LVIII.—*Substituted Dihydrobenzenes. Part II. 1 : 1-Dimethyl- $\Delta^{2:4}$ -dihydrobenzene and 1 : 1-Dimethyl- $\Delta^{2:5}$ -dihydrobenzene.*

By ARTHUR WILLIAM CROSSLEY and NORA RENOUF, Salters' Research Fellow.

THE first part of this research contained an account of the preparation of 1 : 1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene (II) by the reduction of 3 : 5-dichloro-1 : 1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene (I) with sodium in moist ethereal solution (Trans., 1902, **81**, 821):

Shortly after the publication of this work, Harries and Antoni (*Annalen*, 1903, **328**, 88) expressed doubt, not only as to the constitution but also as to the composition of this hydrocarbon. Their

criticisms were, in part, answered at the time (*Ber.*, 1903, **36**, 2692), but it was considered desirable to try to prepare the substance by another method, in the hope that a comparison of the two specimens of the hydrocarbon would throw further light on the problem. Although many processes have been attempted, it is only recently that one has been successfully carried out, with the result that the correctness of the earlier experiments and deductions are completely confirmed, allowing the following conclusions to be arrived at.

1. The dimethyldihydrobenzene described by Crossley and Le Sueur is 1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene, containing as impurity a very small amount of some oxygenated substance, probably a methoxy-compound.

2. The hydrocarbon described in this communication (dimethyldihydrobenzene C and R),* and prepared by the elimination of two molecules of hydrogen bromide from dibromodimethylhexahydrobenzene, is a mixture, in approximately equal quantities, of pure 1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene and pure 1:1-dimethyl- $\Delta^{2:5}$ -dihydrobenzene.

The starting point in the synthesis was again dimethyldihydroresorcin (III), which was first converted into its ethyl ether (IV) (*Trans.*, 1899, **75**, 775), and this by reduction with sodium in absolute ethyl-alcoholic solution into 3-hydroxy-5-ethoxy-1:1-dimethylhexahydrobenzene (V) :

This method of preparing the ethoxy-compound is to be preferred to that originally described (*Trans.*, 1907, **91**, 74), on account of the somewhat larger proportion of the compound produced, and also because the various reactions involved are more readily carried out. The yield of ethoxy-compound is 51 per cent. of the theoretical from the ethyl ether used, and there are also produced a resin, containing 1:1'-dihydroxy-5:5':5':5'-tetramethyldicyclohexane (*Trans.*, 1907, **91**, 71) and a low-boiling liquid, the composition of which is dealt with on page 641.

* To avoid confusion as far as possible, the hydrocarbon described in this communication, which is a mixture of pure 1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene and of pure 1:1-dimethyl- $\Delta^{2:5}$ -dihydrobenzene, is referred to as dimethyldihydrobenzene (C and R), the 1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene, prepared by Crossley and Le Sueur, as dimethyldihydrobenzene (C and S), and the supposed 1:1-dimethyl- $\Delta^{2:5}$ -dihydrobenzene of Harries and Antoni (*loc. cit.*) as dimethyldihydrobenzene (H and A).

When hydroxyethoxydimethylhexahydrobenzene is treated with fuming hydrobromic acid a mixture of bromodimethyltetrahydrobenzene

(VI) and dibromodimethylhexahydrobenzene (VII) results, in which the latter largely predominates. The presence of the former monobromo-derivative is due to the instability of dibromodimethylhexahydrobenzene and its consequent decomposition with loss of the elements of hydrogen bromide. For this reason, it was impossible to prepare the dibromo-compound in an analytically pure condition, as, no matter how often it was distilled, there was always slight decomposition, resulting in the formation of a small quantity of the lower boiling bromodimethyltetrahydrobenzene. Nor could this latter substance be obtained analytically pure, for it behaves in an exactly similar manner on distillation, giving off the elements of hydrogen bromide with gradual formation of dimethyldihydrobenzene.

When dibromodimethylhexahydrobenzene is treated with quinoline it loses readily and completely two molecules of hydrogen bromide, with formation of dimethyldihydrobenzene, and this reaction may take place in two ways, and two ways only, giving rise to 1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene (VIII), or to 1:1-dimethyl- $\Delta^{2:5}$ -dihydrobenzene (IX):

There is no difficulty in proving that the reaction proceeds in both directions, giving rise to a mixture of the two hydrocarbons in approximately equal amounts. At first it was thought that the bromodimethyltetrahydrobenzene might have given only dimethyl- $\Delta^{2:4}$ -dihydrobenzene on treatment with quinoline, and the substance was therefore worked up separately,

without the slightest indication of any difference in the composition of the resulting hydrocarbon. Nor is this to be surprised at, for if the first product of the action of hydrogen bromide on the ethoxy-compound be dibromodimethylhexahydrobenzene, this may lose hydrogen bromide in two ways to give monobromo-derivatives (X and XI) from

which the same mixture of hydrocarbons might result by further loss of hydrogen bromide :

The reasons for believing dimethyldihydrobenzene (C and R) to be a mixture of the two hydrocarbons with the double bonds in the 2:4- (formula VIII) and 2:5- (formula IX) positions respectively are the following.

1. It contains 1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene because it gives the nitrosochloride of this hydrocarbon (Trans., 1902, **81**, 835).

2. When treated with hydrogen bromide it gives a monohydrobromide and a dihydrobromide. The former boils at 82—83°/20 mm., yields on oxidation *as*-dimethylsuccinic acid, $\beta\beta$ -dimethylglutaric acid and the lactone of α -hydroxy- $\beta\beta$ -dimethylglutaric acid, and is therefore identical with the hydrobromide of 1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene (Trans., *ibid.*, p. 833), which hydrocarbon, owing to the fact that it contains a conjugated double bond, is only capable of uniting with one molecule of hydrogen bromide, thus corresponding exactly with the behaviour of $\Delta^{1:3}$ -dihydrobenzene (Trans., 1904, **85**, 1422) in this respect.

The dihydrobromide is obviously that of 1:1-dimethyl- $\Delta^{2:5}$ -dihydrobenzene, which, as it contains two double bonds not conjugated, would unite with two molecules of hydrogen bromide.

3. It absorbs bromine to give two distinct bromides, namely, the liquid dibromide of 1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene (Trans., 1902, **81**, 833), and the solid tetrabromide (m. p. 102°) which must be derived from 1:1-dimethyl- $\Delta^{2:5}$ -dihydrobenzene. Moreover, as the molecular absorption corresponds with three atoms of bromine, it would mean that the mixture consists of the two hydrocarbons in exactly equal amounts. This behaviour is in striking accord with that of dihydrobenzene itself towards bromine, in which case the $\Delta^{1:3}$ variety (XII) absorbs only two atoms to give the solid dibromide (m. p. 108—109°) (Trans., 1904, **85**, 1421), whereas $\Delta^{1:4}$ -dihydrobenzene (XIII) adds

on four atoms of bromine to give a solid tetrabromide melting at 184° (Baeyer, *Annalen*, 1894, **278**, 96).

4. When oxidised with potassium permanganate it yields as main oxidation products *as*-dimethylsuccinic acid and dimethylmalonic acid. The former arises from the 1 : 1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene, because, under the conditions used, this hydrocarbon has been shown by experiment not to give rise to any dimethylmalonic acid, which therefore owes its origin to the oxidation of 1 : 1-dimethyl- $\Delta^{2:5}$ -dihydrobenzene :

5. It gives, when treated with a nitrating mixture, the two possible forms of trinitro-*o*-xylene melting at 71° and 115° respectively. This is an exactly analogous reaction to that recorded by Wallach (*Annalen*, 1890, **258**, 329), where 1 : 3-dimethyldihydrobenzene was converted by a mixture of nitric and sulphuric acids into mono-, di-, and trinitro-*m*-xylenes. Now it was not found practicable to prepare a nitro-derivative from 1 : 1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene (Trans., 1902, **81**, 833), and the experiments have been repeated with fresh quantities of this hydrocarbon again with the same result. The conclusion to be drawn is obviously that the isomeric 1 : 1-dimethyl- $\Delta^{2:5}$ -dihydrobenzene is responsible for the production of the trinitroxylenes in the above-mentioned experiments, during which process a methyl group wanders and, as in other similar cases (Trans., 1904, **85**, 264 ; 1906, **89**, 875), into an ortho-position.

It would appear desirable at this point to give a tabulated comparison of the properties of the dimethyldihydrobenzenes (C and S) and (C and R), also of 1 : 1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene and 1 : 1-dimethyl- $\Delta^{2:5}$ -dihydrobenzene, as far as can be ascertained from the present experiments (see p. 634).

Having acquired this information, the criticisms of Harries and Antoni (*loc. cit.*) may now be answered in detail.*

In the first place, these authors consider that the analyses given by Crossley and Le Sueur (*ibid.*) are midway between those for a dimethyl-dihydro- and a dimethyltetrahydro-benzene. The mean of the two analyses quoted gave C = 88.30 and H = 11.27, and it is obvious from the

	Calculated.		Calculated.	
Difference.	C ₈ H ₁₄ .	Found.	C ₈ H ₁₂ .	Difference.
+1.03	87.27	C = 88.30	88.88	-0.58
-1.46	12.73	H = 11.27	11.11	+0.16

annexed comparison that the numbers do not lie midway between

* The reply to their remarks about dihydrobenzene has appeared (Trans., 1904, **85**, 1404).

	Dimethyldihydrobenzenes.	
	(C and S).	(C and R).
B. p.	111°	111·2°
Sp. gr. at 15°/15°	0·8153	0·8147
Index of refraction	1·4548	1·4535
Molecular refraction	60·217	60·251
Magnetic rotation	11·024	10·450
Colour with H ₂ SO ₄	Blood-red turning to violet-purple	Blood-red turning to violet-purple
Fuming HBr	Monohydrobromide, b. p. 90·5°/86 mm.	Monohydrobromide, b. p. 83°/20 mm. Dihydrobromide, b. p. 137°/25 mm.
Bromine	Dibromide, unstable liquid	Dibromide, unstable liquid Tetrabromide, m. p. 102°
NOCl	Nitrosochloride, m. p. 121°	Nitrosochloride, m. p. 121°
Nitrating mixture.....	No definite product	Trinitro- <i>o</i> -xylenes, m. p. 71° and 115°
Oxidation products	<i>as</i> -Dimethylsuccinic acid	<i>as</i> -Dimethylsuccinic acid, dimethylmalonic acid
Oxidation products of monohydrobromide	<i>as</i> -Dimethylsuccinic acid, $\beta\beta$ -dimethylglutaric acid, lactone of α -hydroxy- $\beta\beta$ -dimethylglutaric acid	<i>as</i> -Dimethylsuccinic acid, $\beta\beta$ -dimethylglutaric acid, lactone of α -hydroxy- $\beta\beta$ -dimethylglutaric acid

1 : 1-Dimethyl- $\Delta^{2:4}$ -dihydrobenzene.	1 : 1-Dimethyl- $\Delta^{2:5}$ -dihydrobenzene.
Hydrobromide, C ₈ H ₁₃ Br. B. p. 83°/20 mm.	Hydrobromide, C ₈ H ₁₄ Br ₂ . B. p. 137°/25 mm.
Nitrosochloride, m. p. 121°	No nitrosochloride isolated
Dibromide, C ₈ H ₁₂ Br ₂ , unstable liquid	Tetrabromide, C ₈ H ₁₂ Br ₄ , m. p. 102°
No nitro-derivatives obtainable	Trinitro- <i>o</i> -xylenes, m. p. 71° and 115°
Oxidation product, <i>as</i> -dimethylsuccinic acid	Oxidation product, dimethylmalonic acid

the calculated figures, the differences in those found and calculated for C_8H_{14} being very large, and the errors are in the wrong direction; for as a rule carbon is found too low and hydrogen too high, and not vice versa. Moreover, if any appreciable quantity of dimethyltetrahydrobenzene had been present it could hardly have escaped detection, as on oxidation it would have yielded $\beta\beta$ -dimethyladipic acid, which presents no difficulty of isolation or identification. This may be noted from the following brief description of some unpublished experiments.

In 1903 an unsuccessful attempt was made to prepare 1:1-dimethylhexahydrobenzene (compare *Trans.*, 1905, **87**, 1487) by the reduction of 3:5-dichloro-1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene (I) with sodium in amyl-alcoholic solution. The resulting hydrocarbon, after distillation over sodium, boiled at 113–114° and gave the following numbers on analysis, C = 87.96, H = 12.15; that is, midway between those calculated for C_8H_{12} and C_8H_{14} . Further, it gave an orange-brown colour with sulphuric acid, and absorbed two atoms of bromine in chloroform solution (molecular absorption, 156.5). This would be in agreement with the supposition that the hydrocarbon was a mixture of 1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene and 1:1-dimethyl- Δ^3 -tetrahydrobenzene, both of which substances would only absorb two atoms of bromine. On oxidation with potassium permanganate a solid was obtained, which was heated with acetyl chloride, and after evaporation of the solvent the residue was treated with dilute sodium carbonate solution, leaving an insoluble portion, which was proved to consist of *as*-dimethylsuccinic anhydride; after acidification of the sodium carbonate solution with dilute sulphuric acid, ether extracted a white solid crystallising from a mixture of chloroform and light petroleum in stellar aggregates of flattened needles melting at 85–86°, nor was this melting point altered on mixing with pure $\beta\beta$ -dimethyladipic acid. (C = 55.15; H = 8.10. $C_8H_{14}O_4$ requires C = 55.17; H = 8.05 per cent., compare also *Trans.*, 1906, **89**, 1556.)

If the above quoted figures for dimethyldihydrobenzene (C and S) are examined, it will be found that they add up to 99.57; and although this hydrocarbon has been prepared by the old method on fifteen different occasions, and each time analysed, the percentages of carbon and hydrogen found have never together formed 100, the deficit in some cases amounting to as much as 0.8–0.9 per cent. It is therefore acknowledged that the hydrocarbon was not and cannot be obtained in an absolutely pure state by the original method, but the impurity is not dimethyltetrahydrobenzene as suggested by Harries and Antoni. The hydrocarbon was prepared by the action of sodium in moist ethereal solution on dichlorodimethyldihydrobenzene (I), and it might therefore be thought that the impurity was

chlorine ; but the most stringent tests failed to reveal the slightest trace of this element. Now when chloroketodimethyltetrahydrobenzene (XIV)

is reduced with sodium in ethyl-alcoholic solution, the chlorine atom is replaced by an ethoxy-group (Trans., 1907, 91, 74), and it seems most probable that a similar type of reaction takes place in the preparation of 1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene by the reduction of dichlorodimethyldihydrobenzene with sodium in moist ethereal solution ; because small quantities of methyl alcohol were added to the ether to facilitate the reaction, and, up to a certain point, the larger the amount of alcohol the more impure was the resulting hydrocarbon. It may therefore be reasonably deduced that the deficit in the above-mentioned analyses is due to oxygen, and that the dimethyldihydrobenzene contains very small amounts of a methoxy-compound, possibly $\text{CMe}_2 \begin{array}{c} \text{CH} : \text{C(OMe)} \\ \text{CH}_2 - \text{CH} \end{array} \text{CH}$, which would account for the error in the analytical figures.

Another suggestion made by Harries and Antoni is that dimethyldihydrobenzene (C and S) is not a true dihydrobenzene, but contains a trimethylene ring as represented in formula XV. Altogether apart from the probable incapability of existence of such a body, it may be

mentioned that the magnetic rotation of the hydrocarbon would have at once proved the presence of a trimethylene ring, and, moreover, we have now evidence that the same dimethyldihydrobenzene is produced by the reduction of dichlorodimethyldihydrobenzene, and by the removal of the elements of hydrogen bromide from dibromodimethylhexahydrobenzene.

This can only be explained if the substance be designated 1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene, and hence the possibility of a trimethylene ring being present in the hydrocarbon is precluded.

Harries and Antoni further point out as a proof that dimethyldihydrobenzene (C and S) is a mixture of the dihydro- and tetra-

hydro-derivatives, that the physical constants lie midway between those of hydrocarbons of the dihydrobenzene series and those of the tetrahydrobenzene series. The specific gravity, 0.814 at 18°/18°, is, however, not very different from that of 1:3-dimethyl- $\Delta^{4:6}$ -dihydrobenzene described by Harries, namely, 0.820 at 18°/18°, and, however plausible the above argument may have appeared at the time, it is no longer tenable; for there can be no doubt that dimethyldihydrobenzene (C and R) does not contain any of the corresponding tetrahydro-derivative, yet its physical data do not differ sufficiently from those of dimethyldihydrobenzene (C and S) to bring it in line with those quoted by Harries and Antoni. (See page 634.)

The whole question is further complicated by the fact that Harries and Antoni prepared a hydrocarbon, which they believed to be 1:1-dimethyl- $\Delta^{2:5}$ -dihydrobenzene, also from dimethyldihydroresorcin as a starting point; but, unfortunately, no information is given as to any derivatives which would enable a comparison to be made with the hydrocarbon having that undoubted structure described in this communication; and it would appear that the present evidence is insufficient definitely to establish the constitution of Harries and Antoni's hydrocarbon. Dimethyldihydroresorcin was first converted into the dioxime, and, after reduction, the dry phosphate of the resulting diamine was distilled:

The single piece of evidence on which the supposed constitution of this substance is based is oxidation, whereby 9 grams gave 0.3 gram of oxalic acid, a small amount of a succinic acid, the presence of which could only be proved by the pyrrole reaction, and 2 to 3 grams of an oily acid, consisting for the most part of malonic acid. It is stated that this latter acid could only have been formed if the hydrocarbon has the constitution represented by formula (XVI); in which

case dimethylmalonic acid should also have been isolated; but Harries and Antoni definitely state that it was impossible to isolate any of this acid. In other words, Harries and Antoni were unable to obtain any oxidation product from the hydrocarbon which contained the *gem*-dimethyl group. Now, although the present authors have oxidised a very large number of derivatives of dimethyldihydroresorcin, they have never failed in any case to isolate either dimethylmalonic acid, *as*-di-

methylsuccinic acid, $\beta\beta$ -dimethylglutaric acid, the lactone of α -hydroxy- $\beta\beta$ -dimethylglutaric acid, or $\alpha\alpha$ - or $\beta\beta$ -dimethyladipic acids, that is, an oxidation product definitely proving the presence of the *gem*-dimethyl group.

It is possible that during the distillation of the diamine phosphate a methyl group has wandered, whence Harries and Antoni's hydrocarbon might have the constitution represented by formula (XVII),

and from which malonic acid could easily result on oxidation.

Nor is there any apparent reason, presuming that a methyl group does not wander, for supposing that the elimination of ammonia from the cyclic diamine would take place in one way and one way only. Harries and Antoni have themselves shown that, when the phosphate of diaminohexahydrobenzene (XVIII) is submitted to dry distillation, ammonia is evolved in both of the possible directions, giving rise to a mixture of $\Delta^{1:3}$ -dihydrobenzene (XX) and $\Delta^{1:4}$ -dihydrobenzene (XIX),

and they therefore conclude that "the *gem*-dimethyl group influences the position taken up by the double bonds,"

If this is so, why does it not influence the position of the double bonds when hydrogen bromide is eliminated from dibromodimethylhexahydrobenzene? For this is a reaction strictly analogous to the

above, which, as proved in this communication, takes place in both ways, giving rise to a mixture of the two possible hydrocarbons in equal amounts. The presence of the *gem*-dimethyl group certainly does not exercise any apparent influence in this case, or in the position of the double bond formed when 3-bromo-1:1-dimethylhexa-

hydrobenzene loses the elements of hydrogen bromide (Trans., 1906, 89, 1556), when again two isomeric hydrocarbons are produced.

The boiling point of dimethyldihydrobenzene (H and A) is 135—137°, agreeing very well with the boiling points of other dimethyldihydrobenzenes, whereas dimethyldihydrobenzene (C and S) boils at 111°, and Harries and Antoni suggest that the low boiling point may be due to the fact that it is a mixture of dimethyldi- and dimethyltetra-hydrobenzenes, but again this argument is not tenable, for dimethyldihydrobenzene (C and R) boils at precisely the same temperature. It is true that this latter hydrocarbon is a mixture of dimethyl- $\Delta^{2:4}$ -dihydrobenzene and dimethyl- $\Delta^{2:5}$ -dihydrobenzene, and we have no information as to the lowering of the boiling point in a mixture of two substances differing in constitution only by the varying positions of the double bonds. It seems hardly likely, however, that this would lower the boiling point by 26°, and it would, indeed, be a most remarkable coincidence if the minute amount of impurity in dimethyldihydrobenzene (C and S) should cause exactly the same lowering in the boiling point of dimethyl- $\Delta^{2:4}$ -dihydrobenzene as would be observed by mixing a pure specimen of this hydrocarbon with an equal bulk of pure dimethyl- $\Delta^{2:5}$ -dihydrobenzene, yet such is the composition of the dimethyldihydrobenzene (C and R). It is hoped that before long further information will be forthcoming as to what influence, if any, the presence of certain groupings exercises on the boiling point of isomeric substituted dihydrobenzenes.

Harries and Antoni state that 2 grams of their dimethyldihydrobenzene gave, on treatment with a nitrating mixture, 0.6 gram of trinitro-*m*-xylene, but they do not give the melting point of the product, and consequently it is doubtful which of the three trinitro-*m*-xylenes (melting respectively at 90°, 125°, and 182°) was obtained. But this might be regarded as a proof that dimethyldihydrobenzene (H and A) does not contain the *gem*-dimethyl group, for although many cases of the wandering of a methyl group in derivatives of *gem*-dimethyldihydroresorcin have been recorded (Trans., 1904, 85, 264; 1906, 89, 875), no single instance has been observed in which a methyl group has wandered into anything but an ortho-position. Moreover, dimethyldihydrobenzene (C and R) undoubtedly contains dimethyl- $\Delta^{2:5}$ -dihydrobenzene, and under the influence of a nitrating

mixture it is this hydrocarbon which is converted into the two possible trinitro-*o*-xylenes, as explained on page 633.

With the statement of Harries and Antoni that dimethyldihydrobenzene (C and S) also gives trinitro-*m*-xylene we cannot agree, as all attempts to nitrate this hydrocarbon under the conditions mentioned by Harries and Antoni, and also under various other conditions, have failed to give any definite nitro-derivative.

EXPERIMENTAL.

Preparation of 1:1-Dimethyldihydroresorcin Ethyl Ether.

The ethyl ether of dimethyldihydroresorcin was originally prepared (Trans., 1899, 75, 775) by the action of ethyl iodide on the silver salt of dimethyldihydroresorcin, but it may be more readily obtained in bulk by direct esterification. For this purpose, large amounts of dimethyldihydroresorcin were heated in quantities of 50 grams with 150 grams of absolute ethyl alcohol and 15 grams of concentrated sulphuric acid for seven hours in a flask attached to a reverse condenser. The major quantity of the alcohol was then evaporated, the residue poured into water, extracted three times with ether, the ethereal solution washed with potassium hydroxide solution (washings = A), then water, dried over calcium chloride, and the ether evaporated, when the residue of 38—40 grams set at once to a solid cake, which, after one crystallisation from light petroleum (b. p. 40—60°), melted sharply at 60°.

On acidifying the alkaline washings, A, 16 grams of dimethyldihydroresorcin were recovered, which were again esterified in the above-described manner, when the total yield of ethyl ether was brought up to 78 per cent. of the theoretical.

Reduction of the Ether with Sodium and Absolute Alcohol.

Four hundred and fifty grams of the ether were dissolved in quantities of 20 grams (1 molecule) at one time in 400 c.c. of absolute ethyl alcohol in a flask attached to a reverse condenser, and 33 grams of sodium (12 atoms) cut in thin slices gradually added; the flask was continuously shaken and heated to expedite the solution of the last portions of the sodium. Water was then added, and sufficient alcohol evaporated to cause the separation of an oil, when the whole was extracted four times with ether, washed with water until no longer alkaline, dried over calcium chloride and, after evaporation of the ether, distilled, when at 33 mm. the following fractions were collected :

Below $130^{\circ} = 61$ grams ; $130-145^{\circ} = 225$ grams ; resinous residue = 31 grams, and after two more distillations :

$87-120^{\circ} = 45$ grams ; $120-135^{\circ} = 2$ grams ; $135-138^{\circ} = 236$ grams.

Fraction $87-120^{\circ}$.—The boiling point of this material, which is identical in composition with the similar low boiling liquid obtained by the reduction of chloroketodimethyltetrahydrobenzene with sodium in alcoholic solution (Trans., 1907, **91**, 74), showed it to be a mixture, but after repeated fractionation a small portion boiled constantly at 85° at 23 mm., and gave the following numbers on analysis :

0.1424 gave 0.3985 CO_2 and 0.1373 H_2O . $\text{C} = 76.32$; $\text{H} = 10.71$.

$\text{C}_8\text{H}_{14}\text{O}$ requires $\text{C} = 76.19$; $\text{H} = 11.11$ per cent.

It was expected that this substance would prove to be 3-keto-1:1-dimethyl- Δ^4 -tetrahydrobenzene, $\text{C}_8\text{H}_{12}\text{O}$ (Trans., 1907, **91**, 78), but the analysis shows it to contain at most traces of this ketone and to have the formula $\text{C}_8\text{H}_{14}\text{O}$. It must therefore be either 3-hydroxy-1:1-dimethyl- Δ^4 -tetrahydrobenzene (XXI), or 3-keto-1:1-dimethyl-hexahydrobenzene (XXII) :

Inasmuch as it did not give a semicarbazone but gave acetyl and benzoyl derivatives, and also as its boiling point is 10° higher than that of keto-1:1-dimethylhexahydrobenzene (Trans., 1907, **91**, 81), it would appear to be 3-hydroxy-1:1-dimethyl- Δ^4 -tetrahydrobenzene.

It is a clear, colourless, limpid liquid, with a strong camphoraceous odour, giving only a faint orange colour with sulphuric acid, and absorbing bromine in chloroform solution without evolving hydrogen bromide. It did not solidify when cooled in a freezing mixture. Unfortunately, the acetyl and benzoyl derivatives could not be obtained in an analytically pure condition, as there was too little of the fraction boiling at 85° at 23 mm. In order to prove the presence of 3-keto-1:1-dimethyl- Δ^4 -tetrahydrobenzene, the fraction $84-86^{\circ}$, giving a marked colour reaction with sulphuric acid, was treated with benzoyl chloride, and, after working up in the usual way, distilled at 25 mm., when about one-third of the liquid passed over below 100° , and the temperature then rose rapidly to 190° (boiling point of the benzoyl derivative). The low boiling liquid was reduced with zinc dust in aqueous alcoholic solution, when a quantity of 1:1'-dihydroxy-5:5:5':5'-tetramethyl- $\Delta^{2:2}$ -dicyclohexene, melting at 148° , was obtained, and from this, by treatment with bromine, the tribromo-

anhydride (?) melting with decomposition at 250° (Trans., 1907, 91, 76).

The fraction $87-120^{\circ}$ therefore consisted of 3-keto-1:1-dimethyl- Δ^4 -tetrahydrobenzene, 3-hydroxy-1:1-dimethyl- Δ^4 -tetrahydrobenzene, and probably also the corresponding saturated ketone and alcohol, the production of which substances necessitates the elimination of the elements of ethyl alcohol from the ethoxy-compound during the process of reduction. If the fraction contained nothing but these substances, then on reduction the whole should be converted into the fully saturated alcohol, and by treating 30 grams with sodium in moist ethereal solution (Trans., 1905, 87, 1494), there were produced 22 grams of 3-hydroxy-1:1-dimethylhexahydrobenzene and 3.5 grams of a resin yielding 1.5 grams of 1:1'-dihydroxy-5:5:5':5'-tetramethyldicyclohexane, melting at 212° (Trans., 1907, 91, 71). The latter substance was also obtained by working up the 31 grams of resinous residue mentioned above.

The fraction $135-138^{\circ}$ was again distilled, when the major portion boiled constantly at 131° at 25 mm.:

0.1229 gave 0.3158 CO_2 and 0.1288 H_2O . $\text{C} = 70.07$; $\text{H} = 11.64$.

$\text{C}_{10}\text{H}_{20}\text{O}_2$ requires $\text{C} = 69.77$; $\text{H} = 11.62$ per cent.

3-Hydroxy-5-ethoxy-1:1-dimethylhexahydrobenzene, which is obtained in 51 per cent. of the theoretical quantity from the ethyl ether used, possesses the properties already ascribed to it (Trans., 1907, 91, 74).

Action of Hydrogen Bromide on Hydroxyethoxydimethylhexahydrobenzene.

Two hundred and fifty grams of hydroxyethoxydimethylhexahydrobenzene were treated with fuming hydrobromic acid exactly as previously described (Trans., 1905, 87, 1497), except that the heating was carried out in glass stoppered bottles instead of soda-water bottles. After several distillations of the product, the following fractions were obtained:

$80-90^{\circ} = 1$ gram; $90-100^{\circ} = 9.0$ grams; $100-110^{\circ} = 24$ grams; $110-120^{\circ} = 11.0$ grams; $120-130^{\circ} = 5.5$ grams; $130-150^{\circ} = 216$ grams.

The residue of 44 grams was not further worked with.

The fraction $100-110^{\circ}$ was twice redistilled, and a portion boiling at $92-93^{\circ}$ at 40 mm. analysed:

0.1431 gave 0.2852 CO_2 and 0.1011 H_2O . $\text{C} = 54.35$; $\text{H} = 7.85$.

0.1866 „ 0.1635 AgBr . $\text{Br} = 37.28$.

$\text{C}_8\text{H}_{13}\text{Br}$ requires $\text{C} = 50.79$; $\text{H} = 6.87$; $\text{Br} = 42.33$ per cent.

As the analytical numbers add up to 99·5, there can be no doubt that the substance contained only carbon, hydrogen and bromine, and consisted mainly of bromodimethyltetrahydrobenzene, mixed probably with some dimethyldihydrobenzene; for on distillation there was always slight decomposition due to loss of hydrogen bromide and formation of small quantities of a lower boiling substance.

The fraction 130—150° was redistilled, when practically the whole boiled between 135—138° at 25 mm.:

0·1599 gave 0·2208 CO₂ and 0·0777 H₂O. C = 37·66; H = 5·39.

0·1318 „ 0·1756 AgBr. Br = 56·69.

C₈H₁₄Br₂ requires C = 35·55; H = 5·18; Br = 59·25 per cent.

The analytical figures add up to 99·74, showing the absence of oxygen, and this material evidently consisted of a mixture of bromodimethyltetrahydrobenzene and dibromodimethylhexahydrobenzene, as the context shows. Further distillation only resulted in the evolution of hydrogen bromide and production of the monobromide of lower boiling point.

Treatment of the Mixed Bromides with Quinoline.

Having proved that the low and high boiling bromides gave the same substance under the influence of quinoline, the whole of the material was treated in the following manner. Forty grams of the bromide and 80 grams of freshly-distilled quinoline were heated in a distillation flask, the neck of which was eight inches long. A reaction set in at 167°, and proceeded quietly at 175°, the hydrocarbon distilling over. Finally, the thermometer was raised out of the liquid, and everything allowed to distil which would do so below a temperature of 200°. As one such treatment did not give a product free from halogen, the distillate was again heated with its own weight of quinoline in the long-necked flask for one and a-half hours at a temperature just sufficiently high to keep the liquid boiling, but not to allow any hydrocarbon to pass over. The temperature was then raised, the hydrocarbon collected, and steam distilled from dilute sulphuric acid to remove quinoline. The product contained the merest trace of bromine, which was entirely removed by distillation in air, when the small residue boiling above 150° was found to contain the bromine. The hydrocarbon (73 grams from 249 grams of bromide) was then fractionated over metallic sodium, using a Young's rod and disk still-head (15 disks):

	1st Fractionation. Grams.	2nd Fractionation. Grams.
111—113°	1	1
113—115°	43·5	50·8
115—120°	16·0	9·5
Residue	9·5	6·0

The portion 113—115° was twice refractionated, when practically the whole distilled between 111° and 112° :

0.1425 gave 0.4635 CO₂ and 0.1462 H₂O. C=88.71 ; H=11.39.
C₈H₁₂ requires C=88.88 ; H=11.11 per cent.

Dimethyldihydrobenzene (C and R) is a clear, colourless, highly refractive liquid, boiling at 111.2° at 749 mm., and possessing a faint odour of garlic, yet strongly resembling turpentine. When dissolved in alcohol and treated with concentrated sulphuric acid, it gives a blood-red colour, rapidly turning to deep plum colour, and then slowly changing to deep violet purple. As proved by the context, it is a mixture of 1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene and 1:1-dimethyl- $\Delta^{2:5}$ -dihydrobenzene in almost equal amounts.

The boiling point of the fractions of the hydrocarbon distilling above 112° was found to be lowered by each further distillation, but the higher fractions were too small to investigate completely. Two of these were analysed and their bromine absorptions determined :

Fraction		Carbon.		Hydrogen.		Bromine absorption.
		Found.	Calc.	Found.	Calc.	
118—121°		88.69	88.88	11.23	11.11	156.8
„	125—130	88.44	88.88	11.48	11.11	156.5

This proves that the whole material had the composition of a dimethyldihydrobenzene, and the presence of the small quantity of this higher boiling substance may be due to polymerisation.

The bromine absorptions were done before it had been noticed that a further amount of bromine is very slowly absorbed by the hydrocarbon (see page 650), and, on repeating the determination with a portion of the hydrocarbon boiling at 120—130°, the first end-point showed a molecular absorption of 159 and the second end-point 235. On evaporating the chloroform mother liquor, the tetrabromide melting at 102° was obtained (see p. 650). The following physical data, kindly sent to us by Dr. F. M. Perkin, refer to the hydrocarbon boiling at 111.2°, and were determined by the late Sir W. H. Perkin.

Density determinations :

$d_{4^{\circ}/4^{\circ}} = 0.82374$; $d_{15^{\circ}/15^{\circ}} = 0.81470$; $d_{25^{\circ}/25^{\circ}} = 0.80737$.

Magnetic rotation :

<i>t.</i>	Sp. rot.	Mol. rot.
15.7	1.4977	10.4505

Refractive value :

$$d_{16.3^{\circ}/4^{\circ}} = 0.81291.$$

Line.	<i>t.</i>	Index of refraction μ .	Specific refraction $\frac{\mu-1}{\alpha}$	Molecular refraction $\frac{\mu-1}{d}p$.	Calculated.
H _{α}	16.3	1.453513	0.55788	60.251	60.2
H _{β}	16.3	1.465146	0.57219	61.796	
H _{γ}	16.3	1.472501	0.58124	62.777	

Dispersion H _{γ} - H _{α} 2.526.

The first specimen of dimethyldihydrobenzene (C and S) examined was in 1902 (Trans., **81**, 836), but, although the numbers were considered to prove definitely that the substance was a dimethyldihydrobenzene, the subsequent comparison of these numbers with the values obtained in the case of dimethyltetrahydrobenzene and dimethylhexahydrobenzene led Sir W. H. Perkin to express the opinion that the dimethyldihydrobenzene contained a small amount of some impurity, which is now admitted (see page 636). It will be noticed that the numbers for pure dimethyldihydrobenzene (C and R) given above do actually differ from those for dimethyldihydrobenzene (C and S) as seen in the following table :

	Density 15°/15°.	Mol. rot.	Mol. refraction $\frac{\mu-1}{d}p$.
C and S	0.8153	11.0240	60.217
C and R	0.8147	10.4505	60.251

As regards the magnetic rotation, this determination completes the investigation of a series of compounds commencing with dimethylhexahydrobenzene and ending with *o*-xylene, and the changes in physical properties following the loss of two, four, or six hydrogen atoms can be followed.

	Mol. rot.	Difference.
Dimethylhexahydrobenzene (Trans., 1905, 87 , 1491).....	8.150	0.753
Dimethyltetrahydrobenzene (<i>ibid.</i>).....	8.903	
Dimethyldihydrobenzene (see above).....	10.450	1.547
<i>o</i> -Xylene (Trans., 1896, 69 , 1241).....	13.345	2.895

These numbers may be compared with another completed set, namely, hexahydrobenzene to benzene :

	Mol. rot.	Difference.
Hexahydrobenzene (Trans., 1900, 77 , 372)	5.664	0.731
Tetrahydrobenzene (Trans., 1898, 73 , 942)	6.395	
Dihydrobenzene (Trans., 1904, 85 , 1417).....	8.093	1.698
Benzene (Trans., 1896, 69 , 1241)	11.284	3.191

It is very interesting to note that when these figures are plotted out they form almost regular curves practically identical in form.

The dotted line shows the course of the curve if the number for dimethyldihydrobenzene (C and S) is included, in which case the form of the curve differs decidedly from that obtained for hexahydrobenzene to benzene.

FIG. 1.

Action of Nitric Acid.—Three grams of the hydrocarbon were added drop by drop to a mixture of 23 c.c. of fuming nitric acid and 11 c.c. of concentrated sulphuric acid, cooled in ice, and allowed to stand twenty-four hours, when an oil had separated. It is important that the addition of the hydrocarbon to the nitrating mixture should be made very gradually, otherwise oxidation takes place very violently with production of flame. The whole was then heated on the water-bath for one hour, poured into water, and the separated oil heated on the water-bath for twelve hours with 30 c.c. of a mixture of one volume of fuming nitric acid and two volumes of concentrated sulphuric acid. On standing twelve hours, compact, needle-shaped crystals had separated, these were filtered off (filtrate = A), washed with water, dried on a porous plate, and purified by crystallisation from ethyl alcohol:

0.1007 gave 15.1 c.c. moist nitrogen at 17° and 752 mm. $N = 17.21$.
 $C_8H_7O_6N_3$ requires $N = 17.43$ per cent.

This nitro-compound crystallised from ethyl alcohol in white, glistening needles melting at 115°, nor was this melting point altered on mixing with pure trinitro-*o*-xylene melting at 115° (Proc., 1908, 24, 58), with which substance it is identical. The amount obtained was 0.4 gram.

The filtrate A (see above) was poured into water and allowed to

stand, when one gram of a solid separated. It was purified by crystallisation from alcohol and the nitrogen determined :

0.1439 gave 21.8 c.c. moist nitrogen at 17° and 748 mm. $N = 17.30$.

$C_8H_7O_6N_3$ requires $N = 17.43$ per cent.

This substance crystallises from absolute alcohol in small, faintly yellow, flattened needles melting at 71°, and is identical with the trinitro-*o*-xylene melting at 71° (Proc., *loc. cit.*).

The nitration was then repeated under the conditions described by Harries and Antoni (*ibid.*, p. 111), when 2 grams of the hydrocarbon gave 0.6 gram of solid which consisted of a mixture of the two trinitro-*o*-xylenes melting respectively at 71° and 115°.

On finding that dimethyldihydrobenzene (C and R) readily gave these nitro-derivatives, whereas it had not been found possible to nitrate dimethyldihydrobenzene (C and S), the latter was again prepared and treated exactly as described above. After heating one hour and pouring into water, 2 grams of the hydrocarbon gave 2.5 grams of a yellow semi-solid, which could not be brought into a crystalline condition, and decomposed with evolution of nitrous fumes without previously melting. After treatment with the second nitrating mixture, only 0.2 gram of a similar yellow material was obtained, from which no definite chemical individual could be isolated.

The nitration of dimethyldihydrobenzene (C and S) was then attempted, using the conditions employed by Harries and Antoni, but not a trace of trinitro-*m*-xylene or any other crystalline substance could be obtained.

A *nitroso-chloride* was prepared as previously described (Trans., 1902, 81, 835), and also by passing nitrosyl chloride into a dry chloroform solution of the hydrocarbon kept below -10° and then pouring into four times the volume of methyl alcohol. By the first method, 4 grams of the hydrocarbon gave 0.1 gram, and by the second method 0.2 gram of a solid crystallising from methyl alcohol in fine, white, silky needles, melting at 121°. As the melting point is also a decomposition point, it varies according to conditions. On heating as rapidly as possible to 100° and then using a very small flame, the above temperature was noted, nor was this melting point altered on admixture with an equal bulk of the nitroso-chloride prepared from dimethyldihydrobenzene (C and S) (Trans., 1902, 81, 835). It is interesting to note the yield of this nitroso-chloride, namely, 0.2 gram from 4 grams of dimethyldihydrobenzene (C and R).

This latter hydrocarbon contains approximately 50 per cent. of 1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene and 1:1-dimethyl- $\Delta^{2:5}$ -dihydrobenzene, and therefore in reality 2 grams of dimethyldihydrobenzene (C and R) give 0.2 gram of the nitroso-chloride, or exactly the same

yield as when prepared from dimethyldihydrobenzene (C and S) namely, 0.5 gram from 5 grams of the hydrocarbon.

Although very careful search was made, no evidence could be obtained of the production of a nitroso-chloride from the isomeric 1:1-dimethyl- $\Delta^{2:5}$ -dihydrobenzene.

Action of Fuming Hydrobromic Acid.—Fifteen grams of the hydrocarbon were treated with hydrobromic acid exactly as previously described (Trans., 1902, 81, 833). The residue was distilled at 22 mm., when 15.5 grams were obtained boiling at 90—130°, and 13.5 grams at 130—132°. After repeated fractionation of the portion boiling at 90—130°, 10 grams passed over constantly at 82—83° at 20 mm., and gave on analysis a number for bromine agreeing with the addition of one molecule of hydrogen bromide to the hydrocarbon. This boiling point is the same as that of the hydrobromide of dimethyldihydrobenzene (C and S) (Trans., 1902, 81, 833), namely, 90.5° at 36 mm. (not 16 mm. as stated), and identity was further proved by oxidation, when there were produced *as*-dimethylsuccinic acid, small quantities of $\beta\beta$ -dimethylglutaric acid, and the lactone of α -hydroxy- $\beta\beta$ -dimethylglutaric acid. The process of oxidation was that previously described (Trans., 1903, 83, 118).

In order to make certain that the hydrobromide boiling at 82—83° at 20 mm. would not combine with more hydrogen bromide, it was again treated with fuming hydrobromic acid and allowed to stand forty-eight hours. The boiling point of the resulting liquid was unchanged, and a bromine determination gave the same value as after the first treatment with hydrobromic acid.

The fraction 130—132° on redistillation boiled quite constantly at 137° at 25 mm.:

0.1869 gave 0.2628 AgBr. Br = 59.83.

$C_8H_{14}Br_2$ requires Br = 59.26 per cent.

The *dihydrobromide* of 1:1-dimethyl- $\Delta^{2:5}$ -dihydrobenzene, in which the position of the bromine atoms is doubtful, is a faintly yellow, highly refractive liquid, turning pale violet on standing, and possessing an odour of turpentine.

Action of Bromine.—The sketch on page 649 is of an apparatus which has been found to give very good results in the determination of the bromine absorption of unsaturated substances.

Into the flask *A* is placed about 30 c.c. of dry chloroform and an accurately weighed quantity (1—1.5 grams) of the substance to be tested, and the flask stoppered securely with an ordinary cork. The dropping funnel, *C*, is then attached to *B* by the ground-glass joint, *eE*, and into *C* is weighed about 25—30 grams of dry chloroform and 3—4 grams of dry bromine. *C* is then attached to *A* by the ground-

glass joint *dd*, and, when the absorption is complete, is again placed in *B* and re-weighed. Any chloroform solution of bromine remaining in the stem of the funnel is prevented from escaping. Without the use of an apparatus with ground-glass joints, it is impossible to obtain accurate determinations, but the apparatus has been found to give reliable and concordant results.

A solution of dimethyldihydrobenzene (*C* and *R*) in chloroform rapidly decolorised a solution of bromine in the same solvent, and

FIG. 2.

a sharp end-point was noted when one molecule of bromine had been absorbed :

1.0747 absorbed 1.6066 Br. Molecular absorption = 161.4.

C_8H_{12} requires 160 for Br_2 and 320 for Br_4 .

This behaviour of the hydrocarbon was not easy to reconcile with the action of hydrogen bromide in glacial acetic acid solution, where roughly one-half of the dimethyldihydrobenzene absorbed two molecules of hydrogen bromide. It was therefore decided, having proved that bromine does not act on glacial acetic acid sufficiently rapidly to

interfere with the reaction, to carry out the absorption in glacial acetic acid solution. Under these conditions, the bromine was readily absorbed, and a pale violet colour produced, which remained up to a point where the solution suddenly acquired a yellow tint, but this point is not as sharp as when chloroform is used as solvent :

1.4385 absorbed 2.3334 Br. Molecular absorption = 175 (theory = 160).

On continuing the addition of bromine, it was absorbed slowly without the evolution of the slightest trace of hydrogen bromide, and a second end-point noted when the bromine was no longer used up, the process occupying about thirty minutes :

1.4385 absorbed 3.3346 Br. Molecular absorption = 250 ($\text{Br}_4 = 320$).

As soon as this second end-point was reached, solid commenced to separate, and, on standing for a short time, 2.1 grams were obtained, which were purified by crystallisation from light petroleum, and the bromine determined :

0.1095 gave 0.1928 AgBr. Br = 74.92.

$\text{C}_8\text{H}_{12}\text{Br}_4$ requires Br = 74.76 per cent.

2 : 3 : 5 : 6 - *Tetrabromo-1 : 1-dimethylhexahydrobenzene*,

is very soluble in the cold in chloroform or benzene, and crystallises from acetone, ethyl acetate, alcohol, acetic acid, or light petroleum (b. p. 40—60°), the crystals melting without decomposition at 102°.

The authors take this opportunity of thanking Prof. W. J. Pope for the following description of the crystals.

The substance crystallises in square, transparent, colourless plates, possessing a calcite-like lustre, and belonging to the orthorhombic system ; the forms present are $b\{010\}$, $c\{001\}$, and $p\{110\}$. Measurements made on two good crystals show the prism angle to be approximately $110 : 110 = 127^\circ 0'$, whence the axial ratio $a : b = 2.006 : 1$ is calculated. The crystals are soft, and show a perfect cleavage parallel to $b\{010\}$; the acute bisectrix is the axis- b , and the optic plane is $c\{001\}$. The optical axial angle is large, and the double refraction is negative in sign.

The absorption was then repeated in chloroform solution, when again a very sharp end-point was observed, the solution becoming yellow :

1.0641 absorbed 1.5762 Br. Molecular absorption = 160.

On further addition of bromine, the latter was absorbed without evolution of the slightest trace of hydrogen bromide, but so slowly that the process could only be followed by comparing the colour of

the solution with that of a solution of potassium dichromate. At the end of two and a-half hours, the reaction was complete :

1.0641 absorbed 2.3213 Br. Molecular absorption = 235.6.

This result obviously means that dimethyldihydrobenzene (C and R) consists of two isomerides approximately in equal amounts, the $\Delta^{2:4}$ -variety absorbing but 2 atoms of bromine, whereas the $\Delta^{2:5}$ -modification absorbs 4 atoms of bromine. No solid separated from the chloroform solution, but on evaporation of the solvent, during which process no hydrogen bromide was evolved, the residue partly solidified and gave 1.6 grams of tetrabromodimethylhexahydrobenzene, melting at 102°.

An attempt was made to isolate the dibromide from the oil out of which the tetrabromo-compound had separated, by preparing a much larger quantity of material and distilling under reduced pressure. The liquid boiled for the most part at 132—133° at 22 mm., the approximate boiling point of a dibromide, but, although it passed over as a pale yellow oil, it rapidly darkened and gave off hydrogen bromide, and on exposure to air decomposed so quickly that it was quite impossible to carry out an analysis. These properties agree with those of the dibromide of dimethyldihydrobenzene (C and S) previously described (Trans., 1902, **81**, 833).

Oxidation with Potassium Permanganate.—Ten grams of the hydrocarbon were suspended in 300 c.c. of water, kept cool in ice, stirred with a turbine, and a cold 4 per cent. solution of potassium permanganate gradually added. After 700 c.c. of the oxidising agent had been used, the reaction took place so slowly that it was allowed to proceed at atmospheric temperature, and was completed when 45 grams of permanganate had been decolorised. After working up in the usual way, 6 grams of an oily residue, smelling of fatty acids, were obtained, which gradually solidified, and, after spreading on porous plate (P), yielded 2.5 grams of solid. Believing this to be *as*-dimethylsuccinic acid (compare Trans., 1902, **81**, 836), it was heated with acetyl chloride for two hours, the solvent evaporated, during which process 0.1 gram of crystals separated, melting at 180—185°, and crystallising from water in the characteristic slabs of crystals of dimethylmalonic acid melting at 190° with evolution of gas and the unmistakable odour of *isobutyric* acid.

The liquid residue from the crystals was distilled, when at 45 mm. all but a small amount passed over below 140°. This was proved to consist of the anhydride of *as*-dimethylsuccinic acid, by boiling with water and saturating the solution with hydrogen chloride. Needle-shaped crystals separated, melting at 140—141°, nor was this melting point altered on admixture with pure *as*-dimethylsuccinic acid.

The residue of the above distillation (0.5 gram) solidified, and, after crystallisation from water, melted at 189—190° with evolution of gas, and consisted therefore of dimethylmalonic acid.

On extracting the porous plate (*P*) with ether, 2.5 grams of an oil were obtained which showed no signs of solidification on standing. It was therefore further oxidised with potassium permanganate by heating on the water-bath, when 1 gram of *as*-dimethylsuccinic acid was isolated from the product.

Dimethyldihydrobenzene (C and S) was prepared and once more oxidised under exactly the above conditions, without, however, the isolation of a trace of dimethylmalonic acid; 6 grams of the hydrocarbon gave 1.5 grams of dimethylsuccinic acid after oxidation in the cold, and a further 0.8 gram after the second oxidation.

RESEARCH LABORATORY, PHARMACEUTICAL SOCIETY,
17, BLOOMSBURY SQUARE, W.C.