III.—On Tolyl-phenyl, a New Hydrocarbon. By Thomas Carnelley, B.Sc., F.C.S.

At the suggestion of Professor Kekulé, to whose kindness I have been much indebted, I undertook to prepare and investigate the hydrocarbon which forms the member intermediate between diphenyl and ditolyl, and the results which I have so far obtained form the contents of this paper.

From its constitution, the name tolyl-phenyl, phenyl-methyl-benzene, $C_6H_4 \begin{cases} CH_3\\ C_6H_5 \end{cases}$, is ascribed to the new hydrocarbon, of which three modifications are possible, viz., those in which the side chains occupy the positions 1:2, 1:3, and 1:4 respectively. It is the (1:4) compound which I have prepared and to some extent investigated. The (1:2) derivative has, however, quite recently been obtained by Barbier (Deut. Chem. Ges. Ber., vii, 1036), by the action of sodium on a mixture of bromobenzene and the liquid modification (1:2) of bromtoluene. The substance he obtained was a liquid boiling at $(258^{\circ}-260^{\circ})$, and was called by him phenyl-cresyl. No derivatives, and scarcely any of the properties of the hydrocarbon itself were described by him in the paper referred to, for he appears to have prepared it chiefly to investigate the action of heat on it.

The hydrocarbon described in the present paper is the (1:4) compound, and was prepared by the action of sodium on a mixture of bromobenzene and pure (1:4) bromotoluene dissolved in pure ether, according to the equation:—

$$C_6H_5.Br + C_6H_4 \begin{cases} CH_3 \\ Br \end{cases} + Na_2 = 2NaBr + C_6H_4 \begin{cases} CH_3 \\ C_6H_5 \end{cases}$$

The reaction had been previously tried by using benzene (dried over sodium) in various proportions, in place of ether, but it was always found that the reaction took place very slowly, and to a partial extent only, even after five or six days' standing in contact with the sodium. With ether, however, the reaction commences shortly after the mixture had been brought in contact with the sodium, and goes on steadily, and even violently, if the vessel be not kept cool, to the end.

The ether used was washed first with dilute caustic soda, and then several times with distilled water, distilled, and then dried first over calcium chloride, and finally over sodium.

The bromobenzene and (1:4) bromotoluene were prepared in the usual manner, the latter being separated from the (1:2) modification by

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crystallising out several times. Previous to being used, they were dried by long standing over calcium chloride.

In all the experiments the two bromides were mixed in molecular proportions as required by the above equation, and the mixture, dissolved in a measured quantity of ether, submitted to the action of a weighed quantity of sodium (rather in excess of the calculated quantity) in a round flask fitted with a reversed condenser and immersed in cold water, to moderate the reaction. The sodium before acting on the mixture, was cut into very thin slices. The following are the experiments made with ether as diluent :---

(a.) 321 grms. C₆H₅.Br 35095

50 ,, $C_0H_4 \begin{cases} CH_3 \\ Br \\ 95 \\ 3 \text{ vols. of ether} \end{cases}$ were used, the sodium being added gradually, during the course of several hours, to the mixture of bromides and ether.

After all the calculated amount of sodium had been added, and the reaction appeared complete, a small additional excess of sodium was added, so as to ensure as much as possible of the bromides being acted on, and the whole allowed to stand over night, when it was found that the last addition of sodium had scarcely been acted on at all. The clear reddish-brown liquid was poured off and distilled on a waterbath till the thermometer rose to 70°, the distillate coming over below this point being used to wash the residue of sodium and sodium bromide; the washings, when clear, were drawn off, and added to the rest of the liquid, which was again distilled till 70° was reached; and this was repeated several times. The crude liquid boiling above 70°, consisted of unchanged bromides, and the products of the reaction, viz., benzene, toluene, diphenyl, tolyl-phenyl, ditolyl and high-boiling products. After one fractionation it gave the following results :--

Grams.

Total hydrocarbon which could be theoretically obtained	
from the amount of bromides used	= 344
Weight of crude hydrocarbon obtained	= 358
· · ·	
Grams.	Calculated amount.
Weight of distillate $(70^{\circ}-200^{\circ})$, consisting of	
benzene, toluene, and unchanged bromides $= 154 =$	44·8 p.c.
Weight of distillate $(200^{\circ}-320^{\circ})$, consisting of	
diphenyl, tolyl-phenyl, and ditolyl $\ldots = 102 =$	29·7 p.c.
Weight of distillate above 320° = 102 =	29·7 p.c.

(b.) $173 \cdot 3 \text{ grms. } C_6H_5.Br$ $188 \cdot 7$, $C_6H_4 \begin{cases} CH_3 \\ Br \\ 51 \cdot 0 \\ 3 \text{ vols. of ether} \end{cases}$ were used, the sodium, cut as before, into thin slices, was added all at once to the ether, and then the mixed

bromides poured on to the top of it. The reaction commenced almost immediately. The mixture was allowed to stand all night, and then the clear liquid poured off and treated as in the previous case. The results obtained were as follows :---

	Calculated
Grams.	amount.
Weight of hydrocarbon theoretically obtainable $= 185.3$	
,, crude hydrocarbon obtained $\dots = 180.0$	
,, fraction $(70^{\circ}-200^{\circ})$ = $77.5 = -77.5$	41·8 p.e.
$,, ,, (200^{\circ}-320^{\circ}) \dots = 48.5 = 1$	26.1 ,,
", ", above 320°	29.1 "
(c.) 91.8 grms. C_6H_5 .Br	
CH_3 were used, and the operation	n carried
100.0 ,, $C_6H_4 \begin{cases} CH_3 \\ Br \end{cases}$ were used, and the operation out as in the previous case.	The re-
27.0 ,, Na sults obtained being as follo	ws :
2 vols. of ether	
a	alculated
	amount.
Weight of hydrocarbon theoretically obtainable = 98.2	
,, crude hydrocarbon got = $114.3*$	
function $(70^{\circ} - 200^{\circ}) - 470$	47.0
$,, ,, (200^{\circ}-320^{\circ})$ = 36.5 =	
", ", above 320° = 30.8 = .	31·3 p.e.
The total of (a) (b) and (c) gives the following :	

The total of (a), (b) and (c) gives the following :--

							Calcu!a	ated
					Grams.		amou	nt.
Theor	retical w	eight of hydrocar	rbon	=	627.0			
		ydrocarbon obtai						
,,		$(70^{\circ}-200^{\circ})$						
,,	,,	$(200^{\circ}-300^{\circ})\dots$		=	187.0	=	29.8	,,
,,	,,	above 320°	• • • • • • • • • • • • • • •	=	187.0	=	29.8	,,

The above figures show that of the three operations, the best result is obtained by using as small a quantity of ether as is sufficient to moderate the reaction, and by acting on only small quantities of the bromides at once.

The different portions of hydrocarbon obtained as above were then

* This rather large excess is probably owing to more of the bromide remaining unchanged than in the previous experiments. submitted to a systematic and oft-repeated fractional distillation, combined with a fractional crystallisation of the diphenyl from the new liquid hydrocarbon, tolyl-phenyl, by the use of a freezing mixture of ice and salt.

The tolyl-phenyl was finally obtained in two portions, boiling at $(258^\circ - 263^\circ)$ and $(263^\circ - 267^\circ)$ respectively, the former containing a trace of diphenyl (and was used in the experiments on the oxidation of the hydrocarbon), while the latter consisted of pure tolyl-phenyl. In all the fractionations with the exception of the first two or three, the temperature always rose suddenly from 267° to above 270°, when ditolyl, which has been given as boiling from 272° to 288°, began to come over. It was difficult, however, to get the tolyl-phenyl quite free from diphenyl, which boils, according to different accounts, from 240° to 254°; whether this end had been attained or not could, however, with some certainty be ascertained by freezing the substance in a mixture of ice and salt, when diphenyl, if present, could be detected by its forming crystals which were not quite colourless, but opaque and milky, and of different form to those of the tolyl-phenyl, which crystallised in moderately large and perfectly clear and colourless octahedrons (?).

The several distillates, after the final fractionation, gave on weighing, the following results :---

		Grams.		Calculs amoun ydroca	t of
(70°—140°) consisting chiefly of benzol and toluol	=	210.0		33·5	p. c.
$(140^{\circ}-230^{\circ})$ consisting chiefly					1
of unchanged bromides \dots (230°–258°) consisting chiefly	=	133.0	=	21.2	,,
of diphenyl (m.p. of crystals -67° (69°)		10.01	*	6.7	
tals = 67° 68°)		42.0	=	0.7	,,
between (258°-270°) consisting chiefly of tolylphenol	_	56.0	=	8.9	••
Ditto $\dots (270^{\circ} - 290^{\circ})$ consisting chiefly					
of ditolyl Ditto Products boiling above 290°.					,, ,,
	-	649.0			

* The three results included in the bracket are a little too high, as they contain, in addition, a very small quantity of hydrocarbon got from a previous operation, but no more, if as much, as would make up for the loss sustained during the successive fractionations of the portions boiling at these temperatures.

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Weight of hydrocarbon which could be obtained
from the weight of bromides acted upon $\dots = 559.0$
Weight of unchanged bromides $\dots = 133.0$
Total $\dots = 692.0$

From the above it will be seen that the yield of the new hydrocarbon was only a very poor one, for supposing that the reaction had gone on theoretically, and that 2 molecules of tolyl-phenyl had been produced to one molecule each of diphenyl and ditolyl, then a yield of 50 instead of about 9 per cent. of the total hydrocarbon ought to have been got. The chief products, however, were in fact benzene and toluene (notwithstanding that all the materials used were very carefully dried) and high-boiling substances, while about $\frac{1}{5}$ of the bromides remained unchanged, even though an excess of sodium was always present.

The pure tolyl-phenyl, obtained as above described, and boiling at $(263^{\circ}-267^{\circ})$ after standing over sodium, was analysed with the following results :---

(a.) Weight of substance taken = 0.1655 grm. (weighed out in small bulb with capillary tube).
 II O abtained at 0.1005 grm.

"	H_2O	optainea	=	0.1032	grm
"	CO_{2}	,,	~	0.5585	,,

- (b.) Weight of substance taken = 0.1620 grm. (weighed out in small bulb with capillary tube).
 - H_2O obtained = 0.1065 grm. CO_2 , = 0.5465 ,
- (c.) Weight taken = 0.1375 grm. This gave 0.0905 grm. H₂O. An accident prevented the determination of the carbon.

(d.) After the hydrocarbon had been distilled over sodium.

Weight taken = 0.1255 grm. (weighed out in a wide open tube).

- ,, of H_2O obtained = 0.0825 grm.
- ,, of CO_2 ,, = 0.4255 ,,

From which it follows :----

,,

"

		Found.			
	Calculated.	(a.)	(b.)	(c.)	(d.)
C_{13}	= 92.86	92.04	92.00		92.47
H_{12}	= 7.14	7.35	7.30	7.31	7.30

Properties of Tolyl-phenyl.—The hydrocarbon is a colourless refractive liquid of a pleasant aromatic odour. It solidifies in a freezing VOL. XXIX.

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mixture to a mass of pretty large colourless crystals (octohedrons?), which melt at (-2°) to (-3°) C. It boils at $(263^{\circ}-267^{\circ})$, uncorrected. It is slightly heavier than water, its spec. grav. at 27° C. being 1.015. It is insoluble in water; soluble in alcohol, ether and glacial acetic acid.

Behaviour on Oxidation.—In order to investigate the behaviour of the new hydrocarbon on oxidation, a few grams of the portion boiling $(258^\circ-263^\circ)$, and containing a trace of diphenyl,* were placed, together with a moderately large quantity of dilute nitric acid (1 to 3.5 of water) in a round flask fitted with a reversed condenser, and gently boiled for six days, the fine needle-shaped crystals of the acid which separated out, being removed after every two days' boiling.

They were freed from unchanged hydrocarbon and nitro compound, which is also formed, by conversion into the sodium salt, from which the acid was obtained by precipitation with hydrochloric acid, in the form of white flakes; it was filtered, washed with cold water and dried.

(a.) A portion of it, after sublimation and twice crystallising from hot dilute alcohol, melted at $(209^{\circ}-211^{\circ})$, and resolidified at $(207^{\circ}-208^{\circ})$.

(b.) Another portion, after twice purification through the ammonium salt, melted at about 217°, and resolidified at 216°; after sublimation however it melted a few degrees lower, viz., at $(211^{\circ}-213^{\circ})$, and solidified at $(208^{\circ}-209^{\circ})$.

In order to avoid the formation of any nitro-compound, from which it was difficult to get the acid free, a small quantity of the hydrocarbon was next oxidised by dissolving in glacial acetic acid, and adding an equal weight of chromic acid. The reaction went on moderately at the ordinary temperature, and was completed by heating for a few minutes. On cooling, the liquid was largely diluted with water, when the acid and unchanged hydrocarbon were thrown down; they were allowed to settle and filtered off; the residue was slightly washed with water, heated with ammonia, and filtered; the filtrate warmed with animal charcoal; the solution again filtered; and the acid precipitated by hydrochloric acid. After washing, drying, &c., it melted at $(208^{\circ}-212^{\circ})$, and on analysis gave the following results :—

	Calculated.	Found.
C_{13}	= 78.78	78.18
H_{10}	= 5.05	5.31
O_2	=	

* (The small quantity of diphenyl which the hydrocarbon used contained, would remain unchanged by boiling with dilute nitric acid, or if oxidised at all would yield benzoic acid, which could be separated from the diphenyl-carbonic acid produced by the oxidation of the tolyl-phenyl.)

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An analysis of the silver salt gave 35.24 per cent. Ag instead of 35.41.

From the above results it follows that the first product of the oxidation of tolyl-phenyl is (1:4) diphenyl carbonic acid, thus—

C_6H_5	C_6H_5
C_6H_4 — CH_3	$\dot{C}_{6}H_{4}$ —COOH.

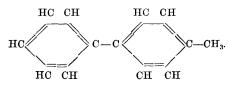
The melting point which I have obtained for this acid varies, however, from 208° to 217°, according to the method of purification; that of (1:4) diphenyl carbonic acid, as found by Schultz (Ann. Chem. Pharm., p. 213, vol. 174) is (216°-217°), and as found by Doebner (ditto, p. 112, vol. 172) (218°-219°). In all its other properties it resembles the (1:4) diphenyl carbonic acid of these chemists. It sublimes readily at a moderately high temperature, forming beautiful needle-shaped crystals; it is almost insoluble in cold water and only difficultly soluble in hot water, from which it separates on cooling in needleshaped crystalline groups; it is less soluble in an acid solution than in pure water, hydrochloric acid precipitating it from solution in the latter; it dissolves easily in alcohol and ether. It forms an almost entirely insoluble calcium salt, a difficultly soluble ammonium salt, and an insoluble white amorphous silver salt. On heating with anhydrous lime, it gives a good yield of diphenyl, together with a small quantity of higher-boiling products; the diphenyl obtained, after purification, melted at 70°-73° and another portion at 71.5°-74.5°, the melting point of diphenyl being 70.5° .

In order to see what the final product of the oxidation of tolylphenyl was, a portion of the hydrocarbon was dissolved in glacial acetic acid and an excess of chromic acid gradually added. After the reaction appeared complete, the liquid was very gently warmed for a minute or two, and when cool largely diluted with water; the greenish-white precipitate produced was separated from the liquid and washed with water; and the acid was extracted by ammonia. From the solution of the ammonium salt the acid was thrown down by hydrochloric acid, and after washing with water, boiled for some time with alcohol, in order to dissolve any benzoic or diphenylcarbonic acid that it might contain; and the residue was filtered off, washed with alcohol, and dried. The acid so obtained was a white powder, quite insoluble in water, and almost entirely so in alcohol and ether. It sublimed at a high temperature without previously melting, the sublimate being a perfectly white crystalline body. On analysis it gave the following—

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		lculated for rephthalic.	Found.
C_8		57.83	58.60
${ m H}_6$	=	3.61	3.81
O4	=		

The properties and composition of the acid prove it to be terephthalic acid; the results therefore show that tolyl-phenyl gives, as a first product of oxidation (1:4), diphenylcarbonic acid, and as a final product terephthalic acid (1:4), from which it follows, as well as from the mode of its formation, viz., from bromobenzene and (1:4) bromotoluene, that its constitution is—



SUBSTITUTION-PRODUCTS.

 α Mononitro-compound, C₁₂H₈.NO₂.CH₃.—This body was obtained by adding one part of nitric acid (spec. grav. 1.45) to one part of the hydrocarbon dissolved in three parts of glacial acetic acid, the mixture being kept cool. After a short time a clear brown liquid, consisting of two parts, was produced, the upper layer forming an oil floating on the lower which consisted chiefly of nitric and acetic acids. On standing, the oily liquid began to deposit a moderate number of well-formed, hard, bright-looking crystals; the greater part of the oil, however, remained fluid, and consisted, it is believed, of a second modification of the mononitro-compound (see below). The whole was allowed to stand for a day and a half, when the crystals were filtered off, well drained and dried between blotting-paper, and dissolved in hot alcohol; on cooling, beautiful, hard, bright, colourless needles crystallised out, which, on separating from the mother-liquor and drying on blotting-paper and over sulphuric acid, melted at 139°-140°; after a second crystallisation they melted at 141°, and on analysis gave the following results :---

Weight of substance taken = 0.1658 gram.

,	H_2O obtained	= 0.0841	,,
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 $,, CO_2 ,, = 0.4441$

0	Calculated.	Found.
$C_{13} =$	73.24	73.05
$H_{11} =$	5.16	5.63
$NO_2 =$		

,,

This body forms beautiful, bright, hard crystals, which melt at 141°. It is insoluble in water, almost insoluble in cold, but moderately easily soluble in hot alcohol.

 α Monoamido-compound, C₁₂H₈.NH₂.CH₃ (?).—The pure solid (α) nitro-compound was gently heated with tin and concentrated hydrochloric acid for a day in a flask with a reversed condenser; after some time, either a double tin-compound, or more probably the hydrochloride of the base (which was subsequently found to be nearly insoluble in dilute hydrochloric acid) was formed, as a white body, soluble to some extent in cold, easily in hot water, only slightly soluble in cold hydrochloric acid, more soluble in the hot acid. After the reduction appeared complete, the liquid (A) was filtered off, the residue B (consisting of tin and the white crystalline body), treated with sulphuretted hydrogen in excess; the sulphide of tin filtered off; and the solution set apart. The residue B, after separation of the metallic tin, was dissolved in hot water, and treated with sulphuretted hydrogen in excess, the liquid was filtered, and the solution added to that obtained from A.

The united liquid was evaporated to dryness; when half way down, and while there was still a large quantity of liquid, the amidohydrochloride partly separated out in small, glistening, silky plates. The residue obtained at the end of the operation was treated with caustic soda and the free base produced dissolved out by ether. The ethereal solution was evaporated to dryness, first at 50° and then at the ordinary temperature, when an oily body was first produced, from which there separated out a small quantity of needle-shaped tufts. The melting point of these, after careful drying, was found to be $93^{\circ}-97^{\circ}$. They were treated with hydrochloric acid, in which they dissolved only after long boiling; on cooling, small, fine, white silky needles were deposited, which were separated from the mother-liquor, washed with a little water, and dried over lime, after which they were found to melt, with blackening, at 280°-283°. An analysis of the very small quantity of it obtained gave 17.17 instead of 16.17 per cent. of Cl as required by the formula C12H8.CH3.NH2.HCl. The amount of substance which I had, however, was much too small to make a good and decisive analysis; that obtained, though it does not establish, yet indicates the composition ascribed to the body.

It is thought that the small yield of base obtained was due to some of the hydrochloride, which is very difficultly soluble in water and hydrochloric acid, remaining behind with the sulphide of tin on the filter in the separation of the tin.

The hydrochloride gives with platinum chloride a crystalline platinum salt, the quantity obtained, however, was too small to analyse.

Jackson (Deut. Chem. Ges. Ber., p. 968, vol. viii) has lately obtained, from a by-product of the manufacture of aniline, a new base which

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has also the composition $C_{13}H_{11}NH_2$, and, like the base I obtained, leaves a brown oil on evaporation of the ethereal solution. Its hydrochloride appears to resemble greatly the hydrochloride of the amido-compound derived from the α -nitro-derivative of tolyl-phenyl, and may possibly be the same substance; but he does not give any melting point either for the base or for the hydrochloride.

 β Mononitro-compound.—The dark red, oily liquid which was obtained in the preparation of the (α) compound, and formed by far the greater portion of the product of the action of nitric acid on the hydrocarbon under the conditions there mentioned, was washed several times with distilled water and then distilled with steam. The distillate, which came over very slowly, was divided into the following fractions:—

1st fraction. Supposed to contain the unchanged hydrocarbon and some nitro-compound. It formed an oil of a light yellow-reddish colour.

2nd fraction. Supposed to consist entirely or chiefly of mononitrocompound. It formed a red oil.

3rd fraction. The residue left in the flask, which might contain a small quantity of dinitro-compound. It was a bright red, oily liquid.

The second fraction of the distillation was freed as much as possible from water, and then dried several times by evaporation from solution in pure ether, then by heating for some time to 100°, and finally over sulphuric acid. The substance thus obtained was a bright red oil, soluble in ether; on analysis it gave the following numbers:—

Weight taken = 0.1892.

,, of H_2O obtained = 0.1145.

,, of CO_2 ,, = 0.5220.

		Calculated for		
	Found.	Mononitro-compound.	Hydrocarbon.	
C	= 75.24	73.24	92.86	
н	= 6.72	5.16	7.14	

From these results it appears that the body consisted chiefly of a liquid modification of the mononitro-compound (for the latter crystallises very readily and in fine crystals), but that it still contained some unchanged hydrocarbon and also was not quite dry.

It boils, with decomposition, between 305° and 325°, but the distillate, mixed as it was with the water from the decomposition, could not be obtained dry enough for analysis.

The first fraction, obtained during the distillation with steam, gave on reduction with tin and hydrochloric acid, a base, the hydrochloride of which, though not very soluble in water, appeared to be more so than that of the α -compound, but the quantity obtained was too small to work with.

Dinitro-compound, C₁₂H₇(NO₂)₂CH₃.—This body was prepared by pouring a mixture of 6 parts of nitric acid (sp. gr. 1.45), and 1 part of concentrated sulphuric acid on to 3 parts of the hydrocarbon contained in a flask and kept cool. A moderate reaction took place, and a dark red fluid was produced. It was allowed to stand at the ordinary temperature for some time, after which, as no crystals had formed, it was placed for a few minutes in a freezing mixture, when it became milky, but did not crystallise; when taken out, however, and allowed to stand for a short time at the ordinary temperature, it first became quite clear again, and soon after began to crystallise, finally becoming almost entirely solid. The mass was heated several times with water, under which it melted, in order to wash out the excess of acid; on cooling, it The solid yellow mass thus obtained was crystallised out re-solidified. five times from hot alcohol, the melting point after each crystallisation being as follows: (1) not taken, (2) 146-150, (3) 152-157, (4) 152-157, (5) 153-156, for the crystals which first separated out, and (153-158) for the general crystallisation.

An analysis of the crystals last obtained gave the following results :---

Weight	of subs	tance	e taker	ı ==	0.1784	grm.
,,	H_2O	obtained		=	0.0680	,,
,,	$\rm CO_2$,,		=	0.3926	"
Calculated.						Found.
C_{13} = 60.46						60.02
H_{10} .		=	3.88			4.24
(NO_2)	$)_2 \ldots$	=				

The dinitro-compound crystallises in groups of very small, fine, white needles, which melt at 153—157. It is insoluble in water, either hot or cold, and melts under the former to a reddish-yellow oil. It is only slightly soluble in cold, but moderately soluble in hot alcohol. I had not sufficient material to investigate the product which this body gives on reduction, but hope shortly to be able to do so.

Owing to the small quantity of hydrocarbon which I had at my disposal, and to the small yield which the reaction gives, I have not been able to make so full an investigation as I should have liked; but I am at present engaged in trying to prepare the hydrocarbon in larger quantity, and by a cheaper method, by passing a mixture of benzene and toluene through a red-hot tube, in a manner similar to that used in the preparation of diphenyl from benzene; and if the method answers, I intend making further investigations with regard to this hydrocarbon and its derivatives.