ABSTRACT OF THESIS

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Address _____

Degree Doctor of Philosophy *Date* August 1962.

Title of Thesis Polycyclic Aromatic Hydrocarbons

The investigation of the reaction of diphenylketene with 2-benzylidene-1-hydrindone has resulted in the discovery of a novel synthesis of polycyclic aromatic hydrocarbons. Diphenylketene reacts with 2-benzylidene-1-hydrindone to give as the main product, 1-diphenylmethylene-2-benzylidenehydrindene. This hydrocarbon, which has diradical properties, undergoes ring-closure with spontaneous dehydrogenation in solution to give 1:4-diphenyl-2,3-benzofluorene. 1-Diphenylmethylene-2-benzylidenehydrindene is a colourless compound giving yellow solutions. That the yellow colour is not due to the tautomerism of this compound in solution to the benzofulvene derivative, 1-diphenylmethylene-2-benzylindene, is indicated by the fact that the 3:3-dimethyl derivative, prepared by the reaction of diphenylketene with 3:3-dimethyl-2-benzylidene-1-hydrindone, which cannot tautomerise, is a colourless compound giving yellow solutions also. Like 1-diphenylmethylene-2-benzylidenehydrindene, the dimethyl derivative undergoes ring-closure with spontaneous dehydrogenation, to give 9:9-dimethyl-1:4-diphenyl-2,3-benzofluorene. 1-Diphenylmethylene-2-benzylindene was synthesised and its solutions were found to be stable, confirming that there is no equilibrium between it and 1-diphenylmethylene-2-benzylidene-hydrindene. Had there been an equilibrium between the two compounds, then 1-diphenylmethylene-2-benzylindene would have been converted into 1:4-diphenyl-2,3-benzofluorene through 1-diphenylmethylene-2-benzylidenehydrindene in solution.

A further example of the ring-closure with spontaneous dehydrogenation of 1-diphenylmethylene-2-benzylidene compounds is the conversion of 1-diphenylmethylene-2-benzylidenetetralin, prepared by the reaction of diphenylketene with 2-benzylidene-1-

Use other side if necessary.

tetralone, into 3,4-dihydro-9,10-diphenyl-1,2-benzanthracene.

Attempted Wolff-Kishner reduction of 2-benzylidene-3-carboxy-1-hydrindone by the Huang-minlon method resulted in the conversion of the hydrindone into 2-phenylnaphthalene derivatives. This novel method of ring-enlargement may be capable of wider application.

Diphenylketene reacts with 2-benzylidene-3-carboxy-1-hydrindone to give the mixed anhydride, which on heating undergoes ring-closure splitting out diphenylacetic acid to give 4-hydroxy-2,3-benzofluorenone. This reaction not only furnishes a novel synthesis of hydroxybenzofluorenones but proves the configuration of the benzylidene group in 2-benzylidene-3-carboxy-1-hydrindone.

Diphenylketene forms an adduct with indene which on alkali hydrolysis gives 1-benzhydrylhydrindene-2-carboxylic acid. The acid, on intramolecular cyclisation, gives 1-keto-4-phenyl-1:4:4a:9a-tetrahydro-2,3-benzofluorene. This is proven by the fact that the ketone on treatment with anisylmagnesium bromide, followed by dehydration and dehydrogenation, gives 1-anisyl-4-phenyl-2,3-benzofluorene, identical with the hydrocarbon obtained by the ring-closure with spontaneous dehydrogenation of 1-diphenylmethylene-2-anisylidenehydrindene, prepared by the reaction of diphenylketene with 2-anisylidene-1-hydrindone. The proof that the diphenylketene-indene adduct is 2,3-benzo-6-keto-7:7-diphenyl-bicyclo- [3,2,0] -hept-2-ene illustrates another novel synthesis of polycyclic aromatic hydrocarbons.

POLYCYCLIC AROMATIC HYDROCARBONS

by

Harry G. Heller, A.H.-W.C.

Thesis presented for the Degree of Doctor of Philosophy

University of Edinburgh

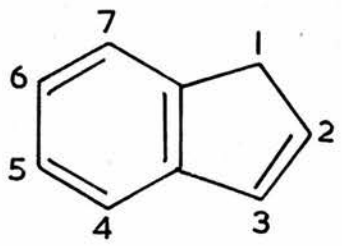
August 1962

To my Mother.

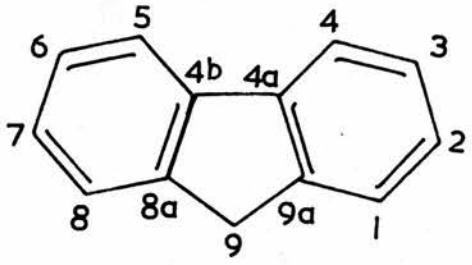
Contents

Nomenclature

The compounds described in this thesis are numbered according to the I.U.P.A.C. Rules 1957 (Handbook for Chemical Society Authors 1960).



Indene



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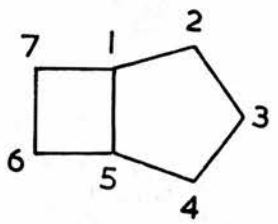
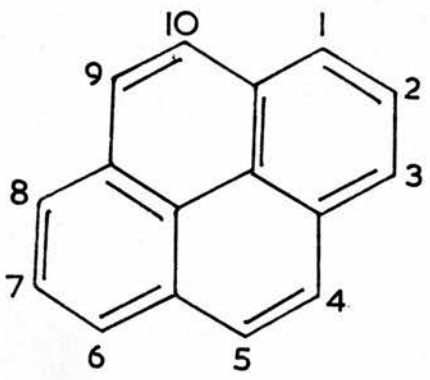


Bicyclo- [3,2,0] - heptane



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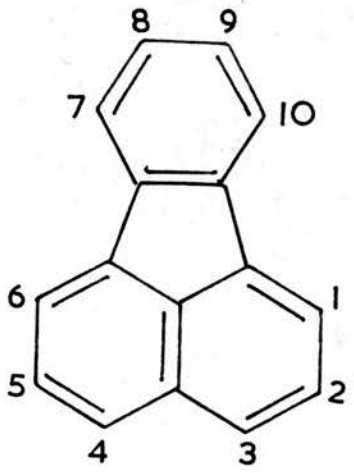
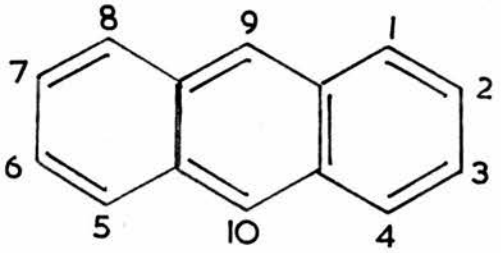
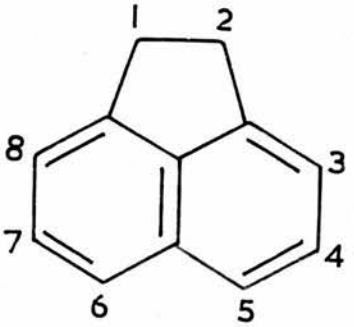


Fluoranthene



Anthracene

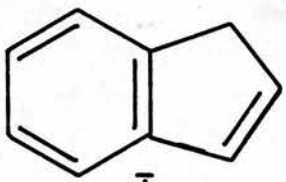


Acenaphthene

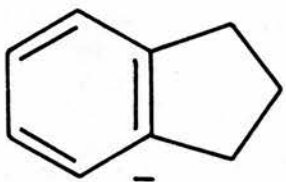
Introduction

This thesis deals mainly with the reaction of diphenylketene with indene and its derivatives, the characterisation of the products and the study of their chemical and physical properties.

The chemistry of indene (I) and its dihydro derivative, hydrindene (II), has been reviewed[1], so that only the salient features of their chemistry relevant to this thesis are given.



I



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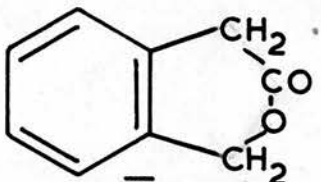
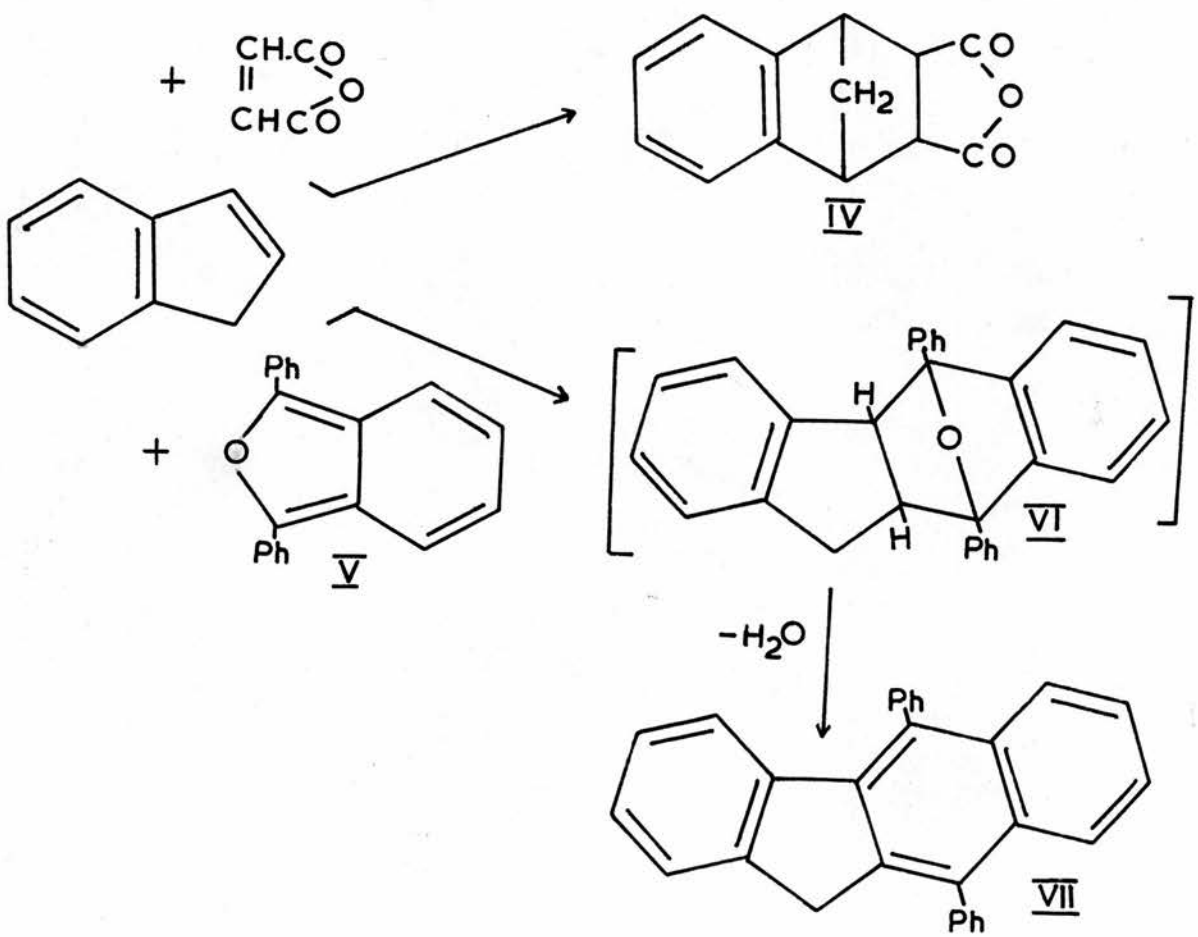


III

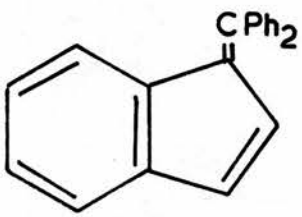
Indene can be isolated from the coal tar fraction b.p. 176-182° and from heavy naphtha[2]. It absorbs oxygen from the air, giving an unstable peroxide, which rearranges to 3-keto-isochroman (III)[3]. Slow polymerisation takes place even at room temperature and in the dark, and amorphous polymers are formed. It forms colourless resins in contact with concentrated sulphuric acid and Friedel-Crafts catalysts.

Indene and its substituted derivatives have the properties of benzene compounds with an unsaturated side chain; they are reduced readily at the 2,3 double bond and form addition compounds there. Hydrogenation with sodium and alcohol[4] or by means of hydrogen and a catalyst[5] transforms indene to

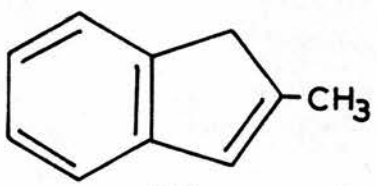
hydrindene. Indene-1-carboxylic acid can be catalytically hydrogenated to hydrindene-1-carboxylic acid[6]. Indene adds smoothly dry hydrogen chloride to give 1-chlorohydrindene[7] and hypobromous acid to yield 1-hydroxy-2-bromohydrindene[8]. At 250°, it adds maleic anhydride, forming cis-4,5-benzo-3:6-endomethylene-1,2,3:6-tetrahydrophthalic anhydride (IV)[9]. In the presence of ethanol saturated with hydrogen chloride, indene forms an adduct (VI) with 2:5-diphenyl-3,4-benzofuran (V), which undergoes spontaneous dehydration to give 1:4-diphenyl-2,3-benzofluorene (VII)[10].



The hydrogen atoms of the methylene group are reactive under the influence of the phenyl group and the double bond, and condensation products with aldehydes and less easily with ketones, can be obtained. These condensation products are the intensely coloured benzofulvenes. Treatment of indene with benzophenone in the presence of sodium ethoxide gives 1-diphenylmethyleneindene, 8:8-diphenylbenzofulvene (VIII), a bright yellow compound[11], 2-Methylindene (IX)[12] and, as is shown in this thesis (p.57), 2-benzylindene do not undergo this characteristic reaction of indene derivatives with benzophenone.



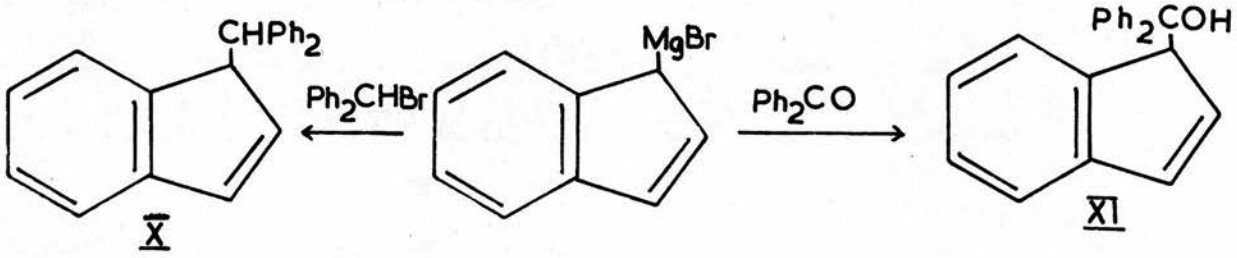
VIII



IX

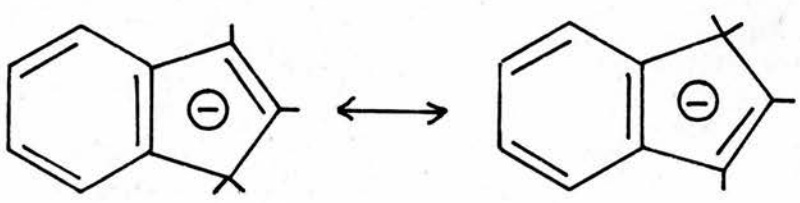
One hydrogen atom of the methylene group in indene can be replaced by sodium, giving 1-indenylsodium, which on treatment with carbon dioxide, followed by acidification, yields indene-1-carboxylic acid[6]. A Grignard derivative is formed on treatment of indene in toluene at 90-100° with ethylmagnesium bromide[13,14]. It reacts with alkyl or aryl halides to give 1-substituted indenes and with ketones to yield benzofulvanols, which on dehydration give benzofulvenes. Like 1-indenylsodium, the

Grignard derivative can be converted to indene-1-carboxylic acid. The Grignard derivative reacts with benzhydryl bromide and with benzophenone to yield 1-benzhydrylindene (X) and diphenylbenzofulvanol (XI) respectively. The latter can be dehydrated to diphenylmethyleneindene (VIII).

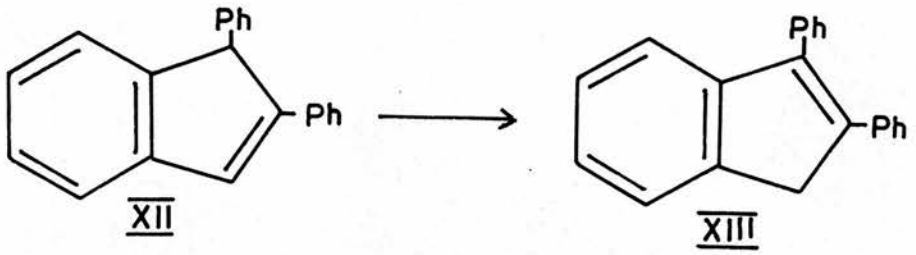


X XI

If the double bond in the five-membered ring could alternate between the 1,2 and 2,3 positions, with a proton oscillating between the 1 and 3 positions, then derivatives containing the same substituent respectively in the 1 and 3, the 4 and 7 or the 5 and 6 positions would be identical. However, the double bond is sufficiently static to permit the separate existence of such pairs of isomers. In alkaline solution however, the mesomeric

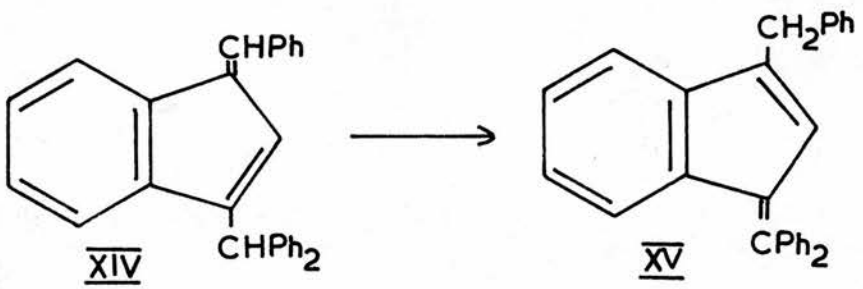


anion is formed and isomerisation readily occurs between the pairs of compounds.1,2-Diphenylindene (XII) can be converted to 2,3-diphenylindene (XIII) by the action of potassium hydroxide[14].



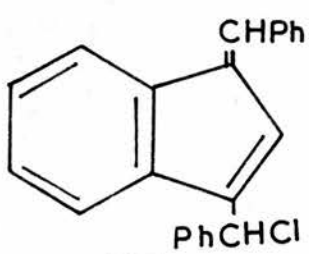
XII XIII

Other types of indene derivatives isomerise under the influence of potassium hydroxide. For example, 3-benzhydryl-1-benzylideneindene (XIV) is converted into 1-diphenylmethylene-3-benzylindene (XV) on boiling with alkali[15].

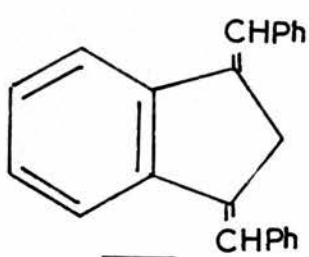


XIV XV

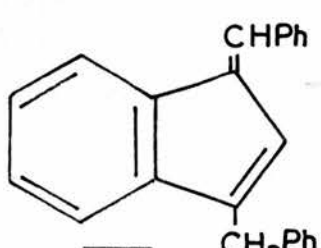
Reduction of 3-(ω -chlorobenzyl)-1-benzylideneindene (XVI) with aluminium amalgam in moist ether gives a sparingly soluble, colourless, monomeric compound, isomeric with 3-benzyl-1-benzylideneindene (XVII), a yellow compound, and transformed to it by heating. The colourless compound is considered to be 1:3-dibenzylidenehydrindene (XVIII) which isomerises when heated[16,17].



XVI

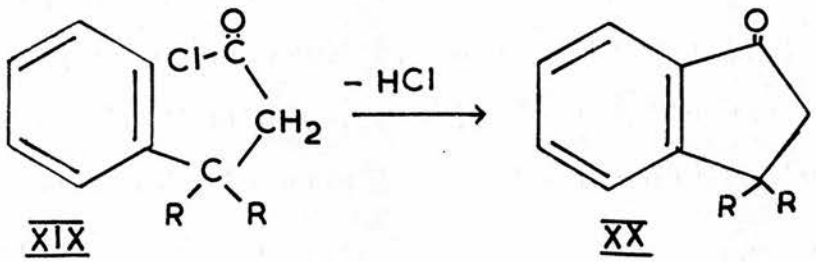


XVIII



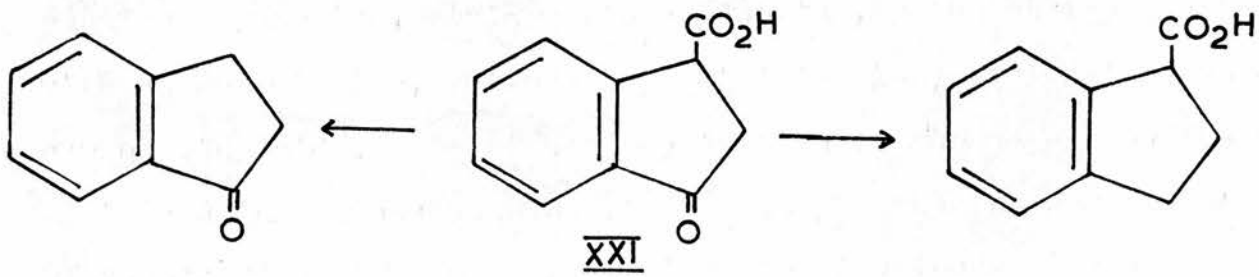
XVII

Many alkyl and phenyl 1-ketohydrindenes have been obtained by the cyclisation of 2-phenylpropionyl chlorides. 1-Hydrindone (XX, R=H) can be prepared in quantitative yield from 2-phenylpropionyl chloride (XIX, R=H) by the Inverse Friedel-Crafts method[18,19] and 3:3-dimethyl-1-hydrindone (XX, R=CH_3) can be prepared from 2-phenylisovaleryl chloride (XIX, R=CH_3)[20].



XIX XX

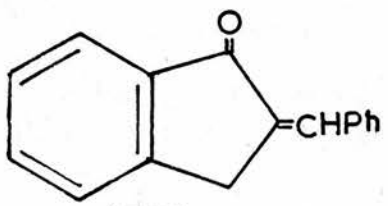
Clemmensen reduction of 1-hydrindone-3-carboxylic acid (XXI), prepared by cyclisation of phenylsuccinyl chloride[21], gives hydrindene-1-carboxylic acid[22]. Ketoacids of this type with substituents in the benzene nucleus, decarboxylate on heating in quinoline in the presence of copper chromite to give 1-hydrindone derivatives[23].



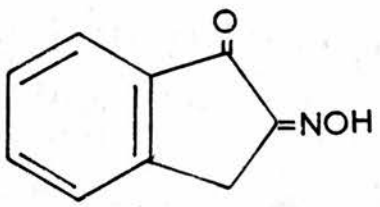
XXI

The methylene group adjacent to the keto group is activated. 1-Hydrindone condenses with benzaldehyde in the presence of alkali to give 2-benzylidene-1-hydrindone (XXII)[24], and with

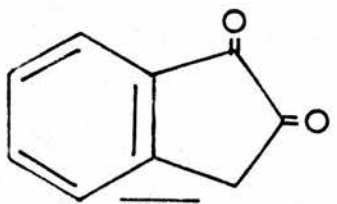
isoamyl nitrite and hydrogen chloride in ethanol to yield hydrindene-1,2-dione-2-oxime (XXIII) which can be hydrolysed to hydrindene-1,2-dione (XXIV)[25].



XXII

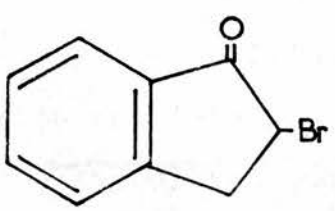


XXIII

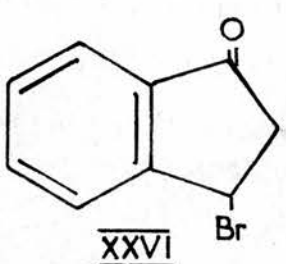


XXIV

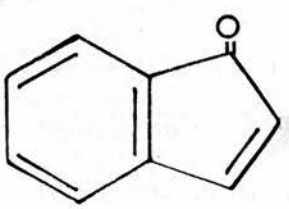
2-Bromo-1-hydrindone (XXV) is formed in quantitative yield from 1-hydrindone and 1 mol. of bromine[26]. 3-Bromo-1-hydrindone (XXVI), prepared by the action of N-bromo-succinimide on 1-hydrindone[27,28], undergoes dehydrobromination when refluxed with symm. collidine, to give indone (XXVII) in good yield.



XXV

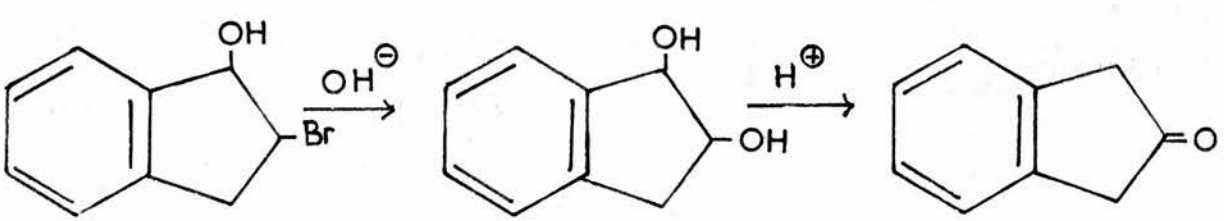


XXVI



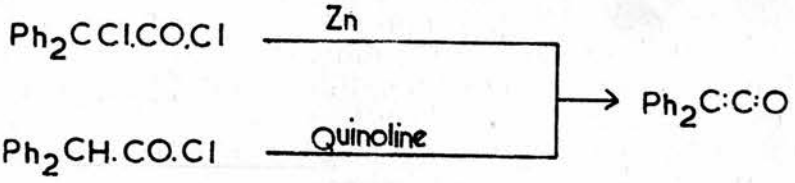
XXVII

2-Hydrindone (XXVIII) can be prepared in good yield by refluxing 1-hydroxy-2-bromohydrindene, first with dilute ethanolic potassium hydroxide and then with dilute sulphuric acid[29].

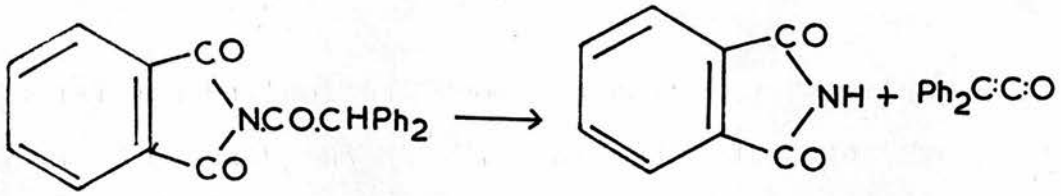


XXVIII

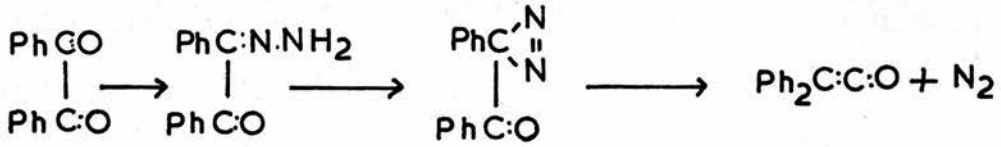
Diphenylketene, $Ph_2C{:}C{:}O$, a yellow liquid, b.p. 146°/12 m.m., which crystallises on refrigeration, was the first ketene to be prepared[30]. It may be obtained from diphenylchloroacetyl chloride by treatment with zinc filings (loc. cit.) or from diphenylacetyl chloride by treatment with tertiary bases, e.g. quinoline[31].



Hura and Dull[32] found that diphenylacetylphthalimide underwent pyrolysis at 300-325° to give phthalimide and diphenylketene in poor yield.



Diphenylketene is best prepared by the thermal decomposition of phenylbenzoyldiazomethane (XXIX) (azibenzil)[33], which is prepared by the oxidation of benzil hydrazone with yellow mercuric oxide in the presence of calcium hydroxide.



XXIX

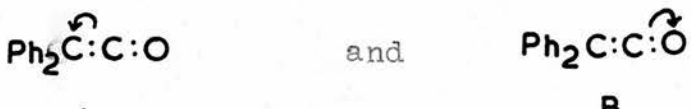
The tendency to polymerise varies considerable for the individual ketenes. The aldoketenes, R.CH:C:O polymerise very readily, even in dilute solutions. The tendency of the ketoketenes, R_2.C:C:O, to polymerise decreases from dibenzylketene to diphenylketene[34].

Polymerisation at 25°

Dibenzylketene	very rapid
Dimethylketene	70% in 6 hours
Allylmethylketene	69% in 1 day
Methylethylketene	52% in 1 day
Diallylketene	75% in 5 days
Diethylketene	28% in 20 days
Dipropylketene	9% in 28 days

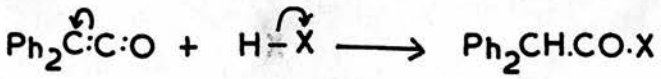
Pure diphenylketene may be kept indefinitely under nitrogen, but in the presence of air, it undergoes autoxidation. The greater stability and the higher reactivity of this compound compared with other members of this class of compounds can be attributed to the influence of the conjugated phenyl groups.

The polarisation of diphenylketene may take place in two ways:

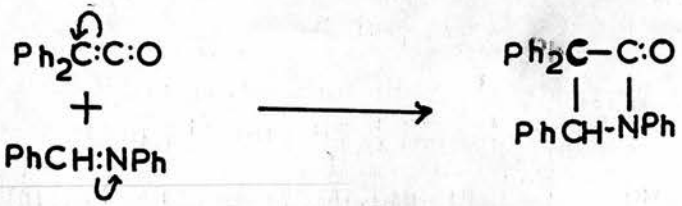


A B

From all the numerous observed examples, in which a dividing addendum adds to the ethylenic centre of the ketene, polarisation occurs exclusively in the direction A. Reactions of this type lead to the production of diphenylacetic acid or its derivatives.



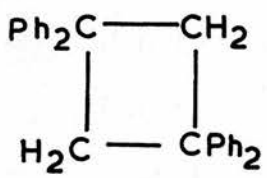
Reactions are known where X = OH, OR, halogen, NH_2, NHR, RCO_2[30]. The addition of Schiff bases takes place so as to give β-lactams, a reaction which proceeds as follows[31]:



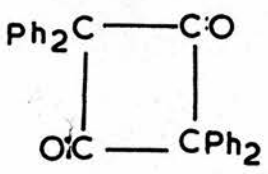
Diphenylketene does not react with carbonyl compounds having an α-hydrogen atom, i.e. aliphatic aldehydes and ketones which can enolise[35]. These carbonyl compounds are considered by Staudinger to catalyse the polymerisation of diphenylketene. Strong polymerisation occurs in the presence of formaldehyde, acetaldehyde, camphor, dibenzylketone, and acetophenone and its derivatives.

Heating paraformaldehyde with diphenylketene for 12 hours at 130° gives the expected product, asym. diphenylethylene, not in the free form, but as the dimer, 1:1:3:3-tetraphenylcyclobutane (XXX). Two polymers of diphenylketene, melting at 244-245° and 176° respectively were isolated

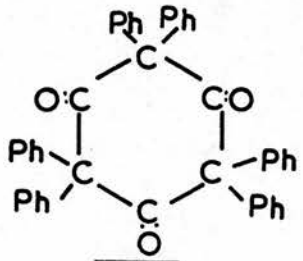
as well. These polymers are the sole products obtained when diphenylketene is heated with acetaldehyde for 18 hours at 120°[35], with quinoline for 80 hours at 170°[36], in the presence of a basic catalyst such as sodium methoxide for 2 hours at 160° or alone for 6 hours at 180-200°[37]. The polymer, m.p. 244-5°, has been shown to be tetraphenyl-1:3-cyclobutane-dione (XXXI) and the polymer, m.p. 176°, to be hexaphenyl-1:3:5-cyclohexane-trione (XXXII)[36,37,39,42].



XXX



XXXI

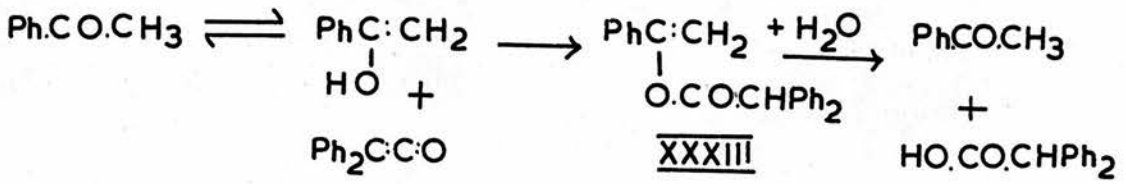


XXXII

On heating diphenylketene with acetophenone at 120° for 18 hours, a third polymer was obtained, melting at 188°. The constitution of this polymer has not yet been elucidated.

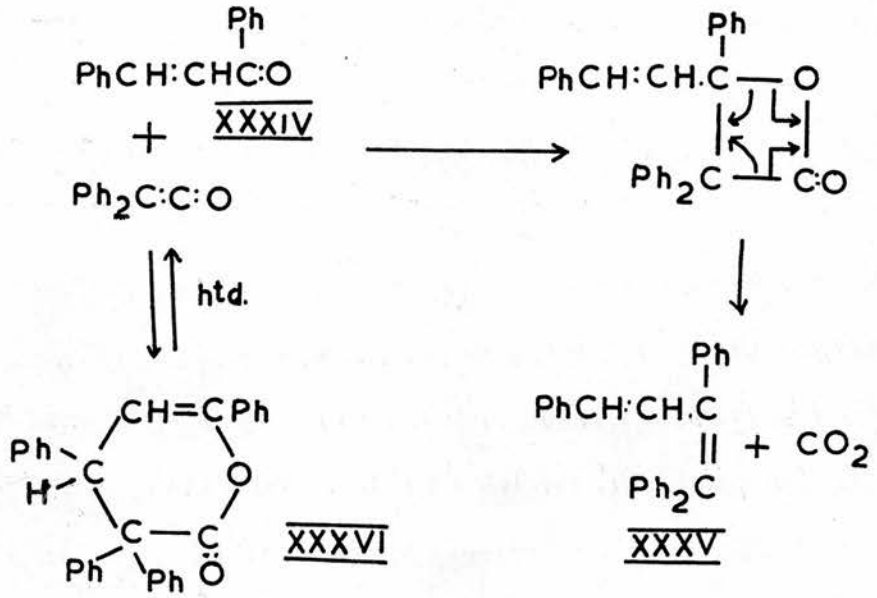
Besides the catalytic influence of aliphatic carbonyl compounds on the polymerisation of diphenylketene, there is the possibility of diphenylketene reacting with the ketone in the enol form, with the formation of an enol ester. Though no enol esters could be isolated, their formation is indicated. The crude product from the reaction of diphenyl-ketene with acetophenone gave a neutral oil, which on hydrolysis with 10% ethanolic potassium hydroxide followed by acidification gave diphenylacetic acid. The neutral oil

might contain the enol ester (XXXIII)[38].

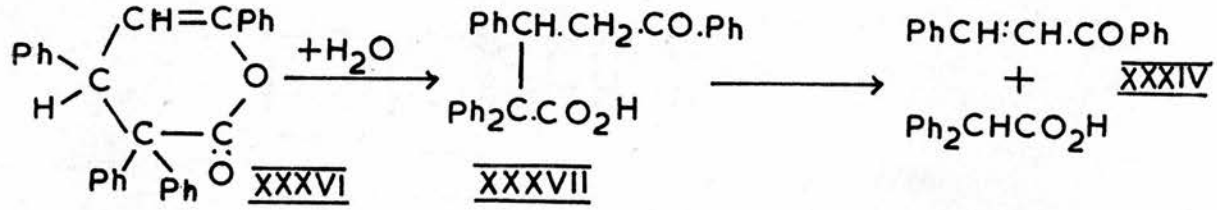


Diphenylketene undergoes 1:2 and 1:4 addition with αβ-unsaturated aldehydes and ketones to give β- and δ-lactones. The β-lactones are unstable intermediates, which decompose to yield a butadiene derivative and carbon dioxide.

The δ-lactones are quite stable. A surprising observation is that on heating them above their melting point, they lose carbon dioxide and give a butadiene derivative like the β-lactones. Staudinger and Endle[40] suggested that on heating, the δ-lactone splits to give diphenylketene and the ketone and that these compounds recombine to give the β-lactone, which yields the butadiene and carbon dioxide. That free diphenylketene was produced, was shown by heating the δ-lactone in the presence of aniline. Diphenylacetanilide was produced. The formation of the δ-lactone is in accordance with Thiele's theory of partial valency for conjugated compounds. The reaction of diphenylketene with αβ-unsaturated ketones is illustrated by the reaction of diphenylketene with benzylideneacetophenone (XXXIV) to give 1:1,2:4-tetraphenylbutadiene (XXXV) and the δ-lactone adduct (XXXVI)[35].



That the δ-lactone has the structure assigned was shown by hydrolysis with ethanolic alkali. 1:1,2-Triphenyl-3-benzoyl-butyric acid (XXXVII) was formed, which can be further hydrolysed to benzylideneacetophenone and diphenylacetic acid[40].

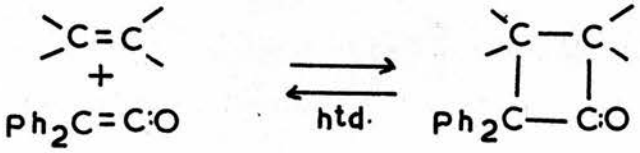


The formation of β- and δ-lactones involves a polarisation of diphenylketene of type A. Diphenylketene does not react with cinnamic acid esters. The alkoxy substituent not only

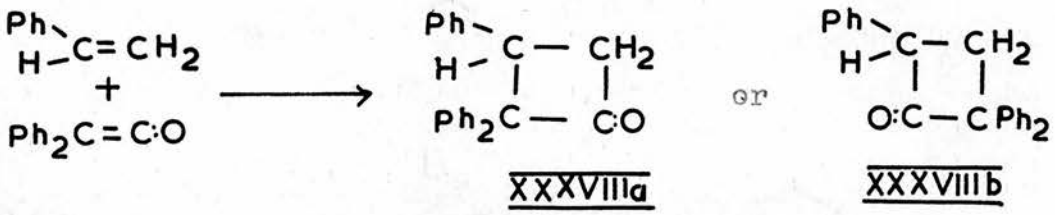
makes the carbonyl group less reactive but also the ethylenic linkage. Neither δ -lactone formation or addition to the double bond occurs.

Diphenylketene reacts with double bonds to yield cyclobutanone derivatives or cyclohexanedione derivatives[41]. The cyclobutanone derivatives dissociate on heating into their components.

In general, the reaction is of the following type:



From styrene, a product is obtained, which could have either of two structures, (XXXVIIIa) or (XXXVIIIb).

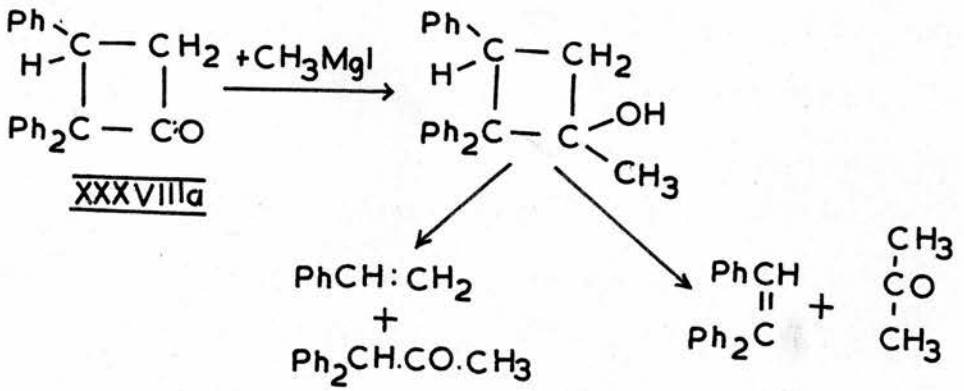


XXXVIIIa

XXXVIIIb

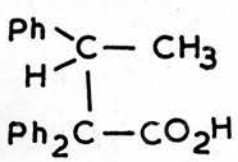
Staudinger and Suter[41] suggested that the adduct had structure (XXXVIIIb) as neither a condensation product with benzaldehyde could be obtained, nor reaction of the carbonyl group with the usual ketone reagents. Treatment of the cyclobutanone with alkali caused ring fission with production of a substituted butyric acid, to which the incorrect structure of 1:1:3-triphenyl-n-butyric acid (XXXIXb) was assigned.

Later Staudinger and Rheiner[42] showed that the adduct had structure (XXXVIIIa), by treating the adduct with methylmagnesium iodide and heating the resulting carbinol.

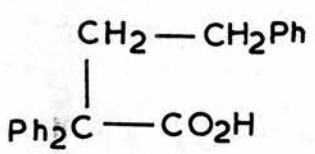


XXXVIIIa

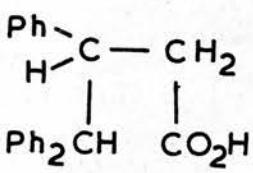
The products produced from the thermal decomposition prove the structure of the adduct. Following from this, the acid produced by hydrolysis of the adduct was assigned the structure of 1:1,2-triphenylbutyric acid (XXXIXa).



XXXIXa

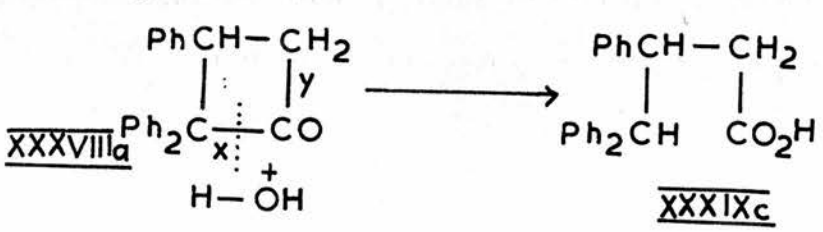


XXXIXb



XXXIXc

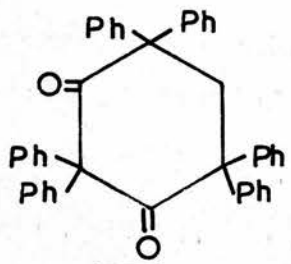
The Bergmanns[43] proved that Staudinger's acid was 2,3:3-triphenylbutyric acid (XXXIXc), indicating that hydrolytic fission occurs at bond x, and not at bond y, as assumed by Staudinger[41,42].



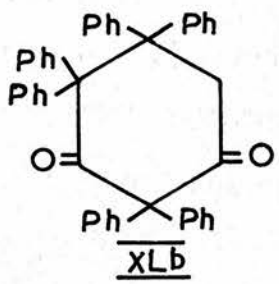
XXXVIIIa

XXXIXc

Asymm. diphenylethylene reacts with two mols of diphenylketene to give a cyclohexanedione derivative, to which structure XLa was attributed after analysis and molecular weight determination[41]. Hydrolytic fission gave an acid, melting at 121-3°.

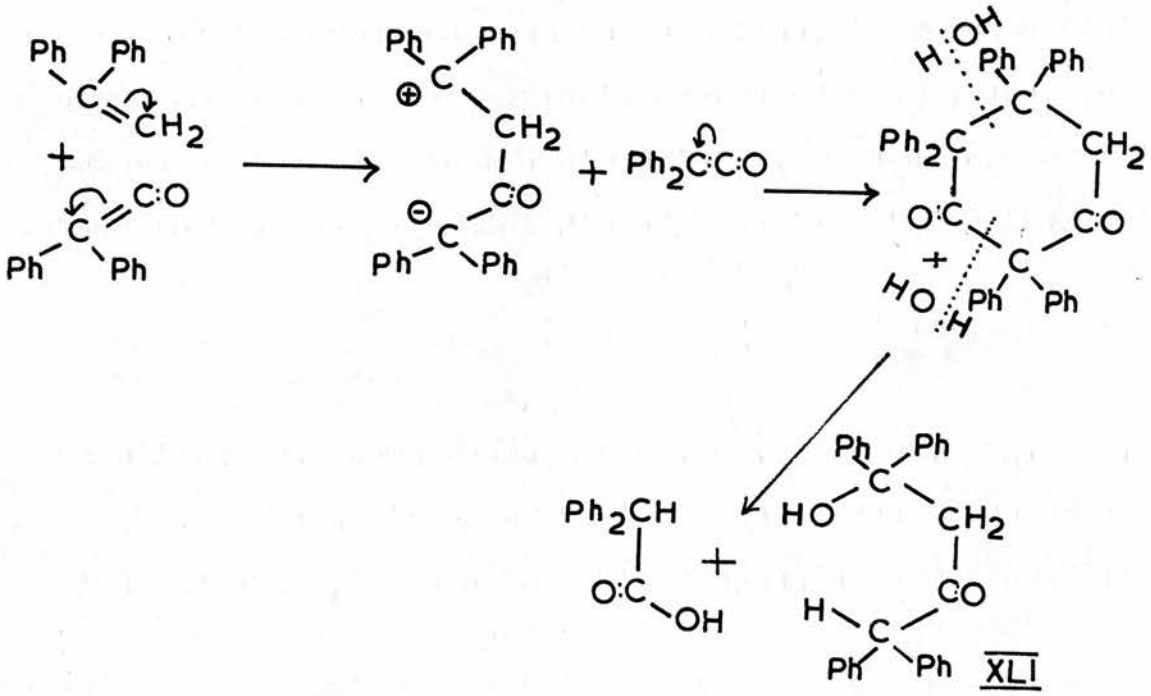


XLa

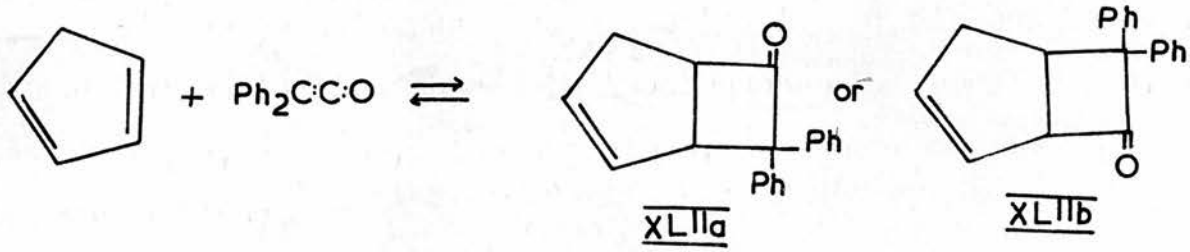


XLb

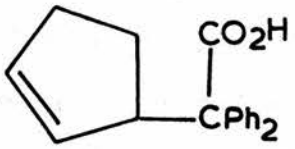
The structure of the cyclohexanedione was reinvestigated by Farooq and Abraham[44]. It had no characteristic reactions of the carbonyl group. It did not react with phenylhydrazine, Grignard reagents or undergo Clemmensen reduction. Alkali hydrolysis gave diphenylacetic acid and a hydroxyketone, which was identified as 1:1:4:4-tetraphenyl-3-ketobutan-1-ol (XLI) indicating that the cyclic diketone had structure XLb. The following mechanism is suggested for its formation:



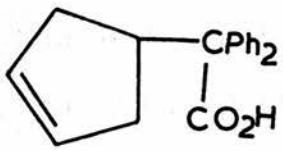
Staudinger and Suter[41] observed that cyclopentadiene reacted with 1 mol of diphenylketene to give an adduct for which structures XLIIa and XLIIb were suggested. The adduct decomposes into its components on heating.



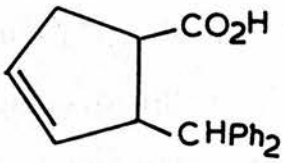
Hydrolysis of the adduct with ethanolic sodium hydroxide gave an acid, thought to be (XLIIIa) or (XLIIIb).



XLIIIa

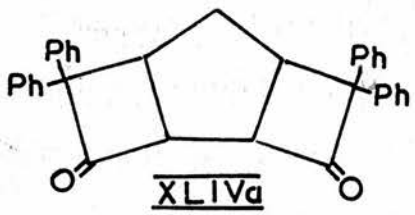


XLIIIb

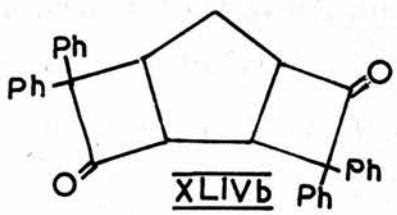


XLIIIc

Simonsen and co-workers[45], Smith and co-workers[46] and Farmer and Farooq[47] have shown that condensation of diphenylketene with cyclopentadiene yields by 1:2-addition 6-keto-7:7-diphenylbicyclo[3,2,0]hept-2-ene (XLIIa) which on alkaline hydrolysis gives rise to two isomeric forms of 2-diphenylmethylcyclopentene-1-carboxylic acid (XLIIIc). The bicyclo compound will add a second molecule of diphenylketene, also by 1:2- addition, to give a tricyclic compound having structure (XLIVa) or (XLIVb).



XLIVa

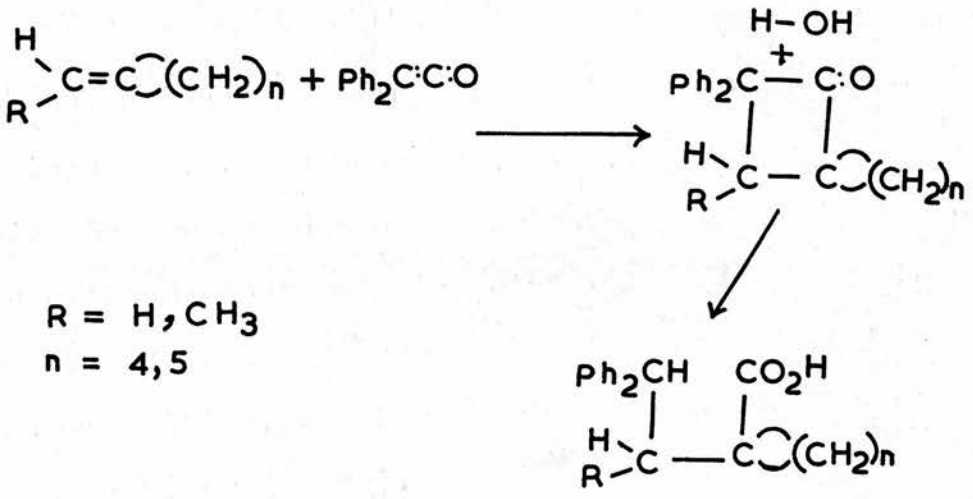


XLIVb

Cyclohexadiene, cyclohexene and cyclopentene are alike in yielding cyclobutanone derivatives. The alkali fission of the cyclobutanone ring occurs in every case between the carbonyl group and the carbon atom having the two phenyl

substituents.

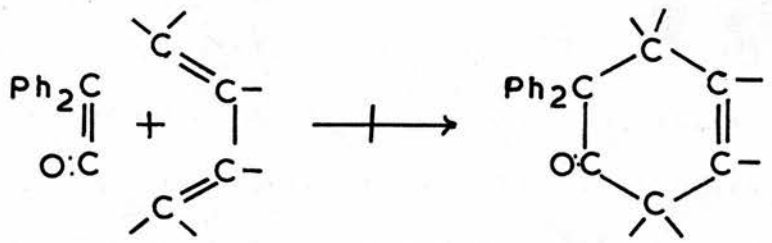
Methylenecyclopentane, methylenecyclohexane, ethylidene-cyclopentane and ethylidene cyclohexane also form substituted diphenylcyclobutanones with diphenylketene, which on alkaline hydrolysis yield substituted butyric acids. Vinylcyclopentane and vinylcyclohexane showed no reaction with diphenylketene[48].



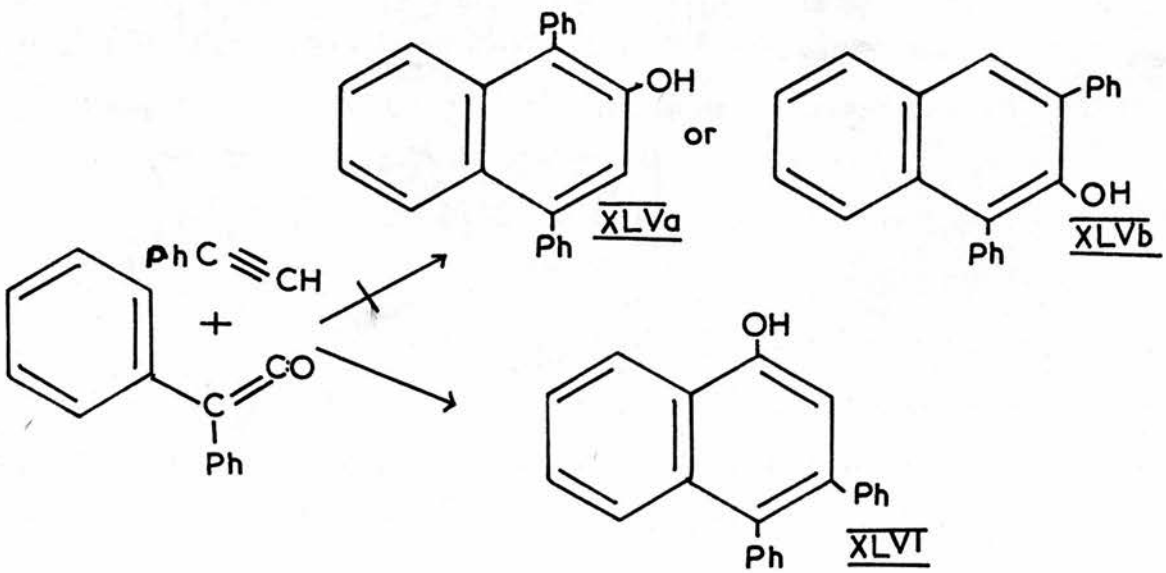
No evidence is given for the structure of the adducts or the butyric acids.

Diphenylketene fails to give adducts with isoprene, methylisoprene[41] or with 1:4-diphenylbutadiene[46]. With butadiene, 2,3-dimethylbutadiene and 1:4-pentadiene, crystalline products are formed, the structures of which have not been established[49]. The analysis of the products indicates the addition of 2 mols of diphenylketene to 1 mole

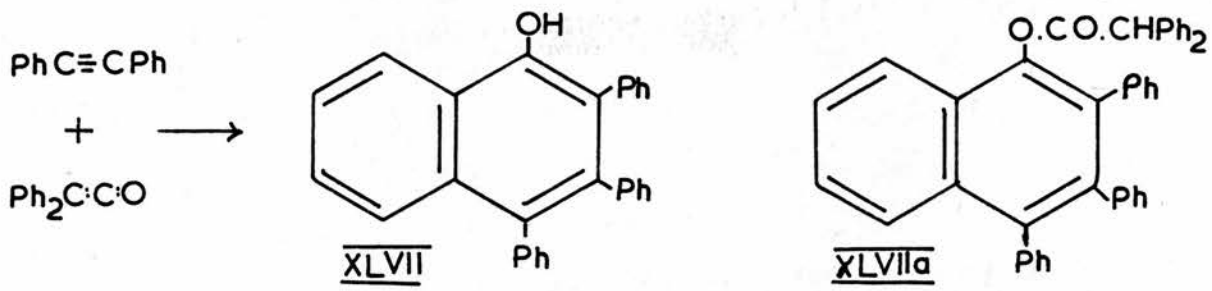
of the butadiene. The compounds show no characteristics of unsaturation and do not give the characteristic reactions of the carbonyl group. It appears that 1:4-addition of diphenylketene to butadienes to give substituted cyclohexenones does not occur.



Smith and Hoehn[50,51] found that diphenylketene condenses with phenylacetylene to form a phenylated naphthol in good yield. The product of a simple addition should have structure (XLVa) or (XLVb) depending on the orientation of diphenylketene during the reaction. In fact, isomer (XLVI) was formed.

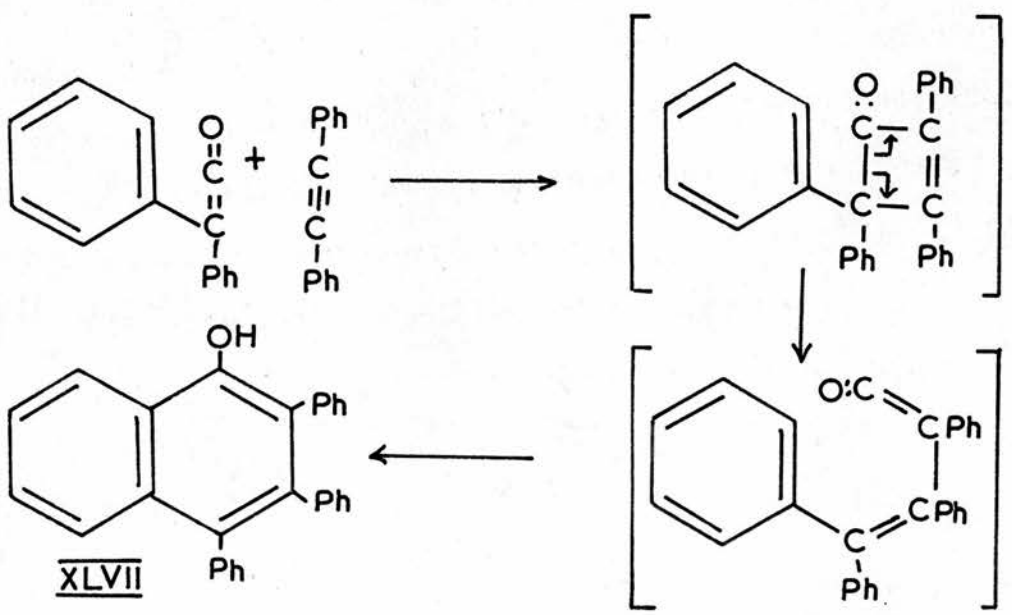


Diphenylacetylene reacted similarly. A mixture of the naphthol (XLVII) and its diphenylacetate (XLVIIa) was obtained.



XLVII XLVIIa

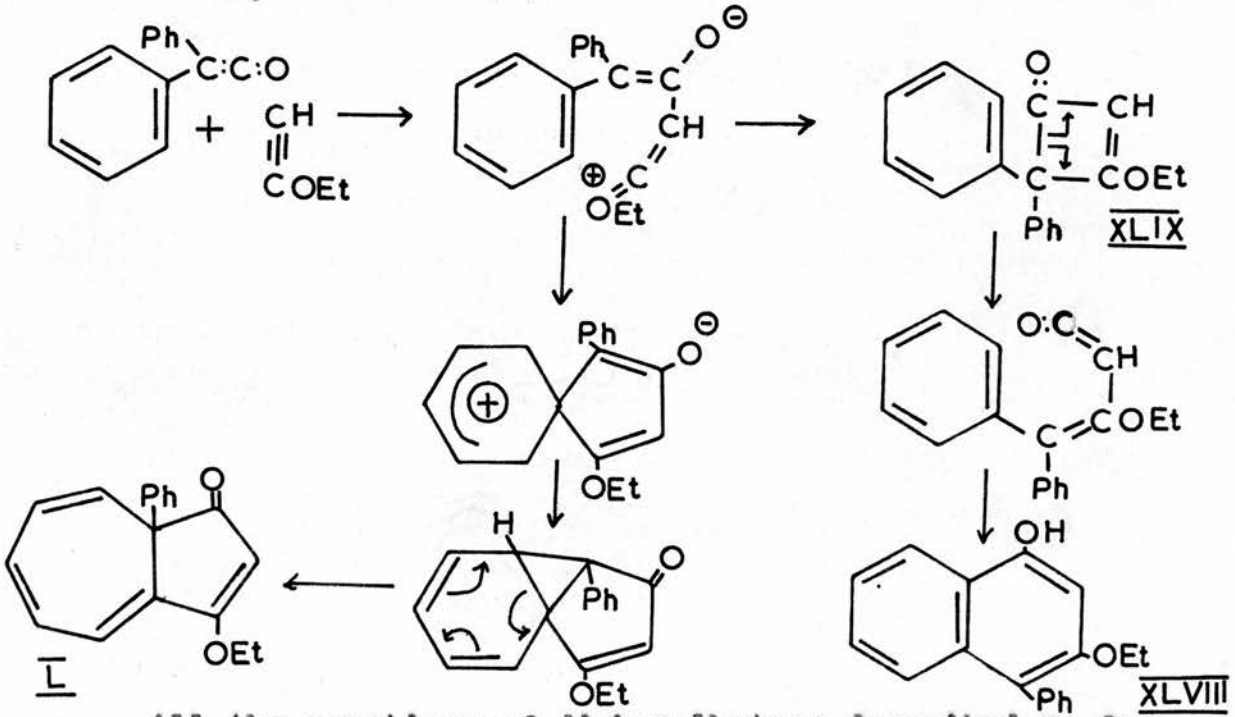
The authors postulated addition of diphenylketene to the triple bond, in analogy to the addition of diphenylketene to double bonds, to give an unstable intermediate cyclobutenone derivative, which however could not be isolated.



XLVII

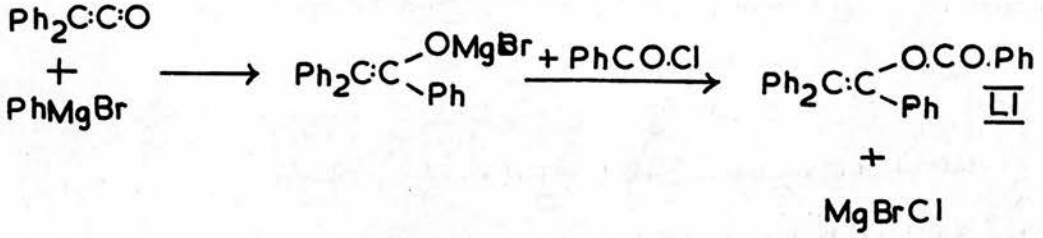
From the reaction of ethoxyacetylene with diphenylketene at room temperature, 1-phenyl-2-ethoxy-4-hydroxynaphthalene (XLVIII) was produced[52]. In an attempt to isolate the

intermediate, 1,1-diphenyl-2-ethoxycyclobut-2-ene-4-one (XLIX) by carrying out the reaction at -20°, a compound of the expected formula was obtained, which could not be rearranged to the naphthol by refluxing in benzene. Independent reinvestigation of this compound by Barton and coworkers[53] and Woodward and coworkers[54] showed it to be the substituted dihydroazulene (L). Woodward and coworkers were able to isolate the butenone (XLIX) as well which on warming in solution or heating above its melting point, rearranges to the naphthol. Woodward postulates the following mechanism for the formation of the ketone (XLIX) and the dihydroazulene (L).

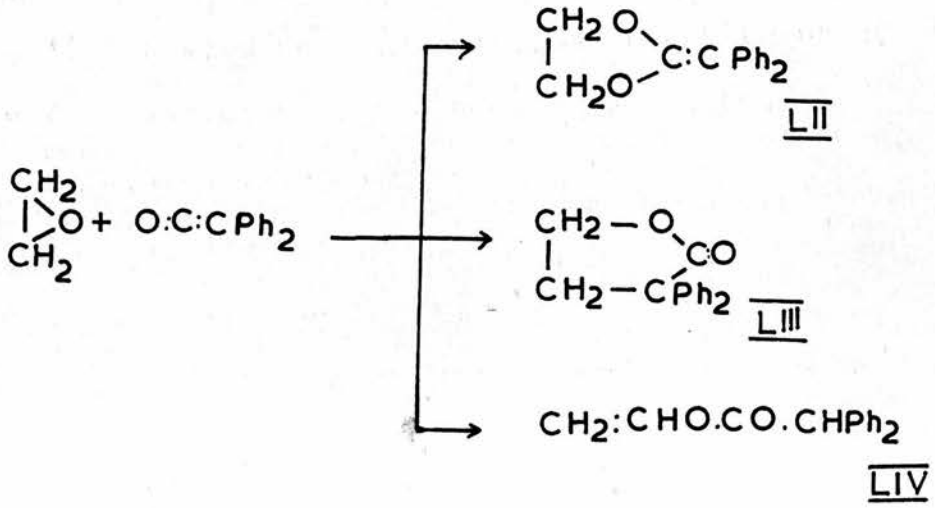


All the reactions of diphenylketene described so far, involve addition across the ethylenic double bond. Very few reactions involving addition to the carbonyl group are known.

Grignard reagents add to the carbonyl group and not to the ethylene group in diphenylketene. This was shown by the fact that the benzoate of triphenylvinyl alcohol (LI) was obtained when the addition compound of diphenylketene and phenylmagnesium bromide was treated with benzoyl chloride[31,55].



From the reaction of ethylene oxide and azibenzil (XXIX) a 50-60% yield of the cyclic acetal of diphenylketene (LII) was obtained, resulting from addition of ethylene oxide to the carbonyl group, and diphenylbutyrolactone (LIII) by addition across the ethylenic double bond. Vinyldiphenyl-acetate (LIV) was isolated from the reaction also[56].



Section 1

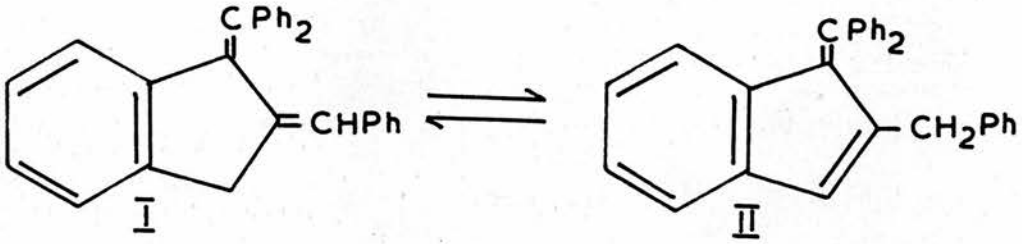
The Reaction of Diphenylketene with 2-Benzylidene-1-hydrindone

Discussion

The aim of this part of the work was to synthesise 1-diphenylmethylene-2-benzylidenehydrindene (I) and to investigate its properties.

By heating 2-benzylidene-1-hydrindone (VI) with diphenylketene at 135-150°, Davison[57] obtained a 50% yield of a colourless hydrocarbon, m.p. 136.5-139°, the analysis of which accorded reasonably with the composition of compound I. The only other product isolated from the reaction was a few milligrams of colourless crystals, m.p. 230-1°.

The compound, m.p. 136.5-139°, was soluble in ethanol giving a bright yellow solution, from which the colourless compound could be recovered unchanged. This reversible colour change suggested that the molecule existed in two tautomeric forms. That more than one form of the compound was present in solution was indicated by the ultraviolet spectrum, which showed the lack of clearly defined maxima and minima. The compound and its solutions did not fluoresce in ultraviolet light. Davison suggested that this hydrocarbon was 1-diphenylmethylene-2-benzylidenehydrindene (I) and that it tautomerised in solution to 1-diphenylmethylene-2-benzylindene (II). This would account for the yellow solution, as compound II is a fulvene derivative, which would be expected to have the characteristic yellow or orange colour of fulvene derivatives.



I II

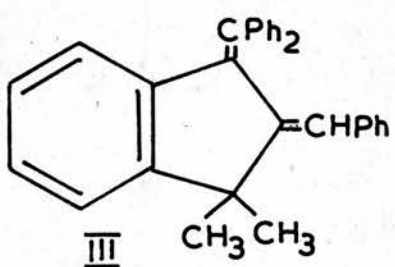
The reinvestigation of these results was tackled in four ways.

1). The repetition of Davison's work to prove the structure of the hydrocarbon, m.p. 136.5-139°, by ozonolysis, Diels-Alder addition and by reduction.

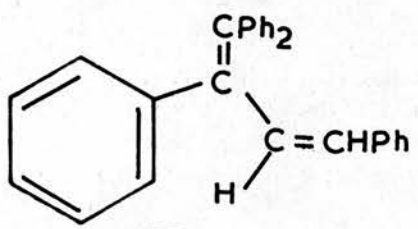
2). The synthesis of 1-diphenylmethylene-2-benzylindene (II).

3). The synthesis of 1-diphenylmethylene-2-benzylidene-3:3-dimethylhydrindene (III), which cannot tautomerise, for comparison of its properties with that of compound I.

4). The synthesis of compound I by an alternative route.



III



IV

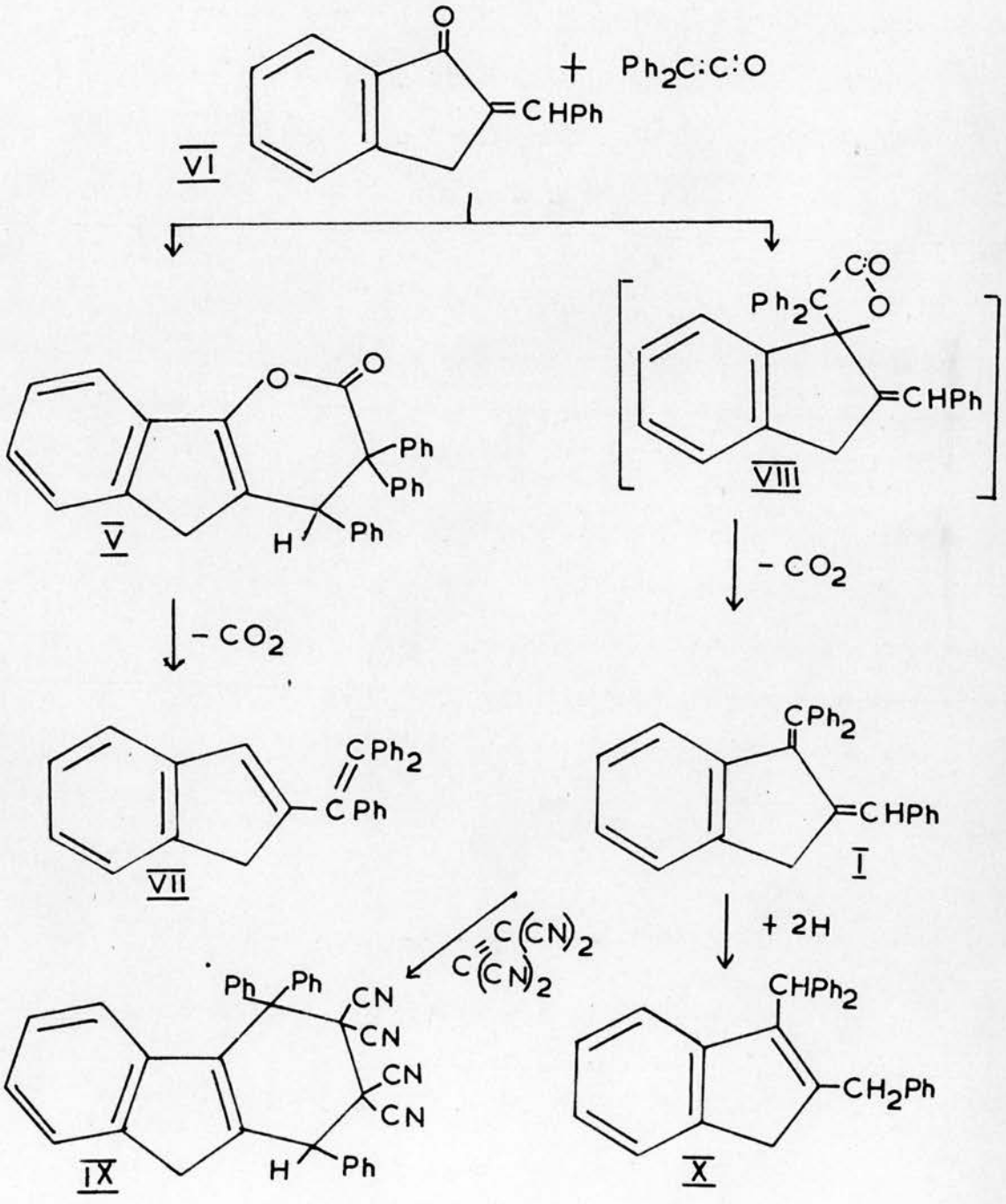
Equimolecular proportions of 2-benzylidene-1-hydrindone (VI) and diphenylketene were heated in an atmosphere of nitrogen in a sealed tube for three and a half hours at 140°. The only product isolated was a small quantity of colourless

crystals melting at 220°, the analysis of which accorded with the composition of compound I. It gave colourless solutions which fluoresced in ultraviolet light. Because of the similarity of its ultraviolet spectrum to that of 1:1,2:4-tetraphenylbutadiene (IV) (Fig. 1) and the proof which follows that the hydrocarbon, m.p. 136.5-139°, is compound I, it is suggested that the compound m.p. 220° might be triphenyl-(2-indenyl)-ethylene (VII), which could be formed theoretically through the intermediate δ-lactone (V) (see scheme A). On repetition of this experiment under identical and different conditions, no trace of this compound could be found and there was insufficient of it for further investigation.

In a second experiment, equimolecular proportions of 2-benzylidene-1-hydrindone (VI) and diphenylketene were reacted together under exactly the same conditions as in the experiment just described. A colourless hydrocarbon melting at 139° having the properties described by Davison, was isolated. Its analysis accorded with the composition of compound I. Small amounts of three other colourless compounds were obtained also. One, m.p. 230°, was shown by mixed m.p. to be the same as that isolated by Davison. The other two compounds melted at 222° and 190° respectively.

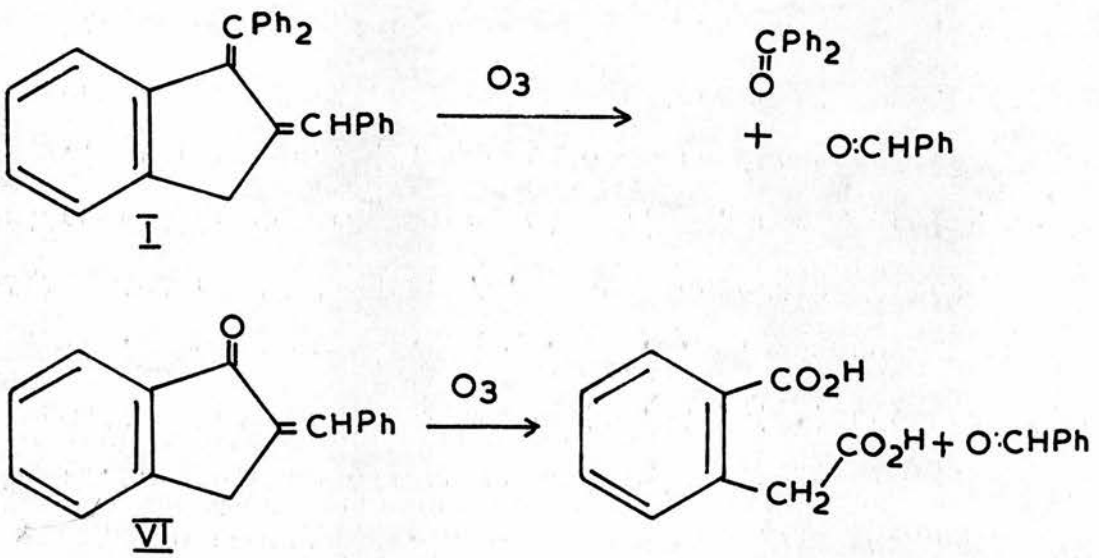
The compound, m.p. 222°, was considered to be the δ-lactone (V) as its infrared spectrum showed a strong carbonyl absorption band at 1775 cms^{-1} and the analysis accorded with

SCHEME A


+ Ph2C:C:O
CHPh
VI
C:O
Ph2C
O
CHPh
VIII
O
O
Ph
Ph
H
Ph
V
- CO2
- CO2
CPh2
CPh
VII
CPh2
CHPh
I
C(CN)2
C(CN)2
+ 2H
Ph
Ph
CN
CN
CN
CN
H
Ph
IX
CHPh2
CH2Ph
X

the structure of the δ-lactone. The compound m.p. 190° was not identified. The compound m.p.230° is discussed on p.43.

Ozonolysis of the hydrocarbon, m.p. 139°, gave benzaldehyde, which was characterised by oxidation to benzoic acid, and benzophenone, which was identified by m.p. and mixed m.p. with an authentic sample and by characterisation as the 2:4-dinitrophenylhydrazone. From the ozonolysis of 2-benzylidene-1-hydrindone (VI), benzaldehyde, characterised as the 2:4-dinitrophenylhydrazone, and homophthalic acid, identified by m.p. and mixed mp. with an authentic sample, were obtained. Homophthalic acid could not be isolated from the ozonolysis of compound, m.p. 139°.



The hydrocarbon, m.p. 139°, did not undergo Diels-Alder addition with maleic anhydride, but gave an adduct with tetra-

cyanoethylene. The analysis and the ultraviolet spectrum of the adduct (Fig. 3) accorded with that of 1:4:4-triphenyl-2:2,3:3-tetracyano-1,2,3,4-tetrahydrofluorene (IX).

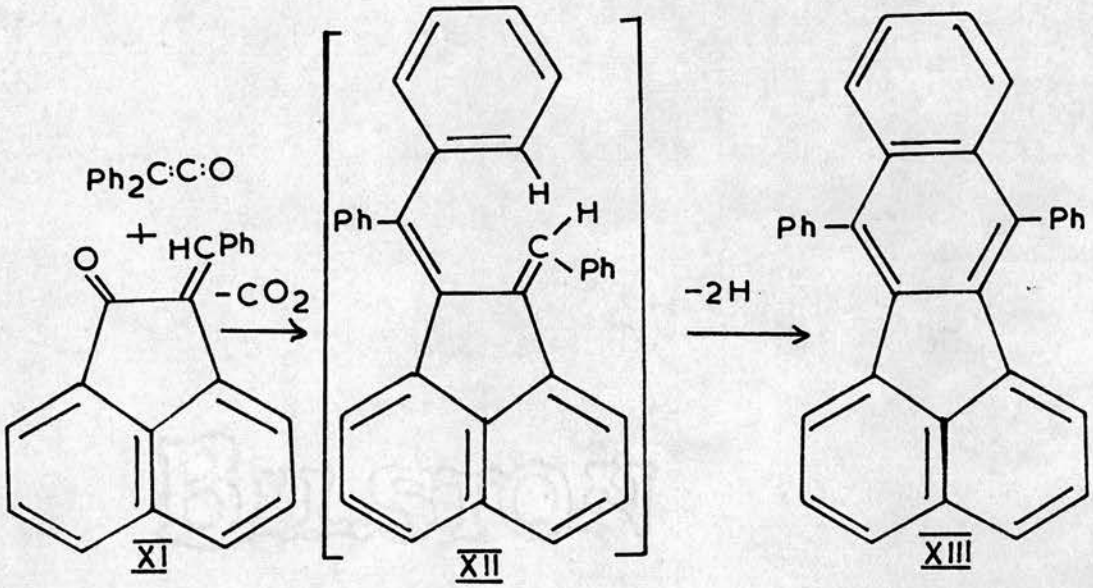
Reduction of the hydrocarbon with aluminium amalgam in moist ether gave 3-benzhydryl-2-benzylindene (X). A mixed m.p. of this compound with 3-benzhydryl-2-benzylindene (X), prepared by a similar reduction of 1-diphenylmethylene-2-benzylindene (II), showed no depression, and their ultraviolet spectra were identical (Fig. 3).

Though hydrogenation of hydrocarbon, m.p. 139°, does not distinguish between compounds I and II, ozonolysis and the formation of an adduct with tetracyanoethylene are proof that the hydrocarbon, m.p. 139°, is compound I.

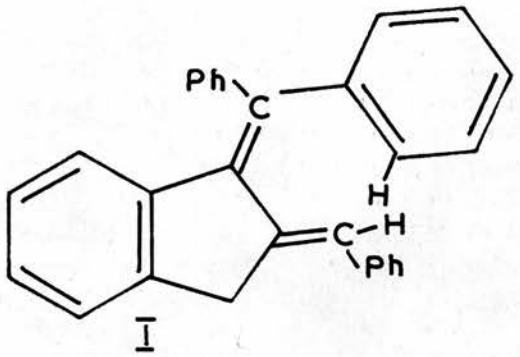
Its ultraviolet spectrum (Fig. 2) was observed in hexane solution. As found by Davison, the spectrum showed a complete lack of clearly defined maxima and minima. This result is surprising, for one would expect compound I to have a characteristic spectrum, similar to that of 1:1,2:4-tetraphenylbutadiene (IV) (Fig. 1). It was observed that the yellow solution became colourless on standing and that the colourless solution had a blue fluorescence in ultraviolet light. The ultraviolet spectrum was observed again and was found to have changed completely, having now well-defined maxima and minima, but was still unlike the spectrum of tetraphenylbutadiene (IV). From the colourless solution,

a hydrocarbon melting at 199° was obtained.

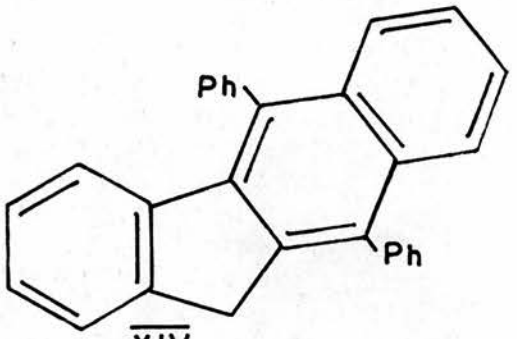
Davison has shown that 1-diphenylmethylene-2-benzylidene-acenaphthene (XII), from the reaction of diphenylketene with 1-benzylideneacenaphthene-2-one (XI), ring-closed spontaneously splitting off hydrogen, to form 7:10-diphenyl-8,9-benzo-fluoranthene (XIII).



This suggested that compound I had undergone ring-closure in solution with spontaneous splitting out of hydrogen to yield 1:4-diphenyl-2,3-benzofluorene (XIV). A mixed m.p. determination of compound, m.p. 199°, with an authentic sample of diphenylbenzofluorene (XIV)[10] gave no depression and the ultraviolet spectra (Fig. 2) of the two compounds were identical.



I



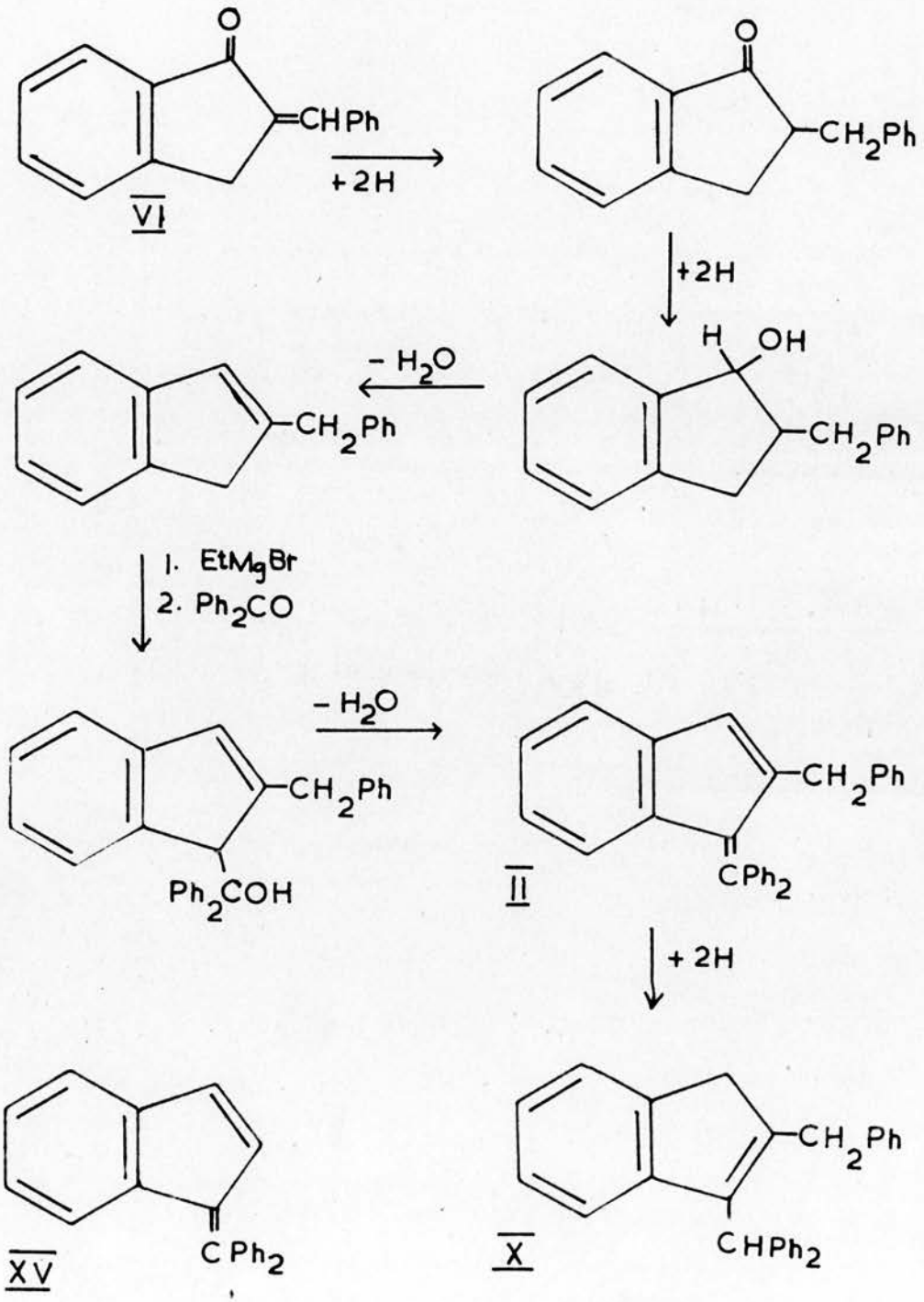
XIV

The possibility of tautomerism between compound I and compound II in solution still exists. It could be argued that in solution, the two tautomers are in equilibrium and as irreversible ring-closure occurs, both tautomers are converted into the benzofluorene (XIV) through compound I. It follows from this argument that compound II would tautomerise partly to compound I,which in turn would ring-close, so that the same effect for either compound would occur.

The synthesis of compound II was carried out as indicated in scheme B and as is described fully in the Experimental Section (pp. 5557). Compound II was obtained as golden yellow prisms melting at 126°. It had a characteristic spectrum (Fig. 4) very similar to that of 1-diphenylmethylene-indene (XV)[11]. Almost a year later, the spectrum of the original solution was reobserved and was found to be completely unchanged, showing that there was no equilibrium between compound I and compound II in solution.

Further proof that the yellow colour of solutions of compound I is not due to tautomerism, is given by the study

SCHEME B

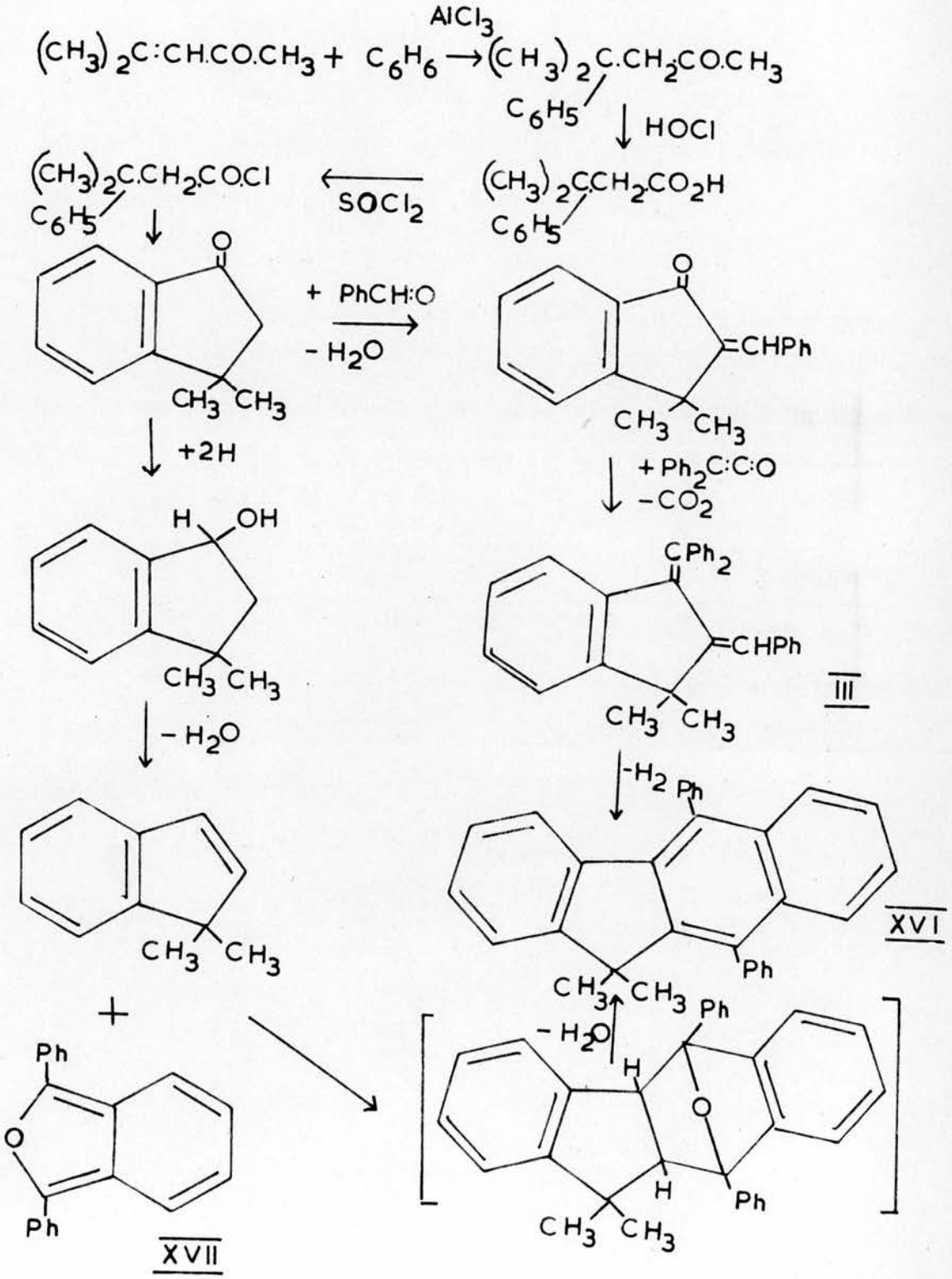

O
CHPh
+2H
VI
O
CH2Ph
+2H
H
OH
CH2Ph
- H2O
CH2Ph
1. EtMgBr
2. Ph2CO
- H2O
CH2Ph
Ph2COH
CH2Ph
CPh2
II
+2H
CPh2
XV
CH2Ph
CHPh2
X

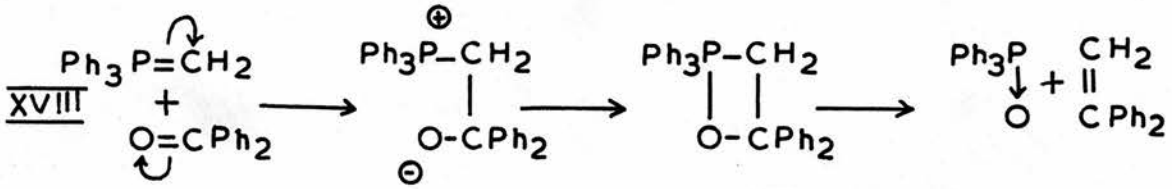
of the properties of 1-diphenylmethylene-2-benzylidene-3:3-dimethylhydrindene (III), which cannot tautomerise. This colourless crystalline compound gives yellow solutions also, which on standing turn colourless. Ring-closure occurs with spontaneous dehydrogenation, to give 1:4-diphenyl-9:9-dimethyl-2,3-benzofluorene (XVI), which was identified by mixed m.p. with an authentic sample, prepared by the action of 2:5-diphenyl-3,4-benzofuran (XVII) with 3:3-dimethylindene. The synthesis of these compounds is indicated in scheme C and described fully in the Experimental Section (pp.58-61).

Though compound, m.p. 139°, has been shown conclusively to be 1-diphenylmethylene-2-benzylidenehydrindene (I) many attempts were made to confirm this by synthesis by an alternative route. All failed and only the more interesting ones are described.

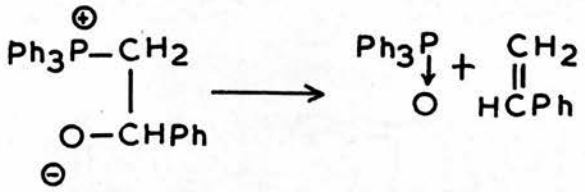
The synthesis of compound I was attempted using the Wittig reaction[38,59]. Triphenylphosphinemethylene (XVIII) reacts with aldehydes and ketones to yield substituted ethylenes and triphenylphosphine oxide. When triphenyl-phosphinemethylene (XVIII) is treated with benzophenone, asymm. diphenylethylene is produced. This surprising result is explained by the following mechanism:

SCHEME C


AlCl3
(CH3)2C:CH.CO.CH3 + C6H6 → (CH3)2C.CH2CO.CH3
C6H5
HOCl
(CH3)2C.CH2CO.Cl
C6H5
SOCl2
(CH3)2C.CH2CO2H
C6H5
+ PhCH:O
- H2O
=CHPh
CH3 CH3
+2H
+ Ph2C:C:O
- CO2
H OH
CPh2
III
- H2O
-H2
Ph
XVI
Ph
CH3 CH3
+
Ph
O
Ph
XVII
- H2O
H
O
H
Ph
CH3 CH3

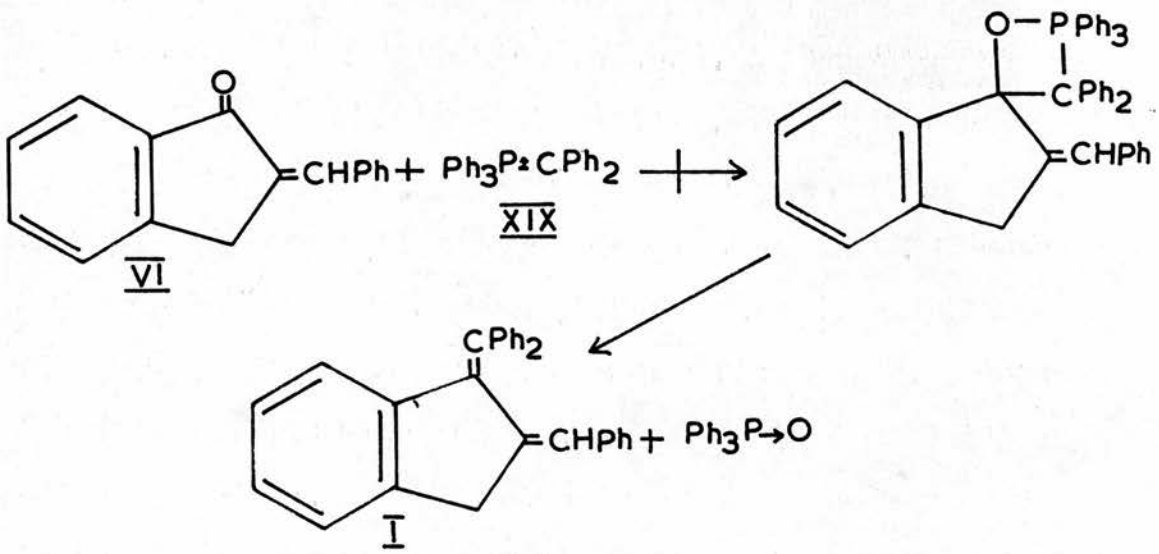


Though the betaine could not be isolated in the above reaction, if benzaldehyde is used instead of benzophenone, the zwitterion can be isolated and characterised as its hydrobromide. This betaine on heating to 60-70° gives styrene and triphenylphosphine oxide.

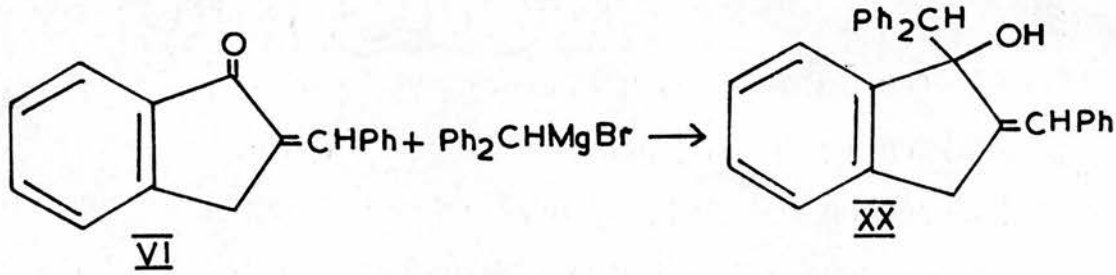


It is reported that triphenylphosphinediphenylmethylene (XIX) does not react with aldehydes and ketones. The stability of this phosphinemethylene (XIX) is attributed to the conjugated phenyl groups. Staudinger[35] has shown that αβ-unsaturated ketones are much more reactive towards diphenylketene than aliphatic or aromatic ketones, so that there was a possibility that the phosphinemethylene (XIX) would react with αβ-unsaturated ketones. Reaction of the phosphinemethylene (XIX) with 2-benzylidene-1-hydrindone (VI) did not occur. Only unchanged ketone, and triphenyl-

phosphine oxide and diphenylmethane, the hydrolysis products of the phosphinemethylene (XIX) were isolated.



The reaction of benzhydrylmagnesium bromide with 2-benzylidene-1-hydrindone (VI) should give 1-benzhydryl-1-hydroxy-2-benzylidenehydrindene (XX) which could be dehydrated to compound I.



Under normal conditions, benzhydryl bromide reacts with magnesium to give the Grignard derivative, which then reacts

immediately with unreacted benzhydryl bromide, so that a quantitative yield of symm. tetraphenylethane is obtained[60].

$$Ph_2CHMgBr + BrCHPh_2 \longrightarrow Ph_2CH.CHPh_2 + MgBr_2$$

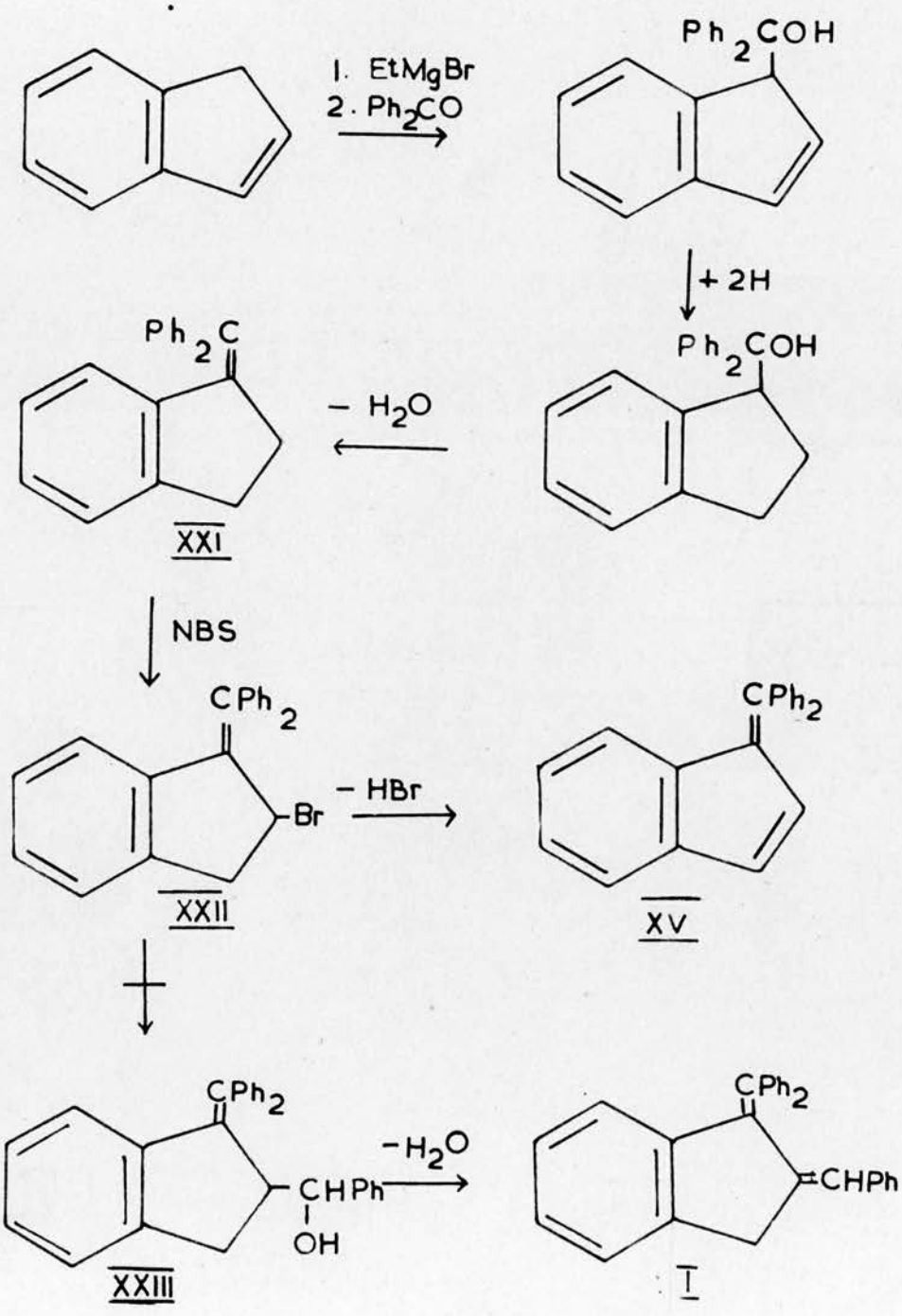
By passing carbon dioxide through the reaction mixture, a small quantity of diphenylacetic acid can be isolated.

A 25% yield of the Grignard derivative is claimed when a cyclic reactor is used[61]. A description of this apparatus is given in the Experimental Section (p. 63). Even by this method no trace of the Grignard derivative could be detected, using Gilman's test[62].

Benzhydryl-lithium could not be prepared, as on treating benzhydryl bromide with phenyl-lithium, tetraphenylethane is produced in over 90% yield[63]. Wittig reports that diphenylmethane reacts with phenyl-lithium in ether at 100° in a sealed tube to give a 46% yield of benzhydryl-lithium. This method was not attempted, as facilities for this experiment were not available.

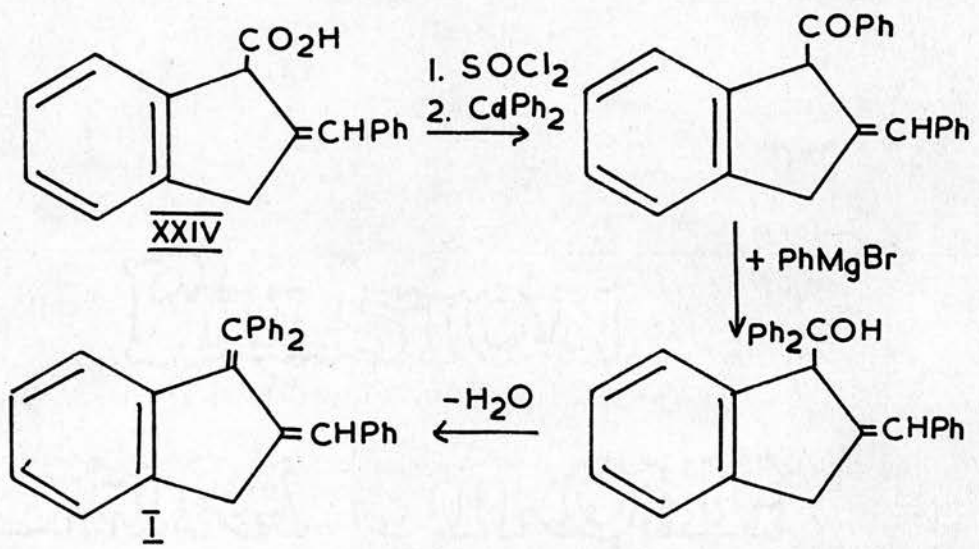
The synthesis of compound I was attempted as indicated in scheme D and as is described in the Experimental Section (pp. 64-65). Bromination of 1-diphenylmethylene-hydrindene (XXI) was accompanied by spontaneous dehydrobromination to give 1-diphenylmethylene-indene (XV) so that the final stages of the synthesis, which consisted of reacting

SCHEME D

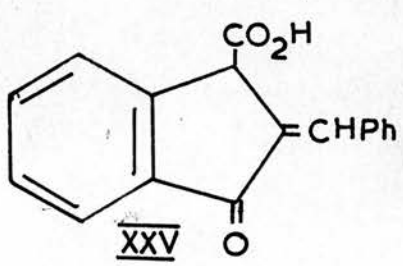

1. EtMgBr
2. Ph2CO
Ph2COH
+2H
Ph2COH
Ph2C
– H2O
XXI
NBS
CPh2
Br
– HBr
XXII
CPh2
XV
CPh2
CHPh
OH
–H2O
XXIII
CPh2
CHPh
I

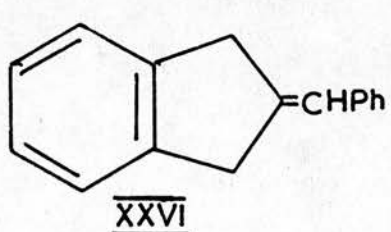
the Grignard derivative formed from the bromo compound (XXII) with benzaldehyde, followed by dehydration of the carbinol (XXIII) produced, could not be carried out.

The synthesis of 2-benzylidenehydrindene-1-carboxylic acid (XXIV) was attempted, as it could be converted to compound I by the following scheme of reactions:

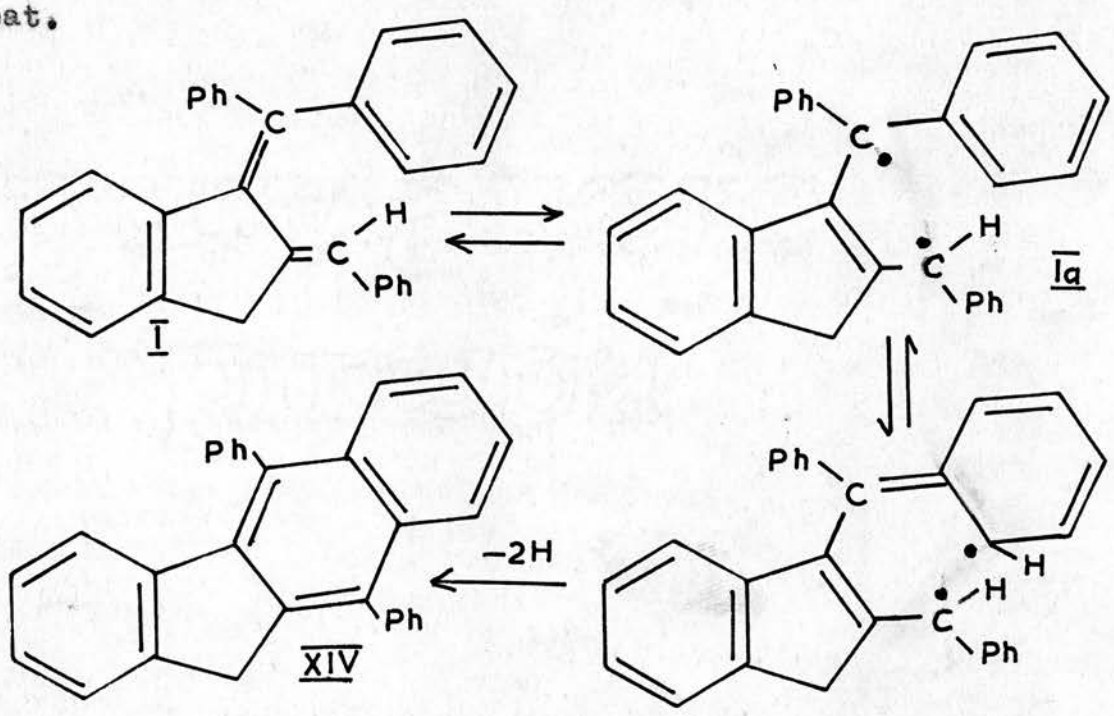


Wolff-Kishner reduction of 2-benzylidene-3-carboxy-1-hydrindone (XXV) did not give the acid (XXIV), but naphthalene derivatives and a small quantity of a compound, m.p. 30°, considered to be 2-benzylidenehydrindene (XXVI). This reaction is discussed separately in Section 2.





1-Diphenylmethylene-2-benzylidenehydrindene (I) gives yellow solutions in organic solvents which are non-fluorescent and do not obey Beer's law. The hydrocarbon turns yellow on exposure to light, is thermochromic, and in solution it undergoes ring-closure with spontaneous dehydrogenation. These properties can be explained by the formation of the diradical Ia in solution, or in the solid state when activated by light or heat.

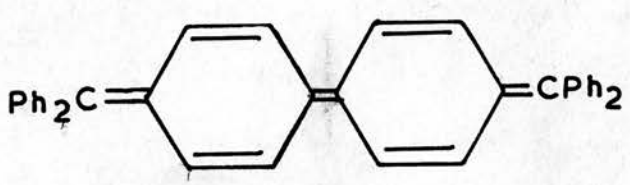


The formation of a diradical would relieve the steric strain in the molecule produced by the interaction of the ortho hydrogen atom of one of the diphenylmethylene phenyl groups with the hydrogen atom of the benzylidene group, as free rotation of the substituents would become possible.

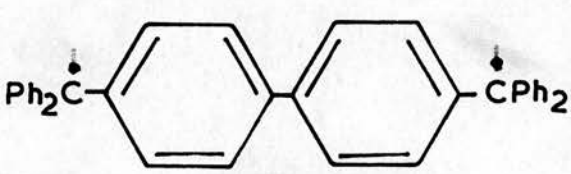
Other hydrocarbons which exhibit a chemical behaviour characteristic of free radicals but contain even numbers of

electrons have been known for almost fifty years[65]. These compounds can have either a quinoidal structure or a diradical structure and considerable confusion is apparent in the literature as to the problem of quinoid-diradical interconvertibility.

Müller and Müller-Rodloff[66] stated as a general rule that a substance is a radical only if no structure with all the electrons paired can be written for it. By this rule, Tschitschibabin's hydrocarbon[65] is not a diradical, because structure XXVII, in which all the electrons are paired, can be written for it. Yet this hydrocarbon, which does not show paramagnetism[66] as true radicals do, has the chemical and physical properties of a diradical, and catalyses the reaction <u>para</u> $H_2 \longrightarrow$ <u>ortho</u> H_2 to some extent[67], which is a standard method of detecting free radicals.



XXVII

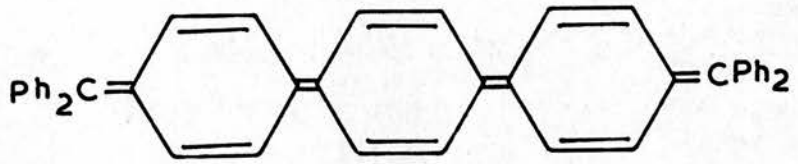


XXVIIa

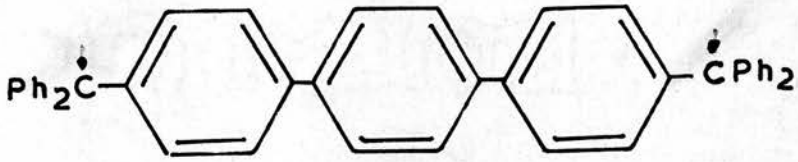
The presence of the diradical (XXVIIa) was claimed to have been detected by electron-spin resonance spectroscopy[68], but it was later reported[69] that the E.S.R. signals obtained may have been due to an impurity. Sloan and Vaughan[70] report

that the electron-spin resonance absorption of this hydrocarbon in benzene solution shows the presence of the diradical in at least 1% concentration.

The Eugen-Müller hydrocarbon[71] can be written in the quinonoid form (XXVIII) or in the diradical form (XXVIIIa).



XXVIII

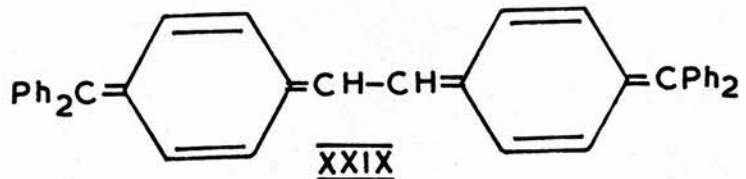


XXVIIIa

It was found to be weakly paramagnetic both in the solid state and in benzene solution. The weak paramagnetism may be explained by partial association of the diradical to give a diamagnetic association product or by the existence of the hydrocarbon in two monomeric forms, the paramagnetic diradical (XXVIIIa) and the diamagnetic quinonoid (XXVIII).

Wittig's hydrocarbon[72] has the properties of a diradical but is diamagnetic in solution[73]. It has been suggested[74]

that the compound is not a diradical as proposed by Wittig, but that it has the quinonoid structure (XXIX).



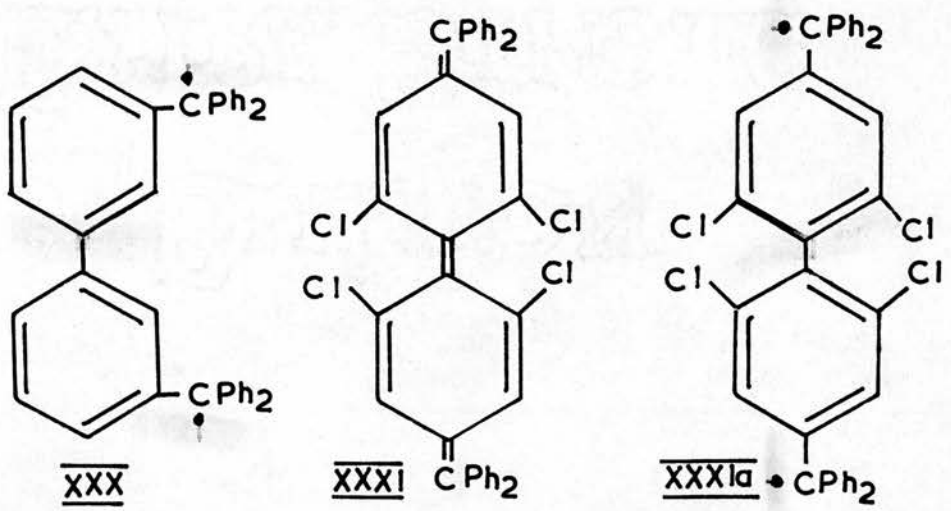
XXIX

By definition, the term diradical describes molecules which contain two unpaired electrons having parallel spins. The two electron spins will couple in a magnetic field to form a resultant vector of S = 1. This total spin will be able to take up three i.e. (2S + 1) different orientations in an applied field and so produce three different energy levels. This state of a molecule is referred to as the triplet state.

Compounds such as fluorescein, which are known to exist in the triplet state, under certain conditions cannot be detected by electron-spin resonance spectroscopy, though their paramagnetism can be detected by magnetic susceptibility measurements[69]. The failure of preliminary electron-spin resonance studies to detect radicals in solutions of 1-diphenylmethylene-2-benzylidenehydrindene I, does not necessarily mean that some of the molecules do not exist in the triplet state in solution, or in the solid state on excitation by light or heat.

Schlenk's hydrocarbon (XXX)[75] like compound I is almost

colourless in the crystalline state, though it gives orange-red solutions. No structure with all the electrons paired can be written for it and it has been suggested that it is in the triplet state[76]. Yet the paramagnetic susceptibility of this compound in benzene at 75°, corresponds only to 6±2% free radicals[77]. It has been suggested that the weak paramagnetism is due to some type of association, the exact nature of which is not known, the association product being presumably diamagnetic.



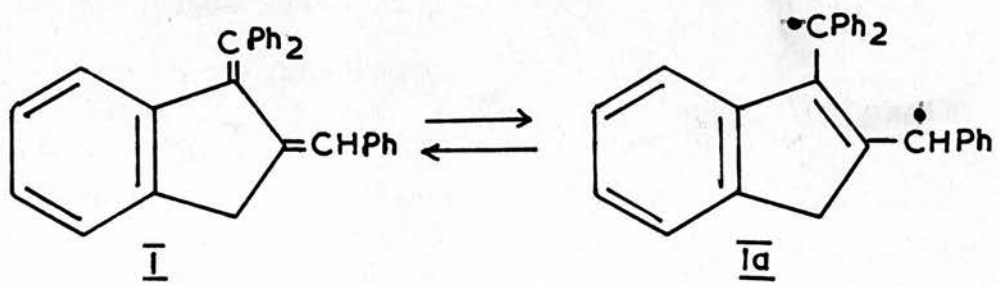
XXX XXXI XXXIa

The compound, known as the Eugen-Müller diradical[77] can be written in the quinonoid form (XXXI) or in the diradical form (XXXIa). However the quinonoid structure is not possible, for in this structure the two central benzene rings must lie in or near a common plane, a configuration prohibited by the steric interference between the bulky ortho-chlorine atoms. The paramagnetic susceptibility of this compound in benzene

at 80° corresponds to 28% free radicals. A true diradical is realised through the effect of isolation.

It can be seen that there exists a class of compounds which can be formulated as diradicals and behave chemically as diradicals, but which do not have two independent electron systems. These compounds, which have failed to show by magnetic susceptibility measurements, the paramagnetism expected of molecules in the highest state, have been termed diradicaloids[78].

A possible explanation for the properties of a compound of this class is that in the ground state the two free electrons are paired so that the substance in this state is diamagnetic but that the paramagnetic triplet state with parallel spins has an energy only slightly higher than the ground state so that a transition into it from the ground state occurs readily. It is suggested that 1-diphenylmethylene-2-benzylidenehydrindene I belongs to this class of compounds. If, like Tschitschibabin's hydrocarbon (XXVII), this compound catalyses the ortho-para-hydrogen conversion, then the weak coupling of the electrons in the ground state would be demonstrated.



I Ia

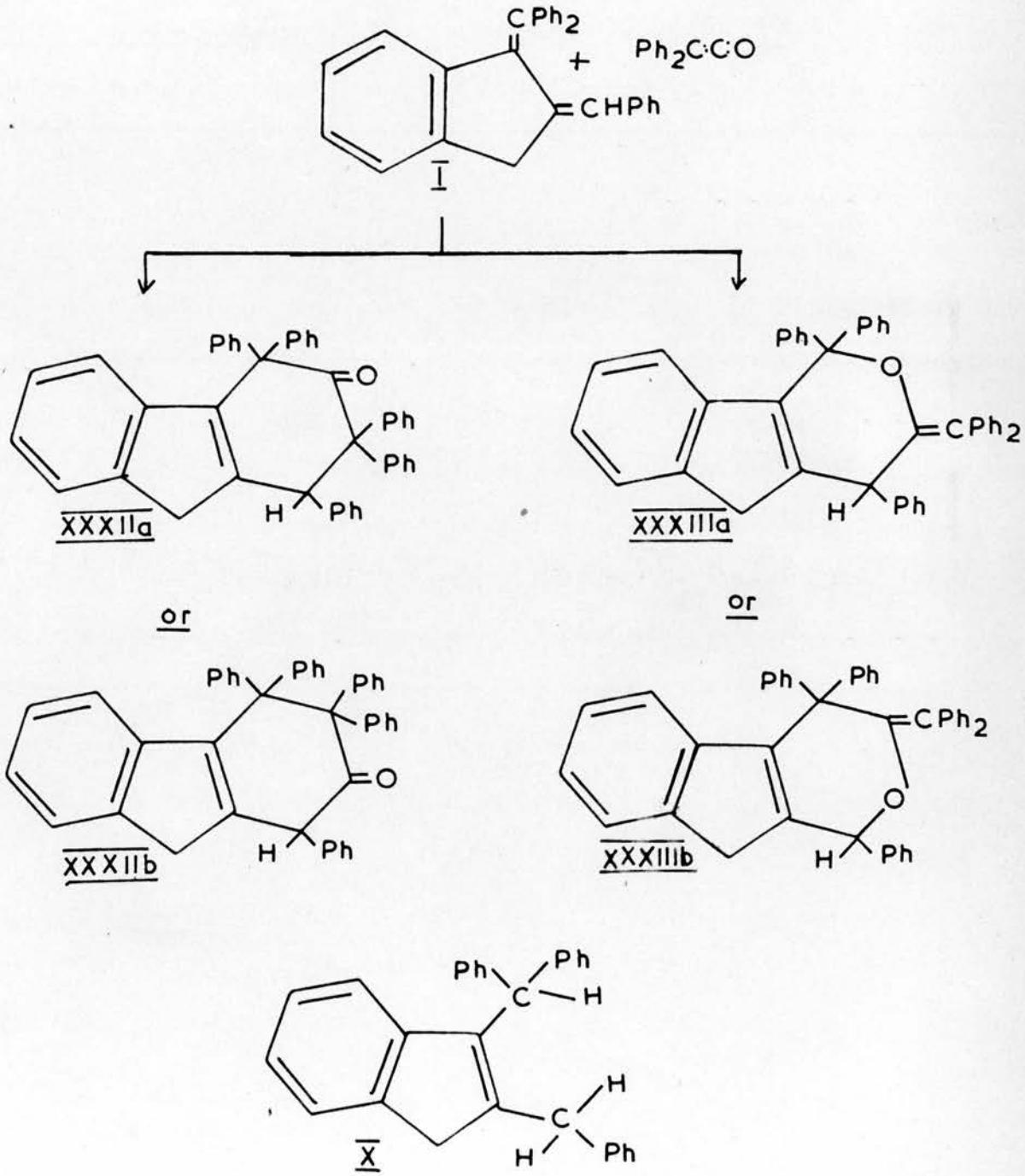
It is pertinent to discuss here the biproduct, m.p. 230°, obtained from the reaction of diphenylketene with 2-benzylidene-1-hydrindone (VI) (see p. 27). As it gave diphenylketene on heating at about 250° in high vacuum, Davison[57] suggested that the compound was an adduct of diphenylketene and 1-diphenylmethylene-2-benzylidenehydrindene I having structure XXXIIa or XXXIIb.

The infrared spectrum of the compound, m.p. 230°, did not show the characteristic carbonyl group absorption band between 1750 and 1650 cms^{-1} and the ultraviolet spectrum (Fig. 6) was very similar to the spectrum of 3-benzhydryl-2-benzylindene (X). It is suggested that the compound m.p. 230° is an adduct of diphenylketene and compound I having the structure XXXIIIa or XXXIIIb.

From the reaction of diphenylketene with 1-benzylideneacenaphthene-2-one (XI), Davison[57] isolated a compound, m.p. 243-5°, which he suggested was an adduct of diphenylketene and 1-diphenylmethylene-2-benzylideneacenaphthene (XII), having structure XXXIVa or XXXIVb, as on heating at about 250° in high vacuum, it gave diphenylketene, and on alkaline hydrolysis 7:10-diphenyl-8,9-benzofluoranthene (XIII). The analysis accorded with that required for the adduct and the ultraviolet spectrum was similar to the spectrum of acenaphthylene (XXXVI).

The infrared spectrum of the compound m.p. 243-5°, did

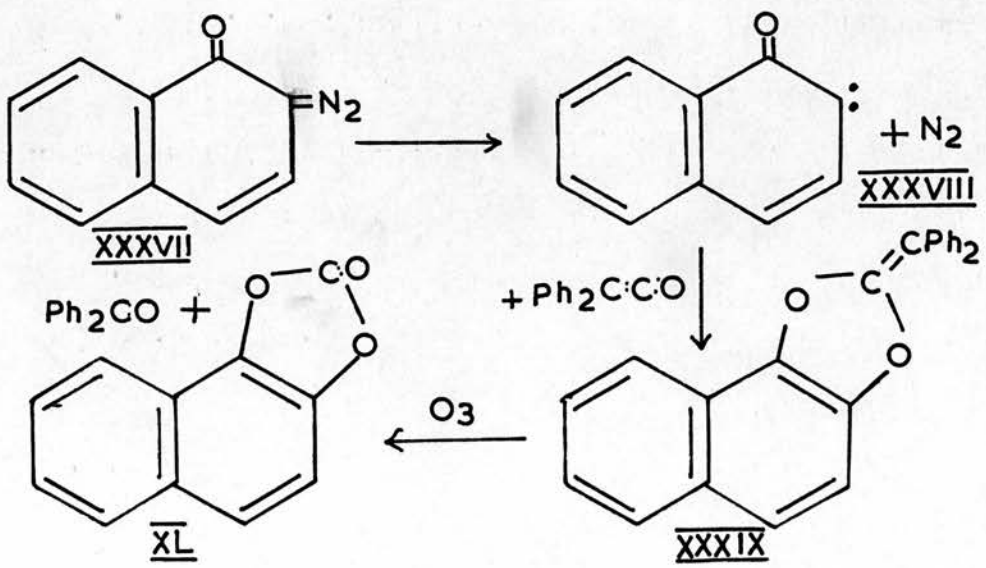
SCHEME E


CPh2
Ph2C:C:O
CHPh
I
Ph
Ph
O
Ph
Ph
H
Ph
XXXIIa
or
Ph
Ph
Ph
Ph
O
H
Ph
XXXIIb
Ph
Ph
O
CPh2
H
Ph
XXXIIIa
or
Ph
Ph
CPh2
O
H
Ph
XXXIIIb
Ph
Ph
C
H
H
C
H
Ph
X

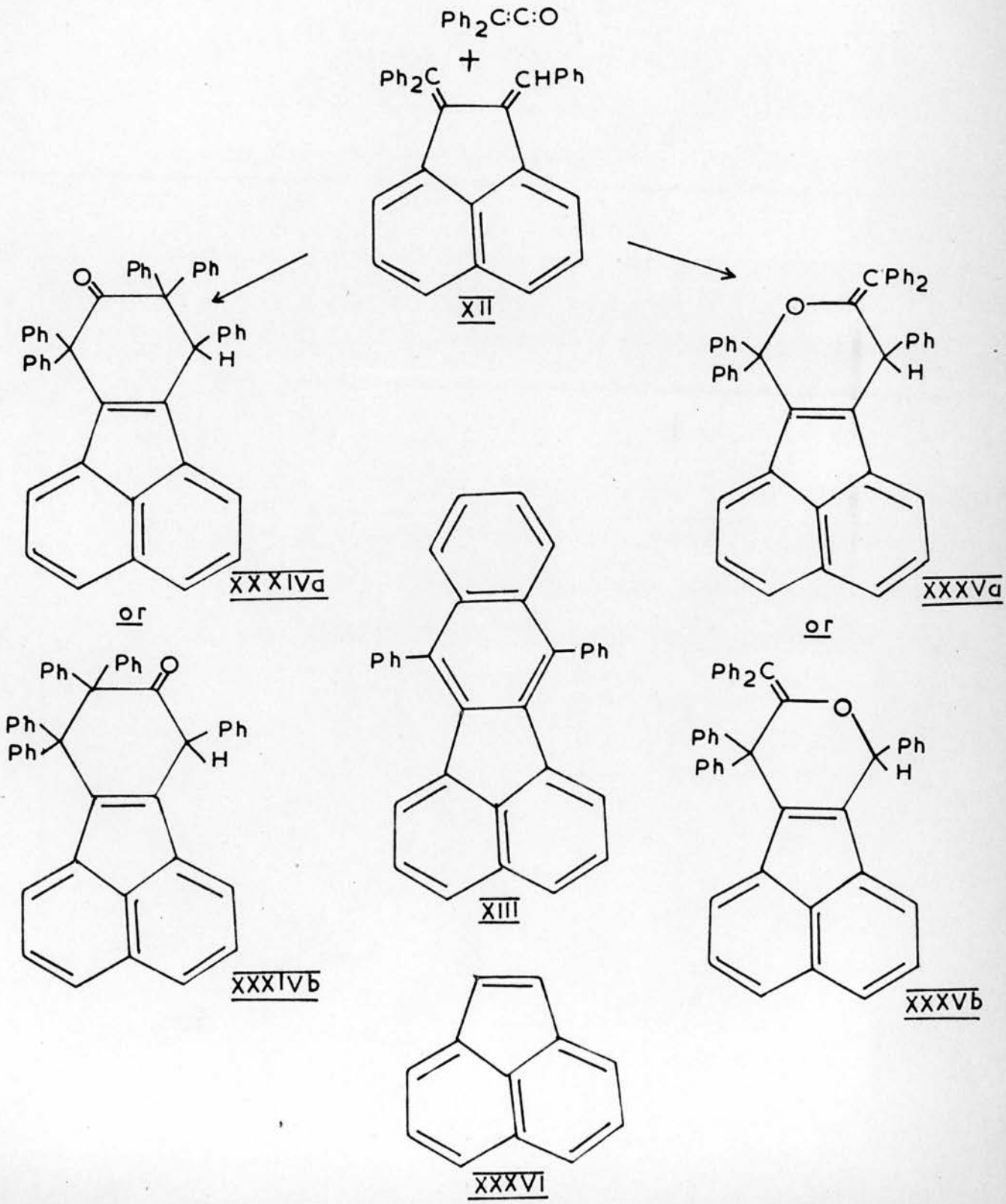
not show the characteristic carbonyl group absorption band between 1750 and 1650 cms^{-1} and it is suggested that this compound is an adduct of diphenylketene and compound XII having structure XXXVa or XXXVb. This suggestion is supported by the fact that ozonolysis of the compound gave benzophenone.

The reaction of diphenylketene with 1-diphenylmethylene-2-benzylidenehydrindene (I) or with 1-diphenylmethylene-2-benzylideneacenaphthene (XII) to give ethers, is further evidence of the diradical nature of these hydrocarbons.

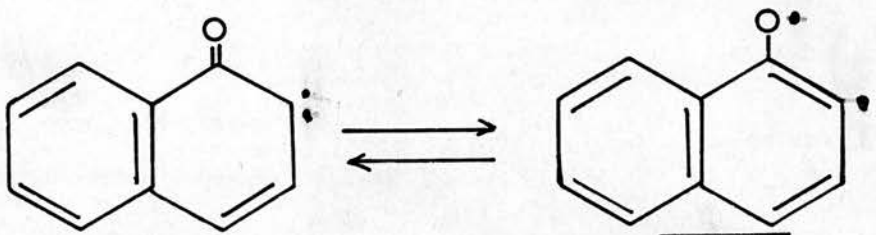
In a literature survey, the only reaction in which addition to diphenylketene has occurred across the carbonyl double bond and not across the ethylenic double bond, is the thermal decomposition of naphthalene-2:1-diazooxide (XXXVII) in the presence of diphenylketene to give 2-diphenylmethylene-naphtho-[1,2]-1:3-dioxole (XXXIX), which on ozonolysis gives 1,2-naphthalenediol carbonate (XL) and benzophenone[79].



SCHEME F

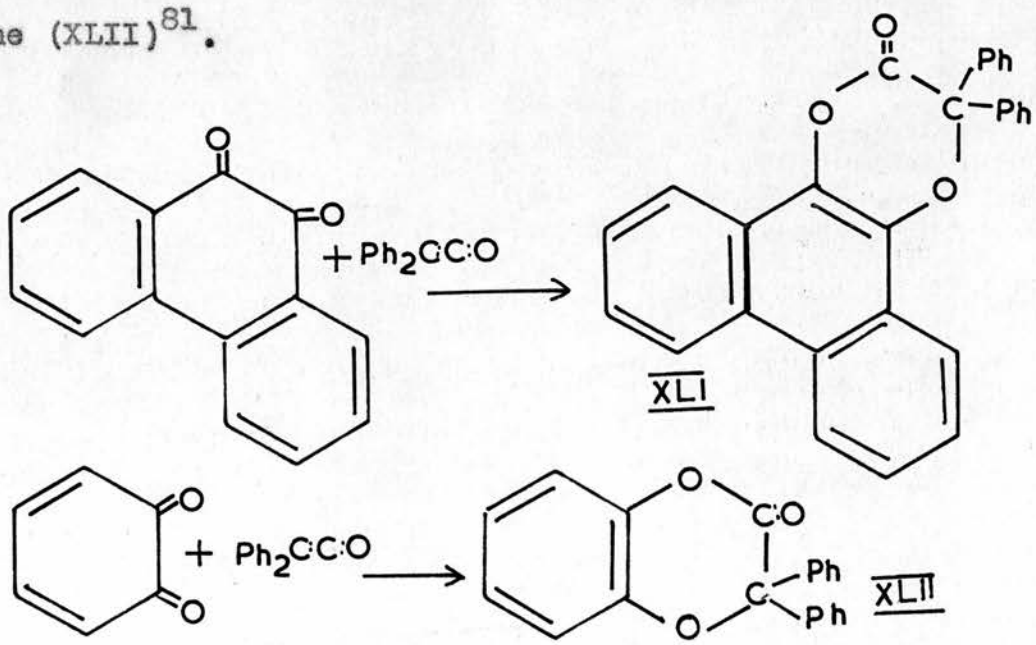

Ph2C:C:O
+
Ph2C
CHPh
XII
O
Ph
Ph
Ph
Ph
H
XXXIVa
or
Ph
Ph
O
Ph
Ph
Ph
H
XXXIVb
Ph
Ph
XIII
CPh2
O
Ph
Ph
Ph
H
XXXVa
or
Ph2C
O
Ph
Ph
Ph
H
XXXVb
XXXVI

It is possible that compound XXXVIII rearranges to the diradical XXXVIIIa and reacts with diphenylketene in this form.



XXXVIII XXXVIIIa

Schönberg and Mustafa[80] report that diphenylketene reacts with 9,10-phenanthrenequinone to give the adduct XLI m.p. 227-230°, but no conclusive evidence for this structure is given. Repetition of this work gave an adduct, m.p. 237°, showing a strong carbonyl band at 1780 cms^{-1} in the infrared spectrum, consistent with the structure XLI. It has been shown that diphenylketene undergoes an analogous reaction with o-benzoquinone to give o-hydroxyphenoxyacetic acid lactone (XLII)[81].



Introduction to Experimental

Melting-points were determined by the capillary tube method using an electrically heated melting-point apparatus.

Analyses were carried out by Drs. Weiler and Strauss, Oxford.

Infrared spectra were determined using a Perkin-Elmer Infrared Spectrophotometer. The intensity of absorption maxima are indicated by strong (s), medium (m) or weak (w). The group to which the absorption is attributed is written below the absorption wave number.

Ultraviolet spectra were determined using a Unicam SP 500 Spectrophotometer. Spectroscopic hexane was used as the solvent unless it is stated otherwise.

Type H alumina, supplied by Peter Spence and Sons, Ltd., was used in chromatography.

Experimental

Preparation of 1-hydrindone

Thiele and Wanscheidt, Ann., 1910, 376, 269.

Intramolecular cyclisation of β-phenylpropionyl chloride (47.5 g.) by aluminium chloride in light petroleum gave a 98% yield (37 g.) of the ketone, m.p. 40° (Lit. m.p. 40°).

Preparation of 2-benzylidene-1-hydrindone (VI)

W.H.Stafford, Ph.D. Thesis (Edin.), 1951, 319.

1-Hydrindone (20 g.) was condensed with benzaldehyde (16 g.) in ethanol (50 ml.) at 20-25° in the presence of 10% w.v. ethanolic potassium hydroxide (3 ml.).
Yield: 29 g., 87%. m.p. 110° (Lit. m.p. 110°[24]).

Ozonolysis of the ketone (0.3 g.) dissolved in hexane (25 ml.) and carbon tetrachloride (15 ml.), followed by steam distillation of the reaction mixture, gave an aqueous distillate having the characteristic odour of benzaldehyde, from which benzaldehyde was isolated as the 2:4-dinitrophenylhydrazone m.p. 238-240°. The mixed m.p. with an authentic sample was not depressed. The residual solution after steam distillation was evaporated to about 2 ml. and filtered hot. The filtrate gave colourless crystals of

homophthalic acid, m.p. 181°. The mixed m.p. with an authentic sample was not depressed.

Preparation of diphenylketene

Organic Syntheses, 1948, 20, 47.

206 g. benzil monohydrazone	200 g. yellow mercuric oxide
115 g. calcium sulphate	750 ml. benzene

Yield: 96 g., 54%, b.p. 106-8°/0.2 m.m.

Preparation of 1:1,2:4-tetraphenylbutadiene (IV)

Staudinger and Endle, Ann., 1913, 401, 271.

Benzylideneacetophenone (7 g.) and diphenylketene were heated under nitrogen in a sealed tube for 3½ hours at 140°. The product was treated with ether and the insoluble material recrystallised from acetone, giving the δ-lactone (1.2 g.), m.p. 194-5° (Lit. m.p. 190°).

Analysis

Found: C, 87.1; H, 5.8.

Calc. for $C_{28}H_{22}O_2$: C, 86.7; H, 5.5%.

Infrared spectrum (cms^{-1}) 1785(s), 1750(m), 1600(w).

(C:O)

The ether solution was evaporated and the residue crystallised from acetone, giving the butadiene (2.4 g.), m.p. 150° (Lit. m.p. 149-150°).

Analysis

Found: C, 93.5; H, 6.1.

Calc. for $C_{28}H_{22}$: C, 93.9; H, 6.1%.

Ultraviolet spectrum - Fig. 1.

The combined filtrates were evaporated to dryness. The residual oil was boiled with 10% w.v. ethanolic potassium hydroxide for one hour, poured into water and extracted with ether. On acidification, an oil separated from the aqueous layer, which solidified on standing and was crystallised from methanol, giving colourless plates, m.p. 147-9°. The mixed m.p. with diphenylacetic acid, m.p. 148°, was depressed to 115-125°. This acid may be 1:1,2-triphenyl-3-benzoyl-butyric acid, $Ph.CO.CH_2.CHPh.CPh_2.CO_2H$.

Analysis

Found: C, 81.8; H, 6.1.

Calc. for $C_{29}H_{24}O_3$: C, 82.8; H, 5.8%.

Infrared spectrum (cms^{-1})

3,400(m), 2,600(w), 1,680(s), 1,250(s), 755, 730, 712.
(free OH) (CO_2H)

Attempted preparation of 1-diphenylmethylene-2-benzylidene-hydrindene (I)

2-Benzylidene-1-hydrindone (VI) (4 g.) and diphenylketene (3.5 g.) were heated under nitrogen in a sealed tube for 3½ hours at 140°. The product was soluble in cold ether. The solvent was evaporated and the residual oil,

on treatment with ethanol gave a solid, m.p. 208-210°. The ethanolic filtrate was evaporated to dryness and the residual oil chromatographed on alumina. Development with light petroleum gave a fraction with a blue fluorescence in ultraviolet light from which a further quantity of solid, m.p. 208-210°, was obtained. Recrystallisation from benzene and light petroleum gave colourless plates, m.p. 220°.

Analysis (Pascher, Bonn)

Found: C, 93.8; H, 5.9.

$C_{28}H_{22}$ requires C, 94.0; H, 6.0%.

Ultraviolet spectrum - Fig. 1.

Preparation of 1-diphenylmethylene-2-benzylidene hydrindene

2-Benzylidene-1-hydrindone (VI) (10.3 g.) and diphenylketene (9.2 g.) were heated under nitrogen in a sealed tube for 3½ hours at 140°. On treatment of the product with ether, yellow crystals (A) (5.5 g.) were obtained. The ether solution on evaporation left a residue which on trituration with light petroleum gave yellow crystals (B)(3 g.). The combined filtrates were evaporated and the residual gum, which could not be induced to solidify, was boiled with 10% w.v. ethanolic potassium hydroxide for 1 hour. The solution was decanted from the tar formed. The aqueous alkaline solution was treated with hydrochloric acid giving diphenylacetic acid, needles from aqueous ethanol, m.p. 148°.

Solid A was boiled with light petroleum (200 ml.). The insoluble material was filtered off and recrystallised

from benzene and light petroleum, giving colourless prisms, m.p. 190°.

Analysis

Found: C, 87.0; H, 6.2.

C, 84.3; H, 5.8%.

Infrared spectrum (cms^{-1})

1705(s) (C:O) 1605(s) (C:C) 770, 765, 760, 750, 710.

The filtrate on cooling gave 1-diphenylmethylene-2-benzylidenehydrindene (3.8 g.) m.p. 139° (orange melt)

Analysis

Found: C, 93.8; H, 6.1.

$C_{29}H_{22}$ requires C, 94.0: H, 6.0%.

Ultraviolet spectrum - Fig. 2.

Solid B was difficult to purify. Repeated crystallisation from benzene and light petroleum gave the δ-lactone (V), colourless needles, m.p. 222°.

Analysis

Found: C, 87.2; H, 5.8.

C, 86.4; H, 5.4.

$C_{30}H_{22}O_2$ requires C, 86.9; H, 5.4%.

Ultraviolet spectrum - Fig. 6.

Infrared spectrum (cms^{-1}) 1775(s), 1670(w)

(C:O)

The combined filtrates from the crystallisations of the δ-lactone were evaporated. The residue was boiled with

ethanol and the insoluble solid crystallised from benzene and light petroleum, giving colourless prisms, m.p. 230°, considered to be the adduct XXXIIIa or XXXIIIb.

Analysis

Found: C, 89.8; H, 5.3.

$C_{42}H_{32}O$ requires C, 91.5; H, 5.7%.

Ultraviolet spectrum - Fig. 6.

Infrared spectrum (cms^{-1})

1630(w), 1600(w), 1210(m), 1180(m), 970(s), 760, 720, 700. (C:C).

From the ethanolic filtrate, compound I (1 g.) was obtained, m.p. 139°, after recrystallisation from isopropanol.

The ultraviolet spectrum of compound I changed with time and showed an isosbestic point at 275 mμ. (Fig. 2).

A solution of the hydrocarbon I (0.1 g.) in hexane (500 ml.) became colourless after two days. From the colourless solution, which had a blue fluorescence, colourless plates, m.p. 199°, were obtained, which were identified by mixed m.p. with an authentic sample as 1:4-diphenyl-2,3-benzofluorene (XIV).

Ozonolysis

Hydrocarbon I (0.1 g.) was dissolved in carbon tetrachloride (25 ml.) and a steady stream of ozone passed through the solution for 45 minutes until a pale yellow ozonide separated. Steam distillation of the reaction mixture

gave an aqueous distillate containing a small quantity of oil which crystallised three months later. The crystals melted at 48° and were shown to be crystals of benzophenone by mixed m.p. with an authentic sample and by characterisation as the 2:4-dinitrophenylhydrazone, m.p. 238°. No other product could be isolated.

Ozone was passed through a solution of the hydrocarbon (0.75 g.) dissolved in carbon tetrachloride (100 ml.) for 25 minutes until the solution became colourless. The reaction mixture was steam distilled. The aqueous distillate had the characteristic odour of benzaldehyde. The distillate was extracted with ether and the ether extracts were evaporated. The residual oil was oxidised with hot aqueous potassium permanganate, decolourised with sulphurous acid and evaporated to small volume. On cooling, benzoic acid separated in needles, m.p. 121°. No other product could be isolated.

Preparation of 1:1:4-triphenyl-2:2,3:3-tetracyano-1,2,3,4-tetrahydrofluorene (IX)

Compound I (0.25 g.) and tetracyanoethylene (0.08 g.) were boiled in benzene (10 ml.) for 4 hours. On cooling colourless needles of the adduct separated, which were crystallised from benzene. The adduct has no distinct m.p.

Analysis

Found: C, 84.2; H, 4.5; N, 10.8.

$C_{35}H_{22}N_4$ requires C, 84.3; H, 4.5; N, 11.2%.

Ultraviolet spectrum - Fig. 3.

Under similar conditions, 1:1:2:4-tetraphenylbutadiene (IV) did not give an adduct with tetracyanoethylene. Compound I and compound IV did not form adducts with maleic anhydride.

Preparation of 3-benzhydryl-2-benzylindene (X)

Compound I (0.2 g.) was dissolved in moist ether (50 ml.) and reduced with aluminium amalgam by Thiele's method[11] for three days. The reaction mixture was filtered and the filtrate evaporated. The residue was crystallised first from ethanol and then from light petroleum, giving colourless crystals, m.p. 115-6°.

Analysis

Found: C, 93.5; H, 6.5.

$C_{29}H_{24}$ requires C, 93.5; H, 6.5%.

Ultraviolet spectrum - Fig. 3.

Preparation of 1:4-diphenyl-2,3-benzofluorene (XIV)

Weiss and Beller, Monatsh. 1932, 61, 143.

2:5-Diphenyl-3,4-benzofuran (XVII) (2.5 g.) and indene (1.25 g.) were suspended in ethanol (30 ml.) and hydrogen chloride passed through the suspension for 1 hour. Yield: 2.8 g. 85%. m.p. 197-9°(after crystallisation from ethanol). (Lit. m.p. 199°).

Analysis

Found: C, 93.9; H, 5.9.

Calc. for $C_{28}H_{20}$: C, 94.5; H, 5.5%.

Ultraviolet spectrum - Fig. 2.

Preparation of 2-benzyl-1-hydrindone

cf. Mills and Akers, J., 1925, 2478.

Hydrogenation of 2-benzylidene-1-hydrindone (VI) (11 g.) in ethanol (100 ml.) with hydrogen at 5 atmos. and palladium on barium sulphate gave benzylhydrindone in 78% yield (8.7 g.), b.p. 206°/12 m.m.

Analysis

Found: C, 86.3; H, 6.3.

Calc. for $C_{16}H_{14}O$: C, 86.4; H, 6.3%.

Ultraviolet spectrum λmax. 283, 240 mμ. ($\log_{10}\epsilon$ 3.52, 4.25)

λmin. 260, 220 mμ. ($\log_{10}\epsilon$ 3.06, 3.89)

Semicarbazone m.p. 199° (Lit. m.p. 198-9°)

2:4-Dinitrophenylhydrazone m.p. 196-7°.

Preparation of 2-benzyl-1-hydroxyhydrindene

2-Benzyl-1-hydrindone (10.1 g.) was added to a solution of aluminium isopropoxide, prepared by dissolving aluminium turnings (4 g.) in isopropanol (80 ml.) in the presence of mercuric chloride (0.2 g.) and carbon tetrachloride (0.8 ml.), and the reaction mixture boiled for 4 hours. The acetone formed was allowed to distil off. Most of the solvent was

evaporated and the residual solution acidified with hydrochloric acid and extracted with ether. The ether extracts were washed with water, dried over sodium sulphate, filtered and the solvent evaporated. The residual oil crystallised from light petroleum in colourless needles (8.2 g.), m.p. 104-5°, 81% yield.

Analysis

Found: C, 85.9; H, 7.4.

$C_{16}H_{16}O$ requires C, 85.7; H, 7.2%.

Preparation of 2-benzylindene

Dehydration of 2-benzyl-1-hydroxyhydrindene (7 g.) with formic acid gave 2-benzylindene (3 g.), b.p. 116°/0.05 m.m., m.p. 48°, 45% yield.

Analysis

Found: C, 92.8; H, 6.8.

$C_{16}H_{14}$ requires C, 93.2; H, 6.8%.

Ultraviolet spectrum - Fig. 3.

Preparation of 1-diphenylmethylene-2-benzylindene (II)

cf. Courtot, Ann. Chim. 1916, 5, 65.

2-Benzylindene (2.06 g.) dissolved in toluene (8 ml.) and ether (4 ml.) was added to a solution of ethylmagnesium bromide, prepared from ethyl bromide (0.8 ml.) in ether (30 ml.) and magnesium (0.25 g.). The ether was distilled off and the toluene solution boiled for 5 hours. The

solution was cooled and a solution of benzophenone (1.8 g.) in ether (20 ml.) was added. The reaction mixture was boiled for 30 minutes, poured on a mixture of ice and dilute hydrochloric acid and extracted with ether. The organic layer was separated, the solvent evaporated and the residual oil heated with formic acid (10 ml.) for 1 hour at 100°. An orange oil was produced. The reaction mixture was poured into water, extracted with ether and the ether extracts washed with sodium carbonate solution. The dried ether extracts were evaporated and the residual oil, dissolved in a small volume of benzene, chromatographed on alumina and developed with light petroleum.

2-Benzylidene (0.5 g.) was recovered from the colourless first fraction. The orange fraction was evaporated and the residue was crystallised from ethanol, giving golden hexagonal prisms, m.p. 126°.

Analysis

Found: C, 94.2; H, 6.0.

$C_{28}H_{22}$ requires C, 94.0; H, 6.0%.

Ultraviolet spectrum - Fig. 4.

Thiele reduction of a sample of compound II with aluminium amalgam in moist ether gave 3-benzhydryl-2-benzylindene (X), m.p. 115-116°, identical with the product obtained by a similar reduction of 1-diphenylmethylene-2-benzylidenehydrindene (I).

An attempt to prepare compound II by boiling equimolecular proportions of benzophenone and indene in ethanolic sodium ethoxide for 10 hours was unsuccessful. Only resinous materials were isolated.

Preparation of β-phenylisovaleric acid

Koelsch and Le Claire, J. Org. Chem. 1941, 6, 525.

Oxidation of 4-methyl-4-phenylpentan-2-one (35 g.), prepared in 45% yield by the dropwise addition of mesityl oxide to benzene containing aluminium chloride at below 10°, with 3.3 N sodium hypochlorite solution (400 ml.) gave a 38% yield (13.4 g.) of β-phenylisovaleric acid, b.p. 158-162°/10 m.m. (Lit. b.p. 155°/10 m.m.).

Preparation of 3:3-dimethyl-1-hydrindone

Koelsch and Le Claire, J. Org. Chem. 1941, 6, 525.

β-Phenylisovaleryl chloride (9.9 g.), prepared by heating the acid with thionyl chloride, was cyclised by aluminium chloride (10 g.) in benzene (50 ml.), giving the ketone in 53% yield (4.3 g.), b.p. 110°/8 m.m. 2:4-Dinitrophenylhydrazone m.p. 270°.

Analysis

Found: N, 15.9. $C_{17}H_{16}N_4O_4$ requires N, 16.5%.

Preparation of 3:3-dimethyl-2-benzylidene-1-hydrindone

A solution of 3:3-dimethyl-1-hydrindone (4 g.), benzaldehyde (2.7 g.) and potassium hydroxide (1 g.) in ethanol (20 ml.), was boiled for 15 minutes and poured into water. The oil which separated, crystallised on standing and was recrystallised from light petroleum, giving pale yellow crystals (1.1 g.), m.p. 79-80°, 18% yield.

Analysis

Found: C, 86.9; H, 6.3.

$C_{18}H_{16}O$ requires C, 87.1; H, 6.5%.

Infrared spectrum (cms^{-1}) 1700(s) (C:O) 1620(s) (C:C) 1580(m) 1320(m) ($C(CH_3)_2$)

The 2:4-dinitrophenylhydrazone crystallised from acetic acid in orange needles and crimson plates.

Analysis

Found: N, 12.9. $C_{24}H_{20}N_4O_4$ requires N, 12.6%.

Preparation of 1-diphenylmethylene-2-benzylidene-3:3-dimethylhydrindene (III).

3:3-Dimethyl-2-benzylidene-1-hydrindone (0.76 g.) and diphenylketene (0.59 g.) were heated under nitrogen in a sealed tube for 3 hours at 158°. The reaction mixture was dissolved in a small quantity of ether and chromatographed on alumina. Development with light petroleum gave an orange fraction which was evaporated. The residue crystallised from benzene and light petroleum in colourless needles, m.p. 223°, which gave yellow solutions in organic solvents.

Analysis

Found: C, 93.3; H, 6.6.

$C_{31}H_{26}$ requires C, 93.4; H, 6.6%.

The benzene and light petroleum mother liquor deposited colourless plates on standing, which on recrystallisation from ethanol melted at 230°. This substance was shown to be 1:4-diphenyl-9:9-dimethyl-2,3-benzofluorene (XVI) by mixed m.p. with an authentic sample.

The hydrindene (III) underwent ring-closure with spontaneous dehydrogenation in hexane solution to give the benzofluorene (XVI).

Preparation of 1:4-diphenyl-9:9-dimethyl-2,3-benzofluorene (XVI)

3:3-Dimethyl-1-hydrindone (5.2 g.) was reduced by aluminium isopropoxide in isopropanol as is described on p. 3:3-Dimethyl-1-hydroxyhydrindene could not be induced to crystallise.

Infrared spectrum (cms^{-1}) 3,300(s) (OH) 1355(m) ($C(CH_3)_2$)

On heating the crude alcohol with formic acid (5 ml.) for 1 hour at 100°, esterification and not dehydration was the main reaction. The formate was an oil with a characteristic odour, b.p. 60-70°/0.5 m.m. It reduced ammoniacal silver nitrate to give a silver mirror.

Analysis

Found: C, 79.3; H, 7.9.

$C_{18}H_{14}O_2$ requires C, 75.8; H, 7.4%.

Infrared spectrum (cms^{-1}) 1720(s) (C:O) 1350(m) ($C(CH_3)_2$) 1175(s) (formate)

The ester (1 g.) and 2:5-dimethyl-3,4-benzofuran (XVII (1 g.) were suspended in ethanol (10 ml.) and hydrogen chloride was passed through the suspension for 1 hour. The product (XVII) on crystallisation from ethanol and re-crystallisation from light petroleum gave colourless plates, m.p. 230°.

Analysis

Found: C, 93.3; H, 6.9.

$C_{31}H_{24}$ requires C, 93.8, H, 6.1%.

Ultraviolet spectrum - λmax. 322, 308, 272, 260 mμ.($\log_{10}\epsilon$ 4.41), 4.36, 4.87, 4.70)

λmin. 315, 293, 265, 240 mμ.($\log_{10}\epsilon$ 4.22, 4.05, 4.69, 4.51)

Attempted preparation of 1-diphenylmethylene-2-benzylidene hydrindene (I) by the Wittig reaction

cf. Coffman and Marvel, J. Amer. Chem. Soc., 1929, 51, 3499.
Harrison, Lythgoe and Tripett, J., 1955, 4016.
Wittig and Schollkopf, Ber., 1954, 87, 1326.

Benzhydryl triphenylposphonium bromide was prepared by boiling a solution of triphenylphosphine (13.1 g.) and benzhydryl bromide (13 g.) in acetone (60 ml.) for 4 hours. The solvent was evaporated. The residue was ground in a mortar and boiled in benzene to remove impurities. Yield: 20 g.

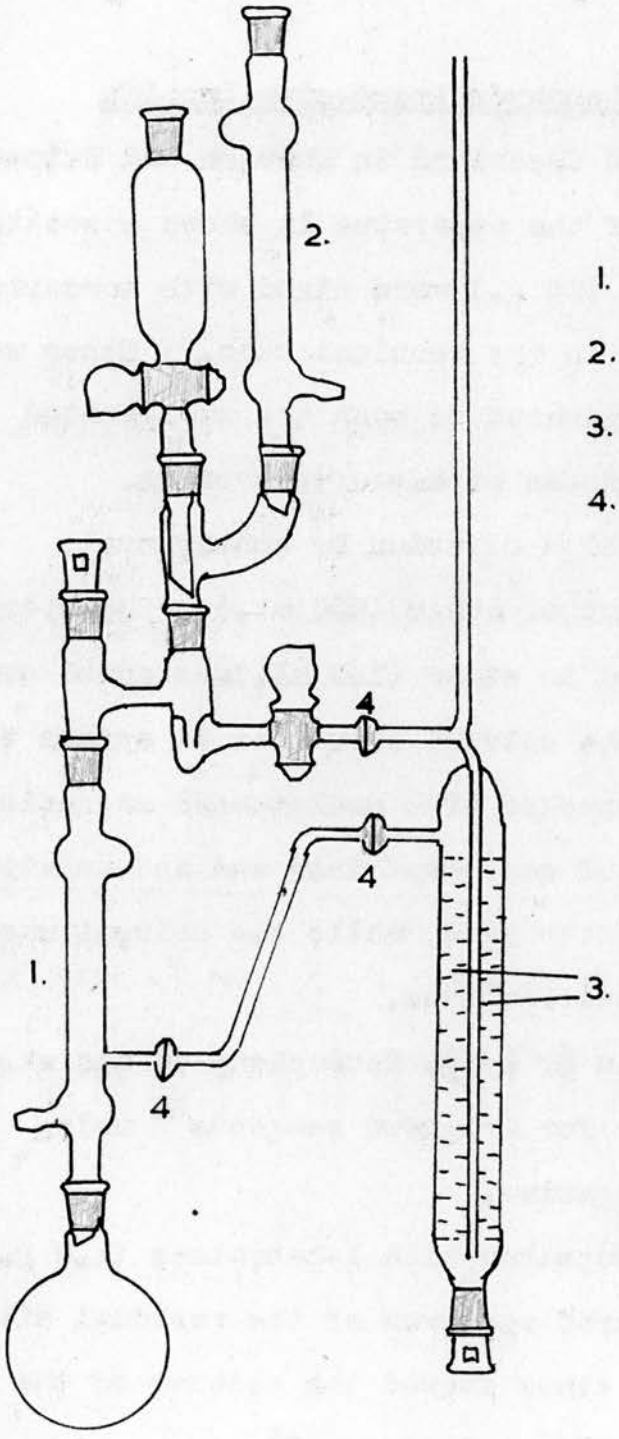
91%, m.p. 277-281° (Lit. m.p. 280°).

A solution of phenyl lithium was prepared by adding finely sliced lithium (3 g.) to bromobenzene (32 g.) dissolved in ether (100 ml.) in an atmosphere of nitrogen. The reaction mixture was boiled for 1 hour and filtered through a sintered glass filter in an atmosphere of nitrogen. The solution was standardised against 1 N hydrochloric acid.

The quaternary compound (11 g. 0.022 M) was suspended in ether (50 ml.) and phenyl-lithium solution (50 ml. 0.035 M) added. The reaction mixture turned bright red. The ether solvent was replaced by benzene (100 ml.) and the hot benzene solution was filtered in an atmosphere of nitrogen to remove lithium bromide. The filtrate deposited bright red needles of triphenylphosphinediphenylmethylene (XIX) on cooling.

2-Benzylidene-1-hydrindone (VI) (4 g. 0.018 M) dissolved in benzene (50 ml.) was added to the suspension of the phosphinemethylene (XIX). The reaction mixture was boiled for 3 hours in an atmosphere of nitrogen. The phosphinemethylene redissolved giving a red solution but no reaction was apparent. The red colour of the solution was expected to disappear as the phosphinemethylene reacted. The reaction mixture was poured into water. The organic layer was separated, washed with water, dried over sodium sulphate, filtered and the filtrate was evaporated leaving a dark yellow oil from which 2-benzylidene-1-hydrindone (2-4 g.)

DIAGRAM I. THE CYCLIC REACTOR



1. Coil Condenser
2. Double Surface Condenser
3. Amalgamated Magnesium
4. Ball Joints

was recovered on trituration with ethanol. The ethanol mother liquors were evaporated, leaving a yellow oil with a disagreeable odour.

Attempted preparation of benzhydrylmagnesium bromide

A cyclic reactor, as described in Kharash and Reinmuth[61], was set up. A diagram of the apparatus is shown opposite.

Magnesium turnings (25 g.) were mixed with mercuric bromide (5 g.) and packed in the vertical tube. Ether was circulated through the apparatus to wash the amalgamated magnesium free from the excess of mercuric bromide.

The system attains high dilution by continuously recycling an initial amount of ether (250 ml.). Benzhydryl bromide (7.4 g.) dissolved in ether (150 ml.)was added over a period of 16 hours to the solvent stream as it enters the top of the vertical tube packed with amalgamated magnesium. The Grignard reagent formed was swept into and accumulated in a flask, heated on a water bath, while the solvent was refluxed back into the reaction tube.

A quantitative yield of symm. tetraphenylethane was obtained. Gilman's test for Grignard reagents[62] using Mischler's ketone, was negative.

The reaction was repeated with 1-tetralone (1.5 g.) in the flask. The infrared spectrum of the residual oil after evaporation of the ether showed the absence of the characteristic hydroxyl band at 3,400 cms^{-1}.

Preparation of diphenylbenzofulvanol

Courtot, Ann. Chim., 1916, 5, 65.

Indene (116 ml.) dissolved in toluene (300 ml.) was added to a solution of ethylmagnesium bromide, prepared from ethyl bromide (75 ml.) in ether (300 ml.) and magnesium (24 g.). The ether was distilled off and the toluene solution boiled for 3 hours. The solution was cooled to 10° and a solution of benzophenone (175 g.) in ether (200 ml.) was added over a period of 1 hour. The reaction mixture was boiled for 2 hours, poured into dilute hydrochloric acid and extracted with ether. The organic layer was separated, washed with dilute sodium carbonate solution and the dried solution evaporated, leaving colourless crystals (175 g.) of the fulvanol. A sample was recrystallised from ethanol, giving prisms, m.p. 130° (Lit. m.p.131-2°).

Dehydration of a sample with formic acid gave 1-diphenylmethyleneindene, m.p. 115-116°, after crystallisation from ethanol (Lit. m.p. 116°).

Preparation of 1-diphenylmethylenehydrindene

cf. Courtot, Ann. Chim., 1916, 5, 65.

Hydrogenation of diphenylbenzofulvanol (29.8 g.) in ethanol (250 ml.) with hydrogen at 5 atmos. and Raney nickel, resulted in a theoretical uptake of hydrogen within 15 minutes. The dihydrobenzofulvanol crystallised from isopropanol in colourless prisms (23.5 g.), m.p. 85° (Lit. m.p. 90°), 78% yield.

Analysis

Found: C, 88.0; H, 6.8.

Calc. for $C_{22}H_{20}O$: C, 88.0; H, 6.7%.

On boiling a solution of diphenyldihydrobenzofulvanol (9 g.) in ethanol (40 ml.) and hydrochloric acid (10 ml.) for 5 minutes, dehydration of the fulvanol occurred and on cooling to 5° a sticky solid separated which on crystallisation from methanol (200 ml.) gave 1-diphenylmethylenehydrindene (XXI) (6.6 g.), m.p. 92° (Lit. m.p. 92°), 77% yield.

Attempted preparation of 1-diphenylmethylene-2-bromohydrindene (XXII)

On warming 1-diphenylmethylenehydrindene (XXI) (1.42 g.) and N-bromosuccinimide (0.89 g.) in carbon tetrachloride (10 ml.), a vigorous reaction occurred with the evolution of hydrogen bromide and the reaction mixture turned orange. It was filtered and the filtrate was evaporated, leaving a quantitative yield of crude 1-diphenylmethyleneindene (XV), which was purified by chromatography on alumina. Recrystallisation from ethanol gave bright yellow needles, m.p. 114-5° (Lit. m.p. 116°).

Ultraviolet spectrum - Fig. 4.

Preparation of 3-benzhydrylindene

Thiele and Merck, Ann., 1918, 415, 267.

1-Diphenylmethyleneindene (1 g.) dissolved in moist ether (40 ml.) was reduced with aluminium amalgam for 30 hours. The reaction mixture was filtered and the filtrate evaporated. The residual oil was crystallised from ethanol giving colourless crystals (0.6 g.), 59% yield, m.p. 112-3° (Lit. m.p. 113-114°).

Ultraviolet spectrum - Fig. 3.

Ozonolysis of the adduct of diphenylketene and 1-diphenylmethylene-2-benzylideneacenaphthene, considered to have structure XXXVa or XXXVb

The adduct (0.1 g.) was dissolved in ethyl acetate (25 ml.) and carbon tetrachloride (25 ml.) and ozone passed through the solution for 30 minutes. Within 15 minutes the yellow solution became colourless. The solution was steam distilled and the aqueous distillate extracted with ether. The ether extract, on evaporation, left an oil which was identified as benzophenone by characterisation as the 2:4-dinitrophenylhydrazone, m.p. 238°. The mixed m.p. with a sample of benzophenone 2:4-dinitrophenylhydrazone was not depressed. No other product could be isolated.

Preparation of 10-(9-hydroxyphenanthryloxy)-diphenylacetic acid lactone (XLI)

cf. Schönberg and Mustafa, J., 1947, 997.

Diphenylketene (2 g.) and 9,10-phenanthrenequinone (1 g.) in benzene (30 ml.) were left in bright sunlight for 3 days. The quinone gradually dissolved and from the brown solution a solid separated, which was crystallised from benzene, giving colourless needles, m.p. 237° (yellow melt) (Lit. m.p. 227-230°).

Analysis

Found: C, 83.5; H, 4.5.

Calc. for $C_{28}H_{18}O_3$: C, 83.6; H, 4.5%.

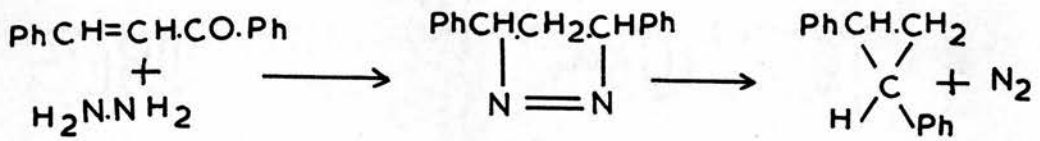
Infrared spectrum (cms^{-1}) 1780(s) (C:O) 1650(w) 1600(w) (C:C)

Section 2

The Conversion of 2-Benzylidene-3-carboxy-1-hydrindone into 2-Phenylnaphthalene Derivatives

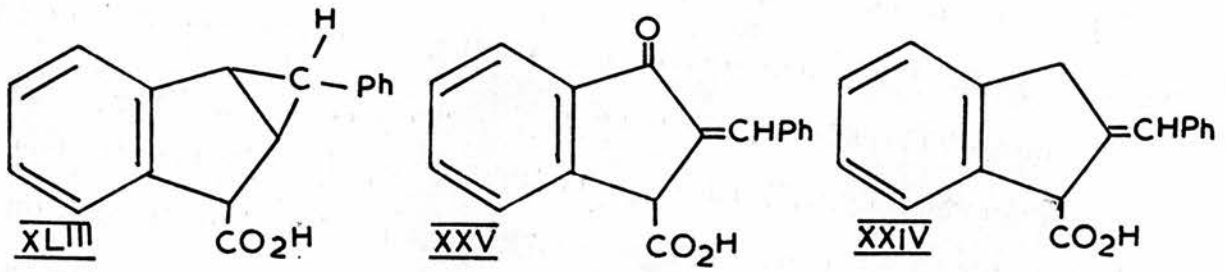
Discussion

The reduction of the carbonyl group to the methylene group through the hydrazone was discovered in 1911 by Kishner[82] and by Wolff[83] in 1912. The reaction, which involves heating the ketone with 100% hydrazine hydrate in the presence of sodium ethoxide in ethanol in a sealed tube is difficult to carry out and safety measures are necessary. In the Huang-minlon modification[84] the carbonyl compound is heated with potassium hydroxide and hydrazine hydrate in a high boiling solvent such as ethylene glycol. Wolff-Kishner reduction of αβ-unsaturated ketones frequently gives either hydrocarbons or cyclopropane derivatives through an intermediate pyrazoline and the Huang-minlon modification of this method yields chiefly cyclopropane derivatives[85]. For example[86], the reduction of benzylideneacetophenone by the Huang-minlon modification gives 1,2-diphenylcyclopropane in 86% yield.



It seemed unlikely that reduction of 2-benzylidene-3-carboxy-1-hydrindone (XXV) would give the cyclopropane derivative (XLIII), as ring strain in the cyclopropane derivative would be considerable and it was hoped that reduction of the keto group would occur to give 2-benzyli-

denehydrindene-1-carboxylic acid (XXIV).



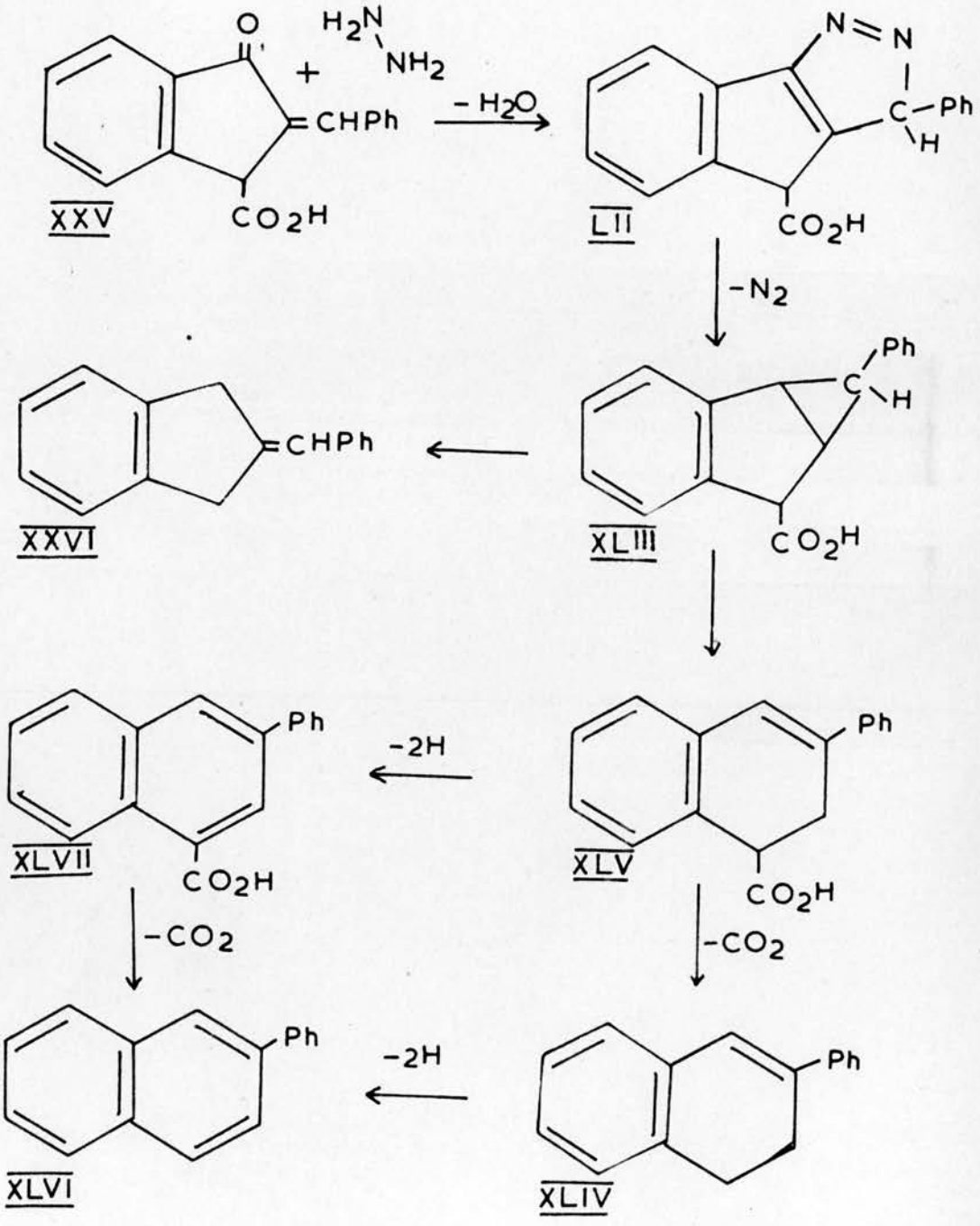
XLIII XXV XXIV

Attempted Wolff-Kishner reduction of the keto acid (XXV) by the Huang-minlon modification gave three products, 1,2-dihydro-3-phenylnaphthalene (XLIV), 1,2-dihydro-3-phenylnaphthalene-1-carboxylic acid (XLV) and a hydrocarbon, m.p. 30°, considered to be 2-benzylidenehydrindene (XXVI) because it differs from the isomeric 2-benzylindene and its ultraviolet spectrum (Fig. 8) indicates that the compound contains a phenyl-conjugated double bond.

The structure of 1,2-dihydro-3-phenylnaphthalene (XLIV) whose m.p. 52° rises to 65-66° when this substance is kept in air or is repeatedly crystallised, was established by dehydrogenation to 2-phenylnaphthalene (XLIV) with N-bromosuccinimide, by mixed m.p. with an authentic sample[87], by characterisation as the trinitrobenzene derivative and by the similarity of its ultraviolet spectrum to that of trans-stilbene (Fig. 8).

The structure of 1,2-dihydro-3-phenylnaphthalene-1-carboxylic acid (XLV) was established by dehydrogenation

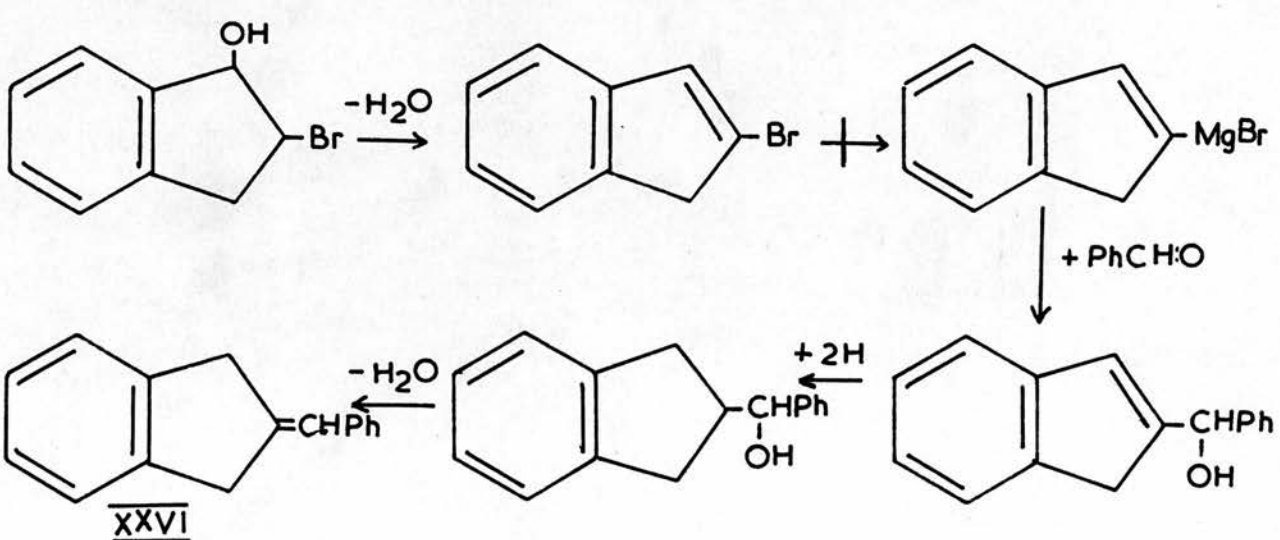
SCHEME G


O
H_2N
NH_2
+
CHPh
$-H_2O$
XXV
CO_2H
N≡N
C
Ph
H
LII
CO_2H
$-N_2$
Ph
C
H
XLIII
CO_2H
CHPh
XXVI
Ph
XLV
CO_2H
Ph
XLIV
Ph
$-2H$
XLVII
CO_2H
$-CO_2$
$-CO_2$
Ph
$-2H$
XLVI

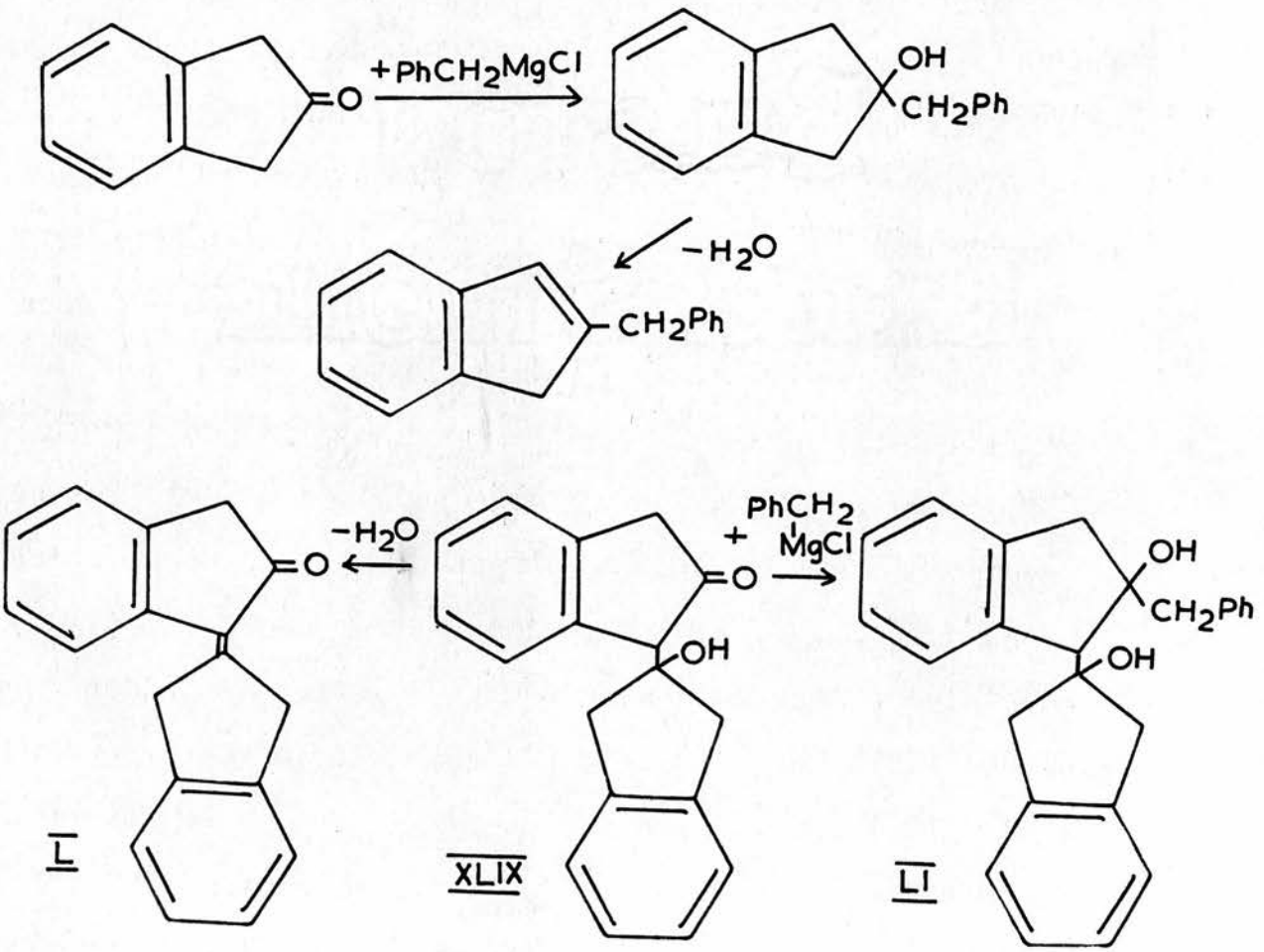
with chloranil to 3-phenyl-1-naphthoic acid (XLVII) and by the similarity of its ultraviolet spectrum to those of 1,2-dihydro-3-phenylnaphthalene (XLIV)(Fig. 9) and trans-stilbene (Fig. 8). Decarboxylation of the acid by heating in 4-methylquinoline and copper bronze gave 2-phenylnaphthalene (XLVI) in nearly quantitative yield in contrast to the 60% yield of naphthalene, obtained from 1-naphthoic acid under the same conditions. 2-Phenylnaphthalene (XLVI) was identified by mixed m.p. with an authentic sample[87].

Attempts to synthesise 2-benzylidenehydrindene (XXVI) by an alternative route, to confirm the identity of compound m.p. 30°, were unsuccessful.

Despite the fact that Porter and Suter[8] report the preparation of indene-2-carboxylic acid from 2-bromoindene through the Grignard derivative, the Grignard derivative could not be induced to form, so that the following scheme of reactions could not be completed.



A further attempt to prepare 2-benzylidenehydrindene (XXVI) by the dehydration of 2-benzyl-2-hydroxyhydrindene (XLVIII) was unsuccessful, since on dehydration of the hydroxy compound (XLVIII) only 2-benzylindene was obtained. In the preparation of benzylhydroxyhydrindene (XLVIII) by the interaction of 2-hydrindone and benzylmagnesium chloride, according to the conditions of the experiment, other products included 1-(2-hydroxyhydrinden-2-yl)-2-hydrindone (XLIX), bis-anhydro-2-hydrindone (L) and the compound (LI) formed from the ketone (XLIX) and the Grignard derivative.

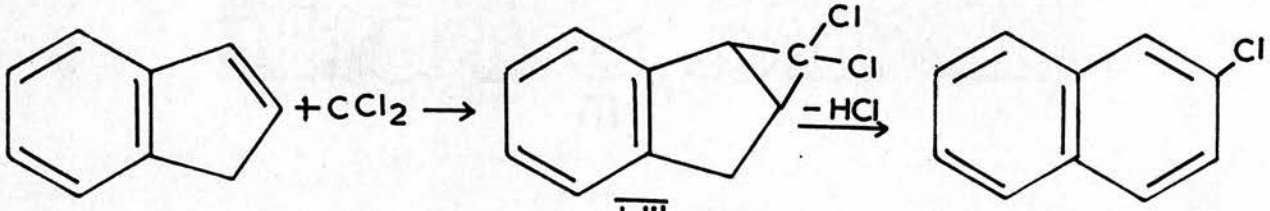


An analogous series of products was obtained by Koelsch and Johnston[12] by the interaction of 2-hydrindone with methyl-magnesium bromide.

2-Hydrindone undergoes self-condensation in the presence of methanolic ammonia to give compound XLIX[64].

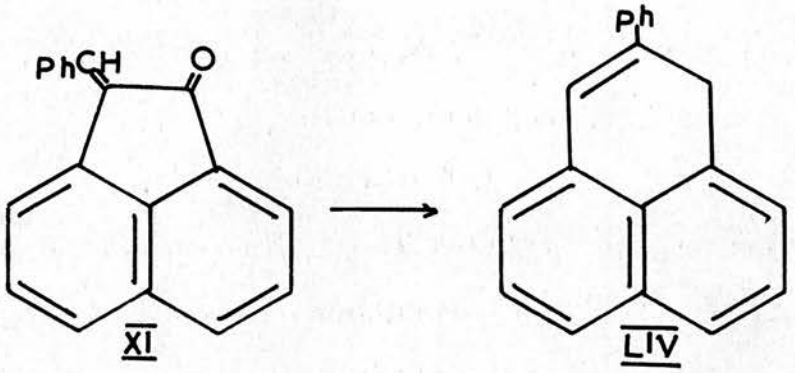
It is probable that 2-benzylidene-3-carboxyhydrindone (XXV) forms the pyrazoline (LII), which loses nitrogen to give 2-benzylidenehydrindene (XXVI) or the cyclopropane derivative (XLIII), the ring strain of which is relieved by rearrangement to a dihydronaphthalene (see scheme G).

This mechanism is supported by the fact that indene reacts with dichlorocarbene to give the cyclopropane derivative (LIII), which can be converted in almost quantitative yield into 2-chloronaphthalene[89, 90].



LIII

The conversion of 2-benzylidene-3-carboxy-1-hydrindone (XXV) to phenylnaphthalene derivatives suggests that it might be possible to evolve a general method of ring enlargement of monosubstituted 2-methylene cyclic ketones by Wolff-Kishner reduction. For example, it might be possible to convert 2-benzylideneacenaphene-1-one (XI) to 2-phenylperinaphthene (LIV) by this method.



XI LIV

Unfortunately many benzylidene ketones dimerise in strongly alkaline solution. By conversion of the ketones first to the pyrazoline and then decomposition of the pyrazoline in the presence of alkali, dimerisation of the ketone might be avoided. On heating the pyrazoline of 2-benzylidene-1-hydrindone with potassium hydroxide in ethylene glycol, only polymeric material could be isolated. Despite the failure of this preliminary experiment, ring enlargement might be possible under different experimental conditions.

Experimental

Preparation of 1-hydrindone-3-carboxylic acid

Vargha et al., Acta Chim. Acad. Hung., 1954, 5, 116.

Phenylsuccinic acid (110 g.) and phosphorus pentachloride (220 g.) were mixed. When the exothermic reaction had subsided, the reaction mixture was heated at 100° for 1 hour and then the phosphorus oxychloride distilled off under reduced pressure.

Anhydrous aluminium chloride (110 g.) dissolved in nitrobenzene (250 ml.) was added to the acid chloride dissolved in nitrobenzene (50 ml.). An exothermic reaction set in and a vigorous evolution of hydrogen chloride occurred. When the initial reaction was over, the reaction mixture was heated at 100° for 1½ hours and the hot solution poured into dilute hydrochloric acid (1½ l.) and steam distilled. When all the nitrobenzene had been removed, the aqueous solution was decanted from tar formed, boiled with charcoal (5 g.) and filtered. On cooling, the product crystallised in colourless plates.

Yield: 48 g. 48%. m.p. 83-4° (Lit. m.p. 83-5°)

Infrared spectrum (cms^{-1})

3,500(m)	2,700(m)	1,720(s)	1,700(s)	1,600(m)	1,250(m)
(OH)	(OH)	(C=O)	(C=O)	(C=C)	(CO_2H)

Preparation of 2-benzylidene-3-carboxy-1-hydrindone (XXV)

1-Hydrindone-3-carboxylic acid (17.6 g.) and benzaldehyde (16 ml.) were dissolved in ethanol (40 ml.). The solution was heated to boiling and 10% w.v. ethanolic potassium hydroxide (100 ml.) added gradually. After the addition of 90 ml., the solution turned from yellow to green. The reaction mixture was boiled for 5 minutes, cooled and filtered. The insoluble residue was rejected. The filtrate was acidified with hydrochloric acid, causing an oil to separate, which solidified on standing. The product was boiled with benzene to remove soluble impurities.
Crude yield: 17.5 g., 66.5%. m.p. 160-3°.
A sample was crystallised from hot benzene (solubility 1 g. in 100 ml. benzene) giving colourless prisms, m.p. 169-170°. Its ultraviolet spectrum (Fig. 7) resembled that of benzylideneacetophenone.

Analysis

Found: C, 77.1; H, 4.5.

$C_{17}H_{12}O_3$ requires C, 77.25; H, 4.6%.

Infrared spectrum (cms^{-1})

2700(w)	1710(s)	1700(s)	1620(s)	1600(m)	1250(s)
(OH)	(C:O)	(C:O)	(C:C)	(C:C)	(CO_2H)

Hydrogenation with hydrogen at 5 atmos. and palladium on barium sulphate gave 2-benzyl-3-carboxy-1-hydrindone colourless needles, m.p. 114-5° after recrystallisation from

benzene and light petroleum. Its ultraviolet spectrum (Fig. 7) resembled that of w-benzylacetophenone.

Analysis

Found: C, 76.8; H, 5.3.

$C_{17}H_{14}O_3$ requires C, 76.8; H, 5.3%.

Infrared spectrum (cms^{-1})

2,700(w)	1,710(s)	1,695(s)	1,600(m)	1,240(s)
(OH)	(C:O)	(C:O)	(C:C)	(CO_2H)

Wolff-Kishner reduction of 2-benzylidene-3-carboxy-1-hydrindone (XXV)

The keto-acid (XXV) (7.92 g.), potassium hydroxide, 99% hydrazine hydrate (4 ml.) and ethylene glycol (40 ml.) were heated gradually to 180° during 1 hour and then boiled for 1½ hours at 195-200° after the water produced and the hydrazine hydrate had been distilled off. The mixture was poured into water, the resulting oil extracted with benzene and washed with 10% w.v. sodium hydroxide and then with water. The extract was dried over sodium sulphate, filtered and the filtrate evaporated. The residual oil was fractionally distilled, to give an oil (3.8 g.) which yielded 1,2-dihydro-3-phenylnaphthalene plates from methanol, m.p. 52°.

Analysis

Found: C, 92.9; H, 6.6.

Calc. for $C_{16}H_{14}$: C, 93.2; H, 6.8%.

Ultraviolet spectrum - Fig. 8.

Repeated crystallisation from ethanol raised the m.p. to 58° giving a mixed m.p. of 58-60° with a sample m.p. 65-66° which had been kept in a stoppered bottle for several years. Both samples, m.p. 58° and 65-66°, gave a trinitrobenzene derivative, m.p. 110-111°, while dehydrogenation of the first-named sample (0.69 g.) by boiling it for 15 minutes with N-bromosuccinimide (0.6 g.) in carbon tetrachloride (20 ml.) gave 2-phenylnaphthalene (XLVI) in 70% yield, m.p. and mixed m.p. 99° after crystallisation from methanol.

In a second experiment, the oil was fractionally distilled, giving two main fractions, b.p. 126-8°/0.5 m.m. and 134-142°/0.5 m.m., the second fraction yielding impure 1,2-dihydro-3-phenylnaphthalene (XLIV). The first fraction (2.17 g.) in ethanol with trinitrobenzene (2.9 g.) gave the adduct of 1,2-dihydro-3-phenylnaphthalene (2.3 g.), m.p. and mixed m.p. 110-111°. The ethanolic filtrate was evaporated giving an oil which was chromatographed in light petroleum on alumina. Development with light petroleum gave a fraction which was shown by infrared spectroscopy to be free from trinitrobenzene. The solvent was evaporated and the residual oil was distilled in a vacuum. The distillate crystallised from ethanol as prisms, m.p. 30°, probably 2-benzylidenehydrindene (XXVI).

Analysis

Found: C, 93.1; H, 6.7.

$C_{16}H_{14}$ requires C, 93.2; H, 6.8%.

Ultraviolet spectrum - Fig. 8.

In one experiment, the aqueous alkaline washings were treated with hydrochloric acid giving 1,2-dihydro-3-phenylnaphthalene-1-carboxylic acid (XLV) needles from aqueous ethanol, m.p. 128-130°.

Analysis

Found: C, 81.4; H, 5.4.

$C_{17}H_{14}O_2$ requires C, 81.6; H, 5.6%.

Infrared spectrum (cms^{-1}) 2,700(w) (OH) 1,700(s) (C:O) 1,600(w) (C:C) 1,250(m) (CO_2H)

The ultraviolet spectrum resembles that of impure 1,2-dihydro-3-phenylnaphthalene, m.p. 58° more closely than that of the pure hydrocarbon, m.p. 52° (see Fig. 9), and this may indicate that the sample contains some dehydrogenated acid. Dehydrogenation of the acid by chloranil in boiling xylene gave 3-phenyl-1-naphthoic acid (XLVII) needles from aqueous ethanol, m.p. 222-4° (Lit. m.p. 221-2°)[88], identical with a sample obtained from the alkaline extract of another experiment.

Analysis

Found: 81.8; H, 4.8.

$C_{17}H_{12}O_2$ requires C, 82.2; H, 4.9%.

Infrared spectrum (cms^{-1})

2,700(w)	1685(s)	1620(w)	1600(w)	1250(s)
(OH)	(C:O)	(C:C)	(C:C)	(CO_2H)

3-Phenyl-1-naphthoic acid (XLVII) (0.25 g.) when boiled in 4-methylquinoline (5 ml.) with copper bronze for 5 hours, gave 2-phenylnaphthalene (XLVI) (0.20 g.), m.p. and mixed m.p. 99°.

Attempted conversion of 2-benzylidene-1-hydrindone (VI) into phenylnaphthalene derivatives

2-Benzylidene-1-hydrindone (VI) (6 g.) and 99% hydrazine hydrate (3 ml.) were boiled in ethanol (15 ml.) in an atmosphere of nitrogen for 2 hours. On cooling the solution to 0°C., no solid separated, indicating that the ketone had been converted to the pyrazoline, as the ketone is sparingly soluble in cold ethanol. The solution was added to potassium hydroxide (1 g.) in ethylene glycol (20 ml.) and the reaction mixture heated at 200° for 1 hour after the ethanol and hydrazine hydrate had been distilled off. The reaction mixture was poured into water and the solid filtered off. The material was insoluble in organic solvents and the m.p. was over 250°, indicating that the product was polymeric.

Preparation of 1-hydroxy-2-bromohydrindene

Porter and Suter, J. Amer. Chem. Soc., 1935, 57, 2024.

Indene (40 g.) was emulsified with water (1 l.) at 90° and bromine solution (880 ml.) prepared by dissolving bromine (20 ml.) in water (1 l.) containing potassium bromide (100 g.), added with vigorous stirring. The product was crystallised from aqueous ethanol. Yield: 38 g. 49%. m.p. 128° (Lit. m.p. 126.8°).

Preparation of 2-bromoindene

Porter and Suter, J. Amer. Chem. Soc., 1935, 57, 2024.

1-Hydroxy-2-bromohydrindene (40 g.) was added to phosphorus pentoxide (14 g.) in carbon tetrachloride (300 ml.). The reaction mixture was refluxed for 2 hours. The carbon tetrachloride solution was decanted and after all the solvent had been evaporated, the residual oil was distilled. Yield: 16.1 g., 43.5%, b.p. 106°/6 m.m..

Attempted preparation of 2-indenylphenylcarbinol

cf. Porter and Suter, J. Amer. Chem. Soc., 1935, 57, 2024.

2-Bromoindene (6 g.) in ether (40 ml.) was added to magnesium turnings (0.75 g.). A few crystals of iodine and a few ml. of ethylmagnesium bromide were added. No reaction appeared to occur, even after refluxing for two hours.

Benzaldehyde (3 ml.) in ether (10 ml.) was added

dropwise with stirring. After boiling the reaction mixture for 5 minutes, it was poured on to dilute sulphuric acid and ice. A gum was obtained which could not be induced to crystallise.

Preparation of 2-hydrindone

Read and Hurst, J., 1922, 2550.

1-Hydroxy-2-bromohydrindene (47 g.) was added to potassium hydroxide (13 g.) dissolved in ethanol (300 ml.). The reaction mixture was boiled for 30 minutes with partial evaporation of the solvent. An excess of dilute sulphuric acid was added and the reaction mixture boiled for a further 30 minutes with evaporation of the rest of the ethanol, and then steam distilled. Yield: 23 g. 79%. m.p. 57.8°. (Lit. m.p. 58°).

Attempted preparation of 2-benzylidenehydrindene (XXVI)

2-Hydrindone (10.2 g.) in ether (200 ml.) was added to benzylmagnesium chloride, prepared from benzyl chloride (9 ml.) in ether (100 ml.) and magnesium (2 g.) to give as the main product 1-(2-hydroxyhydrinden-2-yl)-2-hydrindone (XLIX), m.p. 145°, which with formic acid gave bis-anhydro-2-hydrindone (L), m.p. 173.5°.

Analysis

Found: C, 82.0; H, 6.1.

Calc. for $C_{18}H_{16}O_2$: C, 81.8; H, 6.1%.

Infrared spectrum (cms^{-1}) 3,600(s) (OH) 1760(s) (C:O)

In a second experiment, 2-hydrindone (23 g.) in ether (500 ml.) was added to benzylmagnesium chloride, prepared from benzyl chloride (52 ml.) in ether (500 ml.) and magnesium (11 g.) during 4 hours at 0°. Working up in the usual manner gave a gum, which was dissolved in light petroleum and cooled by acetone-solid carbon dioxide. The resulting gum, on solidification and recrystallisation from light petroleum, gave 2-benzyl-2-hydroxyhydrindene (XLVIII) (6.9 g.), m.p. 82°.

Analysis

Found: C, 86.45; H, 7.2.

$C_{16}H_{16}O$ requires C, 85.7; H, 7.2%.

The combined filtrates were chromatographed on alumina and developed with light petroleum. The first fraction with an intense violet fluorescence in ultraviolet light, gave on evaporation, a solid, part of which dissolved in a limited volume of light petroleum, leaving an insoluble residue. The filtrate, when cooled to 0° gave 2-benzyl-2-hydroxy-hydrindene (2.6 g.) while the residue when crystallised from ethanol yielded 2-benzyl-1-(2-hydroxyhydrinden-2-yl)-hydrindene (LI), m.p. 160°. That the compound m.p. 160° has the proposed structure is indicated by a strong hydroxy

band at 3,400 cms^{-1} but no carbonyl band in the infrared spectrum.

Analysis

Found: C, 84.5; H, 6.5.

$C_{25}H_{24}O_2$ requires C, 84.2; H, 6.8%.

A later chromatographic fraction gave bis-anhydro-2-hydrindone (L), m.p. 173-5°.

Dehydration of 2-benzyl-2-hydroxyhydrindene (XLVIII) (2 g.) with formic acid (5 ml.) yielded only 2-benzylindene (1.4 g.), 76% yield, m.p. 48°, identical with the product obtained by formic acid dehydration of 1-hydroxy-2-benzyl-hydrindene shown by m.p. and mixed m.p. and by comparison of their ultraviolet and infrared spectra.

Section 3

The Reaction of Diphenylketene with 2-Benzylidene-1-tetralone

Discussion

It has been shown in the first section of this thesis that 1-diphenylmethylene-2-benzylidenehydrindene (I) undergoes ring-closure with spontaneous dehydrogenation to give 1:4-diphenyl-2,3-benzofluorene (XIV). It was of interest to investigate whether 1-diphenylmethylene-2-benzylidene-tetralin (LVII) would undergo an analogous reaction to yield 3,4-dihydro-9,10-diphenyl-1,2-benzanthracene (LVIII).

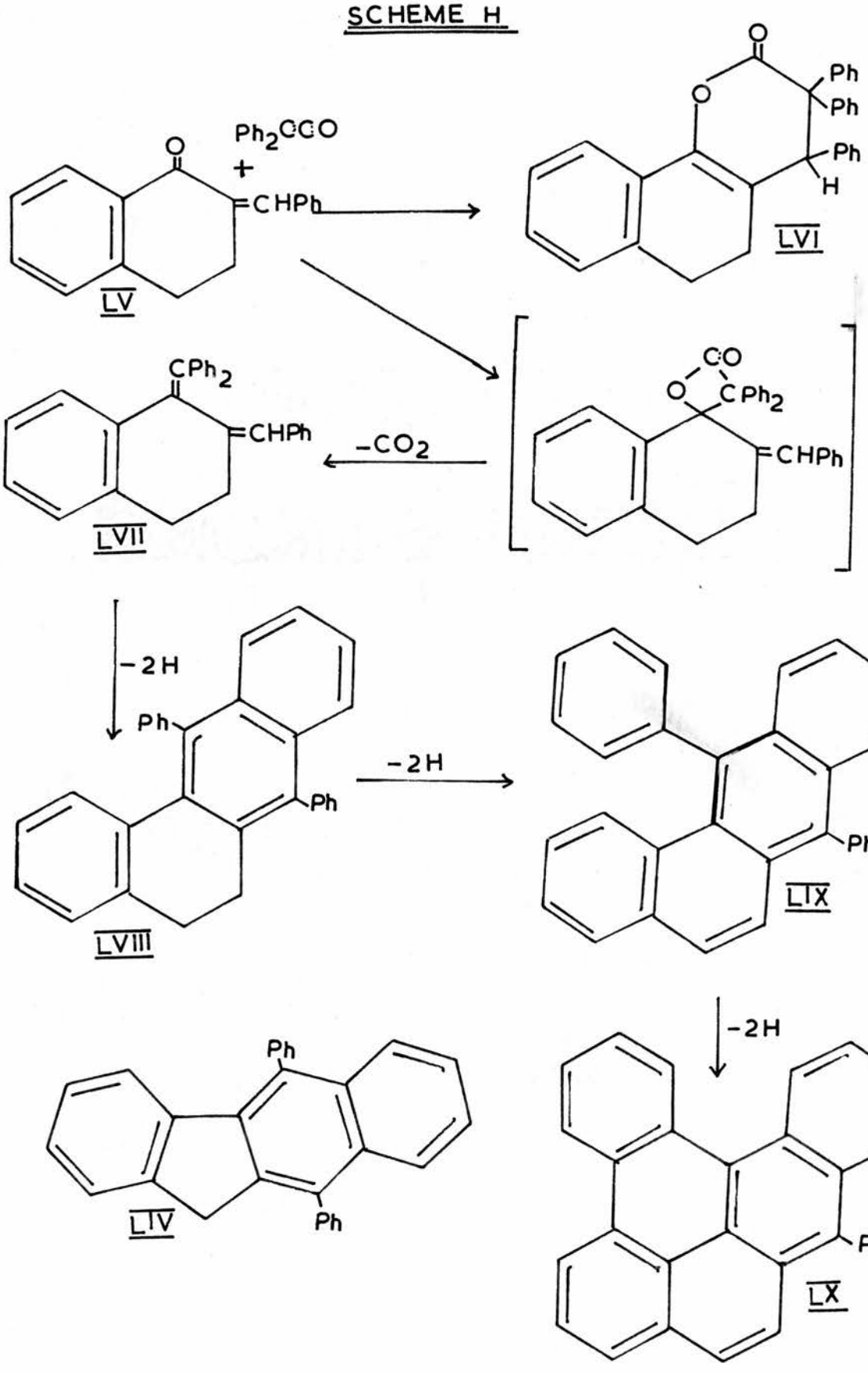
By heating diphenylketene and 2-benzylidene-1-tetralone (LV) under nitrogen for 2 hours at 150° and then for 1 hour at 170°, 1-diphenylmethylene-2-benzylidenetetraline (LVII), the δ-lactone (LVI) and a hydrocarbon, m.p. 284°, were obtained.

1-Diphenylmethylene-2-benzylidenetetralin (LVII) resembled 1-diphenylmethylene-2-benzylidenehydrindene (I) in its physical properties. It was obtained as colourless needles, m.p. 165° (yellow melt), which turn yellow on exposure to light. It gave bright yellow solutions which did not obey Beer's law. On standing, solutions turned colourless and colourless crystals of the hydrocarbon, m.p. 284°, were deposited. It is suggested that the compound, m.p. 284° is 3,4-dihydro-9,10-diphenyl-1,2-benzanthracene (LVIII) and this is supported by the similarity of its ultraviolet spectrum (Fig. 10) to that of 1:4-diphenyl-2,3-benzofluorene (XIV) (Fig. 2), and a

molecular weight determination, which has shown that the compound is a monomer. The compound cannot be 9,10-diphenyl-1,2-benzanthracene (LIX) or 6-phenyl-7,8-9,10-dibenzopyrene (LX) as these compounds have been synthesised and melt at 196° and 242° respectively[91].

An attempt to dehydrogenate the dihydro-compound (LVIII) to the benzanthracene (LIX) by boiling it with chloranil in xylene for 3 hours, was unsuccessful. The dihydro-compound (LVIII) was recovered in over 80% yield. Attempted dehydrogenation of 1-diphenylmethylene-2-benzylidenetetralin (LVII) with chloranil in xylene failed also. Possibly a quinone with a higher redox potential such as tetrachloro-1,2-benzoquinone or tetracyano-1:4-benzoquinone might effect dehydrogenation. Chloranil dehydrogenates tetralin to naphthalene quantitatively when the two compounds are boiled in xylene at 135° for 20 hours, whereas quantitative dehydrogenation occurs when tetralin and tetrachloro-1,2-benzoquinone are boiled in benzene for 2 hours[92].

SCHEME H


Ph2CCO
+
CHPh
LV
Ph
Ph
Ph
H
LVI
CPh2
CHPh
LVII
-CO2
CO
O
CPh2
CHPh
-2H
Ph
Ph
LVIII
-2H
Ph
LIX
-2H
Ph
LIV
Ph
Ph
LX

Experimental

Preparation of 2-benzylidene-1-tetralone (LV)

van Alphen and Prost, Rec. Trav. chim., 1950, 69, 1080.

1-Tetralone (7.3 g.) and benzaldehyde (5.3 g.) in ethanol (20 ml.) were condensed at room temperature in the presence of a few ml. of 10% w.v. ethanolic potassium hydroxide. The product was recrystallised from ethanol. Yield: 8.3 g. 70%. m.p. 105-6° (Lit. m.p. 106-7°).

Preparation of 1-diphenylmethylene-2-benzylidenetetralin (LVII)

2-Benzylidene-1-tetralone (LV) (6.25 g.) and diphenylketene (5.2 g.) were heated under nitrogen for 2 hours at 150° and then for 1 hour at 170°. The reaction mixture was treated with ether and the solid formed filtered off and recrystallised from ethanol, giving colourless prisms (2.85 g.) of the δ-lactone (LVI), m.p. 191°.

Analysis

Found: C, 87.1; H, 5.3.

$C_{31}H_{24}O_2$ requires C, 86.9; H, 5.6.

Infrared spectrum (cms^{-1}) 1765(s) 1680(w) 1600(w) 1120(s) 1135(s)

(C:O) (C:C)

The filtrate was evaporated and the residue dissolved in benzene and chromatographed on alumina. Development with light petroleum gave a bright yellow fraction with a deep blue fluorescence. The solvent was evaporated and

the residue boiled with ethanol (10 ml.). The insoluble material was filtered off and recrystallised from benzene and light petroleum, giving colourless needles, m.p. 284°, considered to be 3,4-dihydro-9,10-diphenyl-1,2-benzanthracene (LVIII).

Analysis

Found: C, 93.0; H, 6.0.

$C_{30}H_{22}$ requires C, 94.2; H, 5.8%.

M.W. found: 380; $C_{30}H_{22}$ requires 382.

Ultraviolet spectrum - Fig. 10. (The compound was very sparingly soluble in organic solvents suitable for spectroscopy.)

The spectrum was taken on a solution of the compound (0.7 mg.) in ethanol (100 ml.).

The ethanolic filtrate gave 1-diphenylmethylene-2-benzylidenetetralin (LVII) (0.62 g.) as colourless needles, m.p. 165° on cooling.

Analysis

Found: C, 93.7; H, 6.1.

$C_{30}H_{24}$ requires C, 93.7; H, 6.3%.

Ultraviolet spectrum - Fig. 10. The spectrum changed with time and showed an isosbestic point at 280 mμ.

The compound (LVII) (0.17 g.) was dissolved in hexane (500 ml.) and exposed to sunlight for 4 days. The solution became colourless and crystals, m.p. 284° separated.

The compound, m.p. 284° (0.03 g.) was boiled with chloranil (0.1 g.) in xylene (2 ml.) for 3 hours. On cooling, the compound was recovered in 84% yield.

1-Diphenylmethylene-2-benzylidenetetralin (LVII) (0.08 g.) was boiled with chloranil (0.1 g.) in xylene (2 ml.) for 3 hours. The reaction mixture was chromatographed on alumina and developed with light petroleum. The fraction with the deep blue fluorescence was evaporated and the residue crystallised from ethanol, giving colourless needles, m.p. 165°. The mixed m.p. with a sample of the tetralin (LVII) was not depressed.

Section 4

The Reaction of Diphenylketene with 2-Benzylidene-3-carboxy-1-hydrindone

Discussion

In an attempt to prepare 1-diphenylmethylene-2-benzylidene-3-carboxyhydrindene (LXI) or the anhydride (LXII), equimolecular proportions of 2-benzylidene-3-carboxy-1-hydrindone (XXV) and diphenylketene were heated under nitrogen for 3 hours at 180-190°. By extracting the reaction product with light petroleum in a soxhlet extractor, two compounds were obtained, a red compound insoluble in petroleum which crystallised from ethanol in red needles, m.p. 265° and a yellow compound soluble in petroleum which crystallised from ethanol in golden-yellow needles, m.p. 195°.

The red compound was soluble in aqueous sodium hydroxide, sodium carbonate and ammonia giving purple solutions but was insoluble in saturated sodium bicarbonate solution. It readily formed a p-nitrobenzyl derivative, and was unaffected by boiling in quinoline with copper bronze. No degradation product could be isolated after attempted ozonolysis. The compound absorbed in the infrared at 3,300 cms^{-1} weakly and at 1700 cms^{-1} strongly, consistent with a compound containing a hydroxy and a carbonyl group. The compound dissolved in concentrated sulphuric acid giving a green solution.

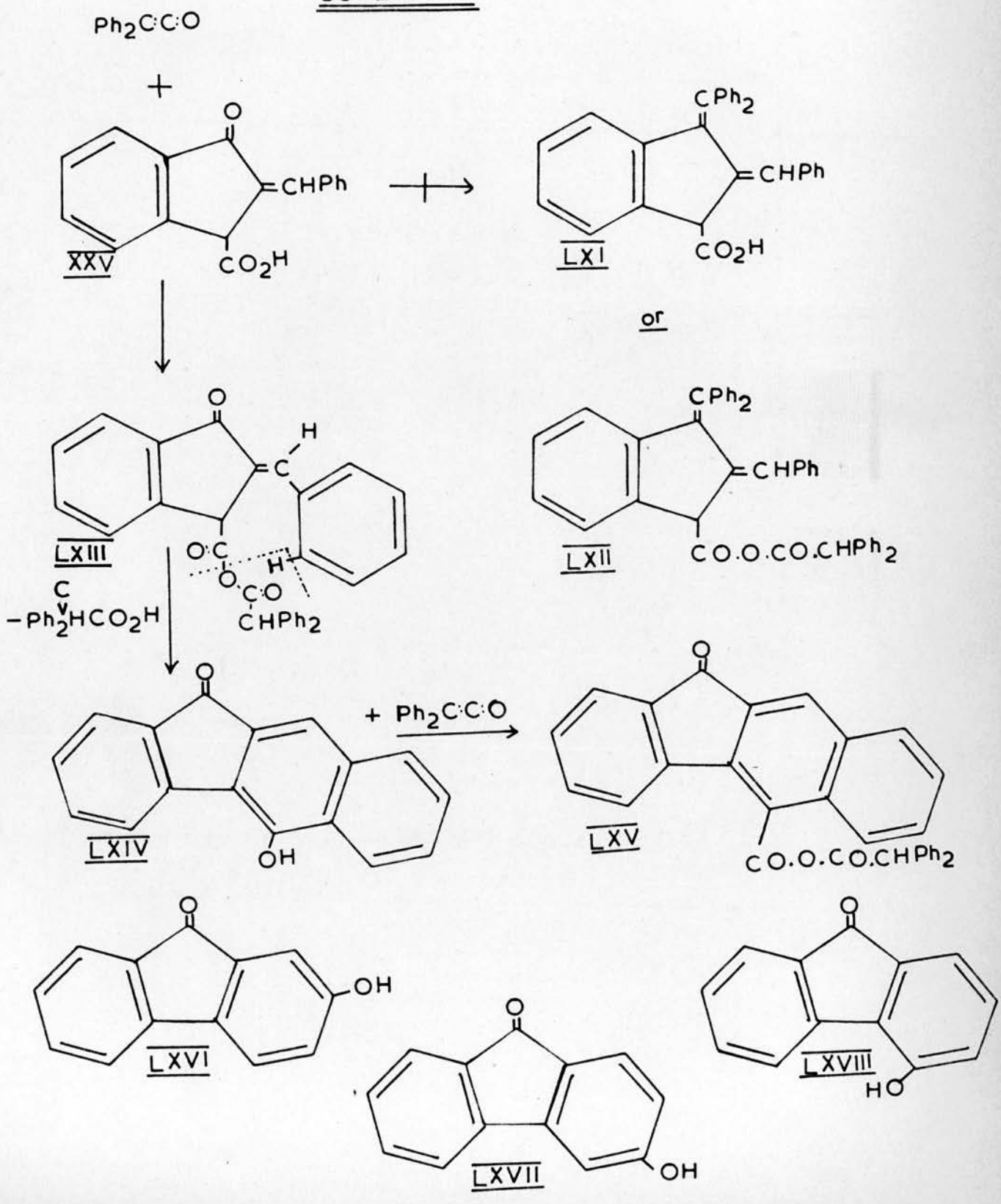
The yellow compound was insoluble in aqueous alkali but on warming with ethanolic potassium hydroxide, it gave a purple solution. The infrared spectrum showed two strong

absorptions at 1750 cms^{-1} and 1710 cms^{-1} suggesting the presence of two carbonyl groups, the former possibly due to the carbonyl stretching vibrations of an ester group. No absorption corresponding to the hydroxyl group was present.

When equimolecular proportions of 2-benzylidene-3-carboxy-1-hydrindone (XXV) and diphenylketene were boiled in benzene for 2 hours, the anhydride (LXIII) was obtained, separating from the solution on cooling. It had no distinct m.p. but decomposed between 180-190° giving the red compound. The benzene solution was extracted with aqueous alkali until the extracts were colourless. On acidification of the purple extracts with hydrochloric acid, the red compound was precipitated. The 'neutral' dried benzene extract after some days deposited diphenylacetic acid and on re-extraction with aqueous alkali, a further quantity of the red compound was obtained.

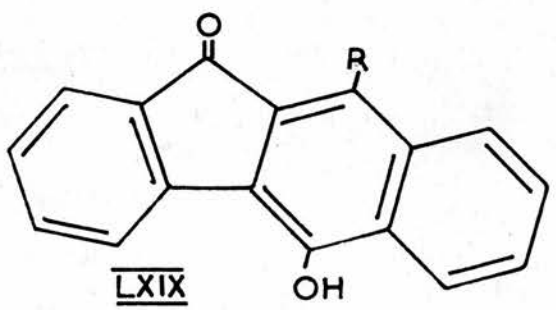
The explanation for these unexpected results is that the red compound is 4-hydroxy-2,3-benzofluorenone (LXIV) and the yellow compound is the diphenylacetate (LXV). 4-Hydroxy-2,3-benzofluorenone (LXIV) is formed by the cyclisation of the anhydride (LXIII) with the elimination of diphenylacetic acid, and the diphenylacetate (LXV) by the reaction of the hydroxy compound (LXIV) with diphenylketene. The proposed structures of the 4-hydroxy

SCHEME I

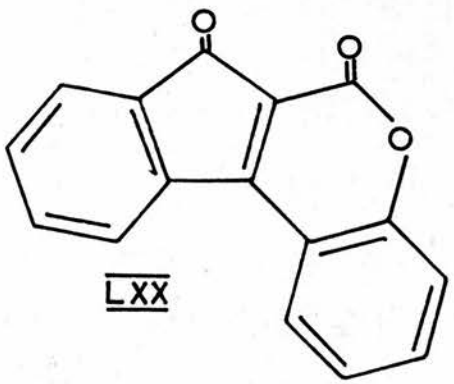

Ph2C:C:O
+
CHPh
CO2H
XXV
CPh2
CHPh
CO2H
LXI
or
H
C
LXIII
O:C
O
C:O
H
CHPh2
CPh2
CHPh
CO.O.CO.CHPh2
LXII
-Ph2HCO2H
+ Ph2C:C:O
OH
LXIV
CO.O.CO.CHPh2
LXV
OH
LXVI
OH
LXVII
HO
LXVIII

compound (LXIV) and its diphenylacetate (LXV) are supported by analyses, by their infrared spectra and by comparison of their ultraviolet spectra and physical properties with compounds of similar structure.

The phenol (LXIV) shares the notable colour of 2-hydroxyfluorenone (LXVI)[93], 3-hydroxyfluorenone (LXVII)[94] and 4-hydroxyfluorenone (LXVIII)[95] which give red solutions in aqueous sodium hydroxide. 1-Phenyl-4-hydroxy-2,3-benzofluorenone (LXIX, R=Ph)[96] is an orange compound which gives a purple solution in aqueous alkali and a green solution in concentrated sulphuric acid. The ultraviolet spectra of this compound and 4-hydroxy-2,3-benzofluorenone are very similar. 1:4-Dihydroxy-2,3-benzofluorenone (LXIX, R=OH) and the monomethyl ether (LXIX, R=$ClCH_3$) are orange compounds giving blue-violet solutions in alkali[97].

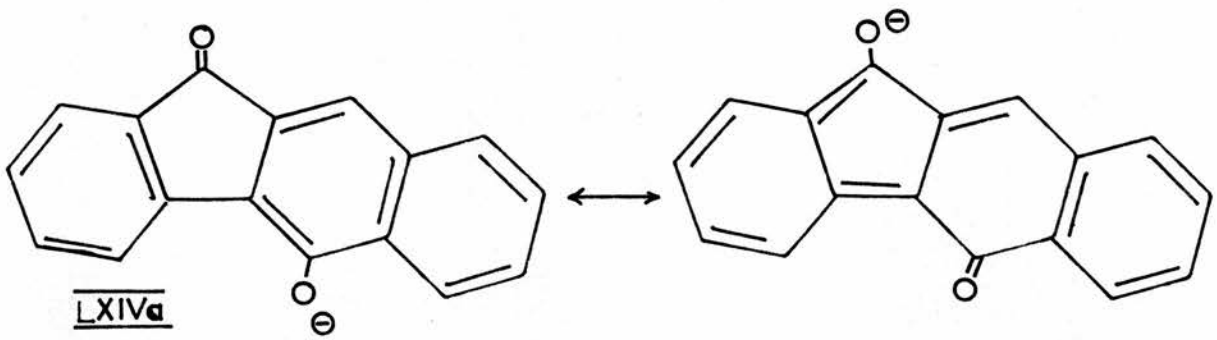


LXIX



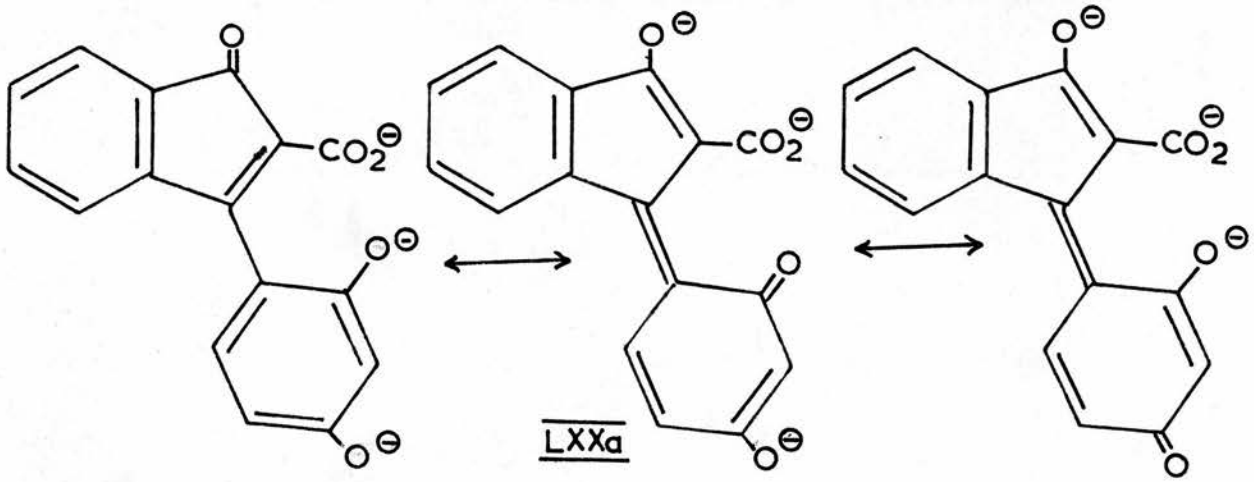
LXX

In the deeply coloured anion of 4-hydroxy-2,3-benzofluorenone (LXIVa), the negative charge is distributed presumably between the two oxygen atoms through the benzene ring.



LXIVa

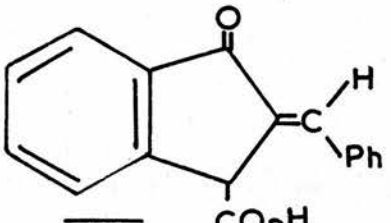
The anions of the hydroxyfluorenones mentioned above contain a similar chromophore. 7-Hydroxy-1-ketoindene-2',3' 3,4-coumarin (LXX)[98] is soluble in aqueous potassium hydroxide giving an intense blue solution. The anion (LXXa) contains a chromophore similar to that of the hydroxyfluorenones.



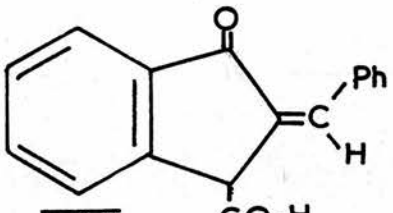
LXXa

The ultraviolet spectrum of the diphenylacetate (LXV) (Fig. 12) is remarkably similar to that of the parent compound 2,3-benzofluorenone (LXXI)[99] and to 1-anisyl-4-phenyl-2,3-benzofluorenone (LXXII). The phenyl substituents in the latter are non-coplanar and show a weak bathochromic effect[100].

This investigation not only introduces a novel synthesis of 4-hydroxy-2,3-benzofluorenone (LXIV), a cyclisation method which might have wider application, but proves that 2-benzylidene-3-carboxy-1-hydrindone has structure XXVa and not structure XXVb.



XXVa



XXVb

Experimental

Preparation of 4-hydroxy-2,3-benzofluorenone (LXIV)

2-Benzylidene-3-carboxy-1-hydrindone (XXV) (3 g.) and diphenylketene (2.4 g.) were heated in an atmosphere of nitrogen in a sealed tube at 180-190° for 3 hours. The product was extracted with light petroleum in a soxhlet extractor for 5 hours and the residue crystallised from ethanol giving bright red needles, m.p. 265°.

Analysis

Found: C, 81.9; H, 3.9.

$C_{17}H_{10}O_2$ requires C, 82.9; H, 4.1%.

Ultraviolet spectrum - Fig. 11.

Infrared spectrum (cms^{-1})

3,300(w)	1700(s)	1650(m)	1600(s)	1530(m)
(OH)	(C=O)		(C=C)	

p-Nitrobenzyl ether, m.p. 215-216°.

The petroleum extract was evaporated to dryness and the residue crystallised from ethanol giving golden-yellow needles of the diphenylacetate (LXV), m.p. 195°.

Analysis

Found: C, 84.8; H, 4.6.

$C_{31}H_{20}O_3$ requires C, 84.5; H, 4.6%.

Infrared spectrum (cms^{-1})

1750(s)	1720(s)	1650(m)	1600(m)	1100(s)
(C:C)	(C=O)			(ester)

Ultraviolet spectrum - Fig. 12.

4-Hydroxy-2,3-benzofluorenone dissolved in aqueous sodium hydroxide, sodium carbonate and ammonia giving purple solutions but was insoluble in saturated sodium bicarbonate solution. It dissolved in concentrated sulphuric acid to give a green solution.

2-Benzylidene-3-carboxy-1-hydrindone (XXV) (6 g.) and diphenylketene (4.4 g.) were boiled in benzene (30 ml.) for 2 hours. On cooling, the anhydride (LXIII (1.5 g.) separated and was recrystallised from benzene giving colourless glistening needles which decompose between 180 and 190°. The compound was insoluble in aqueous ethanol and on heating at 180-190°, it gave an orange solid which dissolved in aaueous alkali giving a purple solution.

Analysis

Found: C, 81.0; H, 5.1.

$C_{31}H_{22}O_4$ requires C, 81.0; H, 4.8%.

Infrared spectrum (cms^{-1})

1820(s)	1750(s)	1705(s)	1640(s)	1600(s)	1050(s)
(C:O)		(C:O)	(C:C)		(anhydride)

The benzene solution was extracted with 10% w.v. aqueous potassium hydroxide until the extracts were colourless. The combined purple extracts were acidified with hydrochloric acid. Fractional crystallisation of the precipitate from benzene and light petroleum gave 2-benzylidene-3-carboxy-1-hydrindone (XXV) (0.7 g.) and 4-hydroxy-2,3-benzofluorenone (LXIV).

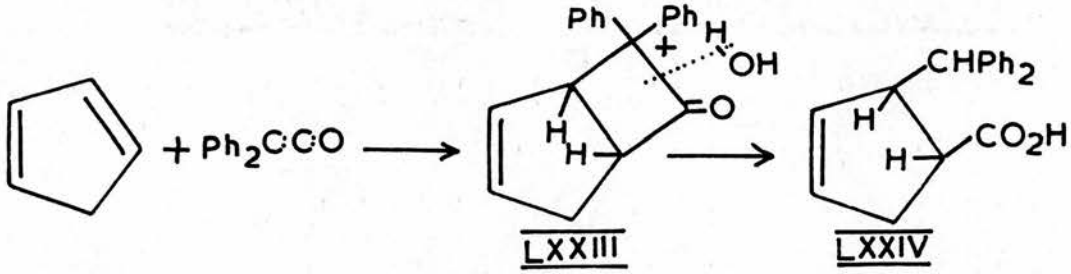
The benzene solution was washed with water, dried over sodium sulphate, filtered and the filtrate left in sunlight for several days. The solution changed from yellow to red and colourless crystals separated, which were identified by m.p. and mixed m.p. as diphenylacetic acid. From a second extraction of the benzene solution with aqueous sodium hydroxide, a further quantity of 4-hydroxy-2,3-benzofluorenone (LXIV) was isolated.

Section 5

The Reaction of Diphenylketene with Indene

Discussion

The addition of diphenylketene to compounds containing a double bond to form cyclobutanone derivatives, has been summarised in the Introduction (pp. 15-20). It has been shown that diphenylketene reacts with cyclopentadiene to give 6-keto-7:7-diphenylbicyclo- [3,2,0] hept-2-ene (LXXIII), which on alkaline hydrolysis gives two isomeric forms of 2-benzhydrylcyclopent-3-ene-1-carboxylic acid (LXXIV).

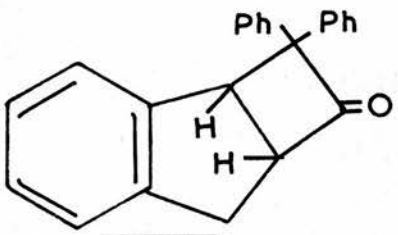


LXXIII LXXIV

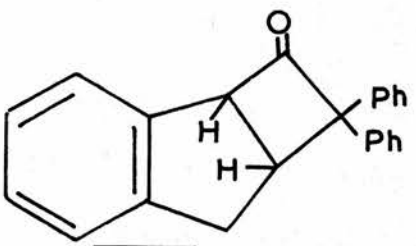
It was of interest to investigate whether diphenylketene would form an analogous adduct with indene and whether this adduct would give the analogous carboxylic acid on ring fission with alkali.

On heating diphenylketene and indene for 4½ hours at 100°, a good yield of an adduct was obtained, for which four structures (LXXVa, LXXVb, LXXVc, LXXVd) are possible. Structures LXXVa and LXXVb are the result of 1,2-addition of diphenylketene to indene depending on the orientation of diphenylketene during the reaction, structure LXXVc is the

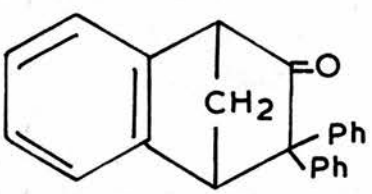
result of a diene reaction between the two compounds, while structure LXXVd is the result of addition of indene to diphenylketene as an active hydrogen compound.



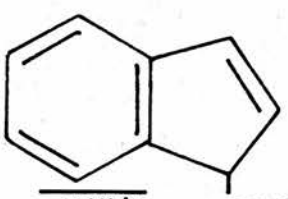
LXXVa



LXXVb

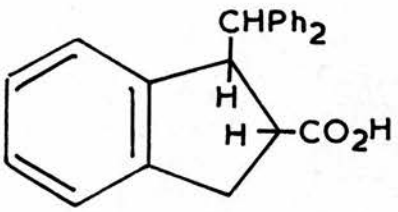


LXXVc

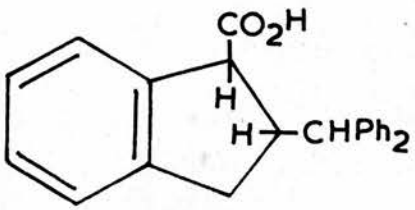


LXXVd COCHPh$_2$

On boiling the adduct with methanolic potassium hydroxide solution, a carboxylic acid was obtained in 89% yield. The analysis of this acid and the fact that it underwent intramolecular cyclisation indicates that the adduct cannot have structure LXXVc or LXXVd and that the carboxylic acid must have structure LXXVIa or LXXVIb depending on whether the adduct has structure LXXVa or LXXVb.



LXXVIa



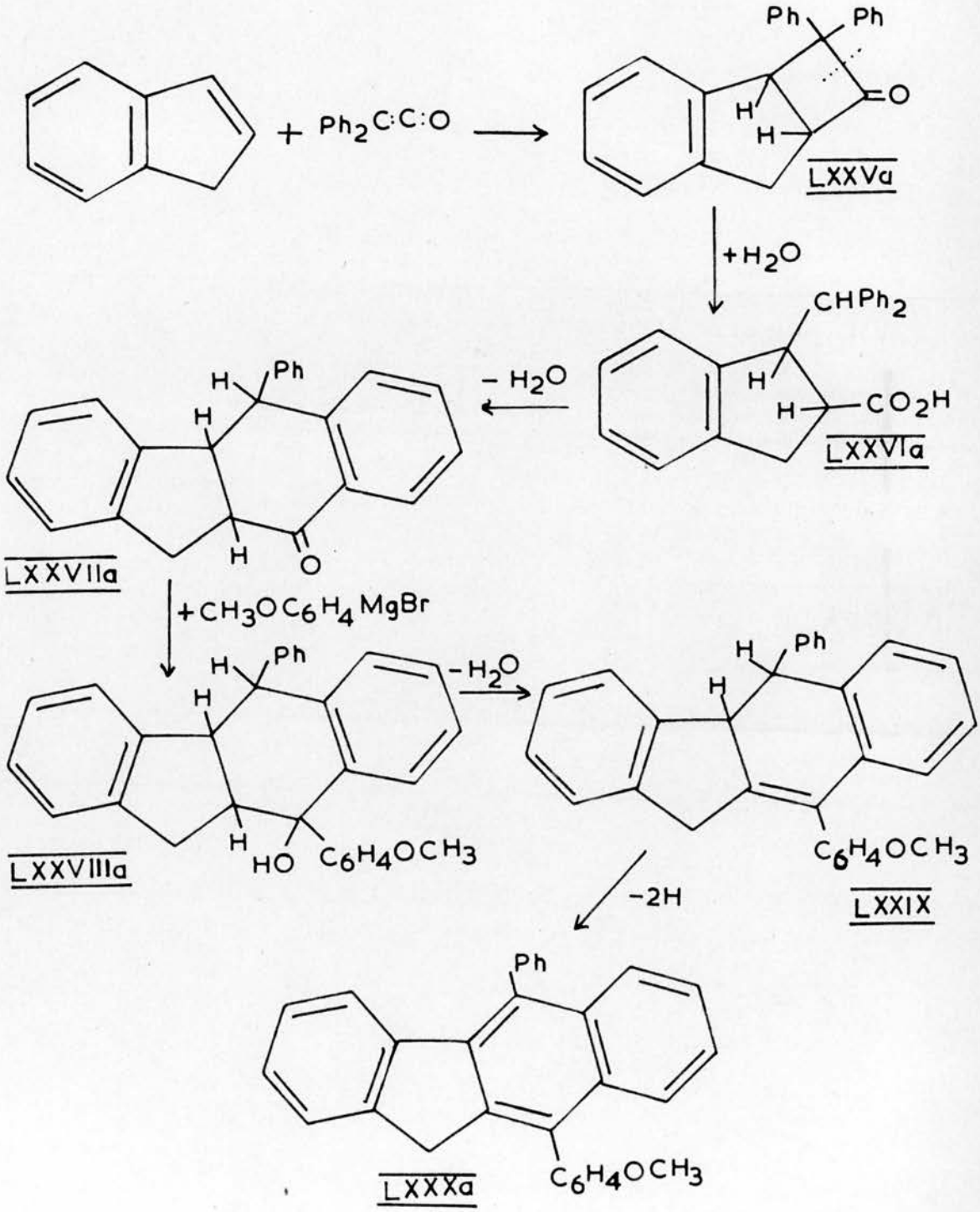
LXXVIb

Cyclisation of the carboxylic acid chloride by aluminium chloride in benzene, trichloroethylene or methylene dichloride gave a ketone melting at 186-7°, while cyclisation in nitrobenzene gave a ketone, m.p. 114°. Cyclisation of the carboxylic acid by anhydrous hydrogen fluoride gave a mixture of the two ketones. Their analyses and the fact that both ketones could be converted into 1-anisyl-4-phenyl-2,3-benzofluorene (LXXXa) prove that the ketones are isomeric forms of 1-keto-4-phenyl-1:4:4a:9a-tetrahydro-2,3-benzofluorene (LXXVIIa), that the carboxylic acid is 1-benzhydrylhydrindene-2-carboxylic acid (LXXVIa) and that the adduct is 2,3-benzo-6-keto-7:7-diphenyl [3,2,0] -hept-2-ene (LXXVa).

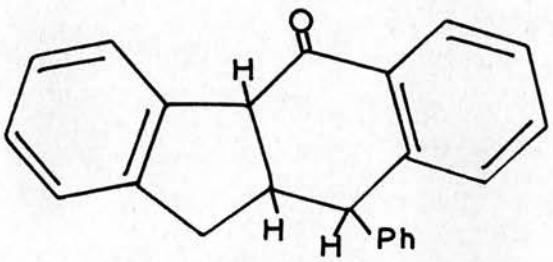
The conversion of the adduct (LXXVa) into 1-anisyl-4-phenyl-2,3-benzofluorene (LXXXa) is indicated in scheme J and is described fully in the Experimental Section (pp.110-116).

If in this scheme of reactions 1-phenyl-4-anisyl-2,3-benzofluorene (LXXXb) had been the final product, it would have meant that the ketone had structure LXXVIIb,

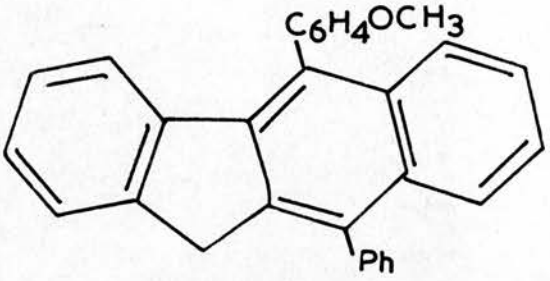
SCHEME J


+ Ph2C:C:O
Ph
Ph
H
H
O
LXXVa
+H2O
CHPh2
H
H
CO2H
LXXVIa
- H2O
H
Ph
H
H
O
LXXVIIa
+CH3OC6H4MgBr
H
Ph
H
H
HO
C6H4OCH3
LXXVIIIa
-H2O
H
Ph
H
C6H4OCH3
LXXIX
-2H
Ph
C6H4OCH3
LXXXa

the acid, structure LXXVIb, and the adduct, structure LXXVb.

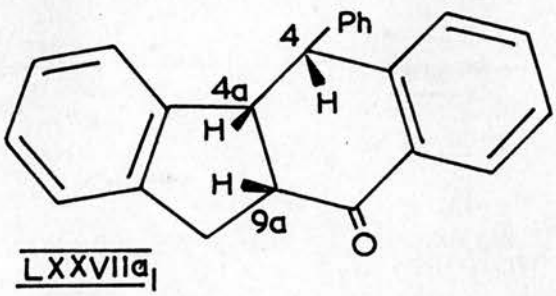


LXXVIIb

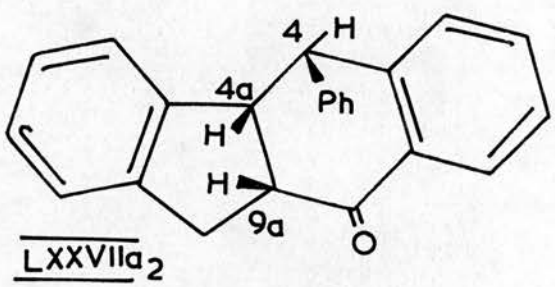


LXXXb

If it is assumed that diphenylketene undergoes cis-addition to indene, then the cis-adduct formed, on hydrolysis will give the cis-acid (LXXVIa). Cyclisation of the cis-acid can give two cis-ketones theoretically. In the ketone $LXXVIIa_1$ the hydrogen atoms at positions 9a, 4 and 4a are on the same side of the ring, while in the ketone $LXXVIIa_2$ the hydrogen atom at position 4 is on the opposite side of the ring to the hydrogen atoms at positions 9a and 4a.



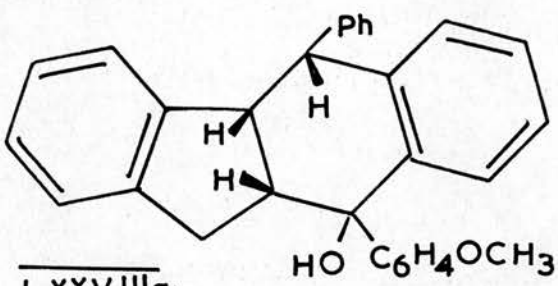
$\overline{LXXVIIa}_1$



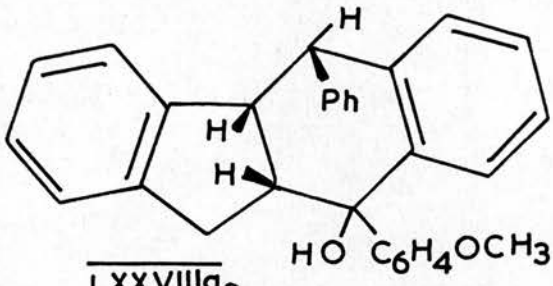
$\overline{LXXVIIa}_2$

The ketones (LXXVIIa), m.p. 186-7° and m.p. 114°, on treatment with anisylmagnesium bromide, gave two isomeric forms of 1-hydroxy-1-anisyl-4-phenyl-1:4:4a:9a-tetrahydro-2,3-benzofluorene (LXXVIIIa), m.p. 214° and m.p. 210°

respectively. The mixed m.p. of the two carbinols was depressed to 187-193°.

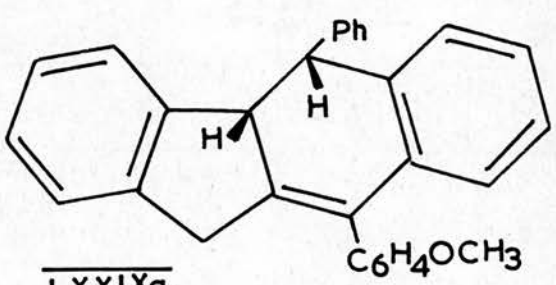


LXXVIIIa$_1$

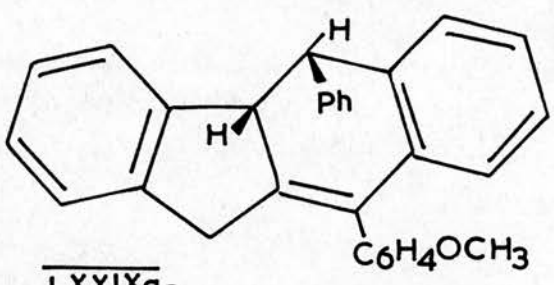


LXXVIIIa$_2$

If the ketones have structures LXXVIIa$_1$ and LXXVIIa$_2$, then the carbinols derived from them will have the structures LXXVIIIa$_1$ and LXXVIIIa$_2$ respectively. On dehydration, carbinol (LXXVIIIa$_1$) will give <u>cis</u>-4:4a-dihydro-4-phenyl-1-anisyl-2,3-benzofluorene (LXXIXa$_1$) and the carbinol (LXXVIIIa$_2$) will give the <u>trans</u>-dihydro compound (LXXIXa$_2$).



LXXIXa$_1$

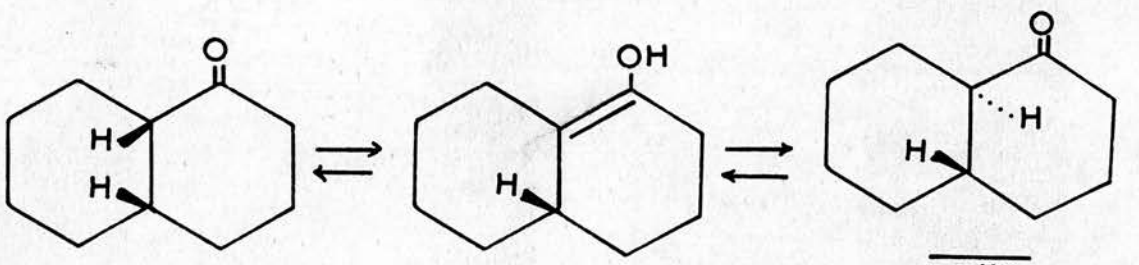


LXXIXa$_2$

In practice, dehydration of the two carbinols by formic acid or by hydrochloric acid in ethanol gave the same dihydro compound, m.p. 168°, as was shown by mixed m.p., and comparison of the ultraviolet and infrared spectra. This proves that the hydrogen atoms in positions 4 and 4a must have

the same orientation in the ketones (LXXVIIa) and in the carbinols (LXXVIIIa). It follows that the two ketones are the cis and trans isomers of structure LXXVIIa. The conversion of the cis-ketone, formed initially from the cis-acid (LXXVa) to the trans-ketone would be facile through the enol form of the ketone, produced in the presence of a strong acid such as anhydrous hydrogen fluoride.

Though this is the probable explanation for the formation of the trans-ketone (LXXVIIa), no directly comparable example could be found in a search through the literature. The explanation is, however, supported by the following examples. cis-α-Decalone (LXXXI) is converted to trans-α-decalone in over 95% yield by distillation at atmospheric pressure. The conversion is considered to occur via the enol form of the ketone[101].

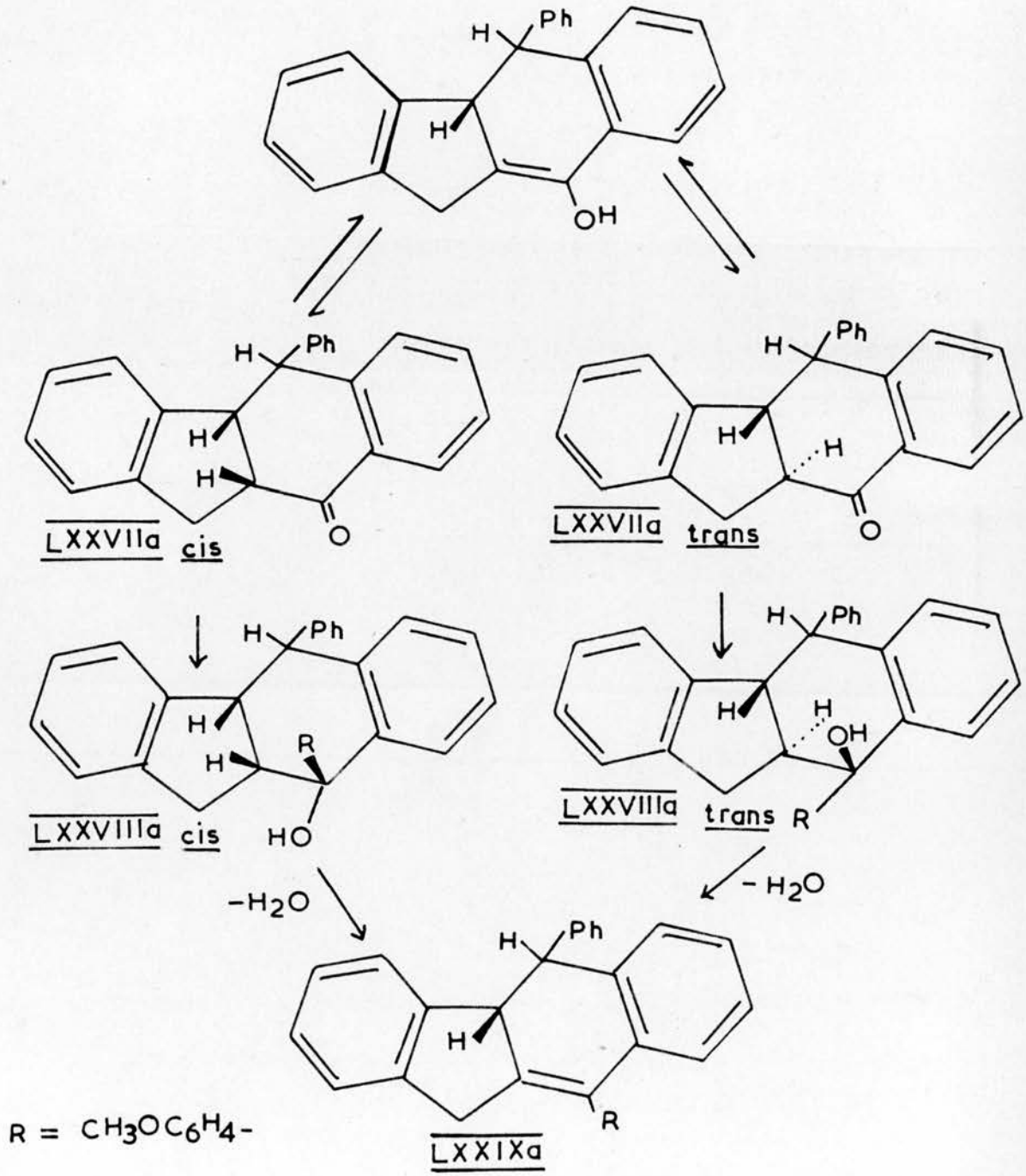


LXXXI cis LXXXI trans

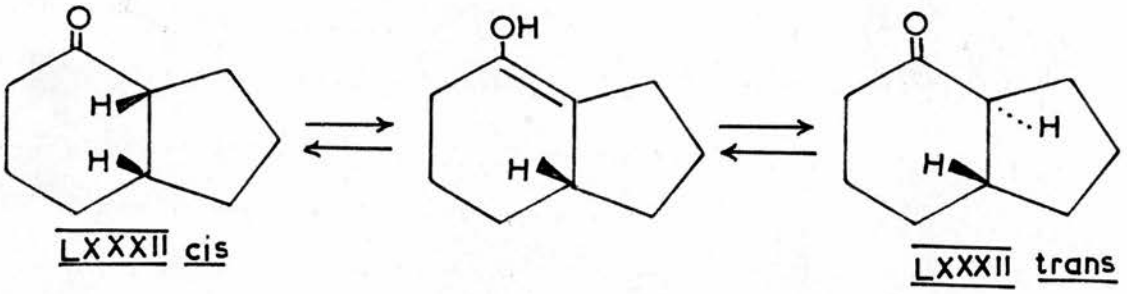
The enol form of the ketone has been isolated as the benzoyl and acetyl esters[102].

cis-α-4-Hydrindanone (LXXII) gives on distillation 15% yield

SCHEME K

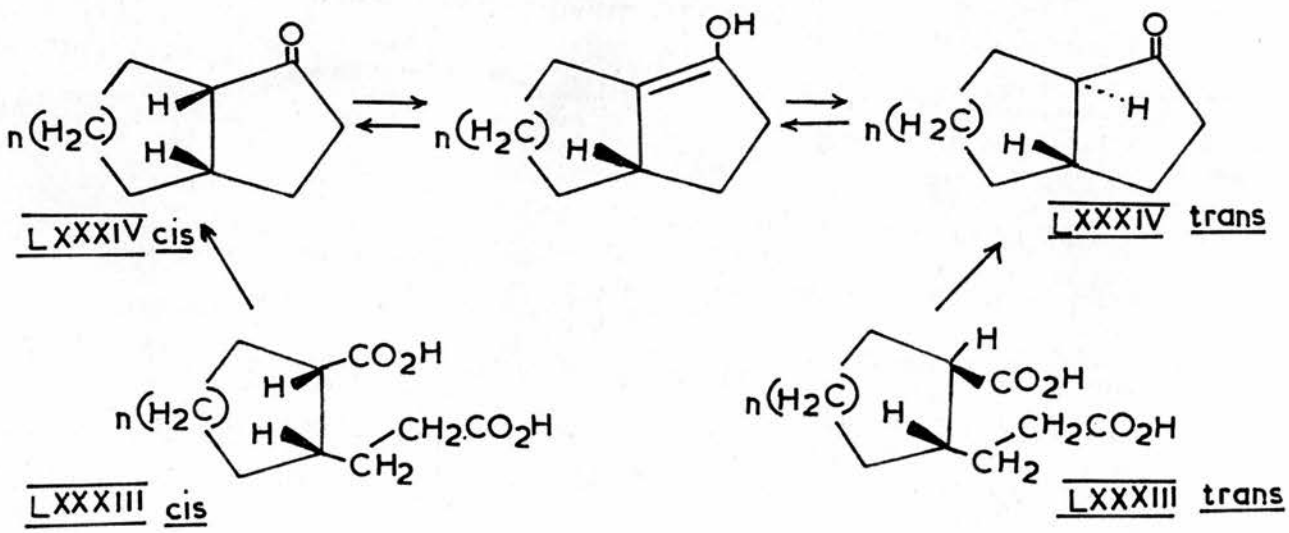

H
Ph
H
OH
H
Ph
H
H
O
LXXVIIa cis
H
Ph
H
H
O
LXXVIIa trans
H
Ph
H
R
H
HO
LXXVIIIa cis
H
Ph
H
H
OH
LXXVIIIa trans R
-H2O
- H2O
H
Ph
H
R
LXXIXa
R = CH3OC6H4-

of the cis-compound and 85% yield of trans-α-4-hydrindanone[103].



LXXXII cis LXXXII trans

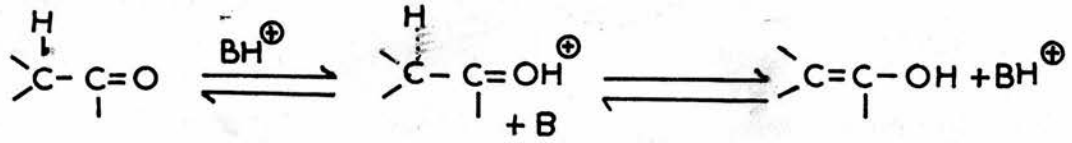
Both cis and trans-cyclohexane-1-carboxy-2-propionic acids (LXXXIII, n = 2) give a mixture of cis and trans-1-hydrindanone (LXXXIV, n = 2) in which the cis form predominates. Both cis and trans cyclopentane-1-carboxy-2-propionic acid (LXXXIII, n = 1) give cis- [3,3,0] -bicyclooctan-4-one (LXXXIV, n = 2) in 70% yield on heating with barium hydroxide at about 300°. The interconversion of the two isomers is considered to occur via the enol form[104].



LXXXIV cis LXXXIV trans

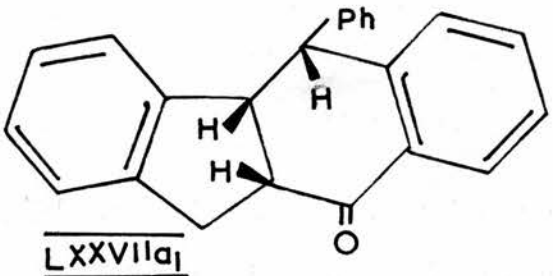
LXXXIII cis LXXXIII trans

The explanation of keto-enol tautomerism put forward for the formation of the cis and trans ketones (LXXVIIa) is the mechanism suggested for the racemisation of optically active ketones by acids[105, 106].

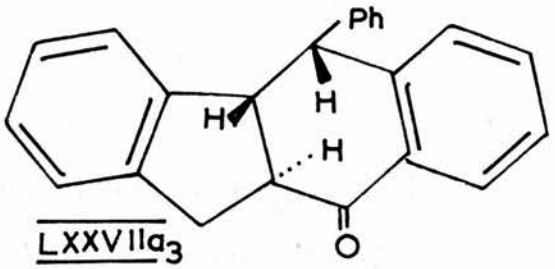


1-Benzhydrylhydrindene-2-carboxylic acid (LXXVIa) has two asymmetric carbon atoms so that four optical isomers are possible, obtainable as two racemic modifications. As cis-addition of diphenylketene to indene is assumed to occur the product obtained by hydrolysis of the adduct (LXXVa), should give the cis-diastereoisomeride, a racemic mixture of enantiomorphic forms. Only one diastereoisomeride was obtained, as expected.

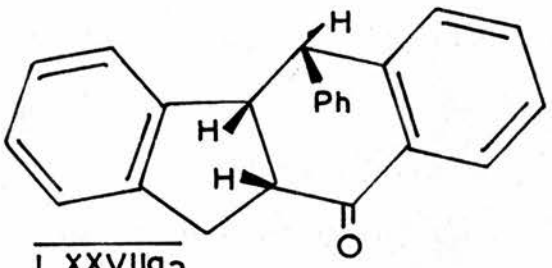
As the ketone (LXXVIIa) has three asymmetric carbon atoms, eight optical isomers, obtainable as four racemic modifications, are possible. Cyclisation of the acid (LXXVIa) would be expected to give four diasterioisomerides, viz.



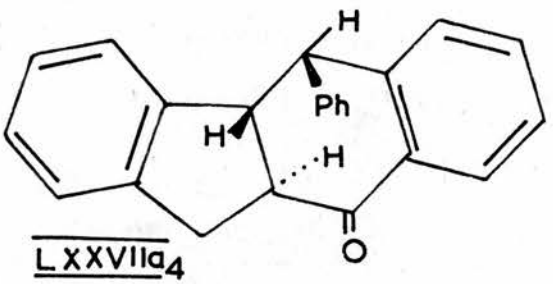
LXXVIIa$_1$



LXXVIIa$_3$



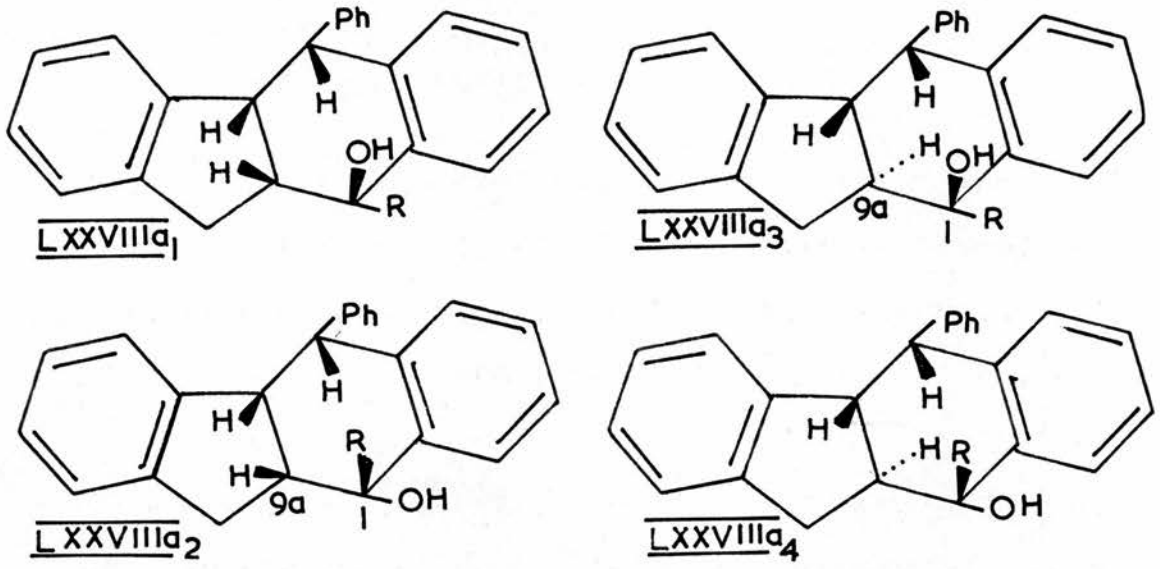
LXXVIIa$_2$



LXXVIIa$_4$

Only two diastereoisomeric ketones are obtained and these must have either structures LXXVIIa$_1$ and LXXVIIa$_3$ or structures LXXVIIa$_2$ and LXXVIIa$_4$. Because of steric effects it is probable that the ketones have structures LXXVIIa$_1$ and LXXVIIa$_3$.

The carbinol (LXXVIIIa) has four asymmetric centres and can give rise to sixteen optical isomers, obtainable as eight racemic modifications. Each of the ketones (LXXVIIa) can give two racemic modifications of the carbinol (LXXVIIIa). If it is assumed that the ketones have structures LXXVIIa$_1$ and LXXVIIa$_3$, then the four diastereoisomeric carbinols which could be formed, have the following structures:-



Only one carbinol was formed from each ketone. The ease of dehydration suggests that both carbinols have the OH group at position 1 and the H atom at position 9a trans to each other, i.e. that the carbinols have the structures LXXVIIIa$_2$ and LXXVIIIa$_3$.

The structure of 1-anisyl-4-phenyl-2,3-benzofluorene (LXXXa) obtained from the adduct (LXXVa) as indicated in scheme J , was determined by m.p. and mixed m.p. with an authentic sample, obtained by the ring-closure with spontaneous dehydrogenation of 1-diphenylmethylene-2-anisylidenehydrindene (LXXXVI), and by comparison of their ultraviolet and infrared spectra.

Compound LXXXVI was prepared by heating diphenylketene and 2-anisylidene-1-hydrindone (LXXXV) under nitrogen

for 3½ hours at 130-140°. The only other product isolated from the reaction was the δ-lactone (LXXXVII).

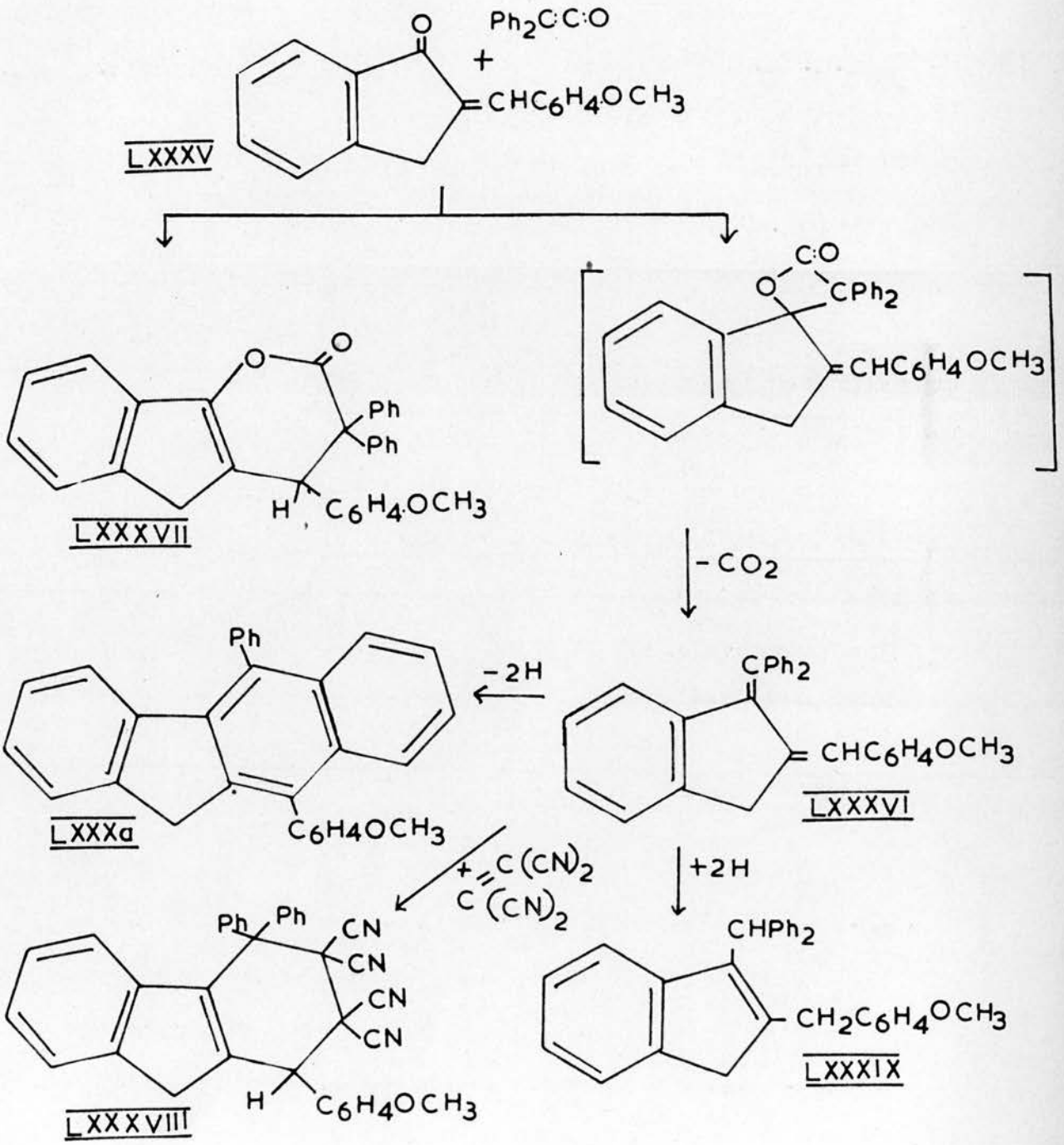
Compound LXXXVI was similar to 1-diphenylmethylene-2-benzylidenehydrindene (I) in chemical and physical properties (p. 37). It was obtained as pale yellow needles, m.p. 186°, which became brighter yellow on exposure to light or on heating. It gave orange-yellow solutions which were not fluorescent in ultraviolet light. The ultraviolet spectrum (Fig. 5) showed no characteristic maxima or minima and solutions did not obey Beer's Law.

It formed an adduct (LXXXVIII) with tetracyanoethylene and on reduction with aluminium amalgam in moist ether, it gave 3-benzhydryl-2-anisylindene (LXXXIX). Ozonolysis of the compound LXXXVI gave anisaldehyde which was characterised as the 2:4-dinitrophenylhydrazone and by oxidation to anisic acid. A solution of compound LXXXVI in hexane became colourless within 24 hours and the solution had a blue fluorescence in ultraviolet light.

A solution of compound LXXXVI in benzene and light petroleum was exposed to daylight for 6 months. From the solution 1-anisyl-4-phenyl-2,3-benzofluorene (LXXXa), m.p. 199°, was isolated, which had the characteristic ultraviolet spectrum of this type of compound (Fig. 5) and a small quantity of 1-anisyl-4-phenyl-2,3-benzofluorenone (LXXII), m.p. 206°.

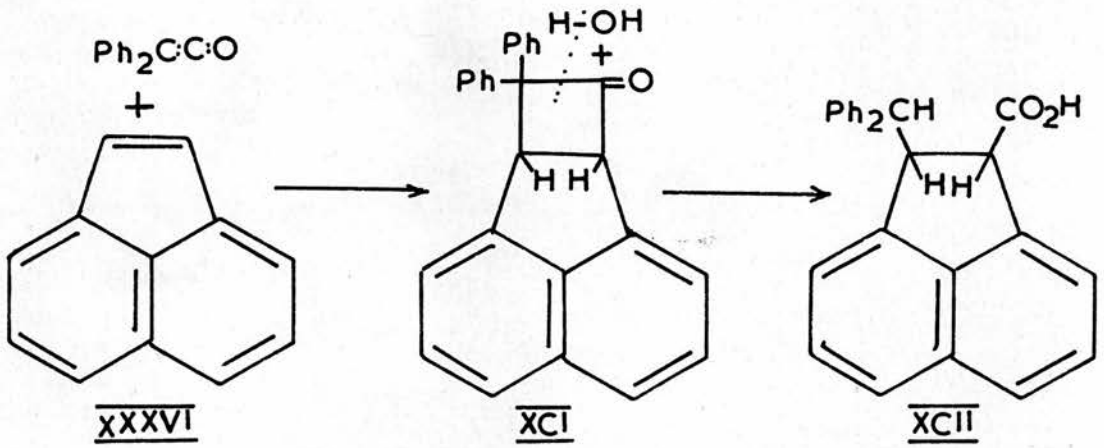
From the condensation of indene with 2-anisyl-5-phenyl-

SCHEME L


Ph2C:C:O
+
CHC6H4OCH3
LXXXV
C:O
O
CPh2
CHC6H4OCH3
O
O
Ph
Ph
H
C6H4OCH3
LXXXVII
-CO2
Ph
-2H
CPh2
CHC6H4OCH3
LXXXVI
LXXXa
C6H4OCH3
+C(CN)2
C(CN)2
+2H
Ph
Ph
CN
CN
CN
CN
H
C6H4OCH3
LXXXVIII
CHPh2
CH2C6H4OCH3
LXXXIX

3,4-benzofuran (XC), a mixture of 1-anisyl-4-phenyl-2,3-benzofluorene (LXXXa) and 1-phenyl-4-anisyl-2,3-benzofluorene (LXXXb) was expected to be formed. Only compound LXXXa could be isolated, together with a colourless compound, m.p. 204-8° which absorbs strongly in the infrared at 1670 cms^{-1} indicating a conjugated ketone. This compound was not identified.

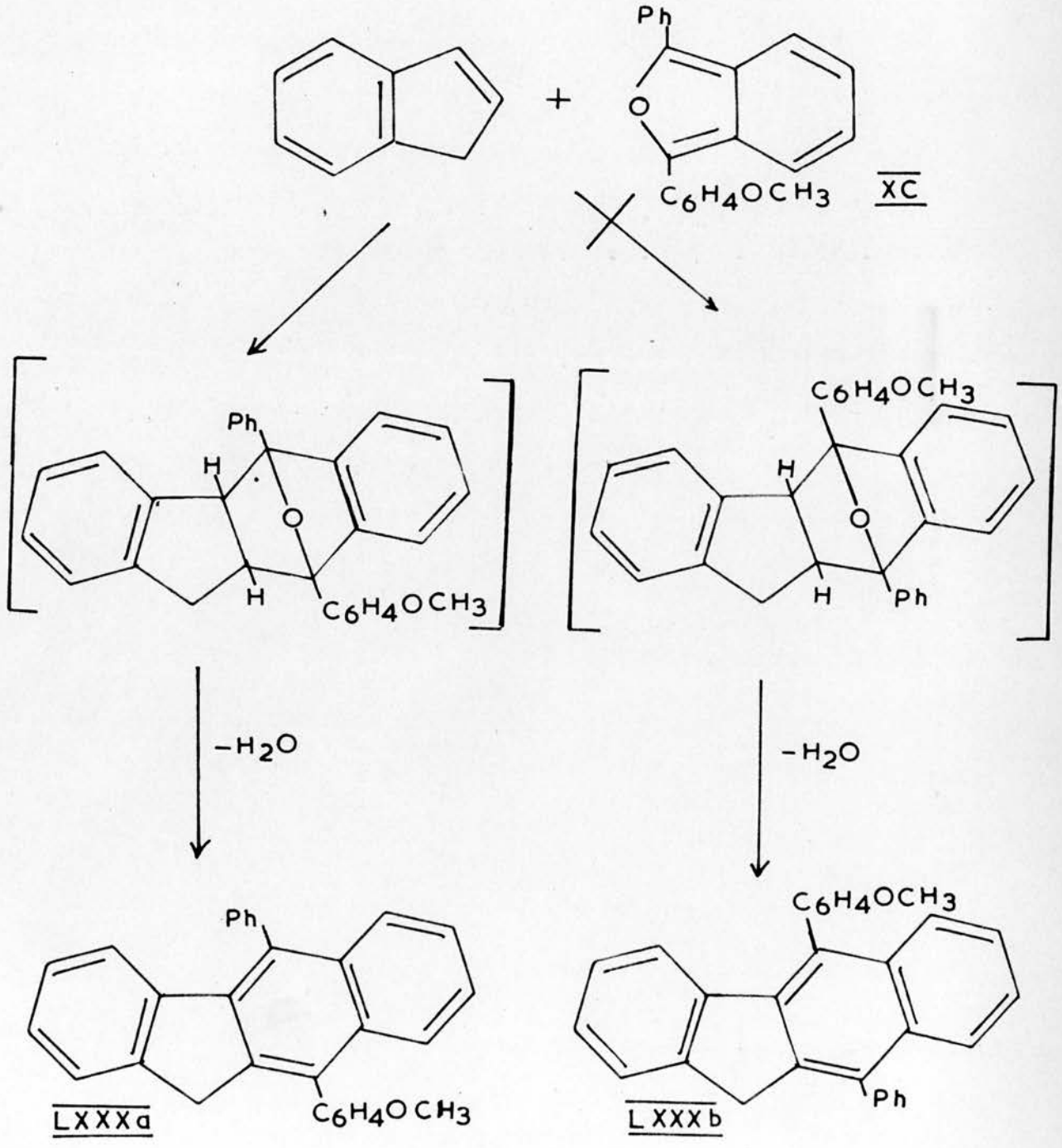
When diphenylketene was heated with acenaphthylene (XXXVI) for 3 hours at 160° an adduct, m.p. 144°, formed, which is considered to have structure XCI. On boiling the adduct with methanolic potassium hydroxide, a carboxylic acid is obtained, considered to be 1-benzhydrylacenaphthene-2-carboxylic acid (XCII).



XXXVI XCI XCII

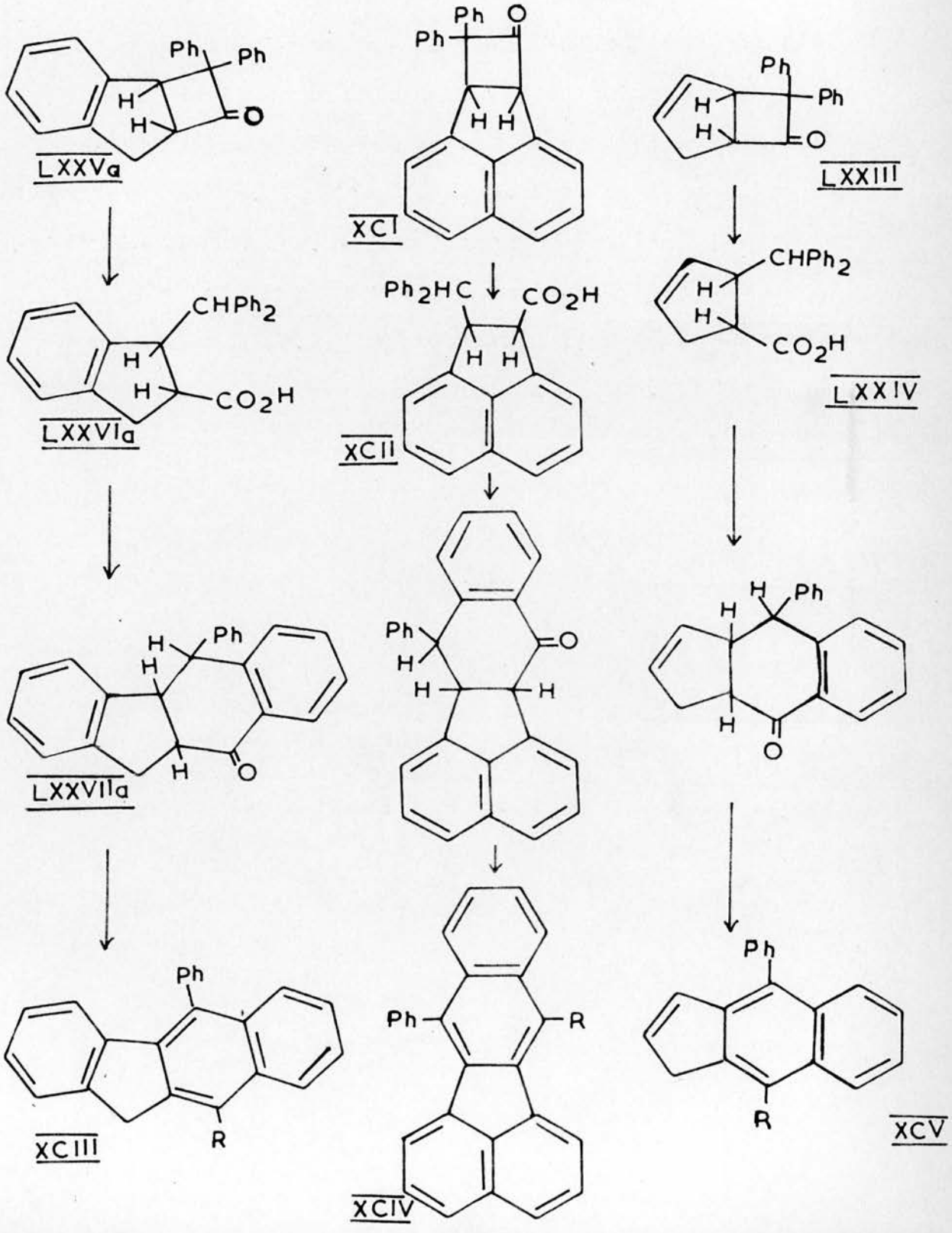
This investigation has shown that diphenylketene forms an adduct with indene analogous to the adduct formed with

SCHEME M



cyclopentadiene. The reactions involved in the proof of the structure of the diphenylketene-indene adduct illustrate a novel synthesis of 1-substituted 4-phenyl-2,3-benzofluorenes (XCIII). It should be possible to extend this synthesis to the preparation of other polynuclear hydrocarbons. For example by an analogous series of reactions, it should be possible to synthesise 7-substituted-10-phenyl-8,9-benzofluoranthenes (XCIV) from the adduct (XCI) of diphenylketene and acenaphthylene and 7-substituted-4-phenyl-5,6-benzindenes (XCV) from the adduct (LXXIII) of diphenylketene and cyclopentadiene.

SCHEME N


Ph
Ph
H
H
O
LXXVa
CHPh2
H
H
CO2H
LXXVIa
H
Ph
H
H
O
LXXVIIa
Ph
R
XCIII
Ph
O
Ph
H H
XCI
Ph2HC
CO2H
H H
XCII
Ph
O
H
H
H
XCIV
Ph
R
Ph
H
H
LXXIII
CHPh2
H
H
CO2H
LXXIV
H
Ph
H
H
O
Ph
R
XCV

Experimental

Preparation of 2,3-benzo-6-keto-7:7-diphenylbicyclo- [3,2,0] - hept-2-ene (LXXVa)

Diphenylketene (69.5 g.) and freshly distilled indene (45.5 g.) were heated at 120° for 4 hours. The product, which solidified on cooling, was washed with a small volume of light petroleum and recrystallised from ethanol.

Yield: 68 g. 61%. m.p. 123°.

Analysis

Found: C, 88.5; H, 5.6.

$C_{23}H_{18}O$ requires C, 89.0; H, 5.9%.

Infrared spectrum (cms^{-1}) 1780(s) (C=O) 1600(m) (C=C) 1580(m)

Preparation of 1-benzhydrylhydrindene-2-carboxylic acid (LXXVIa)

The adduct (LXXV) (62 g.) was boiled with 10% w.v. methanolic potassium hydroxide (250 ml.) for 3 hours. The solution was poured into water (300 ml.), acidified with hydrochloric acid and the precipitated acid filtered off and recrystallised from ethanol (500 ml.).

Yield: 58.5 g. 89%. m.p. 201-2°.

Analysis

Found: C, 83.8; H, 6.0.

$C_{23}H_{20}O_2$ requires C, 84.2; H, 6.1%

p-Nitrobenzyl ester, m.p. 149-150°.

Analysis

Found: N, 3.9. $C_{30}H_{25}NO_4$ requires N, 3.9%.

By evaporation of the ethanolic filtrate, a second crop of crystals (3.6 g.), m.p. 180-6° was obtained. The m.p. of this compound on repeated crystallisation from ethanol remained constant at 180-2°, suggesting that this second fraction was not an impure sample of the first crop of crystals, but an isomer.

Preparation of 1-keto-4-phenyl-1:4:4a:9a-tetrahydro-2,3-benzofluorene (LXXVIIa)

1-Benzhydrylhydrindene-2-carboxylic acid (LXXVIa) (1 g.) was converted into the acid chloride by boiling with thionyl chloride (1 ml.) for 3 hours. After evaporation of the excess thionyl chloride, the acid chloride was cyclised by aluminium chloride (1 g.) in benzene, trichloroethylene or methylene dichloride (20 ml.). The reaction mixture was boiled for 2 hours and poured into ice water. The product on crystallisation from ethanol gave colourless needles (about 50 mg.), m.p. 186-7°.

The carboxylic acid (8 g.) was converted into the acid chloride by thionyl chloride (10 ml.) as described above.

The acid chloride was heated with aluminium chloride (2 g.) in nitrobenzene (20 ml.) for 2 hours at 100°, poured into ice water and steam distilled. The brown gum remaining was dissolved in benzene and chromatographed on alumina. Development with light petroleum gave a pale yellow fraction which was evaporated. The residue, on crystallisation from benzene and light petroleum, gave colourless needles (0.5 g.), m.p. 114°.

The carboxylic acid (17.5 g.) was treated with anhydrous hydrogen fluoride (about 600 ml.) and left for two days. The hydrogen fluoride was evaporated and the residue treated with water (1 l.) and filtered. The residue was dissolved in benzene and extracted with sodium carbonate solution. The aqueous extracts on acidification gave a negligible amount of unchanged acid. The benzene solution was dried over sodium sulphate, filtered and most of the solvent evaporated. On adding light petroleum, discoloured crystals separated which were filtered off.

Yield: 11.4 g. 69%. m.p. 170-180°.

Recrystallisation of a sample from ethanol or light petroleum gave colourless needles, m.p. 186-7°. The mixed m.p. with the ketone obtained by cyclisation of the acid chloride in benzene, trichloroethylene or methylene dichloride, was not depressed.

Analysis

Found: C, 88.7; H, 5.5.

C, 88.4; H, 5.7.

$C_{23}H_{18}O$ requires C, 88.9; H, 5.8%.

Infrared spectrum (cms^{-1}) 1700(s) 1600(m)

(C=O) (C=C)

Reduction of a sample of the ketone with lithium aluminium hydride in ether gave 1-hydroxy-4-phenyl-1:4:4a:9a-tetrahydro-2,3-benzofluorene, colourless needles from aqueous ethanol, m.p. 232°.

Analysis

Found: C, 88.2; H, 6.5.

$C_{23}H_{20}O$ requires C, 88.4; H, 6.5%.

From the filtrate, a second crop of crystals (2 g.) was obtained, m.p. 100-4°, 12% yield. This compound was much more soluble in ethanol or light petroleum than the compound, m.p. 186-7°. Recrystallisation from light petroleum gave colourless needles, m.p. 114°. The mixed m.p. with the ketone obtained by the cyclisation of the acid chloride in nitrobenzene, was not depressed.

Analysis

Found: C, 88.7; H, 5.8.

$C_{23}H_{18}O$ requires C, 88.9; H, 5.8%.

Ultraviolet spectrum - Fig. 12.

Infrared spectrum (cms^{-1}) 1675(s) 1595(m)

(C=O) (C=C)

2:4-Dinitrophenylhydrazone, m.p. 255°.

Preparation of 1-hydroxy-1-anisyl-4-phenyl-1:4:4a:9a-tetrahydro-2,3-benzofluorene (LXXVIIIa)

The ketone (LXXVIIa) m.p. 186-7° (3.1 g.) in benzene (10 ml.) was added to anisylmagnesium bromide, prepared from p-bromoanisole (5.6 g.) and magnesium (0.72 g.) in ether (100 ml.), and the reaction mixture boiled for 15 minutes. Working up in the usual manner gave a white solid, which was recrystallised from ethanol giving colourless prisms, m.p. 214°.

Analysis

Found: C, 85.9; H, 6.3.

$C_{30}H_{26}O_2$ requires C, 86.1; H, 6.3%.

Infrared spectrum (cms^{-1})	3,550(m)	1610(m)	1240(s)
	(OH)	(C=C)	($-OCH_3$)

The ketone (LXXVIIa), m.p. 114° (1.0 g.) in benzene (10 ml.) was added to anisylmagnesium bromide, prepared from p-bromoanisole (3.7 g.) and magnesium (0.72 g.) in ether (100 ml.) and the reaction mixture boiled for 1 hour. Working up in the usual manner gave a white solid, which was crystallised from benzene and light petroleum, giving fine needles, m.p. 210°.

Analysis

Found: C, 86.9; H, 6.6.

$C_{30}H_{26}O_2$ requires C, 86.1; H, 6.3%.

Infrared spectrum (cms^{-1})	3,600(m)	1605(m)	1250(s)
	(OH)	(C=C)	($-OCH_3$)

The mixed m.p. of the two hydroxy compounds was depressed to 187-193°.

Preparation of 1-anisyl-4-phenyl-4:4a-dihydro-2,3-benzofluorene (LXXIXa)

The alcohol (LXXVIIIa), m.p. 214° (1 g.) was heated with 90% formic acid (7 ml.) for 15 minutes at 100° and poured into water.

Yield: 0.9 g. 96%. m.p. 165-8°.

Recrystallisation from ethanol gave colourless plates, m.p. 167-8°. Dehydration of the alcohol could be effected by boiling it in ethanol containing a few drops of hydrochloric acid. On cooling, the product crystallised, m.p. 167-8°.

Dehydration of the alcohol (LXXVIIIa), m.p. 210°, by formic acid or by ethanol containing a few drops of hydrochloric acid gave the same dihydrofluorene, as was shown by m.p., mixed m.p. and by comparison of the ultraviolet and infrared spectra which were identical.

Analysis

Found: C, 89.3; H, 6.1.

$C_{30}H_{24}O$ required C, 89.0; H, 6.0%.

Ultraviolet spectrum - Fig. 12.

Preparation of 1-anisyl-4-phenyl-2,3-benzofluorene (LXXXa)

The dihydro compound (0.4 g.) was boiled with chloranil (0.25 g.) in xylene (3 ml.) for 5 hours and chromatographed on alumina and developed with benzene. The fraction with the

blue fluorescence gave colourless needles, m.p. 199°. The mixed m.p. with an authentic sample of 1-anisyl-4-phenyl-2,3-benzofluorene was not depressed and the ultraviolet and infrared spectra were identical.

Analysis

Found: C, 90.1; H, 5.7.

$C_{30}H_{22}O$ requires C, 90.3; H, 5.5%.

Preparation of 2-anisylidene-1-hydrindone (LXXXV)

Pfeiffer and Mitz, Ber., 1938, 71B, 272.

1-Hydrindone (6.6 g.) was condensed with anisaldehyde (6.8 g.) in ethanol (25 ml.) in the presence of a few ml. of 10% w.v. ethanolic potassium hydroxide.
Yield: 9 g. 72%. m.p. 139-140° (Lit. m.p. 141°).

Preparation of 1-diphenylmethylene-2-anisylidene hydrindene (LXXXVI)

2-Anisylidene-1-hydrindone (LXXXV) (7 g.) and diphenylketene (5.4 g.) were heated together under nitrogen for 3½ hours at 130-140°. The product was boiled with light petroleum (200 ml.) and filtered. Anisylidenehydrindone was recovered from the filtrate in 21% yield.

The residue was crystallised from benzene and light petroleum giving the product (3.1 g.) as pale yellow needles, m.p. 186°.

Analysis

Found: C, 89.0; H, 6.3.

$C_{30}H_{24}O$ requires C, 89.0; H, 6.0%.

Ultraviolet spectrum - Fig. 5.

The filtrate deposited colourless crystals (0.8 g.) on standing overnight, which were recrystallised from benzene and light petroleum, giving the δ-lactone (LXXXVII), m.p. 219°.

Analysis

Found: C, 83.6; H, 5.8.

$C_{31}H_{24}O_3$ requires C, 83.6; H, 5.5.

The infrared and ultraviolet spectra of this compound (LXXXVII) and the δ-lactone (V), formed by the addition of diphenylketene to 2-benzylidene-1-hydrindone, were similar.

Infrared spectrum (cms^{-1}) 1750(s) (C=O) 1660(w) 1600(m) (C=C) 1260(s) (OCH_3)

The hydrocarbon (LXXXVI), m.p. 186° (0.5 g.) was dissolved in benzene and light petroleum and left for 6 months in daylight. The solution was evaporated, and the residual gum dissolved in a small volume of benzene and chromatographed on alumina. Development with light petroleum gave a fraction with a blue fluorescence, which was evaporated. Crystallisation of the residue from ethanol gave colourless needles of 1-anisyl-4-phenyl-2,3-benzofluorene (LXXXa), m.p. 199°.

Ultraviolet spectrum - Fig. 5.

A later bright yellow fraction gave a gum on evaporation, which gave bright yellow needles from ethanol, m.p. 206°, considered to be 1-anisyl-4-phenyl-2,3-benzofluorenone (LXXII).

Analysis

Found: C, 86.4; H, 4.3.

$C_{30}H_{20}O_2$ requires C, 87.4; H, 4.9%.

Ultraviolet spectrum - Fig. 12.

Infrared spectrum (cms^{-1})

1710(s)	1610(m)	1600(m)	1230(s)	760	725	705
(C:O)	(C:C)		(OCH_3)			

Preparation of 1-anisyl-4:4-diphenyl-2:2,3:3-tetracyano-1,2,3,4-tetrahydrofluorene (LXXXVIII)

A solution of compound LXXXVI (0.2 g.) and tetracyanoethylene (0.07 g.) in benzene (10 ml.) was boiled for 1 hour, half the solvent evaporated and light petroleum (5 ml.) added. A solid separated which was recrystallised from benzene and light petroleum giving colourless prisms, having no distinct m.p.

Analysis

Found: C, 81.3; H, 4.6; N, 11.6

$C_{36}H_{24}N_4O$ requires C, 81.8; H, 4.6; N, 10.6%.

Preparation of 3-benzhydryl-2-anisylindene (LXXXIX).

Compound LXXXVI (0.2 g.) was dissolved in moist ether (120 ml.) and reduced with aluminium amalgam by Thiele's method[11] for two days. The reaction mixture was filtered and the filtrate evaporated. The residue was crystallised from ethanol giving colourless needles, m.p. 82°.

Analysis

Found: C, 89.0; H, 6.5.

$C_{30}H_{26}O$ requires C, 89.5; H, 6.5%.

Ultraviolet spectrum - Fig. 5.

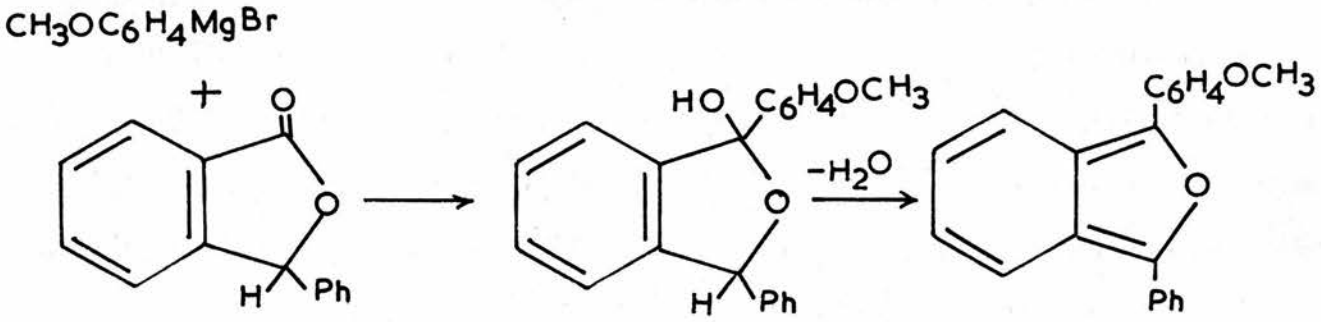
Ozonolysis of 1-diphenylmethylene-2-anisylidenehydrindene (LXXXVI)

Compound LXXXVI (0.5 g.) was dissolved in carbon tetrachloride (100 ml.) and ozone passed through the solution for 20 minutes until the solution became colourless. The solution was poured into water and steam distilled. The first fraction containing the solvent was rejected. The second fraction was extracted with ether and the ether evaporated. Part of the residual oil was oxidised with hot aqueous potassium permanganate, decolourised by sulphurous acid and the solution evaporated to small volume. On cooling, anisic acid, m.p. 184°, separated (Lit. m.p. 184°).

The rest of the oil was converted to the 2:4-dinitrophenylhydrazone, m.p. 254° (Lit. m.p. 254° for anisaldehyde 2:4-dinitrophenylhydrazone).

Preparation of 2-anisyl-5-phenyl-3,4-benzofuran (XC)

cf. Guyot and Catel, Bull. Soc. Chim., 1906, 35, 1127.



Anisylmagnesium bromide, prepared from p-bromoanisole (10.3 g.) and magnesium (1.5 g.) in ether (200 ml.), was added dropwise with stirring to phenylphthalide (9.75 g.) in benzene (150 ml.). When the addition was complete, the reaction mixture was boiled for 10 minutes and poured on to ice and hydrochloric acid. The organic layer was separated and the solvent was evaporated. The residual oil was dissolved in ethanol (100 ml.), hydrochloric acid (1 ml.) added and the solution boiled for 5 minutes. On cooling the bright yellow solution, which had a green fluorescence, 2-anisyl-5-phenyl-3:4-benzofuran separated.

Yield: 6.6 g. 48%. m.p. 95°.

Analysis

Found: C, 84.2; H, 5.6.

$C_{21}H_{16}O_2$ requires C, 84.0; H, 5.4%.

Preparation of 1-anisyl-4-phenyl-2,3-benzofluorene (LXXX)

cf. Weiss and Beller, Monatsh. 1923, 61, 143.

Hydrogen chloride was passed through a suspension of 2-anisyl-5-phenyl-3,4-benzofuran (XC) (3 g.) and indene (1.25 g.) in ethanol for 1 hour. A cream coloured solid (2.2 g.) separated and was dissolved in a small volume of benzene and chromatographed on alumina. Development with light petroleum gave a fraction with a blue fluorescence, which was evaporated. The residue (0.9 g.) was crystallised from light petroleum and then from ethanol giving colourless needles, m.p. 199°. A mixed m.p. with an authentic sample of 1-anisyl-4-phenyl-2,3-benzofluorene prepared by the cyclisation of 1-diphenylmethylene-2-anisylidenehydrindene (LXXXVI) was not depressed. The ultraviolet spectra (Fig. 5) and the infrared spectra of the two samples were identical.

A later chromatographic fraction eluted with acetone gave a white solid (0.5 g.), m.p. 204-8°, which was shown by its infrared spectrum to be a ketone.

Infrared spectrum (cms^{-1}) 1670(s) (C=O) 1600(m) (C=C) 1240(s) (OCH_3) 1770 1710

Preparation of 3,4-(1,2-acenaphthenylene)-2:2-diphenyl cyclobutan-1-one (XCI)

Diphenylketene (2.2 g) and acenaphthylene (XXXVI) were heated at 100° for 3 hours. The reaction mixture was treated with light petroleum and the solid filtered off. The solid (2 g.) was only partly soluble in ethanol leaving an amorphous residue (0.5 g.). The adduct crystallised from ethanol in pale yellow needles (0.6 g.), m.p. 144°.

Analysis

Found: C, 89.8; H, 5.1.

$C_{26}H_{18}O$ requires C, 90.1; H, 5.2%.

Infrared spectrum (cms^{-1}) 1780(s) (C=O) 1600(m) (C=C)

Preparation of 1-benzhydrylacenaphthene-2-carboxylic acid (XCII)

The adduct (XCI) (0.25 g.) was boiled with 10% w.v. methanolic potassium hydroxide (3 ml.) for 30 minutes, poured into water (20 ml.) and acidified with hydrochloric acid. Recrystallisation of the precipitate from ethanol gave colourless prisms of the acid, m.p. 250°.

Analysis

Found: C, 84.8; H, 5.7.

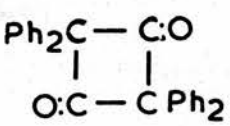
$C_{26}H_{20}O_2$ requires C, 85.7; H, 5.5%.

Section 6

The Reaction of Diphenylketene with 1-Hydrindone and Indone

Discussion

Diphenylketene does not react with carbonyl compounds containing an α-hydrogen atom to give β-lactones or their decomposition products. This work has been summarised in the Introduction (pp. 11-13). When equimolecular proportions of diphenylketene and 1-hydrindone were heated under nitrogen in a sealed tube for 5 hours at 150° an orange compound, m.p. 224°, was formed. Its infrared spectrum was consistent with an αβ-unsaturated ketone structure and the analysis corresponded to $C_{32}H_{22}O_2$, suggesting that the compound was formed by the reaction of 1 ml. of diphenylketene with 2 mols. of 1-hydrindone with the elimination of 1 mol. of water and 1 mol. of hydrogen. The compound gave a yellow solution in ethanol which rapidly decolourised. The dimer of diphenylketene, tetraphenylcyclobutan-1:3-dione (XCIII) and unchanged 1-hydrindone were isolated from the reaction also. The dimer was the sole product isolated from the reaction of diphenylketene with 1-tetralone under similar conditions.

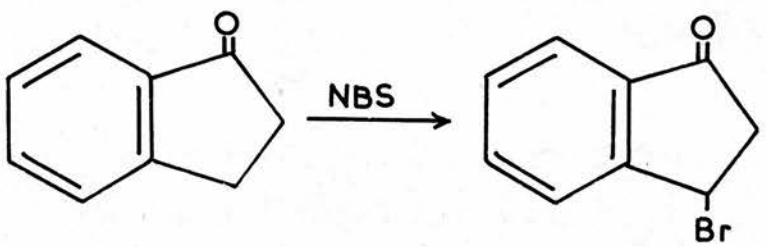


XCIII

1-Diphenylmethyleneindene (XV) could not be isolated from the reaction of diphenylketene with indone. A small quantity of a hydrocarbon, m.p. 182°, was isolated. The ultraviolet spectrum of this compound was very similar to

trans-stilbene and its analysis corresponded to the molecular formula $C_{22}H_{18}$. The structure of this compound was not explained.

Stafford[28] reported that 3-bromo-1-hydrindone could be prepared by boiling 1-hydrindone with N-bromosuccinimide in carbon tetrachloride. It was found that the reaction was facilitated and the yield improved by adding a small amount of benzoyl peroxide to the reaction mixture. In an analogous reaction w-benzylacetophenone was converted into w-(α-bromobenzyl)-acetophenone.

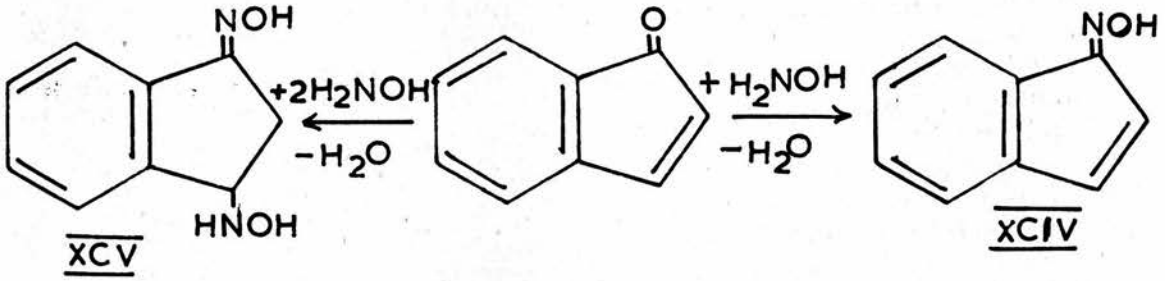


$$Ph.CO.CH_2.CH_2.Ph \xrightarrow{NBS} Ph.CO.CH_2.CHBr.Ph$$

These bromoketones did not form 2:4-dinitrophenylhydrazones, but when treated with 2:4-dinitrophenylhydrazine in hot ethanol containing 1% hydrochloric acid, underwent dehydrobromination to give the 2:4-dinitrophenylhydrazones of indone and benzylideneacetophenone, respectively. Under the same conditions, 2-bromo-1-hydrindone formed a 2:4-dinitrophenylhydrazone without dehydrobromination occurring[28, 107].

Indone, prepared by the dehydrobromination of 3-bromo-1-hydrindone with symm. collidine[108], gave with hydroxylamine

not the oxime (XCIV) but a compound, m.p. 180°, the analysis of which accorded reasonably with structure XCV.



Experimental

The reaction of diphenylketene with 1-hydrindone

1-Hydrindone (1.9 g.) and diphenylketene (2.9 g.) were heated under nitrogen in a sealed tube for 5 hours at 150°. The reaction mixture was treated with light petroleum and ether. The orange solid dissolved leaving a white residue which was recrystallised from benzene and light petroleum giving colourless needles of tetraphenylcyclobutan-1,3-dione, m.p. 245°. (Lit. m.p. 244-5°)[36].

Infrared spectrum (cms^{-1}) 1750(s) 1600(m)
(C:O) (C=C)

The orange filtrate deposited orange needles on evaporation which, on recrystallisation from benzene and light petroleum, melted at 224°.

Analysis

Found: C, 87.5; H, 5.1.

$C_{32}H_{22}O_2$ requires C, 87.6; H, 5.1.

$C_{32}H_{24}O_2$ requires C, 87.2; H, 5.5%.

Infrared spectrum (cms^{-1})

1700(s) 1600(s) 1580(s) 786, 762, 730, 718, 695.
(C:O) (C:C)

A small quantity of 1-hydrindone was recovered on chromatography of the combined filtrates on alumina.

Preparation of 3-bromo-1-hydrindone

cf. Stafford, Ph.D. Thesis (Edin.), p. 185.

1-Hydrindone (10 g.) and N-bromosuccinimide (13.4 g.) were boiled in carbon tetrachloride (75 ml.) in the presence of a small quantity of benzoyl peroxide, for 1 hour. The reaction mixture was cooled to 5° and the succinimide filtered off. The filtrate was evaporated under reduced pressure and the residual oil triturated with light petroleum (20 ml.). The discoloured crystals were filtered off and recrystallised from hexane.

Yield: 9.2 g. 59%. m.p. 50-2° (Lit. m.p. 55°).

A sample of the bromoketone was dissolved in ethanol and a hot solution of 2:4-dinitrophenylhydrazine in ethanol containing 1% hydrochloric acid, was added. The flocculent precipitate was filtered off and recrystallised from acetic acid in orange needles, m.p. 234°. The mixed m.p. with indone 2:4-dinitrophenylhydrazone was not depressed.

Analysis

Found: C, 55.6; H, 3.1; N, 18.9.

$C_{15}H_{10}N_4O_4$ requires C, 58.0; H, 3.3; N, 18.1%.

Preparation of w-benzylacetophenone

cf. Organic Synthesis, 1928, 8, 37.

Hydrogenation of benzylideneacetophenone (41.6 g.) in ethyl acetate (300 ml.) with hydrogen at 5 atmos. and a palladium on barium sulphate catalyst gave an almost

quantitative yield of w-benzylacetophenone (41.6 g.), m.p. 70°. (Lit. m.p. 73°).
Ultraviolet spectrum - Fig. 7.

Preparation of w-(α-bromobenzyl)-acetophenone

w-Benzylacetophenone (4.2 g.) and N-bromosuccinimide (3.6 g.) were boiled in carbon tetrachloride (25 ml.) in the presence of a small amount of benzoyl peroxide, for 30 minutes. Hydrogen bromide was evolved during the reaction.

The succinimide was filtered off. On cooling, the filtrate deposited colourless crystals (1.5 g.) which were recrystallised from carbon tetrachloride giving colourless plates of bromobenzylacetophenone, m.p. 109-111°. (Lit. m.p. 111°)[109].

The filtrate on evaporation gave benzylideneacetophenone, which was recrystallised from ethanol and identified by m.p. 53-5°, and by mixed m.p.

The bromoketone underwent dehydrobromination on addition of ethanolic 2:4-dinitrophenylhydrazine to give the 2:4-dinitrophenylhydrazone of benzylideneacetophenone, m.p. 247-9°. The mixed m.p. with an authentic sample was not depressed.

Preparation of 2-bromo-1-hydrindone

Johnson and Shelberg, J. Amer. Chem. Soc., 1945, 67, 1751.

Bromine (2.1 ml.) was added dropwise with stirring to a solution of 1-hydrindone (4.8 g.) dissolved in ether (200 ml.) at 10°. When the addition was complete, the solvent was evaporated under reduced pressure and the residual oil triturated with light petroleum giving colourless crystals (6.8 g.) of 2-bromo-1-hydrindone, m.p. 37-8°. (Lit. m.p. 38°).

Analysis

Found: C, 49.1; H, 3.0; Br, 32.3.

Calc. for C_9H_7BrO: C, 51.2; H, 3.3; Br, 37.9%.

As found by Ramirez and Kirby and by Stafford, 2-bromo-1-hydrindone forms a 2:4-dinitrophenylhydrazone which does not undergo dehydrobromination, red needles, m.p. 212-3°. (Ramirez and Kirby, m.p. 205-6°[107]; Stafford, m.p. 215°[28]).

Analysis

Found: N, 14.65; Br, 20.75%.

Calc. for $C_{15}H_{11}BrN_4O_4$: N, 14.3; Br, 20.4%.

Preparation of Indone

Marvel and Hinman, J. Amer. Chem. Soc., 1954, 76, 5435.

A solution of 3-bromo-1-hydrindone (8.5 g.) in symm. collidine (30 ml.) and ether (60 ml.) was stirred at room temperature for 4 hours and then poured onto ice. The ether layer was extracted with hydrochloric acid and then

washed with sodium bicarbonate solution, dried over sodium sulphate, filtered and the filtrate evaporated. The residual oil was distilled at 0.5 mm. on a water bath at 80°.

Yield: 3.3 g. 62%.

2:4-Dinitrophenylhydrazone crystallised from acetic acid in orange needles, m.p. 234°.

Analysis

Found: C, 59.0; H, 3.0; N, 17.7.

$C_{15}H_{10}N_4O_4$ requires C, 58.0; H, 3.3; N, 18.1%.

Attempted preparation of indone oxime (XCIV)

Equimolecular proportions of indone and hydroxylamine hydrochloride were dissolved in aqueous ethanol and an excess of 10% w.v. sodium bicarbonate solution added. The yellow solution became colourless and an oil gradually separated which solidified on standing. The solid crystallised from methanol in colourless needles, m.p. 180°. Stafford[28] gives the m.p. of indone oxime as 80°.

Analysis

Found: N, 15.3%.

The reaction was repeated using an excess of hydroxylamine. Crystallisation of the product from methanol gave colourless needles, m.p. 180°.

Analysis

Found: N, 14.8.

$C_9H_{10}N_2O_2$ requires N, 15.7%.

C_9H_7NO requires N, 9.65%.

The reaction of diphenylketene with indone

Diphenylketene (1.3 g.) and indone (1.5 g.) were heated under nitrogen in a sealed tube for 3½ hours at 140-145°. The reaction mixture was treated with ether and the insoluble residue (0.2 g.), m.p. above 260°, filtered off.

The ether solution was evaporated and the residual oil was chromatographed on alumina. Development with light petroleum gave a fraction, which on evaporation gave a small quantity of solid which crystallised from light petroleum as glistening pale yellow needles, m.p. 182°.

Analysis

Found: C, 93.6; H, 6.2.

$C_{22}H_{18}$ requires C, 93.6; H, 6.4%.

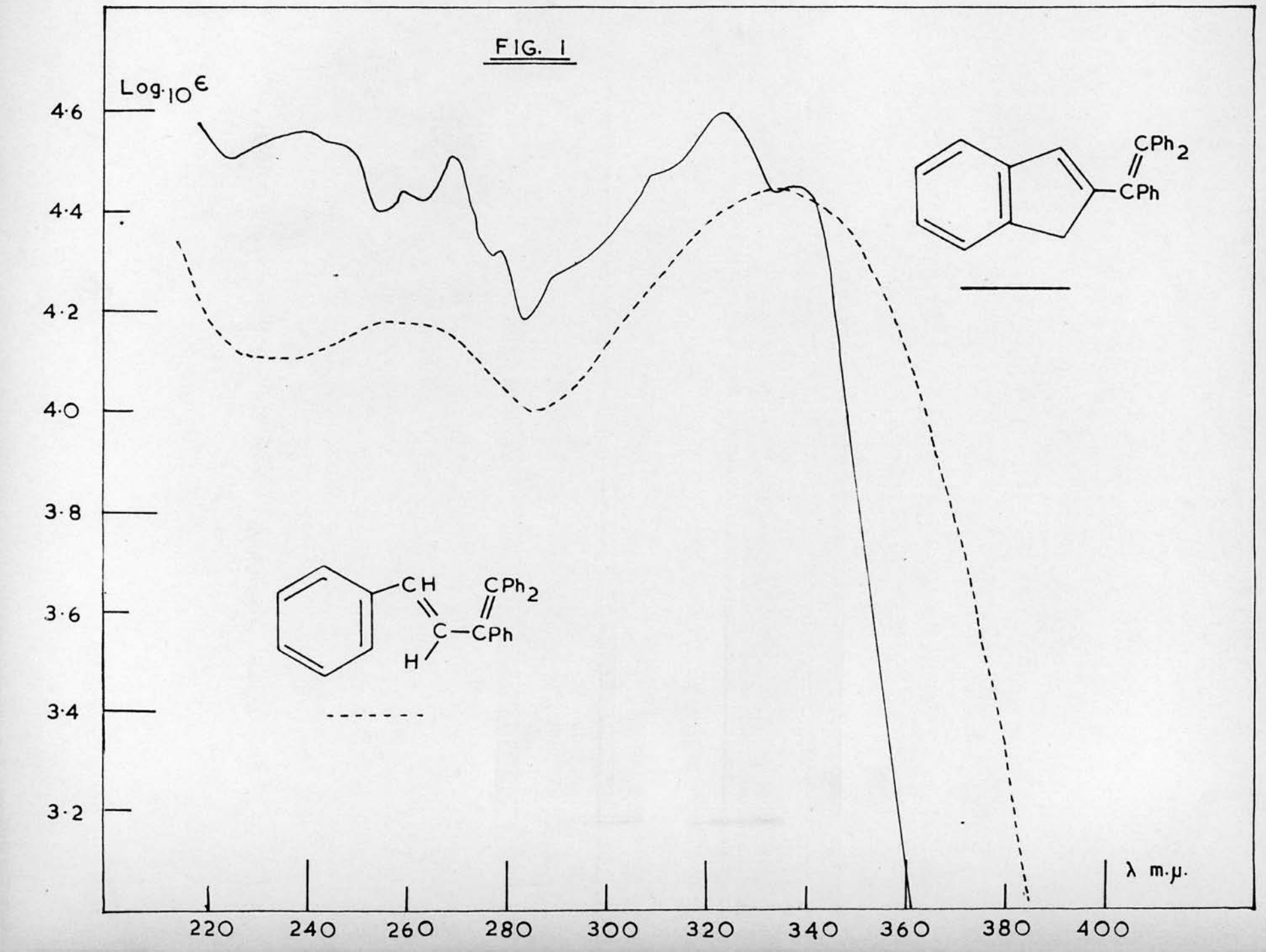
The ultraviolet spectrum was very similar to the spectrum of trans-stilbene (Fig. 7).

λ max. 319, 238 mμ. ($\log_{10}\epsilon$ 4,43, 4.27)

λ min. 262 mμ. ($\log_{10}\epsilon$ 3.10)

Ultraviolet Spectra

FIG. 1


Log·10 ε
4·6
4·4
4·2
4·0
3·8
3·6
3·4
3·2
220
240
260
280
300
320
340
360
380
400
λ m.μ.
CPh2
CPh
CH
CPh2
C—CPh
H

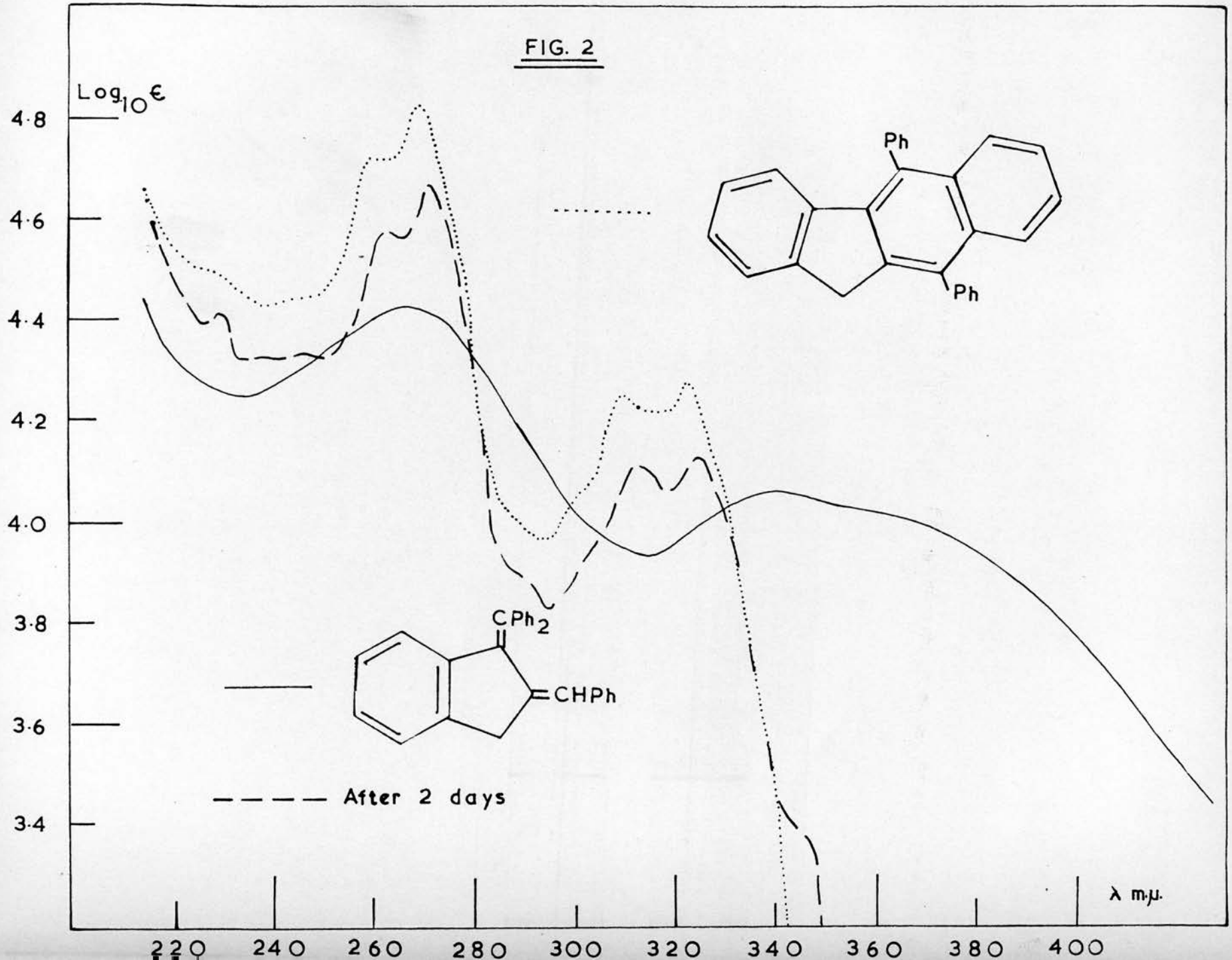
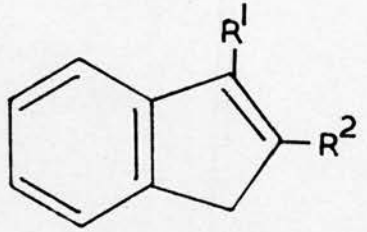
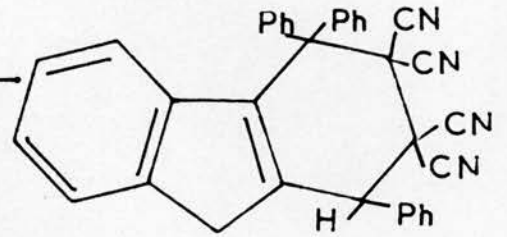


FIG. 2
Log10 ε
4·8
4·6
4·4
4·2
4·0
3·8
3·6
3·4
Ph
Ph
CPh2
CHPh
After 2 days
λ mμ.
220
240
260
280
300
320
340
360
380
400

FIG. 3





—— $R^1 = Ph_2CH-$, $R^2 = PhCH_2-$

····· $R^1 = Ph_2CH-$, $R^2 = H-$

– – – – $R^1 = H-$, $R^2 = PhCH_2-$

Solvent : Chloroform

$Log_{10}\epsilon$

4·6
4·4
4·2
4·0
3·8
3·6
3·4
3·2

220 240 260 280 300

220 240 260 280

λ m.μ.

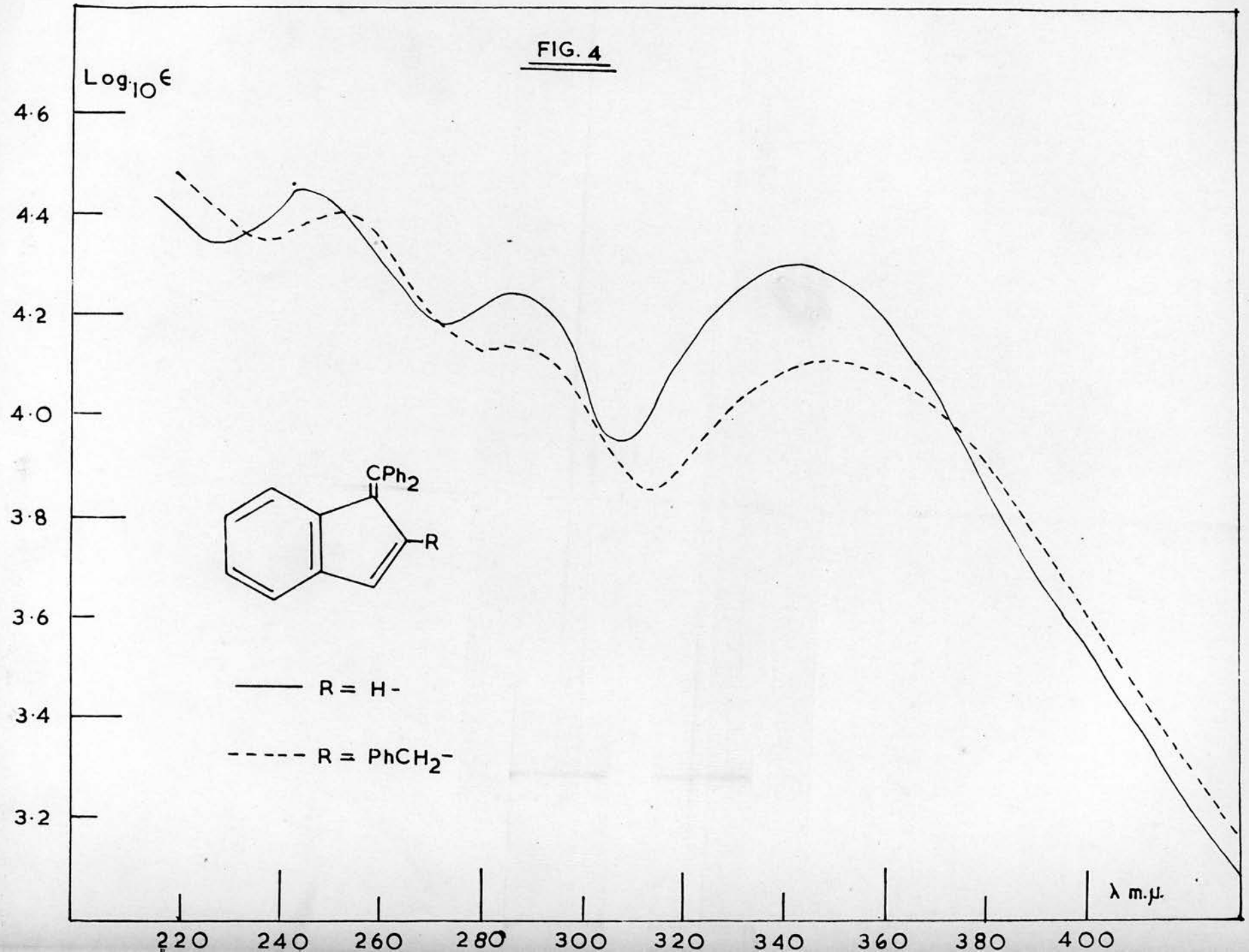


FIG. 4
Log10 ε
4·6
4·4
4·2
4·0
3·8
3·6
3·4
3·2
CPh2
R
R = H-
R = PhCH2-
λ m.μ.
220
240
260
280
300
320
340
360
380
400

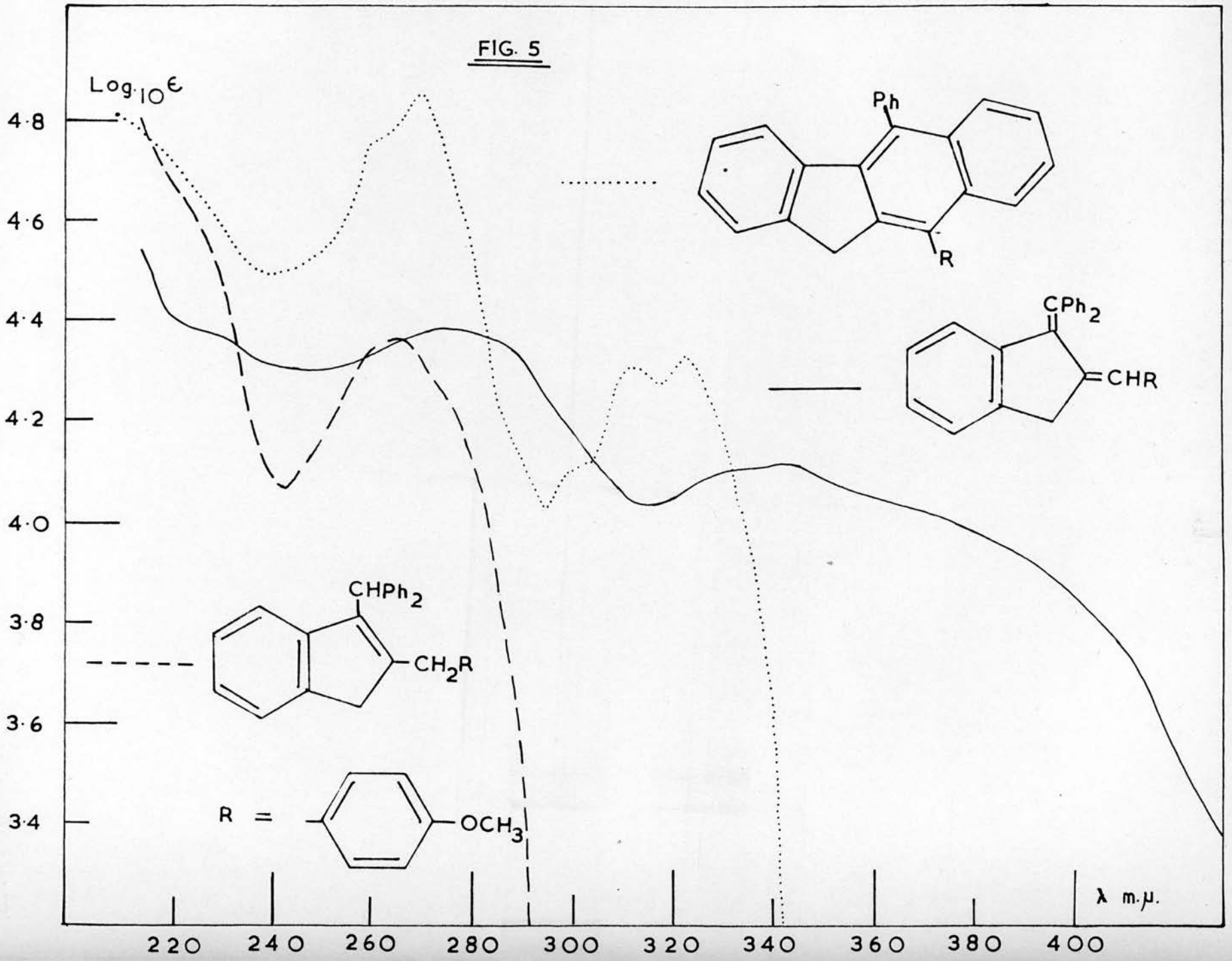
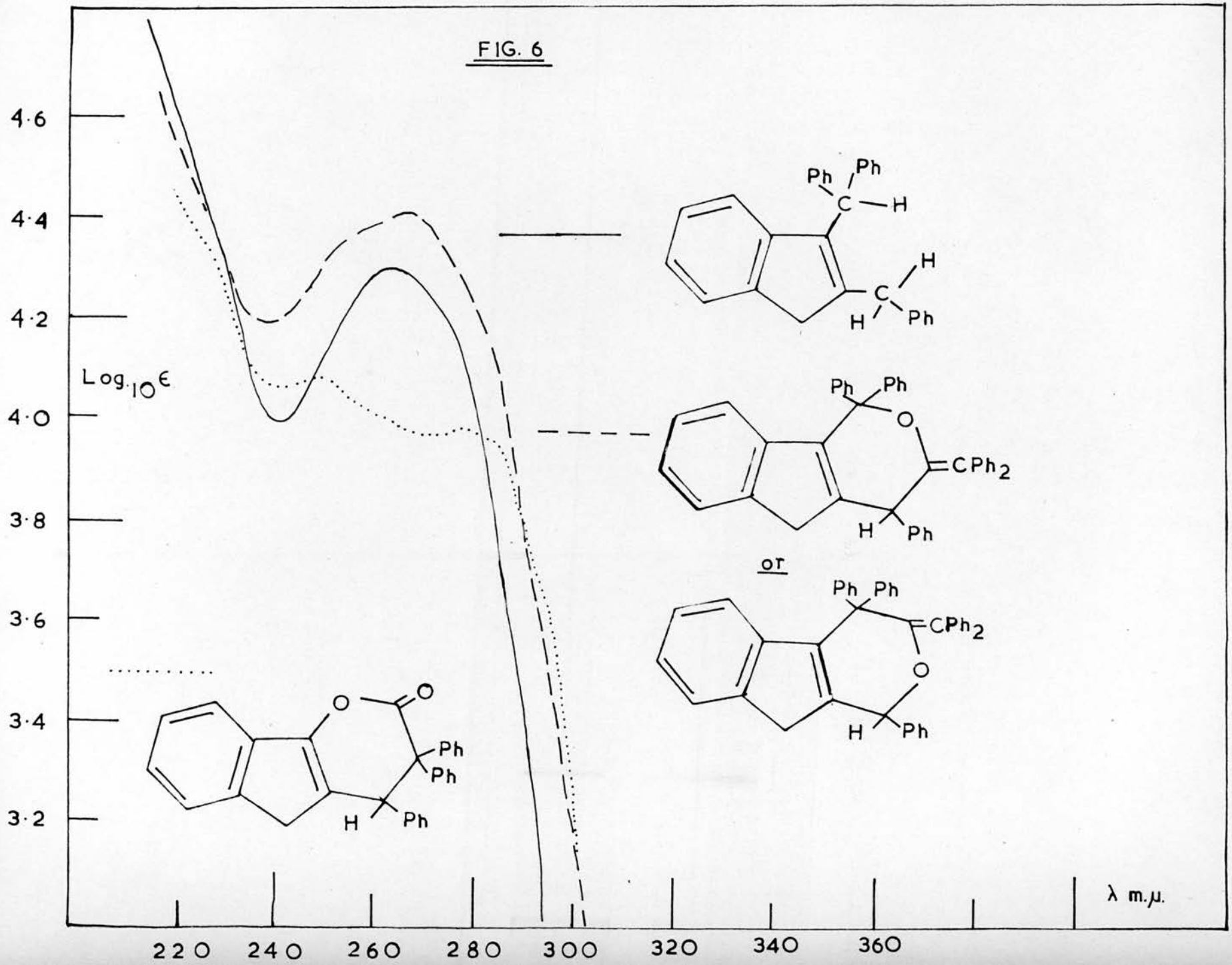


FIG. 5
Log10 ε
4·8
4·6
4·4
4·2
4·0
3·8
3·6
3·4
Ph
R
CPh2
CHR
CHPh2
CH2R
R =
OCH3
λ m.μ.
220
240
260
280
300
320
340
360
380
400

FIG. 6


4·6
4·4
4·2
Log.10 ε
4·0
3·8
3·6
3·4
3·2
220
240
260
280
300
320
340
360
λ m.μ.
Ph
Ph
C
H
H
C
H
Ph
Ph
Ph
O
CPh2
H
Ph
or
Ph
Ph
CPh2
O
H
Ph
O
O
Ph
Ph
H
Ph

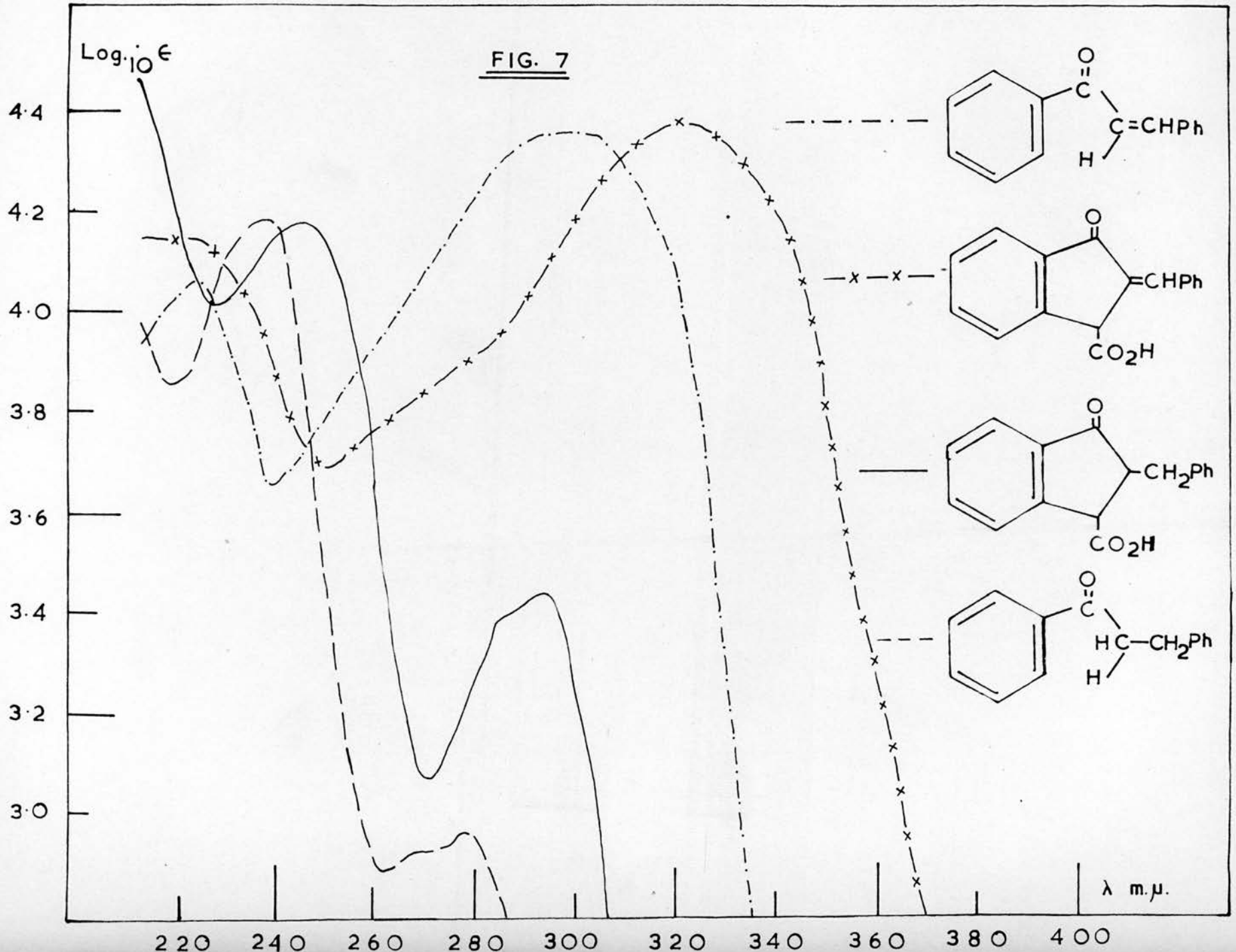


FIG. 7
Log. 10 ε
4·4
4·2
4·0
3·8
3·6
3·4
3·2
3·0
220
240
260
280
300
320
340
360
380
400
λ m.μ.
C=CHPh
H
O
CHPh
CO2H
CH2Ph
CO2H
HC—CH2Ph
H

FIG. 8

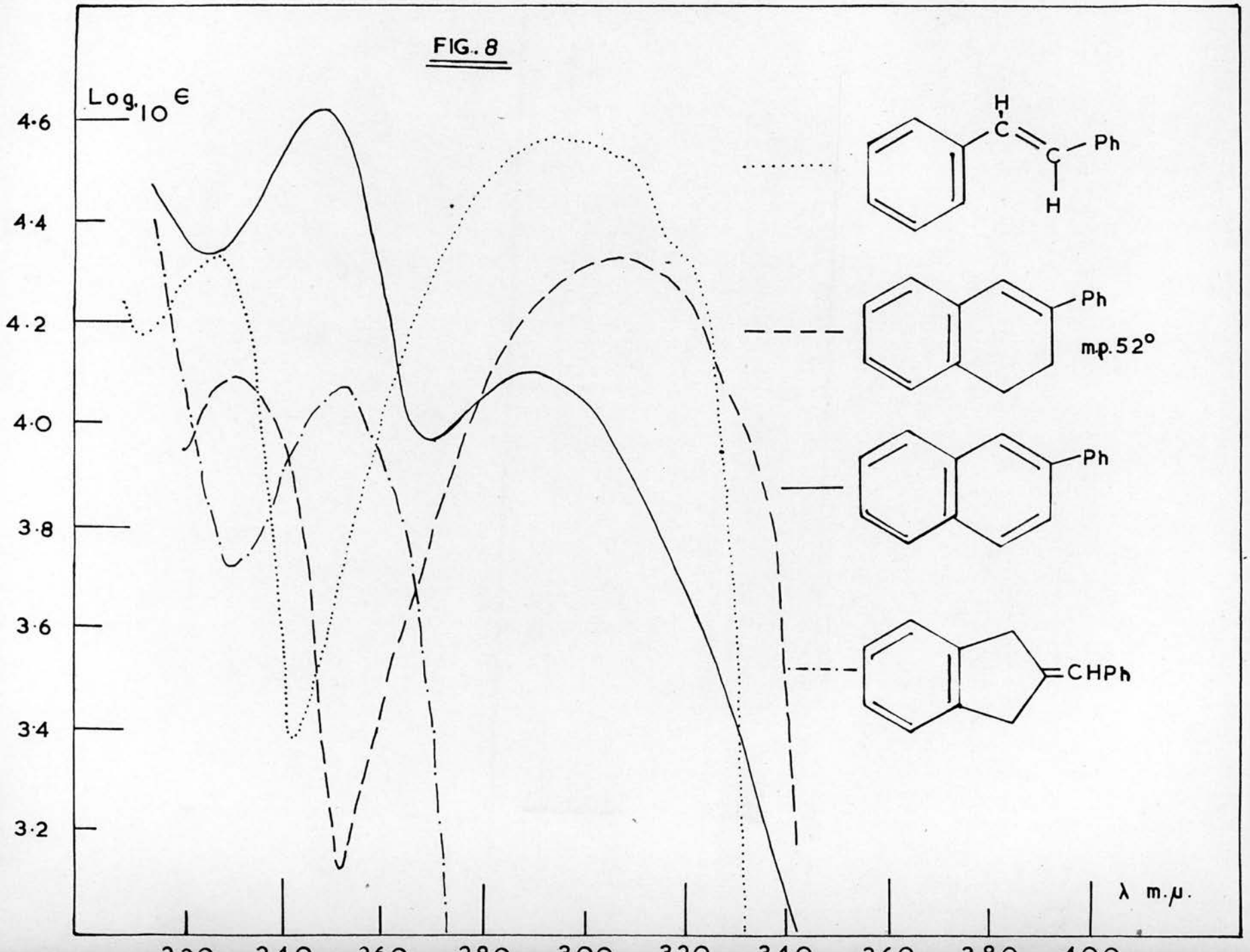
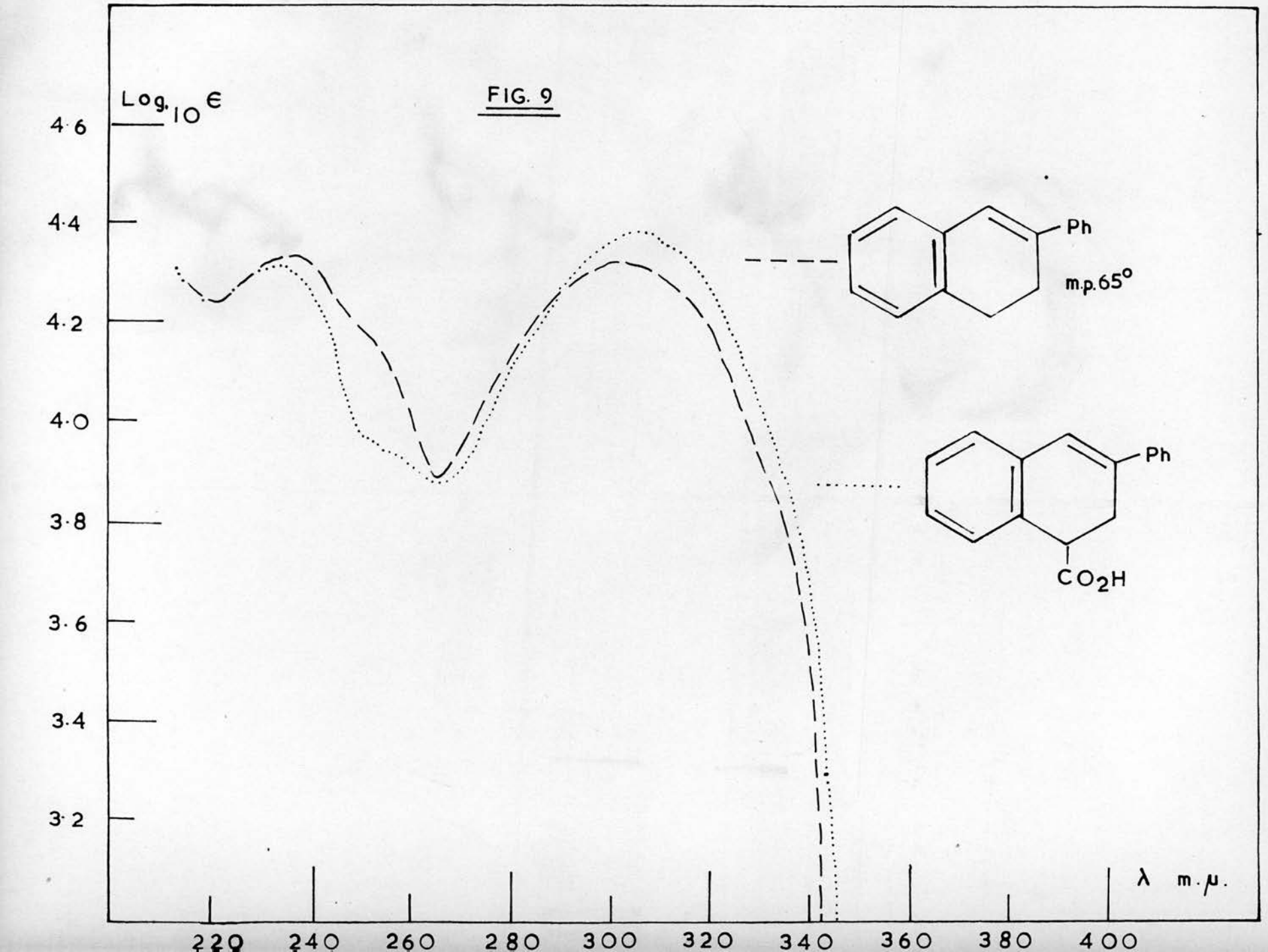

Log10 ε
4·6
4·4
4·2
4·0
3·8
3·6
3·4
3·2
H
C
Ph
C
H
Ph
m.p. 52°
Ph
CHPh
λ m.μ.
220
240
260
280
300
320
340
360
380
400

FIG. 9


Log10 ε
4·6
4·4
4·2
4·0
3·8
3·6
3·4
3·2
Ph
m.p. 65°
Ph
CO2H
λ m.μ.
220
240
260
280
300
320
340
360
380
400

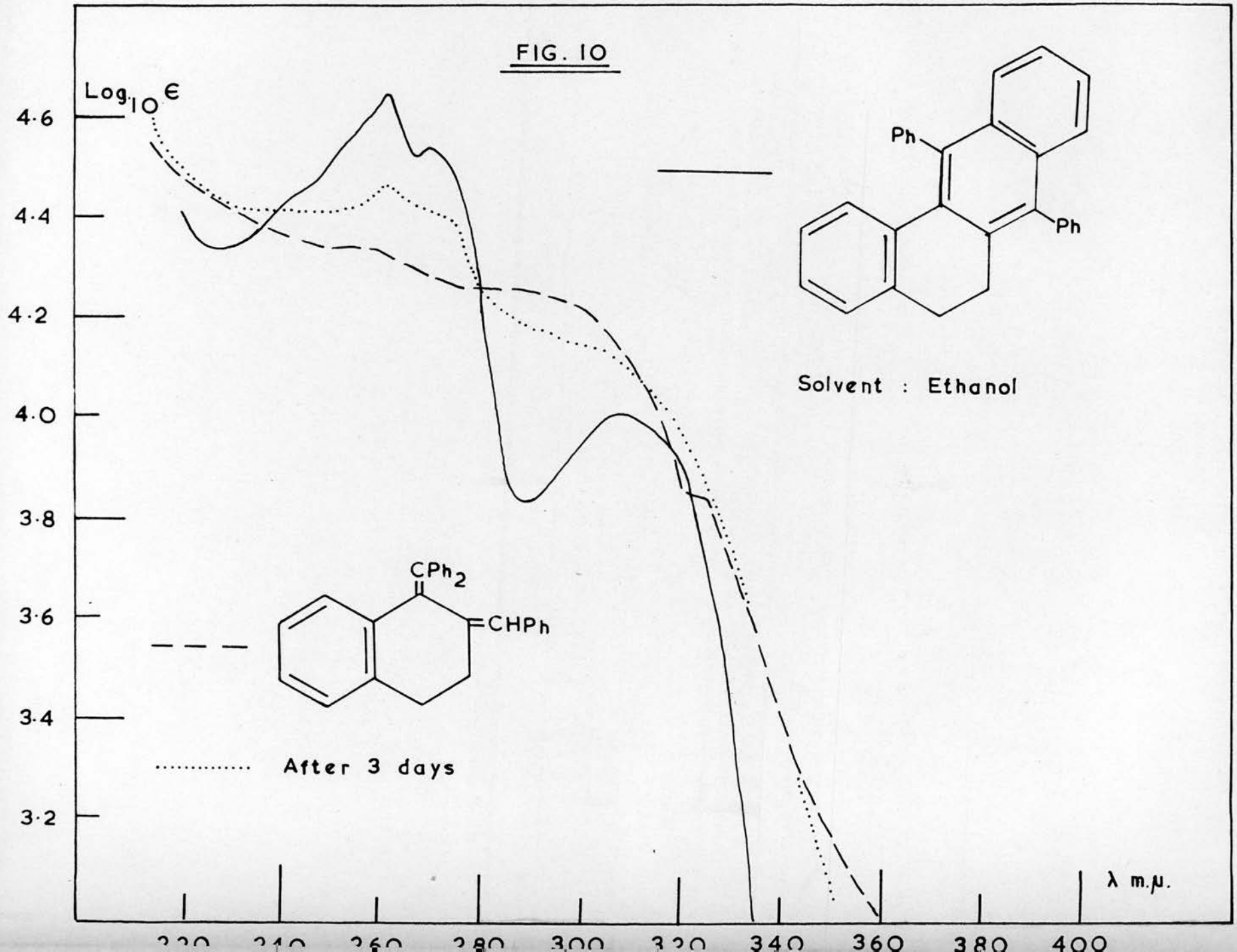


FIG. 10
Log10 ε
4·6
4·4
4·2
4·0
3·8
3·6
3·4
3·2
Ph
Ph
Solvent : Ethanol
CPh2
CHPh
After 3 days
λ m.μ.
220
240
260
280
300
320
340
360
380
400

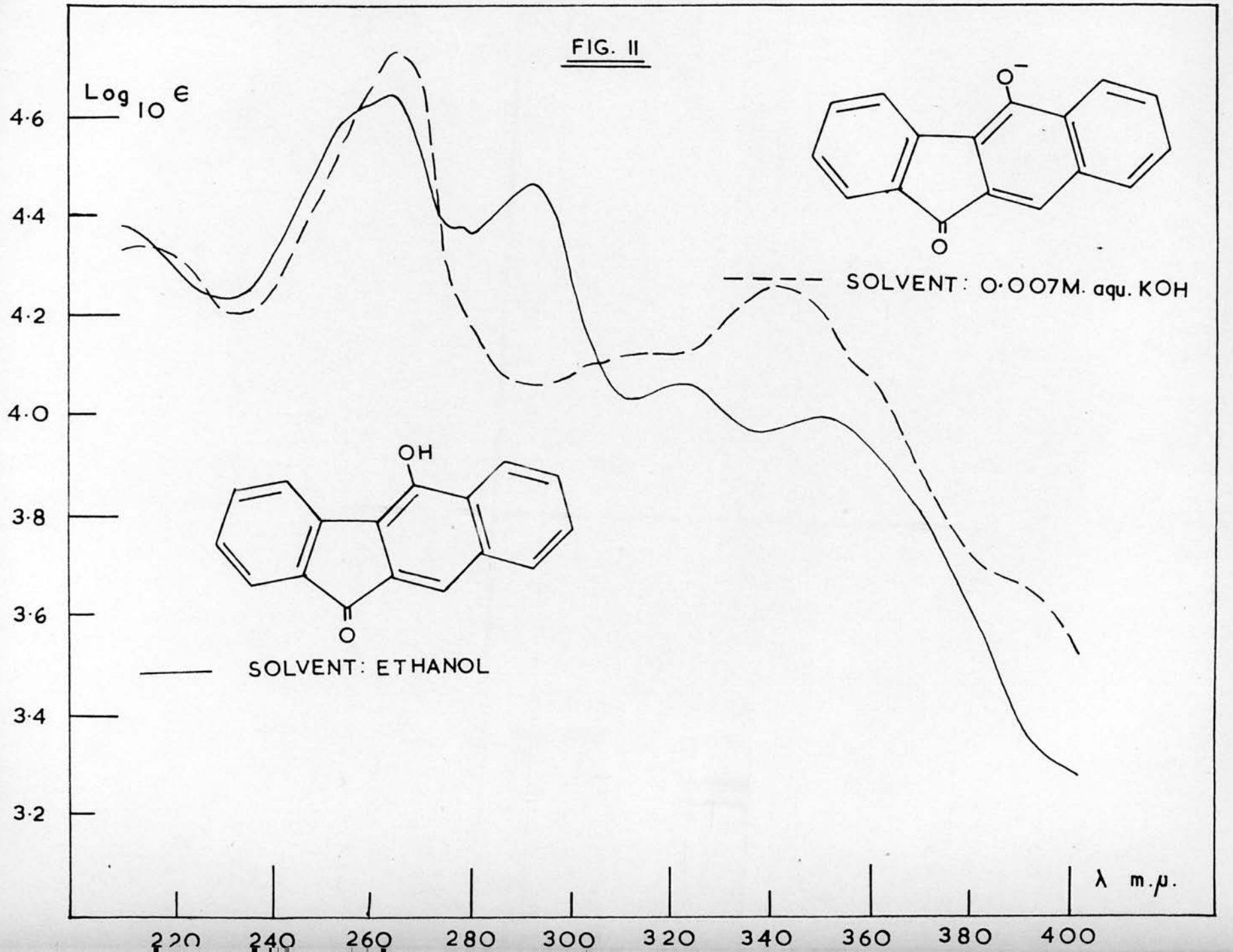


FIG. II
Log 10 ε
4·6
4·4
4·2
4·0
3·8
3·6
3·4
3·2
O⁻
O
SOLVENT: 0·007M. aqu. KOH
OH
O
SOLVENT: ETHANOL
λ m.μ.
220
240
260
280
300
320
340
360
380
400

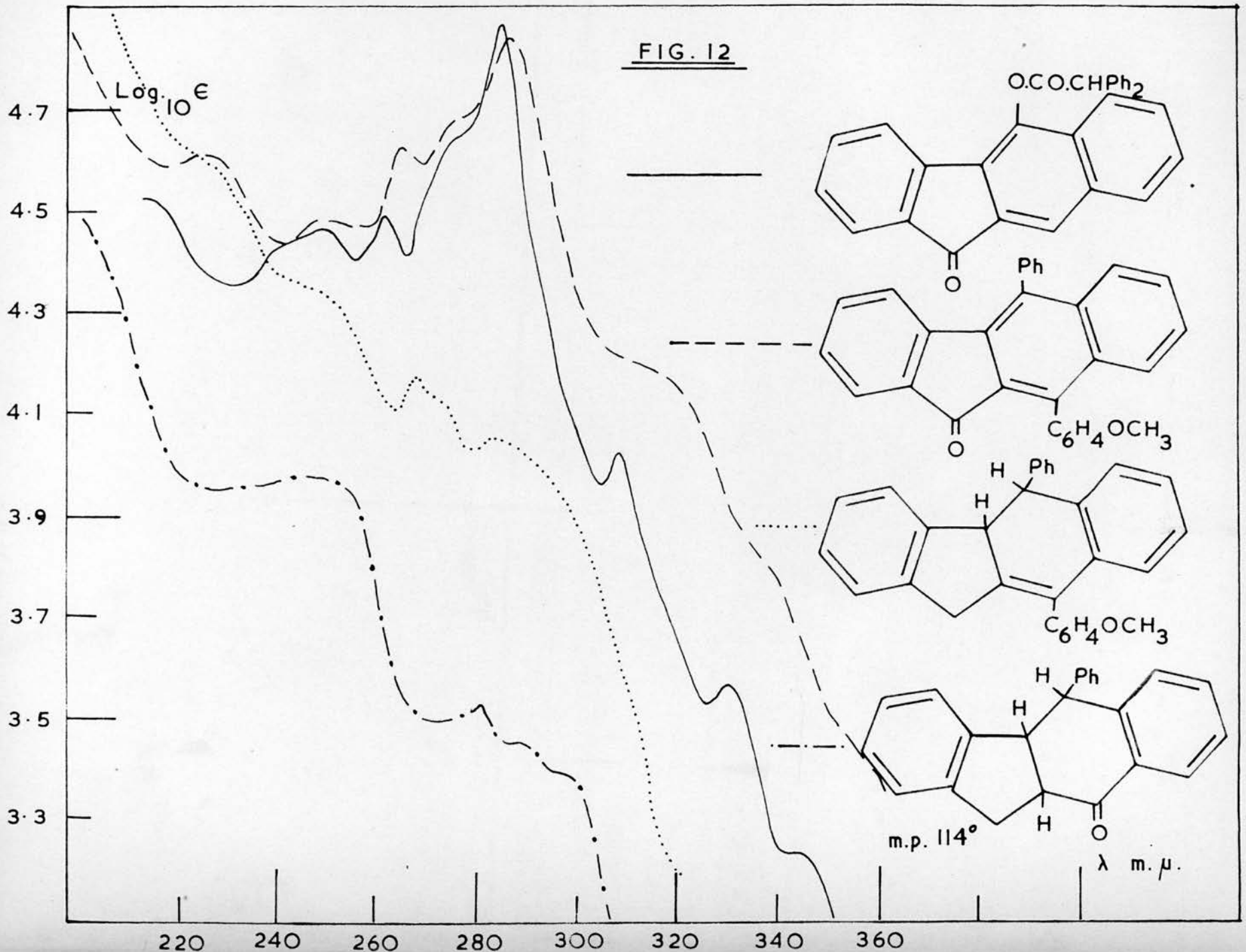


FIG. 12
Log 10 ε
4·7
4·5
4·3
4·1
3·9
3·7
3·5
3·3
220
240
260
280
300
320
340
360
λ m.μ.
O.CO.CHPh2
O
Ph
O
C6H4OCH3
H
Ph
H
C6H4OCH3
H
Ph
H
H
O
m.p. 114°

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