D.Sc.

A. Thomson. 1886

An account of a research on the bromo-derivatives of (a) Diphenyl. (b) Tolylbenzene, and (c) Ditolyl.

{Begun Jany. 1885,
Finished March 1886.}

The hydrocarbons used in the following investigation were obtained by passing the mixed vapours of benzene, and toluene through a red hot tube according to the method described by Professor Carnelley — Chem. Soc. Journ. 37, 701 — to whom I am indebted, (1) for the hydrocarbons used. They were part of the hydrocarbons used in his own work referred to above; (2) for valuable suggestions as to the method of carrying on my research, as also for timely advice at several difficult points in my actual work.

I. The diphenyl, $C_6H_5 . C_6H_5$, after recrystallisation from alcohol, melted at 70° and boiled at 245-245°.

II. The 1.4 tolylbenzene, $C_6H_5 . C_6H_4 . CH_3$ was a colourless liquid boiling at 263-268°, and on oxidation gave first 1.4 phenylbenzoic acid melting at 216-220° and finally terephthalic acid.

III. The 1.2 ; 1.4 Ditolyl $CH_3 . C_6H_4 . C_6H_4 . CH_3$ was a lambent liquid, almost colourless, & boiling at 272-280. It gave on oxidation first 1.2 ; 1.4 tolylbenzoic acid melting at 179-180°, and finally terephthalic acid.

I. Derivatives of Diphenyl

1. Tribromodiphenyl, $C_6H_4Br \cdot C_6H_3Br_2$ = 1.4 ; 1.?.?.

The above compound was got by the action of bromine in excess on a mixture of diphenyl, with the 1.4 tolyl-benzene.

5 grams. of the mixed hydrocarbons boiling at 256-264° were taken and treated with excess of bromine. The product after standing for several hours was gently warmed, and then the excess of bromine and hydrobromic acid removed by repeatedly shaking up with caustic soda. From the crude substance thus obtained the tribromodiphenyl was separated by frequent treatment with alcohol, in which the other substances were much more soluble; and after being recrystalled several times from a large quantity of alcohol, it was finally obtained in colourless silky needles. It melts at 90°, is very sparingly soluble in alcohol even when hot, and is non volatile in steam. On analysis it gave the following results:-

Weight of substance taken = .1775 grams

note 1 page 33) after combustion with lime — see note 1 page 33 — the calcium bromide was extracting by boiling several times with distilled water, and then the bromine precipitated with silver nitrate as silverbromide;

Weight of silverbromide got = .2576 grams

	Calculated	Found
$C_{12}H_7Br_3$	61.38	61.75 per cent. Br.

This tribromo compound was then oxidised with excess of chromic and glacial acetic acids, and gave, on pouring into water a dense white precipitate, easily soluble in warm ammonia. after drying at 100° it was found to melt at 248° and gave on analysis a percentage of bromine required for monobromobenzoic acid. That it was the 1.4 bromo-benzoic acid is shown by comparison of the melting point with that got by Hubner - Berichte 10.1704 - for the parabromobenzoic acid.

(2) Dibromodiphenyl $BrC_6H_4 \cdot C_6H_4Br = 1.4 : 1.4$. after having obtained the tribromoderivative as above described, an attempt was made to get it by the action of bromine on pure diphenyl. The tribromide was not obtained, but two different crystalline modifications of the dipara-dibromodiphenyl were got

5 grams. of the pure diphenyl were dissolved in carbon disulphide, and 16 grams — as the specific gravity of bromine is 2.99 times that of water, the bromine was added from a burette, the number of grams required, divided by 2.99 giving the number of C.C. required — of bromine gradually added to the mixture. a violent reaction took place, though the liquid was kept cool by being placed in cold water. When the action had entirely ceased, the product was digested on a water-bath with a reversed condenser for two days. 1 gram. of bromine

was then added, and the whole heated ~~in~~ a sealed tube for two hours at 90°. On cooling the carbon disulphide was distilled off, and the last traces of bromine removed by caustic soda. After being well washed with water the product was treated with hot alcohol, in which it was for the most part soluble. The insoluble residue on crystallisation from carbon disulphide gave a crop of crystals which were of two kinds, (a) prisms and (b) octohedra. These were separated mechanically, and I have specimens of them in separate bottles, as well as of the tribromodiphenyl.

a <u>The prisms</u> , when recrystallised from carbon-disulphide, were quite free from octohedra, and were drained, washed with hot water in which they were insoluble, and dried. They melted at 162°, and consisted of brilliant, colourless, highly refractive prisms. They were almost insoluble in alcohol, and only moderately soluble in carbon disulphide and cold benzene. A portion recrystallised from benzene gave the following results on analysis:-

Weight of substance taken = ·2345 grams
Weight of silver bromide got = ·2834 "

	Calculated	Found
$C_{12}H_8Br_2$	51·28	51·42 per cent. Br.

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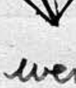
b <u>Octohedra</u>. . These after being picked out from the prisms, were washed with a mixture of alcohol and ether to remove any traces of the prismatic modification which was more soluble therein. after drying they melted at 162. many of the crystals were perfect octohedra. They were insoluble in cold and nearly insoluble in hot alcohol, and were but little soluble in a mixture of alcohol and ether. An analysis of this gave the following result.

Wt. of substance taken = .1985 gram.
Wt. of silver bromide got = .2389 "

	Calculated	Found
$C_{12}H_8Br_2$	51.28	51.19 per cent. Br.

These results show that both prisms and octohedra consisted of dipara-dibromodiphenyl.

Fittig (Annalen 132, 204) and Strasse and Schultz (Annalen 210, 191) give the melting point of this compound as 164°, while Carnelley – see Chem. Soc. Jour. 37-706 – gives the melting point as 162°.

It thus appears that diparadibromodiphenyl exists in two modifications crystallising in different forms, the one in prisms, the other in octohedra. Of these the latter does not seem to have been previously observed, for all published accounts describe dipara-dibromo-diphenyl as crystallising in large colourless prisms, having a splendid lustre and a strong refractive power.

As the other bromo derivatives of

diphenyl had been previously investigated by Schultz and Strasse, and the position of the bromine atoms settled it was considered unnecessary to attempt the preparation of more of these compounds.

The oxidation product of the tribromodiphenyl gives the position of the bromine in one of the phenyl groups, the position of the two bromine atoms in the other group has not been ascertained.

In the case of the dibromodiphenyls, no oxidation was attempted, as these had been already done by Schultz & Strasse, and it was thought to be more important to keep them as specimens.

II. Derivatives of Tolyl Benzene.

1 **Monobromotolyl benzenes**:- To make these 15·5 grams of tolyl-benzene – $Ph.C_6H_4.Me = 1.4$ – were taken, and after dissolving in carbon disulphide were acted upon with 4·9 c.c. of bromine. The chemical action was very violent, the flask having to be kept in cold water and the bromine added very slowly. When the action had ceased the flask was gently warmed for some time, and then the carbon disulphide distilled off. To remove excess of bromine and hydrobromic acid the compound was well washed with caustic soda, and then with water to remove the caustic soda. The semisolid mass, obtained in this way, was next dissolved in hot alcohol, from which on cooling a large crop of crystals (A) separated out first, and then on evaporating the mother liquor a yellowish oil (B) separated out which was more soluble in alcohol than the crystals were.

e note 2. page 33.)

A **The Crystals**. These were purified by being recrystallised from hot alcohol four times, when small pearly plates were obtained melting at 129°, and easily soluble in ether and benzene, but only moderately soluble even in hot alcohol.

an analysis of these crystals gave the following result:-

Weight of substance taken = ·2450 grams.
Weight of silver bromide ppt = ·1845 "

	Calculated	Found
$C_{13}H_{11}Br$	32·39	32·04 per cent. Br.

a part of this crystalline compound was then taken and oxidised with a deficit of chromic and glacial acetic acids, after boiling for an hour the contents of the flask were poured into a large quantity of distilled water, when a yellowish white mass separated out. This was well washed with hot water, and then treated with warm dilute ammonia, when part of it was dissolved leaving a yellowish residue (x). After filtering off the insoluble part, the filtrate was acidified with hydrochloric acid, when a fine white mass separated out, which was easily & completely soluble in ammonia. It melted at 304-306°(Corr.), & otherwise exhibited the properties of monobromoterephthalic acid, giving likewise on analysis a percentage of bromine corresponding to the formula $C_8H_5BrO_4$.

ot 3. page)
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The yellowish residue (x) was then taken and oxidised by boiling for two hours with an excess of Chromium and glacial acetic acids, when an acid was found in all respects similar to the one already found in the first oxidation, viz monobromoterephthalic acid. It would thus appear that in this case there is no intermediate product of oxidation, or if it exists, that it is an unstable compound, being very easily converted into the final oxidation product.

The monobromoterephthalic acid found here & elsewhere in this research — see page 18 — sublimed from a watchglass without melting, & in ascertaining the melting point it had to be done in a sealed tube, as otherwise the acid sublimed up the melting point tube before getting the bath of sulphuric acid to a sufficiently high temperatures. This sublimate was taken on three different occasions, and its melting point determined by heating in a sealed tube. It melted readily and completely to an almost transparent liquid at 243-245°. The amount of material at my disposal did not allow me to make a complete analysis of this sublimate, but it seems to be an anhydride of bromoterephthalic acid, though I am not aware that an anhydride of this acid has hitherto been observed.

B <u>The yellowish oil</u> — page 7 — obtained on evaporating the motherliquor was next taken, and after heating for some time to nearly 100° was thoroughly dried by being left in a desiccator over sulphuric acid for three weeks.

When put in a melting point tube, and suspended in a freezing mixture of ice and salt, the substance solidified to a yellow crystalline mass, which on gently warming melted at 27-30°.

An analysis was then made with the following results:-

Weight of substance taken = ·2160 grams.
Weight of Silver bromide got = ·1626 "

	Calculated	Found
$C_{13}H_{11}Br$ …………	32·38	32·03 percent Br.

This is therefore an isomer of the crystalline monobromotolyl benzene, and differs from it chiefly in having a much lower melting point, and in being much more soluble in alcohol.

2·8 grams of it were oxidised with a deficit of chromic and glacial acetic acids. This on pouring into water gave a white precipitate, mostly soluble in warm dilute ammonia, from which it was reprecipitated on addition of hydrochloric acid. It melted at 193-194° and was found to be difficultly soluble in cold alcohol and benzene, though easily soluble in cold ether. The analysis of this acid gave the following result :-

Weight of acid taken = ·1615 grams
Weight of silver bromide got = ·1077 "

	Calculated	Found
$C_{13}H_9BrO_2$	28·88	28·38 per cent. Br.

1·7 grams of the original substance (B) were then boiled for over two hours with an excess of chromic and glacial acetic acid. on pouring into water, a dense white precipitate was got, readily soluble in ammonia. This was purified in the usual way and dried at 100°, when it was found to melt at 247-249°. an analysis gave a percentage of bromine corresponding to the formula $C_7H_5BrO_2$, which taken along with the melting point shows that the acid is the 1.4 monobromobenzoic acid.

II Dibromotolyl-benzenes.

18·7 grams. of tolyl-benzene – Ph. C_6H_4. Me = 1.4 — were taken and dissolved in carbon disulphide. To the solution was slowly added 13·2 c.c. of bromine, and the rather violent action moderated by keeping the flask in cold water. after allowing the contents to remain together for about 12 hours, the flask was gently heated and the carbon-disulphide distilled off. The residue was well shaken up with caustic soda in the usual way, and after being thoroughly washed with water, it was repeatedly boiled for a considerable time with alcohol, which extracted part of it leaving an insoluble mass B.

A <u>The Crystalline part.</u> This was got as exceedingly beautiful, transparent, ferny plates melting at 113-115, after being purified by repeated crystallisation from alcohol. An analysis gave the following result:-

Weight of the substance taken = ·271 grams
Weight of silver bromide got = ·309 "

	Calculated	Found.
$C_{13}H_{10}Br_2$	49.02	48.52 percent. Br.

„ ·250 of a gramme of this was taken and treated with a deficit of chromic and glacial acetic acids, and the liquid boiled for an hour. On pouring into distilled water a precipitate was got, which after being filtered off was treated with warm ammonia, in which only a part was soluble, an insoluble residue (x) being left.

On acidifying the ammonia solution with hydrochloric acid, a white curdy precipitate was got; which was purified by being several times dissolved in dilute ammonia, and reprecipitated by hydrochloric acid. The purified acid thus obtained melted at 201-204° and sub-

Sublimed in small needle shaped prisms, which were not very soluble in alcohol, though easily soluble in benzene and ether. The acid after being well dried at 100° was analysed with the following result:-

Weight of the acid taken = .1270 grams.
Weight of silver bromide got = .1350 "

	Calculated	Found
$\{C_{13}H_8Br_2O_2$ $\{C_{12}H_7Br_2COOH$	44.94	45.23 per cent. Br.

The residue (x) mentioned above was then boiled for more than an hour with excess of chromic and glacial acetic acids, and on pouring into water gave a white mass, easily & completely soluble in ammonia. This on drying melted at 248-249°, and was in all respects similar to the acid obtained - see page 3 - by the oxidation of the tribromodiphenyl, being therefore the 1.4 bromobenzoic acid. This fact shows us that in the crystalline dibromo compound one of the bromines is in the phenyl-group and one in the tolyl group, and that the one in the phenyl group is in the para position, while the one in the tolyl group may be in the ortho or meta position, the para position being occupied by the CH_3 groups. [See table page 16]

B The mass insoluble in alcohol - see page 12 - was treated with benzene in which it was so easily soluble, that definite crystals could not be obtained. The benzene was evaporated off, and the compound treated with ether, in which it was moderately soluble, and from which it crystallised in needles, almost insoluble in alcohol, but easily soluble in ether, and more so in benzene. The purified crystals melted at 148-150° and gave on analysis the following result:-

Weight of substance used = .313 grams.
Weight of silver bromide got = .358

	Calculated	Found
$C_{13}H_{10}Br_2$	49.02	48.67 percent. Br.

.503 of a gram of this was taken and dissolved in glacial acetic acid and boiled with a deficit of chromic acid. When poured into water a white mass separated, which was partly soluble in ammonia. after filtering off the insoluble part (x), and acidifying the alkaline filtrate with hydrochloric acid, a white mass separated out, easily & completely soluble in dilute ammonia.

The purified acid melted at 231-232°, and was easily and almost completely sublimed from a watch glass. It was much more soluble in alcohol than the corresponding acid melting at 201-204°. An analysis was made and gave the following result :-

Weight of acid taken = .1820 grams

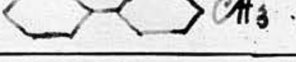
Weight of silver bromide got = .1915 grams

	Calculated.	Found.
$C_{13}H_8Br_2O_2$	44.94	44.74 per cent Br.

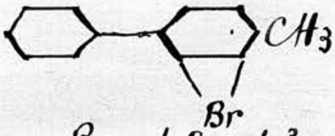
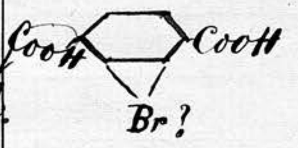
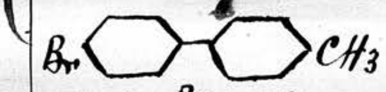
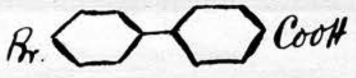
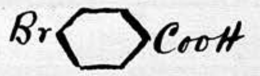
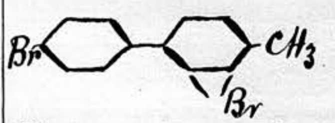
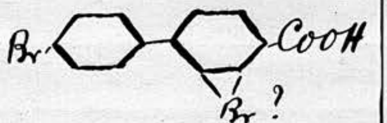
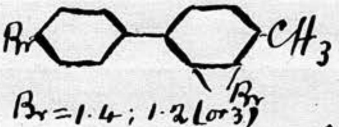
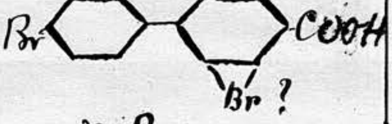
On taking a portion of this acid, and oxidising it with an excess of chromic and glacial acetic acids, and precipitating with water, a substance was obtained, easily soluble in dilute ammonia, and melting at 250-251°. Then the insoluble part x -page 14- was boiled for more than two hours with a large excess of the oxidising agent, and after treatment as above gave a substance melting at 249-251°. An analysis was made of these two, and a percentage of bromine was got corresponding to monobromobenzoic acid.

From this it appears that the difference in melting point, &c. between the two isomeric dibromotolylbenzenes is due to the position of the bromine in the tolyl group i.e. whether it is in the ortho or meta positions, since by the final product of oxidation the position of the bromine in the phenyl group is the same in both, viz in the para position.

Table Shewing the relations of the bromo-derivatives of tolyl-benzene.

Formula = 

. B.P. 263-267°

	The bromo compounds derived from $Ph \cdot \overset{1{\cdot}4}{C_6H_4} \cdot me$.	Oxidation products of these. Intermediate.	Final.
monobromo-Compounds	 Br = 1·2 or 1·3 m.P. = 127-129°	a Separate oxidation product was not obtained.	 m.P. = 304-309°
	 Br = 1·4 m.P.=27-30°	 m.P. = 193-194°	 m.P.=247-249°
× Dibromo-Compounds	 Br = 1·4; 1·2 (or 3) m.P. = 148-150°	 m.P. = 232°	 m.P. 248-251°
	 Br=1·4; 1·2 (or 3) m.P. = 113-115°	 m.P.=201-204	 m.P. = 248-251

× The differences in the isomeric dibromo-comps. seem to be caused by the position of the Br in the tolyl group.

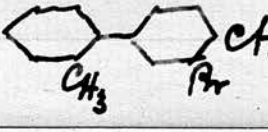
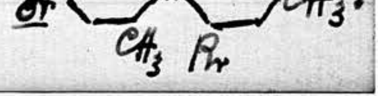
The Bromoderivatives of ditolyl.

I <u>Monobromo-ditolyls</u>. To make these compounds 7·125 grams of the ditolyl – see page 1 – were used. To this were added 2.1 cc of bromine. In this case the chemical action was very violent, and the bromine had to be added drop by drop, the flask containing the ditolyl being meanwhile kept in cold water. The calculated quantity of bromine having been all added, the flask was left for several hours, and then gently heated, after which, the mass was treated with excess of caustic Soda to remove any free bromine, and hydro-bromic acid. a white solid residue was left which was well washed with water, and then boiled in a large excess of alcohol, in which it was entirely dissolved. on cooling a mass of crystals separated out, along with a reddish brown oil, the bulk of which was left in the mother liquor. after the crystalline portion was five times recrystallised from alcohol it was obtained quite free from the oil, (B) and the melting point was constant at 93-95° (Corr.) This compound crystallises in fine interlacing needles, which are only slightly soluble in cold alcohol, but easily soluble in ether and benzene.

This was analysed in the usual way by Combustion with pure Calcium oxide, when the following result was obtained:-

Weight of substance taken = ·1140 grams.
Weight of silver bromide got = ·0829 "

	Calculated	Found
$C_{14}H_{13}Br$	30·94	30·65 per cent. Br.

·119 of a gram. of this compound was then dissolved in a flask by glacial acetic acid, and boiled for an hour with excess of chromic acid. When the contents of the flask were poured into a large quantity of water a white ~~pf~~ precipitate separated from the liquid. This was filtered off, washed, and dried at 100°. On heating a small portion on a watch glass it sublimed without previous fusion, but when put in a sealed tube it was easily fused. Its melting point was determined by heating in a sealed tube in a bath of sulphuric acid, when it was found to melt at 304-309 (corr). From this, and the fact that it was almost insoluble in alcohol though more easily soluble in ether and benzene, it was considered to be monobromo terephthalic acid, the melting point of which is given see Ber., 12. 619 — as 304-305°. This shows that the constitution of this monobromo compound is  or 

The small amount of the crystalline compound at my disposal hindered me from attempting an intermediate oxidation product.

B The oily portion - see page 17 - was thoroughly dried in a desiccator over sulphuric acid, & then a small portion of it cooled to 0°, when it showed no sign of solidification. It differed also from the crystalline compound in being more soluble in the ordinary reagents. an analysis gave the following results:-

Weight of oil taken = ·2934 grams.
Weight of silver bromide got = ·2118 "

	Calculated	Found
$C_{12}H_{13}Br$	30.65	30.75 per cent Br.

·850 of a gram of the oil was taken and treated with a quantity of chromic and glacial acetic acids requisite to convert it into diphenic acid. By pouring into a large excess of water a white precipitate was obtained. a part of which was soluble in warm ammonia. after purifying the acid by redissolving in ammonia and reprecipitating with hydrochloric acid it melted at 215° (corr).

An analysis was then made with the following result:-
Wt. of the acid taken = ·1055 grams.
Wt. of silver bromide got = ·0598 grams.

	Calculated	Found
$C_{14}H_9BrO_2$	24.92	24.17 per cent. Br.

another analysis of this was found impossible owing to the small amount of material obtained.

For the complete oxidation of the liquid monobromo-ditolyl, 1·2 grams of the oil were taken and boiled for two hours with excess of chromic and glacial acetic acids. On pouring into water a dense white precipitate was obtained, easily and completely soluble in warm dilute ammonia, from which it was again precipitated by hydrochloric acid. After being three times treated in this way, it was dried at 100° and its melting point determined = 203° (corr.)

An analysis was then made

Wt. of substance taken = ·118 grams.
Wt. of silver bromide got = ·0893 "

	Calculated.	Found
$C_8H_5BrO_4$	32·65	32·20 per cent. Br.

That this acid is a monobromophthalic acid is shown by its melting point, for in the original liquid bromoditolyl, the bromine must be in the nucleus, in which the methyl is in the orthoposition, otherwise bromoterephthalic would have been obtained on oxidation. Now only two bromophthalic acids are possible viz., $C_6H_3Br(COOH)_2$ = 4·2·1 and 3·2·1.

In doing this part of the research fully a year ago, the only reference that I could find to an acid of the above ~~form~~ composition was in the Annalen 160, 62, and that spoken of by von Pechman in Ber. 12, 2126, who gives an acid of the above composition melting at 138-140°, in which the bromine atom is said to be contiguous to the Carboxyl groups i.e. the 3.2.1 acid, and hence the constitution of the acid obtained by me was thought to be the 4.2.1 acid, since only two of these monobromophthalic acids are possible.

In Chem. Soc. Jour. for 1885 pages 511-515 – the same journal as that in which a part of this research appears – Meldola describes a research by him in which he obtains a monobromophthalic acid melting at 174-176 – anhydride melting at 134-135° – and previously got by Guareschi and Smith. I have also recently obtained the same acid – see page 29 –. That this acid is the 4.2.1 acid I think there is little doubt, though in a paper in this month's – March 1886 – Journal of the Chemical Society there is a paper by Stallard in which he seems to think that the acid got by Meldola is the 3.2.1 and not the 4.2.1 acid. At first I thought that the 174-176 acid must be a mixture of the 203° acid & the 138° acid, but the evidence in support of the separate existence of the 174-176° acid is so strong, that I have come to the conclusion that of the three acids described there is no doubt of its existence. The doubt there is in regard to the acids with melting point 138°, and 203°. Faust gives the acid with m.p. 138, but does not give an anhydride, and the melting point is so near the melting point of the anhydride of Meldola's acid, that one would have thought the mistake was there, but Von Pechmann gives an anhydride of this acid melting at 138° – melting point of the anhydride 60-65° – So that to look at Faust's acid as the anhydride of Meldola's one would be incorrect. At the same time the argument advanced by Stallard from a recent paper by Krüger (Ber. 18. 1755) in regard to the melting points of the isomeric monochlorophthalic acids, obtained by the oxidation of of the 1.2.3 and 1.2.4 monochloroxylenes, would be in favour of the acid melting at 203° as the 1.2.3 acid, without assuming as Stallald does that "during the oxidation process an atomic migration occurs". or the occurrence of substituted phthalic acids produced by secondary reactions.

The real difficulty in connection with this part of my work I am at present unable to explain, and had time permitted I would have repeated my own experiments, and also tried to find by Faust's method the acid described as melting at 138°, as until that is done the difficulty in regard to these two acids cannot be satisfactorily cleared up.

II **Dibromoditolyls**:— $C_{14}H_{12}Br_2$. Two isomers were got having the above formula. For the preparation of these 7.77 grams of ditolyl were weighed out and dissolved in carbondisulphide, and then treated with the calculated quantity - 4.14 cc - of bromine, the liquid as before being kept cool by placing the flask in water. When the action had ceased the carbon disulphide was distilled off, and the excess of bromine removed by caustic soda, and the resulting compound well washed with water. It was then boiled with a large excess of alcohol, in which it was much less soluble than either of the monobromoditolyls. On cooling, a large crop of crystals separated out, and on further evaporation of the mother liquor an oil was obtained, which on analysis was found to be a mixture of dibromoditolyl, & the liquid modification of the monobromo:ditolyl already described, See page 19 et seq.

A <u>The crystalline part</u>, after having been purified by several recrystallisations from alcohol, melted at 156° (corr), and the crystals were found when examined under the microscope to consist of two sets of crystals:- (a) <u>rosettes</u> of almost hair fine needles of brilliant lustre. This modification constituted the great bulk of the compound. (b) a small quantity of minute perfect <u>octohedra</u>. Both sets of crystals seemed equally soluble in alcohol, and I was unable to get them separated. After an analysis by burning with lime in the usual way, the following result was obtained.

Weight of substance taken = ·1790 gram.
Weight of silver bromide got = ·1994 "

	<u>Calculated</u>	<u>Found</u>.
$C_{14}H_{12}Br_2$	47.06	47.42 per cent. Br.

This dibromo-compound behaves in a remarkable manner on oxidation. A portion after being dissolved in acetic acid was boiled for half an hour with a quantity of chromic acid sufficient for oxidation into one of the bromophthalic acids. On pouring the liquid into excess of cold distilled water a thick bright yellow precipitate was obtained, which after washing well with hot water and drying at 100° C melted at

170° (Corr.). This compound did not appear to be an acid as it was quite insoluble in hot ammonia, caustic soda or caustic potash, but dissolved in alcohol to a bright yellow liquid. An analysis was made as follows:-

Weight of the substance taken = ·144 grams
Weight of silver bromide got = ·1479 "

	Calculated	Found
$C_{14}H_6Br_2O_2$	43·71	43·70 per cent. Br.

Another preparation made in exactly the same way gave as melting point 170° and was in all respects similar to the above.

A quantity of the preparation melting at 170° was dissolved in glacial acetic acid & boiled for more than an hour with a large excess of chromic acid. On pouring the liquid into water a yellow precipitate was obtained, which after being well washed with hot water and dried at 100° gave as melting point 201-202° (corr.). Like the former compound it was insoluble in hot ammonia, caustic soda or caustic potash, but soluble in hot alcohol to a bright yellow liquid from which on cooling it crystallised in small yellow needles. It was easily soluble in cold benzene & cold ether to an intensely yellow liquid. To all appearance it seemed identical with the compound previously obtained, and melting at 170°, but its real difference was shown by its melting point 201-202° (corr.) and by its composition which on analysis appeared to be as follows:-

Weight of substance = ·106 grams

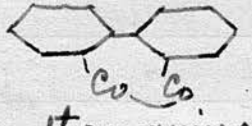
Weight of silver bromide = ·0992

	Calculated.	Found.
$C_{14}H_6Br_2O_4$ or $C_{14}H_8BrO_4$	40·20 40·00	39·82 per cent. Br

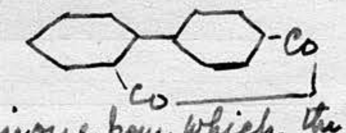
The same compound melting at 201-202 was also obtained by the direct oxidation of the dibromoditolyl with a <u>large</u> excess of chromic and glacial acetic acids.

The compound with the higher melting point - 201-202° - has the percentage of bromine required for dibromodiphenic acid, though its insolubility in caustic alkalies, and its intensely yellow colour make its classification as an acid extremely doubtful.

The compound melting at 170° has the composition of a double ketone. $C_{12}H_6Br_2(CO)_2$, and is therefore isomeric with dibromophenanthraquinone, melting at 230°. (Annalen 167-185)



Phenanthraquinone



Quinone from which the dibromo-compound is obtained with M.P.=170°

If this be so it is an example of the unusual formation of a diketone, in which the two carboxyl groups are not both in the orthoposition.

Quite recently - last month - an attempt was made to prepare another quantity of ~~the~~ crystalline dibromoditolyl, as also to obtain the liquid modification.

8.40 grammes of the ditolyl were taken, and after dissolving in carbon disulphide were treated with a considerable excess of bromine. The whole was left standing in a warm place for four days, and then the excess of bromine removed by caustic soda, after which the resulting compound was well washed with water, & boiled with alcohol, in which it was soluble, & the crystalline compound already described separated out on cooling. This was purified & gave a melting point -156°- corresponding to the quantity obtained ten months previously. This was oxidised with a large excess of chromic acid, and gave a yellow compound corresponding to the one melting at 201-202. If oxidised further than this the compound seemed to be entirely decomposed.

On evaporating down the mother liquor

a considerable quantity of a thick deep-red oil separated out, which was moderately soluble in the usual solvents. On cooling a small quantity in a freezing mixture it solidified, & on gently warming it melted at about 10°. To purify the oil it was boiled several times with alcohol, and then heated to about 100°, & left for two weeks in a desiccator over sulphuric acid to dry it.

On burning with lime the following result was obtained.

Weight of substance taken = ·3020 grams.
Weight of silver bromide got = ·3380 "

	Calculated.	Found.
$C_{14}H_{12}Br_2$	47.06 .	47.62 per cent. Br.

1.97 grams. of the oil were then taken & boiled with a large excess of chromic and glacial acetic acids, & on pouring into water no precipitate was obtained. The compound seemed to have undergone complete oxidation.

2.5 grams. of the oil were then taken & treated with an amount of chromic acid calculated to yield a diphenic acid. On boiling for an hour & then pouring into water a precipitate separated out, which was found partially soluble in warm ammonia, & separated as a white precipitate when the ammonia solution was acidified with hydrochloric acid. This was further purified by being several times dissolved, and reprecipitated as above. It was then found to melt at 171-175°, and on analysis gave the following result:-

Weight of substance used = .0815 grams.
Weight of silver bromide got = .0634 "

	Calculated.	Found.
$C_8H_5BrO_4$	32.65	33.10 per cent. Br.

I was annoyed that the smallness of the material at my disposal did not allow me to further purify this acid, & make another analysis, as it is I cannot help coming to the conclusion that the acid here obtained is the one already referred to, and described by Meldola — Chem. Soc. Journ. 1885, 511-515. — as melting at 174-176°, and corresponding with that previously described by Guareschi and Smith.

Before closing this account I may refer to a law which seems to be applicable to these isomeric compounds, & which may be stated as follows:- If there be two or more isomeric compounds of different melting points, then the solubilities of these compounds are in the inverse ratio of their melting points, i.e. the one with the higher melting point is the least soluble. In the isomeric compounds described in this research this law seems to hold good, and during the Christmas vacation I looked up over 400 examples of isomeric compounds, and in these found only one instance in which the isomer of higher melting point seemed to be the more soluble. I hope to publish an account of this after the summer holidays, but a few examples given here from my note book will illustrate what I mean:-

		References
1	Methoxyhydroxybenzoic acid = 1.4.5. m.P. = 207°. one part soluble in 39 of water at 100°	Chem. Soc. Journ. 34 - 500
	" = 1.3.4. m.P. = 250° " " " " 155 " " " "	"
2	Hydroxyisophthalic acid = 1.3.2. m.P. = 243° one part sol. in 700 of water at 24°	Chem. Soc. Journ. 34. 229
	" = 1.3.4. m.P. = 300° " " " " 3000 " " " "	"
3	β. Stilbene dichloride m.P. = 93-94° soluble in all proportions in alcohol	Chem. Soc. Journ. 32. 622
	α- " " m.P. = 191-192 one part in 10 parts of "	"

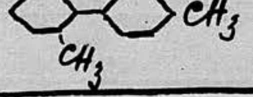
In a great many cases however it is impossible to obtain from the publisheded accounts the absolute solubilities in the different solvents, but the relative solubilities shew the same law. If we represent the solubilities by 1 · 2 · 3 & letting 1 stand for the most soluble, the following method may be employed to shew the same thing:—

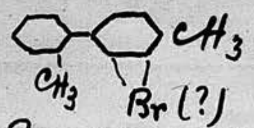
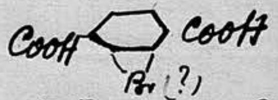
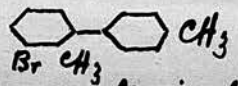
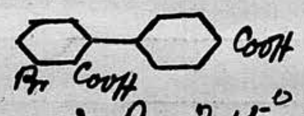
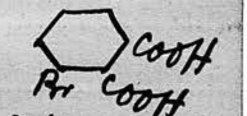
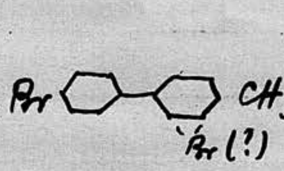
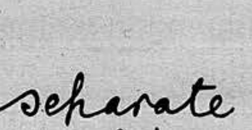
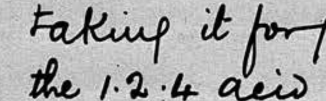
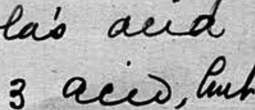
			Solvents used	Order of Solubilities	References
1.	Dimethyl oxalate	m.P. = 51°	water, alcohol & ether	1	Watts Dict. IV, 272
	Isosuccinic acid	m.P. = 130°	"	2	" " VI. 1041
	Succinic acid	m.P. = 180°	"	3	" " " "

Phthalic acid	m.P. = 182°	water alcohol & ether	1	Wislicenus page 653
Isophthalic acid	m.P. = 300°	"	2	" " 655
Terephthalic acid	Sublimes above = 300°	"	3	" " 655

These examples will shew what is meant by the law referred to, and its connection with the isomeric compounds described in this research, seemed to me to justify a single reference to it here.

Table shewing the relations of the bromoderivatives of ditolyl.

Formula =  . B.P. = 272-280.

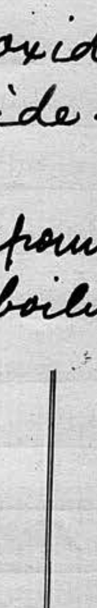
	The bromocompounds derived from $C_6H_4me.C_6H_4me = 1.2:1.4$	Oxidation products of these	
		Intermediate	Final
monobromo-Compounds	 Br = 1.2 or 1.3 m.P. 93.95°	a separate oxidation product was not obtained	 m.P. 304-309°
	*  Br = 1.3 , liquid at 0°	 m.P. = 215°	 m.P. = 203°
Dibromo-Compounds	 position of bromine not got. m.P. = 156°	 m.P. = 170°	 m.P. 201-202°
	*  m.P. = 10°	a separate oxidation product not got	 m.P. 171-175°

*. i.e. taking it for granted that Meldola's acid is the 1.2.4 acid & this one the 1.2.3 acid, but of course this is not yet proved.

See page 2 **Note 1**:- Two different Specimens of Calcium oxide were used in this research both of which were supplied as pure. The first thing that was done with each was to perform a "blank Experiment", by testing with silver nitrate solution a known weight of the lime sufficient to charge the Combustion tubes used. This amount of lime was boiled with distilled water, and the filtrate acidified with pure nitric acid, & then a small quantity of the silver nitrate solution was added. In the first specimen of lime used, the lime was contaminated with a trace of Calcium Chloride, and the weight of silver chloride got in the lime, had to be subtracted from the silver bromide in each analysis.

The second specimen of calcium oxide was found quite free from the chloride.

See page 7 **Note 2**:- In the case of warming the compounds with bromine, as also in the case of boiling with chromic and glacial acetic acids, the following arrangement was used. a flask x which would contain from 100 to 150 c.c. was used, in which the substance to be boiled was placed. This was supplied with a well-fitting cork, through which a piece of



glass-tubing, about 7-10 mm. in diameter & one metre in length was introduced. This acted as a sort of reversed condenser. The volatile compounds got condensed before they reached the top of this tube, and ran back again into the flask x.

See page 8

Note 3: In all these oxidation experiments, the substance was fist of all dissolved in the glacial acetic acids, and then the Chromic acid added very slowly, the flask being well shaken each time after the addition. The Chromic acid used, was pure chromic acid, of a bright red colour, & crystallising in needles. It, as well as the Calcium oxide - see note 1 - was supplied by Burgoyne Burbidges & Co. London, & was kept in a well stoppered glass bottle to prevent the absorption of moisture