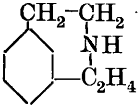
LXVII.—*Conditions of Formation of Rings Attached to the* o-, m-, *and* p-*Positions of the Benzene Nucleus. Part II. The Reduction of* m- *and* p-*Phenylenediacetonitrile.*

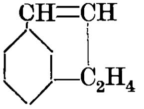
By Alan Francis Titley.

In the course of some work on ring formation, the scope of which is outlined in Part I of this series (J., 1922, **121**, 1562), and a further account of which will be published shortly, it was found desirable to repeat some investigations recently carried out by von Braun and his collaborators.

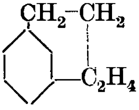
While attempting to prepare *m*-phenylene-ββ′-diethylamine by the reduction of *m*-phenylenediacetonitrile with sodium and alcohol, von Braun, Karpf, and Garn (*Ber.*, 1920, **53**, 98) claimed to have isolated a secondary amine of the composition $C_{10}H_{13}N$, to which they assigned the structure (I), where the heterocyclic ring is joined to the benzene nucleus in the meta-position. From this amine, by thermal decomposition of the quaternary dimethylammonium hydroxide with loss of dimethylamine and water, they stated that they obtained an unsaturated hydrocarbon and, by further reduction, a saturated hydrocarbon, to which they assigned the structures (II) and (III), respectively.



(I.)

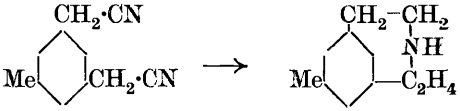


(II.)



(III.)

More recently, von Braun and Engel (*Ber.*, 1925, **58**, 281) have described a homologue of this type, obtained in a similar manner by reducing 5-methyl-1 : 3-phenylenediacetonitrile.



The remarkable ease with which examples of this meta-ring system, generally supposed to be incapable of existence, are formed together with their close structural relationship to the products it was hoped to obtain by the action of sodium on *m*-phenylene diacetic ester (Part I, *loc. cit.*), rendered a re-examination of this work desirable. It was not found possible, however, to confirm the results of von Braun and his co-workers and, in the present paper, evidence is brought forward to show that the amine (I) described by von Braun, Karpf, and Garn (*loc. cit.*) is in reality β-*m*-tolylethylamine (VII), and the unsaturated hydrocarbon derived from it *m*-methylstyrene (IX).*

The reduction of *m*-phenylenediacetonitrile, when carried out in accordance with the directions of these authors and using the same quantities and conditions, led to the formation of a mixture

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* The proof of this paper was sent to Professor von Braun, and he wishes me to say that he has been engaged for some time in repeating the researches in question and has arrived at results which are identical with those contained in the present communication.—W. H. PERKIN.

of products, basic and non-basic. The non-basic substances were removed, together with the excess of alcohol, by steam-distillation of the acidified reaction mixture. These proved to be *m*-tolylacetonitrile (IV), which was identified by conversion into the beautifully crystalline amide, m. p. 141° (compare Radziszewski and Wispek, *Ber.*, 1885 ,**18**, 1281), *m*-xylene (V), identified by b. p. and analysis, and a little unchanged *m*-phenylenediacetonitrile. Considerable quantities of free hydrocyanic acid could also be detected.

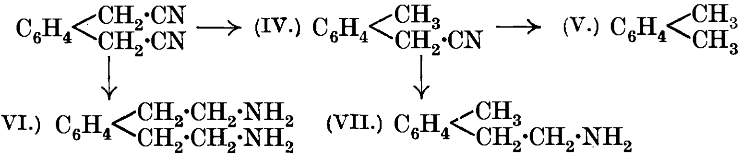
The basic products, after liberation from the acid solution by excess of sodium hydroxide, proved to be a mixture of *m*-phenylene-ββ′-diethylamine (VI), b. p. 162°/18 mm., formed in accordance with the observation of von Braun in a 10—15% yield, and a monoamine of b. p. 97—98°/15 mm., obtained in about 40% yield, which appeared to be identical with the substance $C_{10}H_{13}N$ described by von Braun as a secondary amine.

This monoamine gave a hydrochloride, which crystallised in large, glistening leaflets of m. p. 160°, a sulphur-yellow picrate, m. p. 174°, a benzoyl derivative, m. p. 72°, a phenylthiocarbamide, m. p. 86—87°, a platinum salt which, after blackening between 230° and 240°, melted with vigorous decomposition at 246°, and a quaternary methiodide, m. p. 237°. (The substance described by von Braun as a secondary amine had in almost every respect the same properties, *viz.*, b. p. 97—98°/16 mm., the hydrochloride, m. p. 160°, the picrate, m. p. 176°, the benzoyl derivative, m. p. 72°, the phenylthiocarbamide, m. p. 87°, the platinum salt, m. p. 232°, and the quaternary methiodide, m. p. 236°.)

The amine, however, prepared in this way, did not give analytical results corresponding to the composition $C_{10}H_{13}N$, but invariably showed a higher hydrogen content. It was at first thought that it had the composition $C_{10}H_{15}N$, but careful analyses of several samples, including one prepared from the recrystallised hydrochloride, clearly suggested the composition $C_9H_{13}N$.

On treating a solution of the base in dilute hydrochloric acid with sodium nitrite, a brisk evolution of nitrogen occurred and a pale yellow oil separated. This oil, which had a characteristic pungent and rather sweet odour, dissolved readily in ether and, after shaking with dilute sodium carbonate to remove nitrous acid, gave no response to the Liebermann test.

In view of these results and the nature of the non-basic products of the reaction, it seems quite clear that the normal reduction of *m*-phenylenediacetonitrile to the diamine (VI) is largely accompanied by the conversion of first one and then the other $-CH_2{\cdot}CN$ group into $-CH_3$ groups, the intermediate stage being itself reduced to a monoamine. The process is best made clear by the following scheme:



$$C_6H_4{<}\substack{CH_2{\cdot}CN \\ CH_2{\cdot}CN} \longrightarrow \text{(IV.) } C_6H_4{<}\substack{CH_3 \\ CH_2{\cdot}CN} \longrightarrow \text{(V.) } C_6H_4{<}\substack{CH_3 \\ CH_3}$$

$$\text{(VI.) } C_6H_4{<}\substack{CH_2{\cdot}CH_2{\cdot}NH_2 \\ CH_2{\cdot}CH_2{\cdot}NH_2} \qquad \text{(VII.) } C_6H_4{<}\substack{CH_3 \\ CH_2{\cdot}CH_2{\cdot}NH_2}$$

The monoamine described above, although evidently identical, except in its behaviour towards nitrous acid, with the monoamine (I) of von Braun, is in reality β-*m*-tolylethylamine (VII).

In order to establish the identity of the monoamine beyond question, β-*m*-tolylethylamine was prepared by the reduction of *m*-tolylacetonitrile (IV) with sodium and alcohol. Using approximately twice the theoretical quantity of reducing agent, a yield of about 50% of β-*m*-tolylethylamine was obtained, practically the whole of the rest of the nitrile being reduced to *m*-xylene.

The amine had b. p. 216°/762 mm. and 98°/15 mm. and gave a hydrochloride, m. p. 160°, and a picrate, m. p. 174°, in accordance with the observations of Sommer (*Ber.*, 1900, **33**, 1079).

The benzoyl compound, phenylthiocarbamide, and quaternary methiodide also had the same melting points as the corresponding compounds, prepared from the specimen of monoamine which had been obtained by reducing *m*-phenylenediacetonitrile. There was no depression of the m. p. on mixing samples of these derivatives.

This reduction of the $-CH_2{\cdot}CN$ group to $-CH_3$, although apparently of rare occurrence, is not unknown, and a few instances are recorded in the literature—for example, the reduction of cyanomethylbenziminazole to methylbenziminazole with sodium and alcohol (Bloch, *J. Soc. Chem. Ind.*, 1919, **38**, 118).

β-*m*-Tolylethylamine combines readily with piperonal, the condensation product crystallising well and melting at 53—54°. After being heated in a sealed tube with a slight excess of methyl iodide and then decomposed with aqueous alcohol, the latter yields β-m-*tolylethylmethylamine hydriodide,* m. p. 104°, from which the free base (VIII) was obtained, b. p. 88°/12 mm.

This base was prepared because of the very definite statement made by von Braun regarding the secondary nature of his monoamine. It was thought possible that interaction might occur between β-*m*-tolylethylamine and methylamine, formed by reduction of the free hydrocyanic acid present during the reaction, with the formation of β-*m*-tolylethylmethylamine (VIII), and that this secondary amine ($C_{10}H_{15}N$), in itself and in its derivatives, might closely resemble the primary amine ($C_9H_{13}N$).

$$C_6H_4Me{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2 \xrightarrow{NH_2Me} \underset{\text{(VIII.)}}{C_6H_4Me{\cdot}CH_2{\cdot}CH_2{\cdot}NHMe} + NH_3.$$

This, however, was not found to be the case, since the secondary amine gave a hydrochloride extremely soluble in alcohol and most other solvents, which, when crystallised from chloroform–ligroin, had m. p. 134°. The picrate had m. p. 127°, whilst the benzoyl compound was an oil which could not be induced to crystallise.

No evidence of the formation of any secondary amine by the reduction of *m*-phenylenediacetonitrile was forthcoming, and since the properties of β-*m*-tolylethylamine and its derivatives agree in almost every respect with those of the monoamine described by von Braun, there seems little doubt that the two are identical.

As previously mentioned, von Braun, Karpf, and Garn found that the quaternary ammonium hydroxide of their base, on distillation, lost dimethylamine and water with the formation of an unsaturated hydrocarbon, $C_{10}H_{10}$ (II), which had b. p. 62—63°/18 mm. and added two atoms of bromine with the formation of a dibromide, m. p. 48°.

It was found that the quaternary methiodide of β-*m*-tolylethylamine, on boiling with methyl-alcoholic potash, lost trimethylamine (identified by means of the picrate and platinum salt), with the formation of *m*-methylstyrene (IX), b. p. 62°/18 mm., which by the addition of two atoms of bromine gave the corresponding dibromide (X), m. p. 47° (Müller, *Ber.*, 1887, **20**, 1216, found m. p. 45°).

$$C_6H_4Me{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3,HI \longrightarrow \text{(IX.)}\ C_6H_4Me{\cdot}CH{:}CH_2 \longrightarrow \text{(X.)}\ C_6H_4Me{\cdot}CHBr{\cdot}CH_2Br.$$

The hydrocarbon described by von Braun is stated to have an abnormally low density ($d^{19°}$ 0·900) as compared with " the isomeric hydrocarbons 3-methylindene (*d* 0·968) and Δ^1-dihydronaphthalene (*d* 0·997)," whilst it resembled a styrene in polymerising under the action of light. The density of *m*-methylstyrene was found to be 0·906 at 16° and its tendency to polymerise has been noted by previous workers (Müller, *loc. cit.*).

The saturated hydrocarbon (III) prepared by von Braun had the low density $d^{17·3°}$ 0·852 as compared with 1-methylhydrindene (*d* 0·966) and 1 : 2 : 3 : 4-tetrahydronaphthalene (*d* 0·968), whilst the refractive index was $n_D^{17°} = 1·497$.

The reduction of *m*-methylstyrene to *m*-tolylethane was not investigated, but it may be noted that the density of the latter is recorded by Wroblewski (*Annalen*, 1878, **192**, 198) as 0·869 at 20°. The refractive index of *m*-tolylethane has not apparently been measured, but that of the isomeric *p*-tolylethane is stated to have the value $n_D^{14°} = 1·494$ (Klages and Keil, *Ber.*, 1903, **36**, 1637).

Reduction of p-*Phenylenediacetonitrile.*

The reduction of *p*-phenylenediacetonitrile with sodium and alcohol was also investigated. In this case, the $-CH_2 \cdot CN$ groups are reduced to methyl groups even more readily than those in the *m*-isomeride, a yield of about 50% of β-*p*-tolylethylamine being obtained. The rest of the nitrile was almost wholly reduced to *p*-xylene, whilst no appreciable quantity of *p*-phenylene-ββ′-diethylamine was formed.

The identity of the monoamine was again established by reducing *p*-tolylacetonitrile, which yielded the same product.

β-*p*-Tolylethylamine has b. p. 94—95°/13 mm. and absorbs carbon dioxide rapidly from the air. It forms a sparingly soluble hydrochloride, m. p. 216° (compare Ciesielski, *Anzeiger Akad. Wiss. Krakau*, 1906, 270; *Centr.*, 1907, I, 1793). On treatment with nitrous acid, it passes into an alcohol, which has the same characteristic sweet odour as that derived from β-*m*-tolylethylamine. This β-p-*tolylethyl alcohol* boils at 112°/12 mm. and combines with *p*-nitrobenzoyl chloride, yielding an *ester* which crystallises well and melts at 91°.

The amine forms a *picrate*, m. p. 155°, a platinum salt, m. p. 234°, a *benzoyl* derivative, m. p. 89°, and a quaternary *methiodide*, m. p. 244°. With piperonal, it forms a beautifully crystalline condensation product, m. p. 107°, which, by treatment with methyl iodide in the manner already described, is converted into β-p-*tolylethylmethylamine hydriodide*, m. p. 149°. The free *base* obtained from this had b. p. 96°/12 mm. and yielded a readily soluble *hydrochloride*, m. p. 191°, a *picrate*, m. p. 135°, and an oily benzoyl compound.

The quaternary methiodide of the base, on boiling with methyl-alcoholic potash, was converted into *p*-methylstyrene, b. p. 59—60°/12 mm., which yielded a dibromide, m. p. 45—46° (compare Klages and Keil, *loc. cit.*).

No evidence of any ring formation was obtained during these experiments.

EXPERIMENTAL.

ωω′-*Dibromo*-m-*xylene.*—The bromination of *m*-xylene to the ωω′-dibromo-compound was studied under various conditions, but the best results were obtained by following the directions of Atkinson and Thorpe (J., 1907, **91**, 1696). In this method, *m*-xylene is treated with rather more than the theoretical quantity of bromine required for monobromination, and the mixture of mono- and di-bromoxylenes separated by fractional distillation.

m-Xylene (200 g.) was treated at 130°, under reflux, with dry bromine (405 g.) during about 6 hours. The product was freed from hydrogen bromide by 2 days' standing over solid caustic soda in a vacuum desiccator. The bulk of the monobromoxylene passed over at 110—115°/20 mm., and when the temperature reached 125° the distillation was stopped and the residue in the flask, which solidified almost completely on cooling, was broken up on a Büchner funnel, washed with a little low-boiling ligroin, and recrystallised from acetone. Large, colourless prisms, m. p. 76°, were obtained. The yield of dibromo-compound is about 35%.

The ω-monobromoxylene was refractionated through a column, and the fraction 100—101°/14 mm. collected and used for the preparation of *m*-tolylacetonitrile (see later). The yield of monobromide is about 45% (Found : Br, 43·0. Calc., Br, 43·2%).

*ωω'-Dibromo-*p*-xylene.*—The bromination of *p*-xylene was carried out in the same manner as the above, using a quantity of bromine equal to twice the weight of the *p*-xylene taken. The reaction product solidified completely, and after pressing on a porous plate was extracted with ligroin (b. p. 40—50°) in a Soxhlet apparatus, which dissolved all the monobromide. The crude dibromo-compound crystallised from a small volume of warm chloroform in compact clusters of prisms, m. p. 143—144°.

The monobromo-compound, obtained by evaporation of the ligroin extract, after another crystallisation from the same solvent, separated in very long, colourless needles, m. p. 35·5°.

m-*Phenylenediacetonitrile.*—The conversion of the dibromoxylenes into the corresponding nitriles is usually attended by side-reactions leading to the formation of oily or amorphous by-products. These effects are minimised if the reaction is carried out as rapidly as possible, and the following method was found, in the case of dibromo-*m*-xylene, to give practically quantitative results.

A boiling solution of potassium cyanide (50 g.) in water (110 g.) and ethyl alcohol (350 c.c.) is rapidly stirred mechanically while finely powdered dibromo-*m*-xylene (88 g.) is added as rapidly as the violence of the reaction will permit. The hot solution is filtered at once from traces of brown, amorphous material. A litre of water is then added and the nitrile extracted with ether, dried, and distilled. The nitrile boiled at 230—231°/20 mm. and solidified, on cooling, to a snow-like mass of needles, m. p. 27°. Yield, 47 g.

m-*Tolylacetonitrile.*—Monobromo-*m*-xylene (128 g.) was treated with potassium cyanide (49 g.) dissolved in a mixture of water (120 g.) and alcohol (400 c.c.) in exactly the same manner as the above. The nitrile (yield about 85%) boiled at 245—247°/745 mm. with slight decomposition (compare Radziszewski and Wispek, *loc. cit.*) and was better distilled under reduced pressure; it then had b. p. 133°/15 mm.

p-*Phenylenediacetonitrile.*—The nitrile was prepared in the same manner as the meta-isomeride, the same quantities and conditions being used. The maximum possible yield, however, seems to be about 70%. The remainder of the bromo-derivative is converted into a bright yellow, infusible, amorphous, highly insoluble product, which does not appear to contain any nitrogen or halogen and was not further investigated. The nitrile separates from alcohol in colourless prisms, m. p. 96°.

p-*Tolylacetonitrile.*—This nitrile was obtained from monobromo-*p*-xylene by the usual method. It was found necessary in this case to boil the reaction mixture for a short time to complete the conversion. The nitrile has b. p. 135°/14 mm. and solidifies in ice to a white mass which melts at 17°.

Reduction of m-*Phenylenediacetonitrile.*—Sodium (36·8 g.) in the form of small chips was placed in a 3-litre flask, closed with a cork through which passed an air condenser about 4 feet in length and 1½ inches in diameter. This was itself fitted at the top with a water-condenser. (In some experiments, the sodium was previously granulated under toluene, but this did not appear to affect the yield materially.)

A nearly boiling solution of *m*-phenylenediacetonitrile (14·6 g.) in absolute alcohol (550 g.) was then rapidly added. When the extremely violent reaction had subsided, a solution of 90 g. of concentrated sulphuric acid in 300 c.c. of water was added and the mixture distilled in steam. The acid solution was filtered from traces of a brown, sticky by-product, and, if necessary, extracted with ether. It was then rendered alkaline with caustic soda (30 g.) and thoroughly extracted with ether. After the ethereal solution had been dried with anhydrous magnesium sulphate and the ether removed, 8 g. of a pale yellow oil were obtained, from which 5—6 g. of b. p. 97—98°/15 mm. or 101—102°/18 mm. were isolated (Found: C, 80·1, 80·2; H, 9·8, 9·7; N, 10·25. $C_9H_{13}N$ requires C, 80·0; H, 9·6; N, 10·4%).

The combined aqueous-alcoholic steam distillates from three such experiments were distilled through a column until about three-quarters of the alcohol had been removed. Water was then added to the residue, and the insoluble material extracted with ether. After removal of the ether, about 15 g. of non-basic products were obtained, and from these, by careful fractionation, 8—9 g. of a liquid, b. p. 138—141°/758 mm., which had a xylene-like odour and burned with a smoky flame (Found: C, 90·1; H, 9·3. Calc. for C_8H_{10}: C, 90·6; H, 9·4%).

From the residue about 4—5 g. of a liquid, b. p. 138—140°/18 mm., were obtained which, after shaking with dilute hydrogen peroxide and standing over-night, were converted into a crystalline mass. Recrystallised from hot water, the substance formed colourless leaflets, m. p. 141—142°, and analysis left no doubt that it was identical with *m*-tolylacetamide (compare Radziszewski and Wispek, *loc. cit.*) (Found : N, 9·6. Calc. for $C_9H_{11}ON$: N, 9·7%).

The amine, b. p. 97—98°/15 mm., described above, absorbed carbon dioxide readily from the air, with the formation of a solid carbonate.

The hydrochloride of the base was readily obtained by passing dry hydrogen chloride into its alcoholic solution. It separated in large, transparent laminæ, m. p. 160° (Found : C, 63·4; H, 8·35. $C_9H_{13}N,HCl$ requires C, 63·0; H, 8·2%).

The picrate, obtained by adding an alcoholic solution of the base to a saturated alcoholic solution of picric acid, formed sulphur-yellow needles, m. p. 174° (176° corr.) (compare Sommer, *loc. cit.*) (Found : N, 15·4. Calc., N, 15·4%).

The platinum salt, which separated in small, orange-brown needles on mixing warm solutions of the hydrochloride of the base and chloroplatinic acid, blackened between 230° and 240° and melted with vigorous decomposition at 246° (von Braun found m. p. 232° for this substance) (Found : Pt, 28·85. Calc. for $2C_9H_{13}N,H_2PtCl_6$: Pt, 28·7%).

The benzoyl derivative was best obtained by mixing 1 g. of the hydrochloride with 0·9 g. of benzoyl chloride and adding 15 c.c. of a 5% solution of sodium hydroxide. The sticky, white mass gradually solidified; recrystallised either from a very small volume of alcohol or from alcohol–ligroin, it formed colourless prisms, m. p. 72°.

The phenylthiocarbamide was obtained by boiling a solution of equal weights of the base and of phenylthiocarbimide in alcohol for about 10 minutes and adding ligroin; the thiocarbamide separated in colourless needles, which were recrystallised from a little warm alcohol and then had m. p. 86—87°.

The quaternary methiodide was easily prepared by shaking a mixture of the base (4·5 g.) with methyl iodide (20 g.) and 75 c.c. of a 5% solution of sodium hydroxide. Considerable heat was developed and the quaternary salt was deposited in white crusts. It crystallised from alcohol, in which it was only very moderately soluble in the cold, in colourless prisms, m. p. 237°.

Reduction of m-*Tolylacetonitrile.*—This reduction was carried out in the same apparatus and by the same method as that of the dinitrile already described. Thirty g. of sodium were used to reduce a solution of 15 g. of *m*-tolylacetonitrile in 450 g. of absolute alcohol.

The reaction products were worked up in the same manner, giving a yield of about 7 g. of β-*m*-tolylethylamine, b. p. 98°/15 mm. or 112°/25 mm., and about 5 g. of *m*-xylene (Found : C, 79·9; H, 9·8; N, 10·2. Calc. for $C_9H_{13}N$: C, 80·0; H, 9·6; N, 10·4%).

Condensation of β-m-*Tolylethylamine with Piperonal.*—A mixture of the base (10 g.) with piperonal (11 g.) was warmed on the water-bath for ½ hour. The product, which solidified on cooling, crystallised from about 100 c.c. of hot alcohol in yellowish-white leaflets, m. p. 54° (Found : C, 76·5; H, 6·6. $C_{17}H_{17}O_2N$ requires C, 76·4; H, 6·4%).

β-m-*Tolylethylmethylamine.*—The carefully dried piperonal compound (15 g.) was mixed with an equal weight of methyl iodide and heated for 6 hours in a sealed tube at 100°. The excess of methyl iodide was boiled off and the residue dissolved in about 75 c.c. of 95% alcohol. On diluting the solution with three times its volume of ether, the *hydriodide* of the secondary base was precipitated in needles which, after being washed with ether, were faintly yellow and had m. p. 107° (Found : I, 45·5. $C_{10}H_{15}N,HI$ requires I, 45·8%).

The free *base*, obtained by dissolving the hydriodide in an excess of 10% sodium hydroxide and extracting with ether, had b. p. 88—89°/12 mm. (Found : C, 80·5; H, 9·8; N, 9·6. $C_{10}H_{15}N$ requires C, 80·5; H, 10·1; N, 9·4%).

The *hydrochloride* was best prepared by passing dry hydrogen chloride into a solution of the base in chloroform and adding ligroin, when it separated in greasy-looking leaflets, m. p. 134°. It is very soluble in alcohol and water and is usually obtained from these solvents, on evaporation, as an oil.

The *picrate* separated in orange needles, on mixing strong alcoholic solutions of the base and picric acid, and had m. p. 126—127° (Found : N, 14·7. $C_{10}H_{15}N,C_6H_3O_7N_3$ requires N, 14·8%).

The benzoyl derivative was obtained as a viscous oil on mixing the base with benzoyl chloride and dilute caustic soda. It showed no signs of crystallisation even on cooling in a freezing mixture.

m-*Methylstyrene.*—The quaternary methiodide of β-*m*-tolylethylamine (9 g.) was heated on the water-bath with 25% methyl-alcoholic potash (20 g.) in a small flask fitted with a reflux condenser closed with a cork, through which passed a delivery tube dipping into dilute hydrochloric acid. After 1 hour, when the decomposition appeared to be complete, water was added, the insoluble oily layer extracted with ether, and the ethereal solution washed with very dilute hydrochloric acid, dried, and distilled. The hydrocarbon obtained (3—4 g.) had b. p. 61—62°/18 mm. (Found : C, 91·3; H, 8·5. C_9H_{10} requires C, 91·5; H, 8·5%).

From the hydrochloric acid solution through which the gaseous products of the decomposition had been passed, trimethylamine hydrochloride, m. p. 280° (decomp.) (compare Wagner, *Z. Kryst. Min.*, 1906, **43**, 167) was obtained. The chloroplatinate prepared therefrom formed brown scales, m. p. 242—243° (compare Willstätter, *Ber.*, 1895, **28**, 3287), and the picrate formed golden-yellow prisms, m. p. 216°, from alcohol (compare Delépine, *Ann. Chim.*, 1896, **8**, 452). Conclusive evidence was thus obtained that trimethylamine, and not dimethylamine, is eliminated during this decomposition.

From the density and the observed value of the refractive index ($n_{\mathrm{D}}^{19^\circ}$ 1·54029), von Braun calculated the molecular refraction of his hydrocarbon, assuming, of course, the composition (II), and obtained the value $[R_L]_{\mathrm{D}}$ 45·33, whilst that calculated for the composition $C_{10}H_{10}$ was 42·11. He attributes this large exaltation of 3·2 units to the presence of the meta-ring structure. If, however, the molecular refraction is calculated from the same data, but assuming the composition C_9H_{10}, the value 41·15 is obtained, whilst that predicted theoretically (using Conrady's constants) is 39·70—giving an exaltation of only 1·4 units. This exaltation is of the order to be expected in a substance of the structure (IX) (EM_α for the isomeric β-methylstyrene is 1·01 units).

*αβ-Dibromo-α-*m*-tolylethane.*—*m*-Methylstyrene (1·5 g.) dissolved in 10 c.c. of carbon disulphide was cooled in ice and gradually treated with a solution of 2·1 g. of bromine in 10 c.c. of carbon disulphide. After evaporation of the solvent, the crystalline residue was dissolved in a small volume of warm alcohol, from which it separated in well-formed, large prisms, m. p. 47° (compare Müller, *loc. cit.*) (Found : C, 39·2 ; H, 3·8 ; Br, 57·5. Calc., C, 38·8 ; H, 3·6 ; Br, 57·6%).

Reduction of p-*Phenylenediacetonitrile and* p-*Tolylacetonitrile.*—The reduction of these two substances was carried out in precisely the same manner as that of the meta-isomerides.

The same product, *viz.*, β-*p*-tolylethylamine, was obtained from both, as well as recognisable quantities of *p*-xylene.

The β-*p*-tolylethylamine, obtained in about 50% yield by reducing the dinitrile and in nearly 60% yield from the mononitrile, had b. p. 94—95°/13 mm. (Found : C, 79·6 ; H, 9·7 ; N, 10·7. $C_9H_{13}N$ requires C, 80·0 ; H, 9·6 ; N, 10·4%).

The *hydrochloride*, which is quite sparingly soluble in water and nearly insoluble in cold alcohol, crystallises in large plates, m. p. 216° (Found : C, 63·4 ; H, 8·25. $C_9H_{13}N,HCl$ requires C, 63·0 ; H, 8·2%). The *picrate* forms pale yellow needles, m. p. 155°, from alcohol (Found : N, 15·7. $C_9H_{13}N,C_6H_3O_7N_3$ requires N, 15·4%).

The *benzoyl* derivative is very readily soluble in most solvents, but can be crystallised from a small volume of alcohol in colourless prisms, m. p. 89° (Found : C, 80·5; H, 7·1. $C_{16}H_{17}ON$ requires C, 80·3; H, 7·2%). The quaternary *methiodide* has m. p. 244° and is sparingly soluble in cold alcohol.

On treatment with an excess of an acid solution of sodium nitrite, the amine was converted into β-p-*tolylethyl alcohol,* which had b. p. 112°/12 mm., and when warmed with *p*-nitrobenzoyl chloride was converted into a solid ester, which separated from alcohol in small, colourless needles, m. p. 91° (Found : C, 67·0; H, 5·45. $C_{16}H_{15}O_4N$ requires C, 67·3; H, 5·3%).

With piperonal, the amine formed a beautifully crystalline condensation product, m. p. 107°, only sparingly soluble even in hot alcohol (Found : C, 76·7; H, 6·55. $C_{17}H_{17}O_2N$ requires C, 76·4; H, 6·4%).

β-p-*Tolylethylmethylamine.*—The piperonal compound was heated in a sealed tube with an excess of methyl iodide in the manner previously described. The hydriodide of the secondary base, obtained on decomposition of the product with aqueous alcohol, had m. p. 149°. From this the free base was obtained, b. p. 96°/12 mm. (Found : C, 80·4; H, 10·25; N, 9·4. $C_{10}H_{15}N$ requires C, 80·5; H, 10·1; N, 9·4%).

The hydrochloride is readily soluble in most solvents, but does not exhibit the extreme solubility of the meta-isomeride. It separates from cold alcohol in plates, m. p. 191°. The picrate forms deep orange prisms, m. p. 135°, from alcohol (Found : N, 14·7. $C_{16}H_{18}O_7N_4$ requires N, 14·8%).

p-*Methylstyrene.*—β-*p*-Tolylethylamine hydriodide is readily converted into the hydrocarbon by boiling with 25% methyl-alcoholic potash.

p-Methylstyrene has b. p. 59—60°/12 mm. and does not appear to undergo polymerisation as rapidly as the meta-isomeride (Found : C, 91·2; H, 8·7. C_9H_{10} requires C, 91·5; H, 8·5%).

Treated in carbon disulphide solution with the equivalent of two atoms of bromine, it is converted into αβ-dibromo-α-*p*-tolylethane, m. p. 46° (compare Klages and Keil, *loc. cit.*) (Found : Br, 57·15. Calc., Br, 57·6%).

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THE DYSON PERRINS LABORATORY,
OXFORD.

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