PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XXVII.—*On the Oxidation of Ditolyl.*

By THOS. CARNELLEY, D.Sc. (Lond.), Demonstrator in the Chemical Laboratory of the Owens College.

LAST year I published a paper (*Chem. Soc. Jour.* [2], xiv, 13) on the new hydrocarbon, tolyl-phenyl, in the production of which a quantity of both liquid and solid ditolyl was obtained as bye-product. Almost six months before my paper appeared in the *Journal*, *i.e.*, in the autumn of 1875, I commenced a research on the oxidation of these two ditolyls, and obtained two new acids. I discontinued, however, for some time to work at this subject, as I hoped to obtain a much larger quantity of ditolyl, and intended not to proceed till I had done so. Rather more than a month ago I happened to see a paper by Doebner, on the oxidation of this hydrocarbon, in the *Journal of the Berlin Chemical Society*, ix, 271, in which he describes the oxidation of solid ditolyl (m. p. 121°) to diphenyldicarbonic acid. At the end of his memoir he said he was continuing his research, but does not give any further results. Owing to an oversight, I was unfortunate not to see his paper, which appeared in February, 1876, till a few weeks ago. It is evident, however, from what has been said, that I had succeeded in obtaining two of the products of the oxidation of ditolyl previous to the publication of Doebner's paper, both of them being entirely new acids. As I have not seen any further communication by Doebner on this same subject, I have hastened during the last month to complete my own investigation with what material I had, and without waiting till I had more at command. The following paper contains the results I have obtained:—

According to Zincke (*Deut. Chem. Ges. Ber.*, iv, 396), two isomeric ditolyls are obtained by the action of sodium on the (1 : 4) monobromotoluene—

- (1.) Solid, m. p. 121° , b. p. $283-288^{\circ}$.
- (2.) Liquid, b. p. $283-288^{\circ}$.

The ditolyl got by Fittig from crude monobromotoluene (*i.e.*, a mixture of the (1 : 2) and (1 : 4) isomerides) boiled at 272° , while that prepared from monochlorotoluene boiled at $273-278^{\circ}$. Only a small

quantity of solid ditolyl could be produced by Zincke from crude brom- or chlorotoluene.

The crude ditolyl obtained in the preparation of tolyl-phenyl was fractionated, when from the portions boiling at 270—290° crystals of solid ditolyl separated out, and these, after pouring off the liquid, were recrystallised twice from hot alcohol. The pure solid ditolyl thus obtained melted at 119—120°, and crystallised in hard, white, glistening plates.

The fractions of liquid ditolyl, after the separation of the solid modification, were placed in a freezing mixture, but no further separation of crystals occurred. They were then divided into two portions (1) b. p. 270—280°, (2) b. p. 280—290°. There was nearly an equal quantity of each, the former being rather in excess.

The solid ditolyl and the two fractions of the liquid were then each oxidised separately.

I. OXIDATION OF SOLID DITOLYL, M. P. 121°.

(a.) *Incomplete Oxidation.*—1.147 grams of the hydrocarbon were placed in a flask and dissolved in glacial acetic acid; 2.294 grams of crystallised chromic acid were then added gradually, with frequent shaking. After the somewhat violent action had ceased, the liquid was boiled for about an hour, cooled, and poured into a large quantity of cold water, allowed to settle, and then filtered. The precipitate of acid and unchanged hydrocarbon, after washing, was treated with ammonia and filtered, and the acid thrown down from the filtrate by hydrochloric acid as a white flocculent precipitate; it was filtered off and washed with cold water. The moist acid thus obtained was insoluble in cold, but easily soluble in hot water and in alcohol; after drying, however, it was only difficultly soluble in hot water, and even in boiling alcohol; in ether it dissolved more readily. It forms a very difficultly crystallisable ammonium salt. It melted, with blackening, at 245° C.

It was boiled for some time with alcohol and filtered, and the residue of acid dried. It then melted, with blackening, at 243—244°, i.e., nearly the same as before, from which it was concluded that it was pure. The silver salt was prepared from the ammonium salt by double precipitation with silver nitrate, as a thick, curdy, white precipitate, which was soluble in a moderate quantity of boiling water, and on cooling reprecipitated as a white amorphous powder. The dried salt was analysed.

(1.)	·204	gram salt gave	·0685	gram Ag =	33·58	per cent. Ag.
(2.)	·097	„ „	·0335	„ „	= 34·53	„

	Calculated for $C_{12}H_8 \left\{ \begin{array}{l} CH_3 \\ COOAg \end{array} \right.$	Found.		Mean.
		(1)	(2)	
Per cent. Ag =	33.85	33.58	34.53	34.05

This proves that the first product of oxidation of solid ditolyl is tolyl-phenylcarbonic acid, $CH_3-C_6H_4-C_6H_4-COOH$.

(b.) *Complete Oxidation*.—As all the solid ditolyl I had at my disposal had been used for the previous experiments, it was not possible to investigate the result of the complete oxidation of this hydrocarbon, but this deficiency is supplied by the results obtained by Doebner in the paper already referred to. He found that solid ditolyl, m. p. 121° , on oxidation with excess of chromic acid, gave an acid which was insoluble in all solvents, and neither sublimed nor melted, and formed very difficultly soluble salts, and on heating with excess of lime gave diphenyl. These properties, and the analysis of the ether (m. p. 112°), proved it to be diphenyldicarbonic acid, and identical with the acid obtained from dicyanodiphenyl. The oxidation of solid diphenyl is therefore represented thus—

II. OXIDATION OF LIQUID DITOLYL, B. P. $280-290^\circ$.

(a.) *Incomplete Oxidation*.—2.15 grams of the hydrocarbon were dissolved in glacial acetic acid, and 6.14 grams of chromic acid added gradually, and treated as above described. As the acid thus obtained was not quite colourless, it was dissolved in ammonia and boiled with animal charcoal, filtered, and reprecipitated with hydrochloric acid; m. p. = 176° . The melting point of another preparation was found to be $173-177^\circ$. The acid was insoluble in water and in cold alcohol, but soluble in hot; it formed a soluble ammonium salt, and on precipitation of the latter with barium chloride, it gave a white curdy barium salt, which was but very slightly soluble in water. The silver salt was obtained by double precipitation with silver nitrate as a white flocculent precipitate. Two analyses of this last salt yielded the following results:—

- (1.) .0664 gram of the salt gave .0228 gram Ag = 34.33 p. c. Ag.
 (2.) .0994 ,, ,, .0340 ,, = 34.20 ,,

	Calculated for $C_{12}H_8 \left\{ \begin{array}{l} CH_3 \\ COOAg \end{array} \right.$	Found.		Mean.
		(1)	(2)	
Per cent. of Ag =	33.85	34.33	34.20	34.26
			2 x 2	

These results show that when the liquid ditolyl (b. p. 280—290°) is oxidised with a deficit of chromic acid, the product is an acid having the composition $\text{CH}_3\text{—C}_6\text{H}_4\text{—C}_6\text{H}_4\text{—COOH}$, being isomeric with that obtained by the incomplete oxidation of the solid ditolyl.

(b.) *Complete Oxidation*.—2·2 grams of the hydrocarbon were oxidised in the manner already described, by 24·0 grams (*i.e.* an excess) of chromic acid.

The acid resulting from this oxidation was a white powder insoluble in all the usual solvents; it did not melt, but sublimed without decomposition, in the form of white crystalline grains. By double decomposition of the ammonium salt, a white insoluble silver salt was produced, which on analysis gave 55·65 per cent. of silver, while the silver salt of terephthalic acid requires 56·84 per cent.

The above proves, then, that on complete oxidation, liquid ditolyl, b. p. 280—290°, gives terephthalic acid.

(c.) *Intermediate Oxidation*.—In order to see whether an intermediate acid could be produced of the composition

and isomeric with the diphenyldicarbonic acid obtained by Doebner from solid ditolyl, 2·2 grams of the hydrocarbon were dissolved in glacial acetic acid and oxidised with 15·5 grams of chromic acid. The liquid on cooling was poured into water, and the precipitate of acid filtered off and washed with water. On treating with ammonia it left a rather large residue insoluble even in the boiling liquid. This residue was filtered off and washed; as it was not oily, and was insoluble in alcohol, it could not be unchanged hydrocarbon.

The residue and filtrate were treated separately as follows:—

Residue was warmed with alcohol to dissolve out any unchanged hydrocarbon, and filtered. The alcoholic filtrate on evaporation gave a very small quantity of an oily residue, which was too small to work with. The residue insoluble in alcohol was washed with water and treated with dilute hydrochloric acid, to convert the supposed insoluble ammonium salt into acid; a yellowish-white residue was left, but was too small to do anything with.

The filtrate, treated with hydrochloric acid, gave a white flocculent precipitate, which, after washing and drying, blackened without melting below 270°, and sublimed readily on heating. The acid thus obtained was boiled with a small quantity of alcohol, and filtered, the object being to separate any $\text{C}_{12}\text{H}_8 \left\{ \begin{array}{l} \text{CH}_3 \\ \text{COOH} \end{array} \right.$, that would probably be more soluble than the dicarbonic acid $\text{C}_{12}\text{H}_8 \left\{ \begin{array}{l} \text{COOH} \\ \text{COOH} \end{array} \right.$, if the latter were present.

The *residue* was dried. It sublimed, without melting, in small needles, and blackened at about 230°. The silver salt was prepared in the ordinary way as a white insoluble amorphous precipitate, which yielded, on analysis, the following:—

·0835 gram salt gave ·0394 gram Ag = 47·18 per cent. Ag.

Calculated for $C_{12}H_8 \left\{ \begin{array}{l} COOAg \\ COOAg \end{array} \right. \dots = 47·37.$

The alcoholic filtrate was evaporated to dryness to drive off the alcohol, the residue dissolved in ammonia, and the solution precipitated by hydrochloric acid. The white flocculent precipitate, after washing and drying; blackened at 230°, and did not melt when strongly heated, but readily sublimed. It was difficultly soluble in alcohol or ether, whether hot or cold. The silver salt was prepared and analysed.

·1142 gram salt gave ·0531 gram Ag = 46·50 per cent. Ag. The acid would, therefore, appear to be identical with that in the above residue, except that it contained probably a very small quantity of $C_{12}H_8 \left\{ \begin{array}{l} COOH \\ CH_3 \end{array} \right.$.

The liquid ditolyl, therefore, on oxidation as shown by the above results, gives first $C_{12}H_8 \left\{ \begin{array}{l} CH_3 \\ COOH \end{array} \right.$, then $C_{12}H_8 \left\{ \begin{array}{l} COOH \\ COOH \end{array} \right.$ and finally terephthalic acid $C_6H_4 \left\{ \begin{array}{l} COOH \\ COOH \end{array} \right.$.

III. OXIDATION OF LIQUID DITOLYL, B. P. 270—280°.

This fraction gave exactly the same products on oxidation as that which boiled at 280—290°, proving them to be practically identical.

The above experiments show, therefore, that when sodium acts on parabromo-toluene, two isomeric ditolyls are produced, one of them being, as will be pointed out below, the di-para, and the other the ortho-para-ditolyl. Thus:

The formation of the second of these bodies is probably due to the fact, that in the preparation of ditolyl by different chemists, the solid

(1:4) monobromo-toluene employed was not perfectly pure, but contained a small quantity of the isomeric liquid (1:2), monobrom-compound.

The ditolyl (b. p. 272°) which Fittig obtained by the action of sodium on crude monobromo-toluene (*i.e.*, a mixture of the para- and ortho-compounds), was probably a mixture of the above two ditolyls, the liquid modification, as pointed out by Zincke, being greatly in excess, the solid in fact being produced in only very small quantity. If we make no allowance for a difference in the thermometers, this tends to show that of the two the liquid (1:4) (1:2) ditolyl has rather the lower boiling point, notwithstanding that Zincke found the two hydrocarbons obtained from the nearly pure parabromotoluene to boil at almost the same point, *viz.*, 283—288°, and this is what theory would lead us to expect, for para compounds, as a rule, boil higher than ortho, and therefore probably also higher than ortho-para.

The following formulæ show the manner in which the atoms are arranged in the different compounds which have been mentioned in the preceding pages, together with three others, *viz.*, VIII, IX, and X:—

Diparaditolyl (1:4) (1:4)
 solid.
 M. p. = 121°; b. p. =
 283—288°.

Dipara-tolyl-phenyl
 carbonic acid (or tolyl
 benzoic (1:4) (1:4).
 M. p. = 244°.

Dipara-diphenyl-dicarbonic
 acid (or dibenzoic)
 (1:4) (1:4).
 Does not melt.

Ortho-para-ditolyl
 (1:2) (1:4) liquid.
 B. p. = 283—288°.

Ortho-para-tolyl-
 phenyl carbonic acid
 (1:2) (1:4).
 M. p. = 176°.

Ortho-para-diphenyl
 dicarbonic acid
 (1:2) (1:4).
 Does not melt.

Terephthalic acid
 (1:4).
 Does not melt.

Since the purest para monobromo-toluene gives with sodium the solid ditolyl in by far the greater quantity, it follows that this latter hydrocarbon has the constitution represented by I, and as the acids II and III are derived from it by oxidation, they will also be dipara-compounds. Further, since the ordinary diderivatives of diphenyl are dipara compounds, it is probable that Doebner's dicyanodiphenyl derived from the disulphonic acid is also a dipara-compound; and as it gives the acid III on treatment with alcoholic potash, it is likewise probable that this acid has the constitution given to it above, and is therefore a dipara-compound, as is also proved by its formation from solid ditolyl.

The production of liquid ditolyl from a mixture of ortho- and para-bromo-toluene, and the fact that solid ditolyl is a dipara-compound, show that the former hydrocarbon must be either a diortho- or an ortho-para-compound; while the formation of terephthalic acid, as the final product of oxidation, proves it to be the latter, as shown in IV, and consequently that the two acids V and VI are likewise ortho-para. The only point which remains to be settled is, whether the acid V is—

I think, however, there is no doubt that it is the former, for the ortho-methyl would undergo oxidation the more easily of the two, and would therefore be first oxidised.

The relation of phenanthrene and its derivative, diphenic acid, to the preceding compounds is shown in IX and X, the hydrocarbon

VIII being still unknown. A secondary result of the above experiments is, that they go to confirm in a great measure the generally received constitution of phenanthrene (viz., as a di-ortho-compound IX); for inasmuch as it yields on oxidation diphenic acid, it cannot be either a di-para- or an ortho-para compound, for, if so, it would yield, not diphenic acid, but one of the acids III or IV. It must, therefore, be a di-ortho, a di-meta, a meta-para, or a meta-ortho compound. That it cannot be a di-para-compound is shown by the fact that diphenic acid may be converted into phenyl-benzoic acid, $\text{C}_6\text{H}_4 \left\{ \begin{array}{l} \text{COOH} \\ \text{C}_6\text{H}_5 \end{array} \right.$, which latter is not a para-compound, being isomeric with the para-phenyl-benzoic acid obtained from (1:4) tolylphenyl.

With respect to the four remaining possible constitutions for phenanthrene, its whole chemical character shows that it stands in the same relation to naphthalene as the latter to benzene (Schorlemmer), and it is therefore almost certainly a di-ortho compound. The fact that diphenic acid melts indicates also that it is probably di-ortho.

I intend, if possible, to prepare di-ortho-ditolyl from orthobromotoluene, and to investigate its products of oxidation, one of which should be diphenic acid, if phenanthrene be really a di-ortho compound.