ON THE ACTION OF SODIUM METHOXIDE AND ITS HOMOLOGUES ON BENZOPHENONE CHLORIDE AND BENZAL CHLORIDE.

THESIS

presented by

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INTRODUCTION.

In a paper "On Benzophenone Chloride and the Formation of Anthraquinone in the Preparation of Benzophenone," 1) published by Kekulé and Franchimont in 1872, they state that "we have among other things, tried the action of sodium ethoxide, silver acetate, and silver benzoate on benzophenone chloride, but have not yet arrived at any definite results." On repeating this experiment, the following reaction was found to take place

$$(C_6H_5)_2CCl_2 + 2NaOC_2H_5 = (C_6H_5)_2C(OC_2H_5)_2 + 2NaCl$$

and by replacing the sodium ethoxide by the sodium compounds of other alcohols, the corresponding derivatives were obtained.

As these substances bear the same relation to benzophenone that acetal bears to acetaldehyde, the study of the corresponding derivatives of benzaldehyde was entered upon.

The first method by which these compounds were prepared was the action of benzal chloride on sodium methoxide and its homologues according to the equation:-

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1) Ber. 1872, 5. 909

$$C_6H_5.CHCl_2 + 2NaOCH_3 = C_6H_5CH(OCH_3)_2 + 2NaCl.$$

In this way Wicke[1] obtained dimethoxy-, diethoxy-, and diamoxybenzylidenes.

Some years later, Limpricht in a research on the chlorine substitution products of toluene[2] repeated Wicke's work, but was unable to obtain products free from chlorine. It was therefore thought advisable to try these experiments again under various conditions. Following the instructions of Wicke, it was found that the reaction took place under ordinary pressure as represented, but that the benzal chloride only disappeared on repeated treatment with sodium methoxide. The yield of diethoxybenzylidene obtained by this method was not large and from the product of the action of sodium benzoxide on benzal chloride, pure dibenzoxybenzylidene could not be isolated, but stilbene was found to be present in small quantity. The formation of stilbene may be expressed by the equation

$$2C_6H_5.CHCl_2 + 4C_6H_5CH_2ONa =$$

$$4NaCl + C_6H_5.CH{:}CH.C_6H_5 + 2C_6H_5.CH_2OH + 2C_6H_5.CHO$$

On the other hand, when benzal chloride was heated with sodium ethoxide under pressure, quite a different reaction took place, ethyl chloride, benzaldehyde and sodium chloride being the products.

The change may be represented thus:-

$$C_6H_5.CHCl_2 + C_2H_5ONa = C_2H_5Cl + C_6H_5.CHO + NaCl.$$

By the use of sodium compounds of different alcohols, the corresponding chlorides were produced. In the paper already referred to, Limpricht notes the production of ethyl chloride and benzaldehyde by heating benzalchloride and ethylic alcohol to a temperature of 140°, but does not

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1) Ann. 1857, 102.356 2) Ann. 139, 319

appear to have observed it when using the sodium derivative of alcohol.

That this reaction does not apply to the phenols would appear from the work of Fosse,[1] who obtained dibenzoxy-ethylidene by heating together ethylidene chloride and sodium phenate in sealed tubes at 120° according to the equation-

$$CH_3.CHCl_2 + 2C_6H_5ONa = CH_3.CH(OC_6H_5)_2 + 2NaCl$$

As in benzophenone chloride and benzal chloride, both halogen atoms are attached to the same carbon atom, it was thought that it would be interesting to see what happened when the halogen atoms are attached to different carbon atoms. In the case of ethylene dibromide, it would appear that the following reaction takes place-

$$CH_2Br.CH_2Br + 2C_2H_5ONa = CH_2(OC_2H_5).CH_2(OC_2H_5) + 2NaBr$$

though the author had been unable to find a reference on this point. The product, diethoxy ethylene has, however, been prepared by Henry[2] from an intermediate product in the way represented by the equation

$$C\,H_2I.CH_2O\,C_2H_5. + C_2H_5ONa = CH_2(OC_2H_5)CH_2(OC_2H_5) + NaI.$$

But on heating ethylene dibromide with sodium ethoxide under pressure, it was found that acetylene was produced, reaction taking place thus:-

$$CH_2Br.CH_2Br + 2C_2H_5ONa = C_2H_2 + 2C_2H_5OH + 2NaBr$$

The production of acetylene in a similar fashion, using sodium isoamoxide instead of ethoxide is recorded by Sawitch[3]

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[1] Comptes rend. 130. 725 and 1194

[2] " " 100 1007

[3] Jahresbericht,1861, 646

I was led to the study of the action of sodium methoxide and its homologues on benzophenone chloride by the negative results obtained in the course of an investigation the object of which was the synthesis of ethylic β-phenyl-α carboxy-cinnamate. In my first experiment, benzophenone chloride and ethylic malonate, in molecular proportions, were brought together in presence of a dehydrating agent, in the hope that they might react according to the equation

$$(C_6H_5)_2CO + CH_2(COOC_2H_5)_2 = (C_6H_5)_2C:C(COOC_2H_5)_2 + H_2O$$

But in no case did they do so, at least to any appreciable extent. When glacial acetic acid or acetic anhydride was used as the dehydrating agent, only a very slight change was apparent and almost all the benzophenone and ethylic malonate was recovered. On zinc chloride or aluminium chloride being added along with either of the above, a certain amount of a dark brown sticky substance was formed, which could not however be made to crystallise, as it always separated from solvents in a gummy form. Here also most of the benzophenone and ethylic malonate were unchanged although the experiments were made under different conditions and at various temperatures.

As these methods did not afford the wished for result, it occurred to me that it might be attained according to the following equation:-

$$(C_6H_5)_2CCl_2 + CNa_2(COOC_2H_5)_2 = (C_6H_5)_2C:C(COOC_2H_5)_2 + 2NaCl$$

Accordingly benzophenone chloride was added to a mixture of ethylic disodiomalonate and ethylic alcohol, and in this way a beautiful crystalline compound was obtained, which proved to be, however, not ethylic β-phenyl-α-carboxy-cinnamate, but diethoxydiphenylmethane. The ethylic disodiomalonate had apparently given up its sodium to the alcohol, and the sodium ethoxide reacted on the benzophenone chloride according to the equation (p. 1).

As the compounds produced in this manner bear the same relation to benzophenone as the acetals to acetaldehyde, the names ketal and aldal are proposed for the derivatives of ketones and aldehydes respectively. Until a few years ago very few aldals and ketals were known, but since 1896 the number has been largely increased by the introduction of new or improved methods of preparation. Of these the most important are those of Claisen and Fischer.

By the action of ethylic orthoformate on aldehydes or ketones, Claisen 1) has obtained a series of aldals and ketals, e.g.

$$C_6H_5.CHO + (C_2H_5O)_2CH.OC_2H_5 = C_6H_5.CH(OC_2H_5)_2 + H.COOC_2H_5$$

$$(CH_3)_2CO + (C_2H_5O)_2CH.OC_2H_5 = (CH_3)_2C(OC_2H_5)_2 + H.COOC_2H_5$$

Fischer's method, on the other hand, is only a modification of the method first made use of by Geuther 2) who prepared acetal by heating acetaldehyde with three times its volume of alcohol under pressure and also in presence of acetic acid.

$$CH_3CHO + 2C_2H_5OH = CH_3.CH(OC_2H_5)_2 + H_2O$$

In the latter case the ethylic acetate, which is formed, was rather troublesome to separate. In presence of mineral acids, such as sulphuric acid, Geuther found the yield of acetal comparatively small, as they hydrolyse it very easily. By making use of a one per cent solution of hydrochloric acid gas in absolute alcohol, Fischer 3) has found that in many cases action takes place at ordinary temperature and in others on heating. Any unchanged aldehyde is easily removed in the form of the hydroxylamine compound and as a rule large yields of the aldal are obtained.

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1) Ber. 1896 29, 1008 & 2931
1898,31, 1010

2) Ann. 126, 63.

3) Ber. 1897, 30, 3053
1898, 31, 545 & 1989

This action does not, however, occur with ketones as is indicated by Fischer, and is here shown in the case of benzophenone in the experimental part of this paper.

In the following pages the experiments with benzophenone chloride are described in Part I., those with benzal chloride at ordinary pressure in Part II., and those with benzal chloride at increased pressure in Part III.

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EXPERIMENTAL.

PART I.

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On the Action of Sodium Methoxide and its HomologueS on Benzophenone Chloride.

DIMETHOXYDIPHENYLMETHANE,

$(C_6H_5)_2C(OCH_3)_2$

The benzophenone chloride required for the synthesis of this substance was prepared according to the directions of Kekulé and Franchimont, molecular proportions of benzophenone and phosphorus pentachloride being heated to a temperature of 140° - 150° for two hours, and the resulting product being then distilled under reduced pressure. In this way, 35 grams of a colourless oil distilling at 204° - 206° under 50 mm. pressure were obtained from 27 grams of benzophenone. On redistilling this oil, the temperature remained steadily at 201° - 202° under 35 mm. pressure. The fraction 201° - 202° weighed 33 grams, a yield corresponding to more than 90 per cent of the theoretical. Benzophenone chloride thus prepared is a colourless oil, showing a bluish fluorescence and having only a very faint odour.

For the preparation of dimethoxydiphenylmethane, 4.6 grams of sodium were dissolved in 44 grams of absolute methylic alcohol, and 23.7 grams of benzophenone chloride were then added to the cold solution, the mixture being shaken well. After standing in the cold for two hours, a vigorous action took place, which had to be moderated by cooling; a white powder separated from the solution, and when cold the whole became nearly solid. After adding 50 grams of methylic alcohol and boiling for three hours, the solution showed a neutral reaction. On cooling, beautiful prismatic crystals, apparently rhombic, separated from the solution, some exceeding an inch in length. To separate the new substance from the sodium chloride, the mixture was again heated and filtered through a hot filter, the solid residue being repeatedly extracted with methylic alcohol until no more dissolved. After concentration, the alcoholic solution afforded an abundant crop of crystals, and by concentrating the mother liquor, more crystals were obtained; a repetition of the process yielding almost all the substance in the form of colourless crystals. After drying between filter paper, the crystals melted at 106° - 107°. In this way 18.5 grams were obtained, corresponding to 81 per cent of the calculated quantity. The analysis of the substance gave the following results:-

I. 0.2022 grams substance gave 0.5826 grams CO_2 & ·1290 gram
II. 0.2064 " " " 0.5937 " " "0.1311 " H

	Theory for $C_{15}H_{16}O_2$	Found I	Found II
C	78.95 per cent	78.58	78.45 per cent
H	7.01 " "	7.08	7.0I " "

The number 2I4.5 was obtained by the cryoscopic method, using benzene as the solvent, the calculated molecular weight being 228. 0.1428. grams subs. dissolved in 12.29 grams benzene depressed the freezing point 0.271°.

Under ordinary pressure, the substance distilled without decomposition at 288°- 290°, the distillate crystallising at once and melting sharply at 106°.5 - I07°. From an ethereal solution, brilliant crystals were obtained. For the crystallographic examination, I am indebted to Dr. Hugh Marshall of Edinburgh University.

Dimethoxydiphenylmethane.

Crystallised from methylic alcohol.

System and Class :—Rhombic bipyramidal.

$a : b : c = 0{\cdot}4662 : 1 : 2{\cdot}6210.$

Forms observed :—$c\{001\}$, $q\{011\}$, $o\{111\}$.

On some large crystals from ether, faces of a fourth form, $o'\{113\}$, truncating the edge $c : o$, were also observed.

FIG. 1.

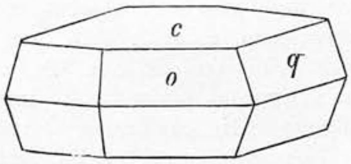

Table of Angles.

Angle.	*n.*	Measured.	Mean.	Calculated.
111 : 011	14	63° 27′—63° 31′	63° 29′*	—
001 : 011	12	69 2—69 12	69 7*	—
111 : 001	7	80 50—80 55	80 53	80° 50½′
111 : $1\bar{1}1$	3	49 17—49 20	49 18⅓	49 18½
111 : $01\bar{1}$	9	70 32—70 37	70 34	70 33
001 : 113	1	—	64 5	64 11½

The faces are bright and give good reflections, but become dull on exposure to air. The habit is generally tabular on the basal pinacoïd, or somewhat prismatic along the *a*-axis.

The crystals are brittle, and show no well-marked cleavage.

The optical axes lie in the plane (100). On examining through *c* in sodium light, the axes themselves cannot be observed owing to the large axial angle. A determination of the latter in bromonaphthalene gave 87° 15′, so that *c* is probably the obtuse bisectrix. Double refraction is strong.

The crystals from the ethereal solution were comparatively stable in air, but in an exsiccator over sulphuric acid, they steadily lost weight, until benzophenone was formed. In a comparative experiment, A was in an exsiccator with sulphuric acid, while B was in an exsiccator not containing sulphuric acid or any dehydrating agent.

	A	B
Weight of powdered crystals	0.4401 grams	0.2763 grams
Decrease in weight after 6 days	0.0212 "	0.0007 "
" " " " 12 "	0.0503 "	0.0016 "
" " " " 18 "	0.0713 "	0.0025 "
" " " " 25 "	0.0920 "	0.0043 "

In A a slight vacuum formed each day, and after six days the powder had deliquesced all over. In B no change was observable. After twenty-five days, the daily loss in weight of A scarcely exceeded half a millegram, and in three days after, the weight became constant. Thus A was found to suffer a decrease of 0.0920 grams or 20.90 %. while B only lost 0.0043 grams or 1.5 % in weight. The decrease in the case of A corresponded closely with that calculated for the change from $(C_6H_5)_2C(OCH_3)_2$ to $(C_6H_5)_2CO$, namely 20.18 p.c. On the addition of a minute particle of benzophenone crystal to A, the oil at once crystallised in a fan-like form. The crystals melted at 48°- 48°.5 and on analysis gave the following figures:-

0.1940 grams substance gave 0.6079 grams CO_2& 0.0972 grams H_2O

	Theory for $C_{13}H_{10}O$	Found
C	85.71 per cent	85.46
H	5.49 " "	5.56

Evidently the substance in presence of sulphuric acid lost methylic ether and became benzophenone. To find out whether this separation occurs in the absence of absorbing agents, a small quantity of the substance was placed in a thick walled tube of about 35 cc. capacity, one end of which was drawn out, and exhausted to a pressure of 40 mm. and then sealed up. After standing a couple of days, the substance showed no apparent change. The tube was then connected by rubber tubing to a glass tube filled with mercury. On the point of the drawn out tube being broken beneath the rubber, the mercury rushed up and nearly filled it. That the volume of gas left was air and not ether vapour was shown by subjecting it to pressure and cold, when it behaved as a permanent gas.

The crystals of dimethoxydiphenylmethane were quite insoluble in water, but very easily soluble in ether, hot methylic and ethylic alcohols, much less so in cold. They were unaffected by boiling water, and were volatile with steam. In one experiment, 2 grams of the substance were distilled with steam, and from the distillate 1.9 grams were recovered, corresponding to 95 per cent of the original quality. A trace of gummy substance remained in the distilling flask. The substance was not affected by aqueous or alcoholic solutions of caustic alkalies; acids, on the other hand, completely decomposed it. In some molecular weight determinations by the cryoscopic method, acetic acid was used as the solvent and results were obtained, which pointed to dissociation. In the case of diethoxydiphenylmethane(see below) this was confirmed by the recovery of benzophenone from the acetic acid solution. The dissociation is also shown by the following nitration experiment, in which 4,4' and 3,3' dinitrobenzophenones were produced,as well as by the direct formation of diphenylmethylenanilide by the action of aniline.

NITRATION OF DIMETHOXYDIPHENYLMETHANE.

2 grams of dimethoxydiphenylmethane were slowly added to 25 cc. of fuming nitric acid cooled by ice, the crystals dissolving without apparent change. After standing for a day, the solution was poured on to crushed ice, by which means a white curdy precipitate was formed. The weight of

dried precipitate was 2.1 grams. It dissolved easily in hot ethylic alcohol, and from the solution there separated simultaneously pale yellow leaflets and needle-like crystals, neither of which showed a constant melting point. Thinking this might be due to a mixture of isomers, analysis of different portions of the substance, which had been kept in desiccators until of constant weight, were made.

I. 0.3082 grams substance gave 27.9 cc. of moist nitrogen measured at 13° and 757 mm.

II. 0.2287 grams substance gave 20.4 cc of moist nitrogen measured at 13° and 759 mm.

Calculated for $C_{13}H_8N_2O_5$	Found	
	I	II.
N 10.30 per cent	10.66	10.52

As dinitrobenzophenone exists in several modifications further efforts were made to separate the possible isomeric forms. From a fairly concentrated solution of nitric acid, glistening crystals resembling sand were deposited. They melted at 189°– 190° and crystallised from hot glacial acetic acid in fan shaped groups of needles, thus agreeing with the properties of 4,4' dinitrobenzophenone. 1)

On heating the mother liquor from above and diluting it with hot water, a second crop of crystals, consisting of rosettes and needles, was obtained. Recrystallised from glacial acetic acid, they softened at 137° and melted at 149° thus conforming with the description of the properties of 3,3' dinitrobenzophenone.

Neither of these bodies is appreciably volatile with steam and both are very difficultly soluble in ether.

DIPHENYLMETHYLENANILIDE.

$(C_6H_5)_2.C:N.C_6H_5$

This substance was formed when dimethoxydiphenylmethane

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1) Stadel, Ber. XXVII, 2110.

was heated with three times its weight of aniline. At about 60° the solid had all dissolved, and at 175° crystals began to separate and slight ebulition occurred. After being kept at 180° for five minutes, the product was allowed to cool,filtered with the aid of a pump and the residue washed with dry ether. From a hot methylic alcohol solution of the residue, glistening yellow plates separated, showing a melting point of 113 - 113.5°. Rohde[1] gives 112 - 113°

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DIETHOXYDIPHENYLMETHANE.

$(C_6H_5)_2C(OC_2H_5)_2$.

As previously stated, this was first prepared by the action of benzophenone chloride on ethylic disodiomalonate mixed with ethylic alcohol, the quantities taken being those required by the above equation (p 4). After the action was finished, the alcohol was distilled off and the residue poured into water. The oil, which separated from the water, was dried and then fractionally distilled under reduced pressure. When placed in a freezing mixture, the fractions which came over between 180° and 220° , under a pressure of 40 mm., crystallised, and by recrystallisation from hot ethylic alcohol, brilliant crystals were obtained, which agreed in all their properties with those prepared in the manner described below and on analysis afforded the following figures:- 0.2196 grams substance gave 0.6374 grams CO_2 and
0.1540 " H_2O

	Theory for $C_{17}H_{20}O_2$	Found
C	79.69 per cent	79.16
H	7.81 " "	7.79

In preparing diethoxydiphenylmethane from benzophenone chloride and sodium ethoxide, the process used was exactly similar to that described under dimethoxydiphenylmethane,

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[1] Ber. XXV, 2056.

the quantities taken being 4.6 grams of sodium, 72 grams of ethylic alcohol and 23.9 grams of benzophenone chloride. After two hours heating in a water bath, the solution, which was neutral was filtered through a hot filter and the residue extracted several times with hot ethylic alcohol. On adding hot water to the hot alcoholic solution, from which the excess of alcohol had been distilled, until the turbidity at first produced just disappeared, almost all the substance separated on cooling in long prismatic crystals; in this way 22.5 grams were obtained, or 88 per cent of the theoretical yield. On analysis the following results were obtained:- 0.2170 grams substance gave 0.6318 grams CO_2 and .1538 grams H_2O

	Theory for $C_{17}H_{20}O_2$	Found
C	79.69 per cent	79.40
H	7.81 " "	7.87

The molecular weight as determined by the cryoscopic method, using benzene as the solvent, was found to be 236.2 instead of 256. 0.1582 grams substance dissolved in 11.161 grams benzene depressed the freezing point 0.300°.

The crystals melted at 51.5 - 52°, forming a colourless oil, which distilled unaltered at 294°- 295°. The colourless distillate crystallised on the introduction of a crystal particle, the crystals again melting at 52°. They were comparatively stable in air, but in an exsiccator over sulphuric acid, they behaved like the dimethoxy-compound. 0.2555 grams lost 0.0732 grams in weight after sixteen days in an exsiccator over sulphuric acid, thereafter remaining constant. This corresponds to a decrease of 29.65 per cent, the calculated decrease for $(C_6H_5)_2C(OC_2H_5)_2$ when it loses $(C_2H_5)_2O$ being 29.81 per cent. The analysis of the residue gave numbers which agree well with those required for benzophenone:-

0.1823 grams substance gave 0.5705 grams CO_2 and 0.0922 gm H_2O

	Theory for $C_{13}H_{10}O$	Found
C	85.71 per cent	85.35
H	5.49 " "	5.62

Diethoxydiphenylmethane is quite insoluble in water, but is very easily soluble in ether, light petroleum, hot methylic and ethylic alcohols, less so in cold. It is volatile with steam. It is not affected by boiling aqueous or alcoholic solutions of caustic alkalies, but it is decomposed by acids. Thus by the action of acetic acid, benzophenone was formed, the melting point (48°– 49°) and the numbers obtained on analysis agreeing well with those required by that compound. Acetic anhydride also split it up, the same product being produced.

On recrystallisation from hot absolute ethylic alcohol, very perfect crystals were obtained. I have also to express my thanks to Dr.Hugh Marshall of Edinburgh University for the following crystallographic examination:-

Diethoxydiphenylmethane.

Crystallised from ethylic alcohol.

System and Class :—Monoclinic prismatic.

$a : b : c = 1{\cdot}5016 : 1 : 1{\cdot}2740.$

$\beta = 106° \, 26\tfrac{1}{2}'.$

Forms observed :—$a\{100\}$, $c\{001\}$, $r\{10\bar{1}\}$, $p\{110\}$, $\omega\{11\bar{1}\}$. A few crystals also showed minute faces of the form $o\{111\}$ (determined by zones).

FIG. 2.

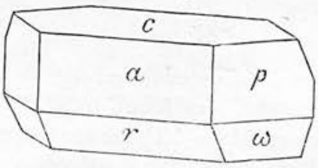

Table of Angles.

Angle.	n.	Measured.	Mean.	Calculated.
100 : 110	15	55° 7′— 55° 25′	55° 13½′*	—
100 : 001	8	73 24 — 73 36	73 33½*	—
$\bar{1}11 : \bar{1}10$	12	36 24 — 36 49	36 39*	—
$001 : \bar{1}01$	5	46 36 — 47 5	46 49	46° 57½′
001 : 110	11	80 26 — 80 54	80 40	80 42½
$100 : \bar{1}11$	7	109 50 —110 3	109 56	110 0
$110 : \bar{1}11$	6	65 33 — 65 44	65 36	65 40
$\bar{1}01 : \bar{1}11$	8	47 32 — 47 45	47 42	47 40
$\bar{1}01 : \bar{1}10$	—	—	—	73 10

The crystals are often tabular on the basal pinacoïd, or prismatic along the axis of symmetry. The best reflections are given by the faces of the forms p and ω. The faces soon become dull if left exposed to air.

There is no well-marked cleavage.

When examined through the basal pinacoïd in convergent polarised sodium light, one bisectrix is seen to be almost normal to that form. The axes themselves lie in the plane (010), but are not observable.

DIPROPOXYDIPHENYLMETHANE.

$(C_6H_5)_2C(OCH_2.CH_2.CH_3)_2$.

In preparing this substance, 3.7 grams of sodium were dissolved in 40 grams of ethylic alcohol, and to the cold product 19 grams of benzophenone chloride were added. The mixture was gradually heated up to a temperature of 95° , when a violent action took place, and then kept at 120° for seven hours, at the end of which time, the supernatant liquid still gave an alkaline reaction. It was filtered from the salt which had separated, the latter being washed three times with small quantities of propylic alcohol. The filtrate was then distilled under reduced pressure, propylic alcohol distilling at a temperature between 35° and 45° under 40mm. pressure. The residue in the distilling flask, which was a viscous brown oil, was diluted by the addition of a little ethylic alcohol, filtered from some salt, and subjected to fractional distillation under diminished pressure. 7.9 grams of a colourless oil boiling at 200°- 210° under 40 mm. pressure were collected, representing 35 per cent of the theoretical quantity obtainable.

The yellowish, semi-solid residue showed a strongly alkaline reaction, and was distilled with steam. From the milky distillate crystals separated, which melted at 32°- 35° and boiled at 204° under 40 mm. pressure. They amounted to nearly 1 gram.

By cooling the fraction boiling at 200-210° under 40 mm. pressurein a freezing mixture, a white powdery mass was obtained, which , on recrystallisation from light petroleum, formed colourless prismatic crystals melting at 33° - 34.5°, and on analysis gave the following numbers.

0.2026 grams substance gave 0.5982 grams CO_2 and 0.1576 gm. H_2O

	Theory for $C_{19}H_{24}O_2$	Found
C	80.28 per cent	80.53
H	8.45 " "	8.64

Dipropoxydiphenylmethane is insoluble in water, but extremely easily soluble in methylic and ethylic alcohols, ether, benzene, light petroleum, &c. It is rather unstable, the faces of crystals very soon becoming dull. Well formed crystals were very difficult to obtain. Of many attempts, only one in which a light petroleum solution was allowed to remain outside on a cold winter night was successful. Subsequent attempts in spring and summer were fruitless.

ATTEMPT TO PREPARE DI-ISOPROPOXYDIPHENYLMETHANE.

In this experiment, 2.3 grams of sodium were dissolved in 60 grams of isopropylic alcohol, and to the cold product, which had separated into a white crystalline powder and a yellowish liquid, 12.8 grams of benzophenone chloride were added. No action took place in the cold, but on heating, a violent action set in, ebulition proceeding for about five minutes. A white salt separated and the liquid darkened in colour. The mixture was then heated in water bath for 8 hours. After filtration, the liquid was distilled under reduced pressure, isopropylic alcohol boiling at 27° under a pressure of 47 mm. The residue was a brownish oil, which on mixing with a little hot water, crystallised out on cooling. These crystals melted at 47° - 49° without further recrystallisation and also agreed in crystalline form with benzophenone. In this way 7.6 grams crystals were recovered, the total possible quantity of benzophenone being 9.1 grams.

It is thus evident that the compound desired, though probably formed in the above reaction, is very unstable.

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DI-ISOBUTOXYDIPHENYLMETHANE.

$(C_6H_5)_2C[OCH_2.CH.(CH_3)_2]_2$

The preparation of this substance was effected in the way previously described. The quantities taken were 3.7 grams of sodium, 41 grams of isobutylic alcohol and 19 grams of benzophenonechloride. When the sodium compound melted a brisk action took place, but was not complete after heating to a temperature of 130° - 150° for seven hours, the liquid still showing an alkaline reaction. The salt was removed by filtration and the liquid then distilled under diminished pressure. The isobutylic alcohol boiled at 54-55° under 85 mm. pressure. The temperature then rose rapidly to 199° and 16.5 grams of a thick colourless oil were collected having a boiling point between 199° and 210° at 35 mm. pressure. When placed in a freezing mixture this oil became a thick jelly, in which minute needles appeared on scratching. After standing at ordinary temperature for eighteen days, the small bunches of needles which had grown were filtered off, dried on a porous plate and as no sharp melting point was obtained, dissolved in ether. The ethereal solution deposited silky needles after being in an exsiccator for a week. The dry crystals which weighed 0.8 gram, melted between 62° and 64° but on exposure to the air, the melting point fell, and, as will be shown later, the substance decomposed with the formation of benzophenone. A combustion performed a week after the separation of the crystals gave the following figures:-

0.2682 grams substance gave 0.8313 grams CO_2 & 0.1657 grams H_2O

	Calculated for $C_{21}H_{28}O_2$	for $C_{13}H_{10}O$	Found
C	80.76 per cent	85.71	81.53
H	8.97 " "	5.49	6.86

The substance was apparently mostly benzophenone.

Being so small a quantity, no experiments to ascertain the reason for the difference in melting point of these crystals from that of those described below could be made. The oil from the above mentioned crystals was again distilled under a pressure of 35 mm., when eleven grams or 44 per cent of the theoretical quantity came over between 203° and 215°, mostly at 210°. By cooling in a freezing mixture, small diamond shaped plates crystallised from the oil, which gradually became solid throughout. After drying on a porous plate, the solid melted between 36° and 38°, but the melting point was lowered by exposure. From an ethereal solution crystals melting at 35° - 37° and from a light petroleum solution crystals melting at 35° - 36° were obtained.

Analysis of the crystals of melting point 36° - 38° gave the following numbers.

0.2041 grams substance gave 0.6017 grams CO_2 and
0.6144 " H_2O

I. 0.2076 grams substance gave 0.6131 grams CO_2 and
0.1669 " H_2O

	Calculated for $C_{21}H_{28}O_2$	Found I	Found II.
C	80.76 per cent	80.40	80.54
H	8.97 " "	8.95	8.92

The following experiment is a further proof that the substance really has the formula attributed to it. 0.2660 grams of the crystals in a platinum boat were placed in an exsiccator over sulphuric acid and weighed every second day. The crystals soon deliquesced, then became entirely liquid, meanwhile steadily losing weight for nearly three weeks. At the end of the fourth week the weight had become constant and on introducing a particle of benzophenone, the reddish brown oil crystallised. The loss in weight amounted to 0.1080 grams or 40.6 per cent. The loss in weight caused by di-isobutoxydiphenylmethane splitting off diisobutylic ether is 41.6 per cent. An analysis of the residual product proved it to be impure benzophenone.

0.1562 grams substance gave 0.4858 grams CO_2 & 0.0794 grams H_2O

	Calculated for $C_{13}H_{10}O$	Found
C	85.71 per cent	84.82
H	5.49 "	5.65

In this respect therefore the diisobutoxy derivative agrees with the dimethoxy and diethoxy compounds.

Di-isobutoxydiphenylmethane is exceedingly soluble in the ordinary organic solvents. Though it crystallises more readilythan the propoxy compound, it is difficult to work with in summer weather on account of its low melting point and ready dissociation.

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ATTEMPT TO PREPARE DI-AMOXYDIPHENYLMETHANE.

The quantities used in this experiment were 2.8 grams of sodium, 50 grams of amylic alcohol (B.P.129.5 – 130.5°) and 13.6 grams of benzophenone chloride. The mixture was heated---after a rather violent action had taken place---in an oil bath at 135 – 145° for five hours. Dry ether was then added to the still alkaline product and the solution was filtered from the salt. On fractional distillation at a pressure of 40 mm.

3.0 grams of oil boiling at 200 – 220°
10.2 " " " " " 220 – 235°
and 4.3 " " " " " 235 – 260°

were obtained. The two latter portions formed a jelly when placed in a freezing mixture, but no crystals separated. On exposure to winter cold during the Christmas vacation, small groups of stellate needles had grown. After drying between filter paper these crystals melted at 66° – 67°. However, only a very small quantity was obtained and further efforts to get more were fruitless. An analysis gave figures which lie between those required for the amoxy compound and benzophenone.

0.1268 grams substance gave 0.3887 grams CO_2 & 0.0745 grams H_2O

	$C_{23}H_{32}O_2$ Calculated for	$C_{13}H_{10}O$	Found
C	81.65 per cent	85.71	83.60
H	8.87 " "	5.49	6.53

DIPHENOXYDIPHENYLMETHANE.

$(C_6H_5)_2C(OC_6H_5)_2$.

After several preliminary experiments, the following process for obtaining the above named substance was adopted. 4.6 grams of sodium were added to a solution of 18.9 grams of phenol in 81 grams of dry ether placed in a flask with a reflux condenser attached. Owing to the insolubility of the sodium phenoxide, more ether was added and the mixture boiled for eight hours with frequent shaking. At the end of that time traces of sodium still remained unchanged. 23.7 grams of benzophenone chloride were then added and the mixture warmed in a water bath. As no action appeared to take place, the ether was distilled off. When it had nearly all passed over, a violent ebulition set in, vapours of phenol being evolved, and the residue in the flask became like tar. The product was heated for an hour and a half in an oil bath at 115°, and when cold extracted with ether. The ethereal extract was repeatedly shaken with water until the washings no longer reacted alkaline. From the first washings, phenol separated as an oil on the addition of hydrochloric acid. After drying the ethereal extract and distilling off the ether, there remained an uninviting, thick brown oil, which would neither solidify on cooling in a freezing mixture, nor on the introduction of particles of benzophenone or phenol. After trying to crystallise it from alcohol, ether, chloroform and other solvents, it was found that, by the addition of light petroleum to the ethereal solution, small crystals separated and after several days a product very like treacle filled the bottom of the beaker. This was spread on a porous plate and then dissolved in a large volume of chloroform and boiled under a reflux condenser with animal charcoal to decolourise it. Repeated boilings reduced the colour of the solution to a light yellow and on the addition of a light petroleum light yellow sandy crystals separated. After several recrystallisations the substance softened at about 260° and melted at 285° - 287°.

Analysis showed the peculiar combination of two molecules of ether with one of diphenoxydiphenylmethane.

0.1330 grams substance gave 0.3862 grams CO_2 &
0.0943 " H_2O

	Calculated for $C_{25}H_{20}O_2, 2C_4H_{10}O$	Found
C	79.20 per cent	79.19
H	8.00 " "	7.89

The ether of crystallisation was expelled by heating in a steam oven. A portion of the substance, which had already lost in weight by standing in an evacuated desiccator for several days, lost more than 20 per cent in weight by heating in a steam oven. The theoretical loss is 29.6 per cent

The results of an analysis of a portion of substance which had been heated in a steam oven until of constant weight were:-

0.1418 grams substance gave 0.4412 grams CO_2 and
0.0800 " H_2O

	Calculated for $C_{25}H_{20}O_2$	Found
C	85.22	84.85
H	5.68	6.26

Diphenoxydiphenylmethane is very easily soluble in alcohol and ether, moderately in chloroform and difficultly in light petroleum.

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DIBENZOXYDIPHENYLMETHANE.

$(C_6H_5)_2C(OCH_2.C_6H_5)_2$

The method of preparing this substance differed slightly from the above mentioned. 2.3 grams of sodium were dissolved in 53 grams of benzylic alcohol, and to the cold solution, which resembled glycerine in consistency, 12.8 grams of benzophenone chloride were added. After being heated for nine hours in a water bath, the mixture had become a solid jelly, but still gave a strongly alkaline reaction with litmus; to complete the change, the mixture was heated in an oil bath at 205 - 210° for five hours, but even at the end of that time the reaction was still faintly alkaline. On adding ether to the white jelly-like product, a white powdery solid separated. The ethereal solution, which was neutral, was filtered off and the residue extracted with ether several times. After distilling off the ether, a yellow oil remained, which on standing yielded a crop of fine prismatic, needle-like, crystals. The oil was separated from the crystals by filtration with a filter pump, and the crystals dried between filter paper. On fractional distillation, the oil was found to be benzylic alcohol, distilling under a pressure of 60 mm. at 142°. The crystals were recrystallised from methylic alcohol, in which they are only sparingly soluble when cold, but more readily when hot. They melted between 104° and 105°. In this manner a yield corresponding to more than 60 per cent of the theoretical was obtained, although it may probably be increased by modifying the conditions of the experiment.

An analysis gave the following results:-

0.2076 grams substance gave 0.6457 grams CO_2 & 0.1188 g. H_2O

	Calculated for $C_{27}H_{24}O_2$	Found
C	85.26 per cent	84.83
H	6.32 " "	6.36

This substance was easily soluble in hot ethylic alcohol and light petroleum, but much less so in cold. On exposure to the air, the crystals lost their brilliancy and deliquesced. When distilled under the ordinary pressure, decomposition appeared to take place, the temperature rising steadily from 260° to above 360°, and the distillate forming a colourless fragrant smelling liquid, which crystallised only very partially even after the introduction of a crystal of the original substance. Under a pressure of 40 mm. it distilled without decomposition at about 305°, the distillate being colourless and solidifying at once to crystals which melted at 103°- 105°.

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ACTION OF ETHYLIC ALCOHOL ON BENZOPHENONE.

From the easy dissociation of the above described compounds it was thought possible that they might be formed directly from benzophenone, and the corresponding alcohol, but this proved not to be the case as is here shown. In this experiment 5 grams of benzophenone crystals were boiled for three hours with 20 grams of ethylic alcohol and allowed to stand over night. No crystals having appeared, most of the alcohol was distilled off. The residual oil did not crystallise on standing, but on the addition of a particle of benzophenone , a rapid growth of crystals took place. After drying, they melted at 48 - 49°, and were evidently unchanged benzophenone. A further crop of crystals from the mother liquor, brought the amount recovered up to 4.8 grams.

ACTION OF 1.% SOLUTION OF HYDROCHLORIC ACID. IN METHYLIC ALCOHOL ON BENZOPHENONE.

As E.Fischer mentions that the use of 1 per cent alcoholic solutions of hydrochloric acid is particularly adapted to the production of aldals and only infers that it is not applicable for the production of ketals, the following experiments showing its inapplcability in the case of benzophenone were performed.

Five grams of benzophenone were dissolved in 100 cc. of a one per cent solution of hydrochloric acid gas in methylic alcohol and the mixture allowed to stand at ordinary temperature for five days. Most of the alcohol was then removed by distillation and the residue crystallised on cooling. The crystals were separated from the mother liquor, which afforded a second crop on standing, the amount recovered being 4.9 grams. After drying, the crystals melted at 48 - 49°. (Benzophenone M.P.48°), hence the benzophenone was unacted upon.

A similar experiment, in which 5 grams benzophenone and 40 cc. of a 1.5% solution of hydrochloric acid gas in methylic alcohol were heated in a sealed tube to a temperature of 75 - 90° for 12 hours, also resulted in the recovery of the whole of the benzophenone unchanged.

LIST OF NEW COMPOUNDS PREPARED FROM BENZOPHENONE CHLORIDE.

NAME	FORMULA	MELTING POINT.
Dimethoxydiphenylmethane	$(C_6H_5)_2C(OCH_3)_2$	106.5 - 107°
Diethoxy " "	$(C_6H_5)_2C(OC_2H_5)_2$	51.5 - 52°
Dipropoxy " "	$(C_6H_5)_2C(OCH_2.CH_2.CH_3)_2$	33 - 34.5°
Diisobutozy " "	$(C_6H_5)_2C[OCH_2.CH(CH_3)_2]_2$	35 - 36°
Diphenoxy " "	$(C_6H_5)_2C(OC_6H_5)_2$	285 - 287°
Dibenzoxy " "	$(C_6H_5)_2C(OCH_2.C_6H_5)_2$	104 - 105°

EXPERIMENTAL.

-:÷ PART II.÷:-

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ON THE ACTION OF SODIUM METHOXIDE AND ITS HOMOLOGUES ON BENZAL CHLORIDE AT ORDINARY PRESSURE.

As the products obtained in these experiments were not all of the same character, they will be described under the heading of the sodium derivative of the alcohol which acted upon benzal chloride.

SODIUM METHOXIDE.

This experiment was carried out according to the instructions of Wicke 1). 23 grams of sodium were dissolved in 250 cc. of methylic alcohol, 80.5 grams of benzal chloride added to the solution, and the mixture heated in a water bath for fifteen hours. As it was thought possible that

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1) Annalen der Chemie 102,356.

methylic chloride might be formed, as is the case when the action takes place under pressure, an apparatus for collecting gas was attached to the end of the reflux condenser, but no gas was evolved. After removing the alcohol by distillation, the residue, which was alkaline, was mixed with water, and the oil, which separated, extracted by ether. The ethereal extract was dried over calcium chloride, the ether removed and the residue subjected to fractional distillation under diminished pressure. In this way a colourless oil, not boiling at any constant temperature, was obtained, which distilled between 190 and 210° under ordinary pressure.

On testing the various fractions, chlorine was found to be present in all. Only after heating this oil with fresh quantities of sodium methoxide in alcoholic solution several times, could it be obtained free from chlorine. This purification was carried out by my former assistant, Dr. A. Jamieson Walker, who also analysed the pure compound, which distils unaltered at 198°, thus agreeing with the number given by Fischer 1). Wicke mentions 208° as the boiling point, but gives no analysis, and his product probably contained a quantity of unchanged benzal chloride (Boiling Point 206°)

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SODIUM ETHOXIDE.

In this experiment 23 grams of sodium were dissolved in 230 grams of ethylic alcohol, and to the cold solution, 80.5 grams of benzal chloride (Kahlbaum) were added. The mixture was heated in a water bath for 24 hours, no violent action taking place, but salt gradually separating. At the end of this time the liquid was still alkaline. The alcohol having been distilled off in the water bath, the product was mixed with water, the oil which separated being extracted three times with ether. The ethereal solution

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1) Ber. 31, 549

was washed twice with water, after which it showed a neutral reaction, dried over calcium chloride, and the ether evaporated off. The residual oil was then distilled under a pressure of 45 mm., the following fractions being collected:-

up to 90°	1.3	grams.
90 - 125°	15.8	"
120 - 125°	19.1	"
125 - 128°	19.8	"
128 - 175°	15.6	"
175 - 220°	.2	"

The residue in flask was dark brown in colour and semi-solid.

The above fractions were redistilled at a pressure of 749 mm., and tested for the presence of chlorine with the following results:-

up to 206°	3.6	grams	much chlorine
206 - 207°	14.1	"	" "
207 - 210°	15.8	"	" "
210 - 213°	16.7	"	" "
213 - 218°	8.6	"	" "
218 - 220°	4.1	"	trace of "
220 - 300°	6.3	"	" " "

Supposing the chlorine to be still present as benzalchloride, all the fractions boiling up to a temperature of 220° were added to a solution of 9 grams of sodium in 100 gram of alcohol and the mixture heated on the water bath for 17 hours. During the heating a quantity of salt separated and the liquid darkened in colour. The product was treated as before and the oil obtained, yielded 51.1 grams of colourless liquid boiling at 135 - 140° under a pressure of 75 mm.

This oil still contained traces of chlorine. An effort to separate a constant boiling product using a Young's pear shaped still-head gave the undermentioned fractions at 770 mm., namely:-

up to 210°	3.4	grams	
210 - 214°	17.2	"	
214 - 216°	15.8	"	
216 - 220°	6.2	"	(some of this was lost)

As all these fractions contained a little chlorine, they were mixed together and for the third time boiled with sodium ethoxide (4.5 grams sodium in 45 grams alcohol) for 16 hours and subsequently treated as before.

The fractions obtained were:-

212 - 215°	6.2 grams
215 - 217°	13.3 "
217 - 219°	12.6 "
219 - 222°	4.2 "

As they all still showed the presence of traces of chlorine, the action of zinc dust and an alcoholic solution of potassium hydrate was tried upon the two latter fractions. The quantities employed were 5 grams of potassium hydrate dissolved in 20 grams of ethylic alcohol with sufficient water to make a solution, 5 grams of zinc dust and 16 grams of the oil. The mixture was kept at ordinary temperature for five days, then after heating under a reflux condenser for an hour in a water bath, the alcohol was distilled off, the residue mixed with water, extracted with ether, the ethereal extract dried over calcium chloride and the ether removed by evaporation. The resulting product now boiled at a temperature between 216° and 220°, but chiefly at 217°, 13 grams being obtained. In order to make certain of the absence of chlorine, a Carius estimation was carried out,

0.5890 grams substance gave 0.0004 grams ash + silver

paragraph chloride (Ash = 0.00011 grams). It is very curious Wicke does not speak of the difficulty of getting rid of the chlorine compounds in this reaction. On the other hand Limpricht, who repeated Wicke's work, but heated the mixture of sodium methoxide, benzal chloride and alcohol to 140° was unable to obtain products free from chlorine, the amount of chlorine varying between 7.5 and 18.7 per cent.

The absence of chlorine having been established, the liquid was once more fractionally distilled and 7.5 grams of liquid boiling at 216 - 217° were collected. Wicke, with whom Fischer agrees, mentions 222° as the corrected boiling point of Diethoxybenzylidene. (The temperatures throughout this investigation are uncorrected.)

A combustion of this portion was performed with the following results:-1)

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1) (Foot note see next page.)

0.2400 grams substance gave 0.2000 grams water and 0.6450 grams carbonic anhydride.

	Calculation for $C_{11}H_{16}O_2$	Found
C	73.33 per cent	73.29
H	8.88 " "	9.25

NOTE The combustion of this substance was a matter of some difficulty because on heating, it apparently splits off ethylic ether, which if allowed to pass over rapidly causes the per centage of carbon to come out low. The following analyses of portions which were free or as nearly as possible free from chlorine illustrates this fact.

I. 0.3745 g. of subst. of B.P.217-219° gave 0.9706 grams CO_2 & 0.2933 grams H_2O
II. 0.1690 " " " " " " 0.4397 " " " 0.1360 " "
III. 0.6398 " " " 216-220° 1.6868 " " " 0.5056 " "
IV. 0.5438 " " " 216-217° 1.4243 " " " 0.4255 " "

	Calculated for $C_{11}H_{16}O_2$	Found I.	II.	III.	IV.
C	73.33	70.68	70.90	71.93	71.43
H	8.88	8.70	8.94	8.77	8.67

In the above four analyses, the combustion was carried out at an ordinary rate, an hour to an hour and three quarters being taken between the introduction of the substance and the removal of the absorption apparatus. In the combustion mentioned in the text, the time was extended to two hours and a half. This observation was also made by Dr. A Jamieson Walker when burning dimethoxybenzylidene.

TEXT. Diethoxybenzylidene is a colourless liquid with a fragrant odour. It is not soluble in water, but is miscible with the ordinary organic solvents. It is stable in the presence of alkalies, but is readily decomposed by acids. With a saturated solution of sodium bisulphite it soon yields the benzaldehyde compound.

Assuming that the fractions 215 - 222° weighing 30.1 grams in all, consisted of pure diethoxybenzylidene, the yield would be 33 per cent of the theoretical. This is therefore not so convenient a method as Fischer's for the preparation of this substance.

SODIUM BENZOXIDE.

The quantities used in this experiment were 4.6 grams of sodium, 50 grams of benzylic alcohol, and 16.1 grams of benzal chloride. The mixture was heated in an oil bath to a temperature of 206 - 210° for five hours, during which a quantity of solid matter separated. When cold, a large volume of ether was added and the solution filtered, the salt being washed several times with ether. After removal of the ether, the yellow oil which remained was distilled under a pressure of 55 mm., the following fractions being collected:-

100 - 125°	17.6 grams
125 - 140°	12.6 "
140 - 200°	7.2 "
200 - 270°	11.1 "

The residue in the distilling flask was a viscid mass.

The last portion i.e. that boiling at 200 - 270° smelt of benzaldehyde and contained some chloride.

The whole liquid was next distilled at ordinary pressure (774 mm.) the following fractions resulting:-

up to 195°	6.2 grams
195 - 200°	14.5 "
200 - 205°	6.5 "
205 - 230°	8.7 "
230 - 300°	5.7 "

These fractions were successively distilled under a pressure of 60 - 65 mm., but no separation was effected.

The distillate was collected in the following fractions:-

up to 115°	9.3 grams
115 - 120°	12.3 "
120 - 195°	11.9 "
195 - 260°	5.3 "
260 - 300°	6.8 "

The first two fractions were found to be free from chlorine and as they distilled at 195 - 202° under ordinary pressure (149 mm.) were probably benzylic alcohol. The other portions all contained chlorine.

By cooling the last fraction in a freezing mixture, a small quantity of crystals separated. These were filtered off, dried on a porous plate, and, without further purification, the melting point was found to be 112 - 115°. Suspecting the presence of stilbene and benzoic acid, which both melt at 120°, a few tests were performed to prove the presence or the absence of each. The crystals did not dissolve in solutions of either sodium hydrate or carbonate nor did they react acid to litmus, but they did decolourise a solution of bromine in carbon disulphide, thus indication the absence of benzoic acid, and the presence of stilbene. They were then purified by recrystallisation from hot ethylic alcohol. The glistening leaflets of which only a minute quantity was obtained melted sharply at 120° and on analysis gave the following figures:-

0.0316 grams substance gave 0.1078 grams CO_2 and
0.0246 grams H_2O

	Calculated for $C_{14}H_{12}$	Found
C	93.33 per cent	93.02
H	6.67 " "	8.65

With the idea of removing any benzoic acid and possibly chlorine compounds from the fractions 195 - 260° & 260 - 3 an ethereal solution of them was shaken with aqueous solutions of sodium carbonate and hydrate, dried and, after removal of the ether, distilled under a pressure of 85 mm. The quantities of distillate collected were:-

up to 160°	1.6 grams
160 - 200	0.3 "
200 - 240	5.5 "

On mixing the last portion with some light petroleum and cooling it in a freezing mixture, there separated some crystals, which when dry weighed 0.11 gram.

An ice-cold ethereal solution of bromine was immediately decolourised by a similar solution of these crystals. After standing four hours in the cold, the silky needles, which had been deposited from the solution, were filtered off and dried on a porous plate. The weight of crystals obtained was 0.124 gram, and they melted at $236 - 237^{\circ}$. As stilbene dibromide melts at 237° this confirms the results of the analysis.

From the mother liquor of the stilbene, no constant boiling liquid could be isolated and it still contained a considerable quantity of chlorine. The action of sodium benzoxide on benzal chloride would thus appear to be a rather complicated one, the formation of stilbene only taking place in very small quantity.

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EXPERIMENTAL.

PART III.

In the following experiments the mixture of the chloride and the sodium derivative of the alcohol was heated under pressure, the operation being conducted in sealed tubes.

SODIUM METHOXIDE

In this experiment 41.4 grams of benzal chloride were added to a solution of 6 grams of sodium in 60 grams of methylic alcohol, and the mixture was sealed up in a tube and heated to a temperature of 100 - 105° for six hours. On the tube being opened, only a slight pressure was exerted, but a considerable quantity of a white salt had separated. The tube was again sealed and heated to 150° for three hours. On reopening, a strong pressure was exerted by the gas in the tube, and the liquid contents were faintly acid. After standing for a few minutes the contents of the tube began apparently to boil, a brisk evolution of gas taking place for more than an hour. This gas had a pleasant ethereal odour, burned with a green edged flame, did not make lime water turbid and was not absorbed by sulphuric acid, thus showing that it was probably methylic chloride and did not contain either carbonic anhydride or an unsaturated hydrocarbon. That the gas was almost certainly methylic chloride is shown by the production of corresponding ethylic, propylic and benzylic chlorides under similar conditions.

The residue was filtered with the aid of the pump and the liquid thus obtained was distilled under reduced pressure, the following fractions being collected:-

below 35°	at 80 mm. pressure	21.7 grams
35 - 105	" 75 " "	5.1 "
100 --105	" 65 " "	18.8 "

The residue in the distilling flask was a dark brown pitchy mass.

These fractions on redistillation at ordinary pressure gave the following fractions:-

66 - 67°	13.3 grams
67 - 70	6.1 "
70 - 170	3.3 "
170 - 179	2.2 "
179 - 182	12.4 "
182 - 195	8.5 "

The last three fractions had the characteristic odour of benzaldehyde and the crude product so obtained corresponds to a yield of 87% of the theoretical.

From the residue a small quantity of a crystalline acid melting at 121° was obtained, (Benzoic acid M.P.121°) probably formed by the oxidation of the aldehyde.

SODIUM ETHOXIDE

This experiment was carried out in a similar manner to the previous one, the quantities taken being 4.6 grams of sodium, 47 grams of ethylic alcohol and 32.0 grams of benzal chloride. The mixture was heated to 150 - 160° for seven hours. No pressure of gas was shown on opening the tube, but on heating it to 55° a large volume of gas was liberated. The gas, which measured 2250 cc. was collected in a gas holder. After passing it through two wash bottles containing sulphuric acid, some of the dry gas was liquefied in U tubes immersed in a freezing mixture. About 4 cc. of the colourless, very mobile liquid which was obtained in this way, evaporated very rapidly when removed from the freezing mixture. The vapour burned with a green edged flame and was evidently ethyl chloride. The volume of gas measured was about half the volume which should theoretically have been obtained.

The contents of the tube were next filtered with the aid of the pump and after distilling off the unchanged alcohol from the filtrate the following fractions were collected:-

80 - 180°	5.4 grams
180 - 185	11,1 "
185 - 210	6.3 "

The residue was dark brown in colour and resembled pitch. It did not give evidence of the presence of chlorine as shown by the sodium test. On heating alone, it gave off a very acrid odour. (Melting point of Benzoic acid 120°) A solution obtained by boiling it with water and filtering hot, deposited glistening leaflets, which melted at 121°. The three fractions above mentioned were again distilled with the following results:-

up to 100°		2.1 grams
100 - 175°		1.0 "
175 - 180°		8.7 "
180 - 185°		3.6 "
185 - 210°		5.5 "
residue	about	2.5 "

Only a trace of chlorine was found in the fraction boiling between 185 & 210°, hence unchanged benzal chloride can only be present in very small quantity. That this portion was mainly benzaldehyde was shown by the amount of sodium bisulphite compound formed on shaking some with a saturated solution of that reagent. Assuming the fractions boiling between 175 and 210° to have been chiefly benzaldehyde, the yield was nearly 84 per cent of the theoritical.

SODIUM PROPOXIDE

In this experiment the quantities used were 4.6 grams of sodium, 50 grams of propylic alcohol and 32.2 grams of benzal chloride. The mixture was heated up to 150° for 7 hours. No gas escaped on opening the tube. The tube was then connected with a condenser to which two U tubes immersed in a freezing mixture were attached, and in order to heat it, it was placed in the outer jacket of a V. Meyer vapour density apparatus filled with water. When the temperature of the water rose to 55°, bubbles of gas began to come off and after heating for an hour and a quarter during which, the temperature gradually rose to 97° all the gas seemed to have been evolved. The weight of the condensed liquid in the U tube was 11.4 grams. It was then fractionally distilled, a Linnemann column being used. The temperature which rose to 43° before any liquid distilled over, remained constant at 46° for some time, and then rose rapidly to 90°. The fractions collected were:-

Bar = 767 per cent43 - 48° (chiefly 46°) 4.4 grams
48 - 97° (chiefly 90-94) 6.4 "

The former was a colourless, mobile, strongly refractive and pleasant smelling liquid resembling propyl chloride in all its properties. (Propyl chloride B.P. 46°) A yield of 4·4 grams propyl chloride corresponds to 28 per cent of the theoretical. The latter portion was chiefly propylic alcohol.

The residue in the tube was mixed with about 250 cc. of water and extracted with ether eight times. The ethereal extract which reacted neutral to litmus, was dried over calcium chloride and after expelling the ether by heating in the water bath, was distilled. The series of fractions obtained may be grouped thus:-

up to 105°	26 grams
105 - 175°	1.1 "
175 - 230°	18.5 " "

The first portion consisted mainly of propylic alcohol, while the last had a strong odour of benzaldehyde and was found to contain a considerable quantity of chlorine. In order to get a rough estimate of the quantity of benzaldehyde present, the last portion was shaken with a saturated solution of sodium bisulphite, the crystalline compound thus formed, filtered with the aid of a pump, washed twice with ethylic alcohol and dried on a porous plate. The weight of the dry bisulphite compound was 9.6 grams or 23 per cent of the theoretical.

SODIUM BENZOXIDE.

In this experiment, 4.6 grams of sodium were dissolved in 50 grams of Benzylic alcohol, and to the cold solution which had solidified in cooling, 32.2 grams of Benzal chloride were added, the mixture then being heated in a sealed tube to a temperature of 150 - 160° for eleven hours. On opening the tube, slight pressure was noticeable, a combustible vapour escaping. A small quantity of thin glistening leaflets which had crystallised on the upper part of the tube proved to be insoluble in cold water, readily soluble in hot water, and in caustic soda solution, from which they were reprecipitated by the addition of hydrochloric acid. After drying the crystals between filter paper, they softened at 90° and melted at 118°, agreeing generally therefore with the properties of benzoic acid, which melts at 120°. The contents of the tube were then filtered with the aid of the pump and the oil thus obtained subjected to fractional distillation under reduced pressure.

Fractions were collected

up to 85° at from 70 to 60 mm. pressure
85 - 105° " 60 mm pressure
105 - 120° " " " "
120 - 140° " " " "

The first fraction was slightly milky, the middle ones were clear and colourless, and as the last fraction was being collected, drops crystallised in the condenser. Redistillation at ordinary pressure yielded fractions-(1) up to 135° (2) 135 - 167° (3) 167 - 179° (4) 179 - 182°, all of which were slightly turbid. After treatment with calcium chloride, the turbidity disappeared and on again being distilled at ordinary pressure the following fractions were collected:-

up to 162°
162 - 176° 7.2 grams
176 - 178° 20.0 "

As this last fraction was expected to be benzyl chloride chlorine estimations were made, the results being:-

(1) 0.2673 grams substance gave 0.2330 grams Ag Cl.
(2)& 0.2207 " " " 0.1918 " " "

Calculated for C_7H_7Cl Found
Cl 28.06 per cent (1) 21.5 per cent
(2) 21.5 " "

AS the liquid probably contained benzaldehyde, it was shaken up with a saturated solution of sodium bisulphite, and the colourless crystalline substance so obtained, filtered off and proved to be the benzaldehyde bisulphite compound. The oil was then separated by the addition of water and extraction with ether. After drying the ethereal extract over calcium chloride, the ether was expelled and the residue distilled under a pressure of 70 mm., when it came over between 100 & 110°. Unfortunately some was lost; but of the remaining 8.7 grams, there distilled at ordinary pressure (761 mm) 1.8 grams below 176°, & 5.7 grams at 176-177°

The latter portion showed all the properties of benzylchloride the boiling point of which is given as 179° and a chlorine determination gave concordant figures.

0.2635 grams substance gave 0.2967 grams Ag Cl

	Calculated for $C_6H_5.CH_2Cl$	Found
Cl	28.06 per cent	27.90 per cent

In another experiment in which the same quantities were used, the components were thoroughly mixed by stirring with a glass rod before sealing off the tube. After heating to 150 - 155° for eleven hours, the white solid which had separated, was filtered with the aid of a pump from the brown liquid, washed with a little benzyl alcohol and dried. It weighed almost 12.0 grams, theory requiring 11.7 grams. It was entirely soluble in water, did not char or volatilise on heating and behaved generally like sodium chloride.

The filtrate on distillation under a pressure of 50 mm. was divided into following fractions:-

(1)	up to 95°	6.7 grams
(2)	95 - 107°	19.4 "
(3)	107 - 121°	12.9 "
(4)	121 - 160°	6.1 "

From fractions (1), (2), & (3), 18.2 grams of the sodium bisulphite benzaldehyde compound were obtained corresponding to a yield of 43.4 per cent of the theoretical.

After repeating the distillation and treatment with sodium bisulphite, 11.8 grams or 46 per cent of the theoretical yield of benzyl chloride, boiling at 175 - 176° under 748 mm. pressure, were obtained. An estimation of the chlorine in this substance gave the following figures:-

0.2165 gram substance gave 0.2403 gram AgCl

	Calculated for $C_6H_5CH_2Cl$	Found
Cl	28.06 per cent	27.5

Note on the Analysis of Benzal and Benzyl Chlorides.

As Wicke states that the chlorine in benzal chloride is completely precipitated by the addition of an alcoholic solution, of silver nitrate, it was thought that the Carius' method of estimating halogens might in the case of this compound and of benzyl chloride be replaced by the more direct process. The following experiments, which show that the precipitation is very incomplete in the case of benzyl chloride and slightly so in that of benzal chloride, were carried out.

To an alcoholic solution of the chloride, an excess of an aqueous alcoholic solution was added, the mixture being well stirred and heated to boiling. The precipitate was then treated in the usual manner.

0.3280 grams benzyl chloride gave 0.3623 grams AgCl

	Calculated for $C_6H_7.CH_2Cl$	Found
Cl	28.06 per cent	22.4

(1) 0.6302 grams benzal chloride gave 1.0907 grams AgCl

(2) 0.4226 " " " " .7314 " " "

	Calculated for $C_6H_5.CHCl_2$	Found	
		(1)	(2)
Cl	44.09 per cent	42.98	42.97

An attempt was also made to estimate the chlorine in benzal chloride by reduction with sodium amalgam. The chloride was covered with about 150 cc. of water and 40 grams of 5 per cent sodium amalgam were gradually added in small portions at a time. The sodium chloride formed was estimated in the usual way. The figures obtained thus in two experiments were (1) 0.7012 grams benzal chloride gave 0.4654 grams AgCl (2) 1.3776 " " " " 0.9345 " "

Calculated for $C_7H_6Cl_2$	Found	
	(1)	(2)
44.09 per cent	16.5	16.8

Both the above methods were therefore inapplicable, and the Carius method had to be resorted to.

ON THE ACTION OF SODIUM ETHOXIDE ON ETHYLENE DIBROMIDE UNDER PRESSURE.

In this experiment, 23.5 grams of ethylene dibromide were mixed with 5.75 grams of sodium dissolved in 57.5 grams of ethylic alcohol and sealed up in a tube. After remaining at ordinary temperature for two days, during which a quantity of salt separated, the mixture was heated to 120 - 130° for seven hours. On the tube being opened, a gas escaped under slight pressure. This gas possessed all the properties of acetylene. It burned with a brilliant, white, luminous flame. It decolourised bromine water, forming oily drops having a peculiar odour. It produced a deep red precipitate in an ammoniacal solution of cuprous chloride and a yellowish white precipitate in a similar solution of silver nitrate, both of which were explosive when dry.

The filtrate from the salt distilled at a temperature of 68 - 70° and in this way nearly all the alcohol was recovered.

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