CIII.—*Substituted Dihydrobenzenes. Part III. The So-called 1:1-Dimethyl- $\Delta^{2:5}$ -cyclohexadiene of Harries and Antoni.*

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IN Part II of this work (Trans., 1908, **93**, 637), wherein the properties of 1:1-dimethyl- $\Delta^{2:4}$ -cyclohexadiene and 1:1-dimethyl- $\Delta^{2:5}$ -cyclohexadiene were described, the opinion was expressed that the evidence then forthcoming was insufficient definitely to establish the constitution of the hydrocarbon designated 1:1-dimethyl- $\Delta^{2:5}$ -cyclohexadiene by Harries and Antoni (*Annalen*, 1903, **328**, 88), although showing that the hydrocarbon could not have the structure assigned to it. Further work has now been carried out with the hydrocarbon, and direct evidence is forthcoming that it is a mixture of 1:2-dimethylcyclohexadiene and 1:3-dimethylcyclohexadiene, and very probably does not contain any of the isomeride with the methyl groups attached to the same carbon atom.

The hydrocarbon was prepared according to the directions of Harries and Antoni (*loc. cit.*, p. 109), by reducing 400 grams of the dioxime of dimethyldihydroresorcin * in quantities of 5 grams

* The oxime was obtained in 85 per cent. of the theoretical amount by dissolving 20 grams of dimethyldihydroresorcin in absolute alcohol, adding 28 grams of dry, powdered hydroxylamine hydrochloride, 42 grams of dry, powdered potassium acetate, and allowing to stand for three days. The whole was then heated to the

at one time. The phosphate of the resulting 3:5-diamino-1:1-dimethylcyclohexane, isolated as fine white, silken needles by crystallisation from diluted alcohol, was submitted to the process of dry distillation, when 30 grams of hydrocarbon were obtained, giving numbers on analysis agreeing with those required for a dimethylcyclohexadiene:

0.1793 gave 0.5834 CO₂ and 0.1811 H₂O. C=88.74; H=11.22.

C₈H₁₂ requires C=88.88; H=11.11 per cent.

The non-constant boiling point at once gave indications that the substance was not homogeneous; at the first distillation the largest amount boiled from 134—138°, and after repeated fractionation somewhat lower; but no portion of constant boiling point could be obtained, the hydrocarbon passing over anywhere from 126—136°.

The hydrocarbon gave marked colour reactions, which agreed closely with those given by Harries and Antoni (p. 118) for 1:2- and for 1:3-dimethylcyclohexadienes; the colour with sulphuric acid was yellowish-red, and certainly not raspberry-red.

Attempts to prepare a nitrosyl chloride from the hydrocarbon gave negative results.

Harries and Antoni believed their hydrocarbon to have the double bonds in the 2:5 position, that is to say, that the elimination of ammonia from the cyclic diamine had taken place in one way

only, and this despite the fact that in other cases quoted by them the elimination of ammonia took place in two ways, giving hydrocarbons isomeric by reason of the different positions of the double bonds which they contained. If their hydrocarbon had the above formula, it should readily absorb 4 atoms of bromine, whereas if the double bonds were in the 2:4 position (Thiele linking), it would be expected to only absorb 2 atoms of bromine. This was shown

boiling point of alcohol, filtered, washed with a little hot alcohol, the filtrate evaporated to about 100 c.c., and then diluted to 500 c.c. with water, when the oxime (m. p. after recrystallisation, 175—176°) crystallised out in flattened needles.

In the preparation of the base after steam distillation, the residue was acidified, when a little more than 100 grams of solid were obtained, soluble in potassium hydroxide, re-precipitated by acid, and crystallising from dilute formic acid in stout, transparent needles. These contained nitrogen, but had no definite melting point, and decomposed somewhat violently on heating, so that it was extremely difficult to obtain concordant results on analysis. For these reasons, the material was not further examined.

in Part II of this research to be the case with 1:1-dimethyl- $\Delta^{2:5}$ -cyclohexadiene and 1:1-dimethyl- $\Delta^{2:4}$ -cyclohexadiene respectively.

In order to test the point, a chloroform solution of bromine was added to a solution of the hydrocarbon in dry chloroform, when a pale violet colour was developed, gradually deepening, then becoming green, once again changing to deep violet, which suddenly became pale reddish-brown, and hydrogen bromide was evolved. At this point the molecular absorption was 162. Bromine was then taken up very slowly by the solution, and the absorption could only be followed by comparing the colour with that of a solution of similar tint (see Trans., 1908, **93**, 650). The absorption was finally complete after three hours, but as a considerable amount of hydrogen bromide was evolved in the latter stages, not much reliance is to be placed on the fact that the final molecular absorption was 256.

A similar result was obtained when the reaction was performed in glacial acetic acid solution, the first number being 163 and the final one 265. No solid product was obtained on evaporating either the chloroform or acetic acid solutions.

These experiments prove that the substance does not consist of a single hydrocarbon with the double bonds in the 2:5-position, and therefore capable of absorbing 4 atoms of bromine, but that it is mixed with an isomeride with the double bonds in the Thiele position, capable of absorbing, therefore, only 2 atoms of bromine.

Further, if the hydrocarbon were 1:1-dimethyl- $\Delta^{2:5}$ -cyclohexadiene, then, on treatment with a mixture of nitric and sulphuric acids, it would give the two isomeric trinitro-*o*-xylenes (Trans., 1908, **93**, 634), but it does not; for on nitrating 2 grams as described (*ibid.*, p. 646), 0.2 gram of a nitro-product was obtained, which crystallised from alcohol in glistening needles melting at 181–182°, nor was this melting point altered on mixing with pure trinitro-*m*-xylene (m. p. 182°).

The process of oxidation is usually recognised as one of the chief aids in elucidating the structure of organic substances. Now, the present authors have oxidised with potassium permanganate many hydroaromatic hydrocarbons, alcohols, and ketones containing the *gem*-dimethyl group, and, in all cases, have succeeded in isolating a product which definitely established the presence of this grouping. Thus 1:1-dimethyl- $\Delta^{2:4}$ -cyclohexadiene gives *as*-dimethylsuccinic

acid (Trans., 1908, **93**, 633), and other examples are mentioned in the following references: Trans., 1903, **83**, 110; 1905, **87**, 1488; 1906, **89**, 1556; 1907, **91**, 63.

If, therefore, the hydrocarbon of Harries and Antoni is 1:1-dimethyl- $\Delta^{2:5}$ -cyclohexadiene, it should yield on oxidation with potassium permanganate, dimethylmalonic acid (compare Trans., 1908, **93**, 651):

but Harries and Antoni state (p. 112) that they could not with certainty prove the presence of this acid among the oxidation products of their hydrocarbon with potassium permanganate. The present authors have been equally unsuccessful, for on oxidising 9 grams of the hydrocarbon with potassium permanganate, the only definite product isolated was acetic acid, although evidence was obtained of the presence of a succinic acid and also of traces of phthalic and isophthalic acids. In other words, no single piece of evidence has been obtained which directly establishes the presence of the *gem*-dimethyl group in the hydrocarbon.

When dilute nitric acid is used as an oxidising agent, the result is in some cases the breaking down of the hydrocarbon at the double bonds, as with $\Delta^{1:3}$ -cyclohexadiene (Trans., 1904, **85**, 1423), or the oxidation results in the production of an aromatic carboxylic acid as with cantharene, which gives *o*-toluic and phthalic acids (Piccard, *Ber.*, 1879, **12**, 579), or with 1:3-dimethylcyclohexadiene, which gives toluic and isophthalic acids (Wallach, *Annalen*, 1890, **258**, 329).

Although in certain cases, where concentrated nitric acid or a nitrating mixture has been used, a wandering of a methyl group has been observed when both methyl groups are attached to the same carbon atom (Trans., 1908, **93**, 646), it does not appear that such wanderings have ever been brought about under the influence of dilute nitric acid; but in order to obtain some further evidence on this point, 2 grams of 1:1-dimethyl- $\Delta^{2:4}$ -cyclohexadiene (Trans., 1902, **81**, 821), prepared by the action of sodium in moist ethereal solution on 3:5-dichloro-1:1-dimethyl- $\Delta^{2:4}$ -cyclohexadiene, were oxidised with dilute nitric acid. On evaporation to dryness, 0.8 gram of solid remained, which was proved to consist of a mixture of dimethylmalonic and dimethylsuccinic acids by the method already described (Trans., 1902, **81**, 829), and no evidence was obtained of the production of an aromatic carboxylic acid. In this case, therefore, oxidation takes place at the double bonds, and a methyl group does not wander.

It appeared, therefore, that if it were possible to produce a toluic or phthalic acid from the hydrocarbon of Harries and Antoni by oxidation with diluted nitric acid, direct proof would be established that it does not contain the *gem*-dimethyl group. Moreover, it is

evident from the following passage (p. 101) in the paper by Harries and Antoni that they would have accepted such evidence as showing that in the production of their hydrocarbon a methyl group had wandered: "We have considered the possibility that, as a consequence of the high temperature attained during the dry distillation of the phosphate of 3:5-diamino-1:1-dimethylcyclohexane, our dimethylcyclohexadiene has undergone a change, consisting in the wandering of a methyl group from the 1:1- to the 1:2-position. We have, however, relinquished this opinion. Piccard has shown that cantharene can be easily converted into *o*-toluic and phthalic acids by means of dilute nitric acid, but from our dimethylcyclohexadiene, under similar conditions, no *o*-toluic acid could be obtained."

Yet the true explanation of the matter is that a methyl group does wander in the formation of the hydrocarbon, as proved by the following experiments, where, using as little as 3 grams of the hydrocarbon, appreciable quantities of ortho- and *iso*-phthalic acids have been isolated on oxidation with dilute nitric acid followed by potassium permanganate, as recommended by Wallach (*Annalen*, 1890, **258**, 329).

Three grams of the hydrocarbon were added to 30 c.c. of a mixture of one volume of fuming nitric acid and two volumes of water, when the whole gradually became hot, a reaction set in, and an oil separated. After heating six hours on the water-bath, all the oil had disappeared, and on standing overnight a white solid (0.4 gram) had separated, and a further 0.3 gram was obtained by evaporating the solution. This softened when heated in a capillary tube at 90°, began to melt at 180°, and was not completely melted until 220°, and consisted probably of a mixture of toluic and phthalic acids (compare Wallach, *ibid.*). The solid was suspended in water and oxidised with potassium permanganate by heating on the water-bath, etc. On evaporating the resulting liquid to a small bulk and acidifying, 0.2 gram of solid resulted (Filtrate=A), which was sublimed in two fractions; the first gave the fluorescein reaction and had a very indefinite melting point, shrinking at 180–200° and melting at 250–280°. It evidently consisted of a mixture of phthalic and *isophthalic* acids. The second fraction did not give the fluorescein reaction, did not melt at 300°, and gave the following figures on analysis:

C=57.63; H=3.85.

$C_8H_6O_4$ requires C=57.83; H=3.61 per cent.

These data prove that the substance is either *isophthalic* or *terephthalic* acid; but inasmuch as trinitro-*m*-xylene is obtained on nitrating the hydrocarbon, it would be *isophthalic* acid. The

filtrate A (see above) was extracted ten times with ether, the solution dried, and evaporated, when the residue (0.2 gram) solidified immediately. After crystallisation from hydrochloric acid, it melted at 183—184°, nor was this melting point altered on mixing with pure phthalic acid. Moreover, it gave a marked fluorescein reaction, an anhydride melting at 128—129°, and from this an anilic acid crystallising in glistening, transparent prisms melting at 166—167°. The melting points of the anhydride and the anilic acid were not altered on admixture with specimens of these derivatives prepared from pure phthalic acid. Obviously during dry distillation of the phosphate of 3:5-diamino-1:1-dimethylcyclohexane a methyl group must wander, partly into an ortho- and partly into a meta-position. The wanderings of methyl groups which have so far been noticed by the present authors (Trans., 1904, **85**, 264; 1906, **89**, 875; 1908, **93**, 633) have only taken place into an ortho-position, but the cases are not exactly parallel, for in the above instance the wandering concerns the passage of a saturated hydroaromatic substance into an unsaturated hydroaromatic substance, whereas in the other instances hydroaromatic substances are converted by the change into members of the aromatic series. There is, moreover, another possibility, namely, that instead of only one group wandering, both groups swing into ortho-positions, one to the carbon atom A, and the second to the carbon atom B:

The positions of the methyl groups in the resulting hydrocarbon would then be 1:3, and this process would not necessitate the assumption that a methyl group wanders into a meta-position.

Action of Dehydrating Agents on Methylheptenone.

Having shown that the hydrocarbon of Harries and Antoni consisted of a mixture, containing as one constituent 1:3-dimethylcyclohexadiene, it appeared to be desirable to compare the properties of these two hydrocarbons more closely, particularly regarding their behaviour on oxidation with potassium permanganate.

1:3-Dimethylcyclohexadiene is said to have been obtained pure by the action of dehydrating agents on methylheptenone, and sulphuric acid was first employed, as recommended by Verley (*Bull. Soc. chim.*, 1897, [iii], **17**, 180). One hundred and twenty grams of methylheptenone gave 48 grams of a hydrocarbon boiling not

very constantly at 130—132°, having a decided odour of xylene, and giving the following figures on analysis:

0·1223 gave 0·3960 CO₂ and 0·1304 H₂O. C=88·30; H=11·84.

C₈H₁₂ requires C=88·88; H=11·11 per cent.

C₈H₁₄ „ C=87·27; H=12·73 „

This suggested that the hydrocarbon was a mixture of dimethylcyclohexadiene and dimethylcyclohexene, which would not be altogether surprising, as in such reactions sulphuric acid has been shown to act as a reducing agent (Wagner, *Ber.*, 1894, **27**, 1638). Zinc chloride was next used as recommended by Wallach (*Annalen*, 1890, **258**, 326), but again analysis showed the resulting hydrocarbon (b. p. 131—133°) to be a mixture:

0·1110 gave 0·3600 CO₂ and 0·1162 H₂O. C=88·45; H=11·64.

Finally phosphoric oxide was employed, without, however, producing any appreciable difference in the composition of the hydrocarbon (b. p. 130—133°), as is seen from the following figures:

0·1163 gave 0·3764 CO₂ and 0·1223 H₂O. C=88·26; H=11·68.

On communicating these results to Professor Wallach, he replied that the hydrocarbon obtained by the dehydration of methylheptenone is not homogeneous (compare Wallach, *Terpene und Campher*, p. 351). During the reaction considerable quantities of *m*-xylene are produced, but no hydrogen is liberated, and it is probably used up in reducing the dimethylcyclohexadiene to dimethylcyclohexene. We wish to thank Professor Wallach for his courtesy in supplying us with this information and for allowing us to make this statement. As Professor Wallach is at present working out this problem, we have no intention of continuing on the same lines, and simply place on record a few results of our incompleted experiments.

Oxidation of the Hydrocarbon with Potassium Permanganate in Aqueous Solution.—Seventeen grams of the hydrocarbon were oxidised at atmospheric temperature with a 4 per cent. solution of potassium permanganate solution. The reaction proceeded very slowly, and was not completed until thirty-four hours, facts which are alone sufficient to show that the substance contained something less readily oxidised than a dimethylcyclohexadiene. On completion of the reaction the liquid had a decided odour of xylene, and it was therefore distilled in a current of steam, when, after separating and drying the liquid lighter than water, 2 grams of *m*-xylene were obtained. This was proved by the facts that it did not decolorise a solution of bromine in chloroform, it boiled at 136—139°, and

on treatment with a nitrating mixture gave an almost theoretical yield of pure trinitro-*m*-xylene melting at 182°.

After working up the residue of the steam distillation in the ordinary way, there was obtained 0.7 gram of a solid, which sublimed in colourless, fern-like aggregates of needles. These did not melt at 300°, and on treatment with phosphorus pentachloride, and then pouring into methyl alcohol, gave sheaves of fine silken needles melting at 64–65° (methyl *isophthalate*, m. p. 64–65°), thus proving that the original solid consisted of *isophthalic acid*. On steam-distilling the liquid from which the *isophthalic acid* had separated, 2.7 grams of a volatile fatty acid were obtained, probably acetic acid, and the residue of the distillation yielded, on extraction with ether, 3 grams of an oil, which contained a ketonic acid.

Oxidation of the Hydrocarbon with Potassium Permanganate in Acetone Solution.—Fifteen grams of the hydrocarbon were suspended in a mixture of 500 c.c. acetone and 100 c.c. of water, and powdered potassium permanganate gradually added. The whole was filtered from manganese dioxide, distilled in a current of steam, and after evaporation to a small bulk, extracted ten times with ether (extracted liquid=B), the ethereal solution dried over potassium carbonate, and the ether evaporated, when the residue solidified at once (1.8 grams). It was purified by fractional extraction and crystallisation from light petroleum (b. p. 40–60°), when there was obtained a solid crystallising in transparent, silken needles, melting at 90°:

0.1029 gave 0.2511 CO₂ and 0.1024 H₂O. C=66.55; H=11.05.

C₈H₁₆O₂ requires C=66.66; H=11.11 per cent.

This substance sublimes in transparent needles, does not absorb bromine, and does not give a colour with concentrated sulphuric acid. It is evidently the crystalline glycol mentioned by Wallach (*Terpene und Campher*, p. 351), and is probably also the indifferent crystalline substance mentioned by Harries and Antoni (p. 114), who prepared the so-called 1:3-dimethylcyclohexadiene from methylheptenone, without, however, observing it to be a mixture.

There is produced, in addition to this substance, a second neutral compound, which has a lower melting point, but has not been further investigated.

The liquid B (see above) was acidified and extracted with ether, when 1 gram of an oil was obtained, which contained a ketonic or ketonic acids, because it gave the iodoform reaction, and also a semicarbazone or mixture of semicarbazones, crystallising from dilute alcohol and melting at 129–131°, but not becoming clear until 182°, when gas was evolved.

It would appear, therefore, that the hydrocarbon prepared by

the dehydration of methylheptenone contains considerable quantities of *m*-xylene and dimethylcyclohexene, and probably not more than 30 to 40 per cent. of dimethylcyclohexadiene.

In comparing the properties of this hydrocarbon with a dimethylcyclohexadiene prepared by Harries and Atkinson (*Ber.*, 1902, **35**, 1175), Harries and Antoni say that the former is more easily converted into trinitro-*m*-xylene than the latter. This is not surprising considering that, as now shown, the former contains considerable quantities of *m*-xylene.

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