10. *The Action of Sodium on* o-*Xylylene Dibromide.**

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Sodium reacts with o-xylylene dibromide in boiling dioxan to give a 6% yield of s-*dibenzcyclooctadiene* (I) and much smaller yields of di-o-tolylethane and s-*tribenzcyclododecatriene* (II). In boiling ether no apparent reaction occurs unless a small quantity of ethyl acetate is added, whereupon o-xylene (5%), di-o-tolylethane (6%), the dodecatriene (II), and a product which may be 3 : 4 : 7 : 8-*dibenzoxacyclo*-$\Delta^{3:7}$-*nonadiene* (III) are formed, together with a high yield of an amorphous product having a composition identical with that of (III).

The stereochemistry of the hydrocarbons (I) and (II) is discussed; the structure of (I), which can theoretically exist in two isomeric forms, is established.

When a solution of o-xylylene dibromide in dry dioxan was refluxed in the presence of an excess of " powdered " sodium, a slow but spontaneous reaction occurred, which was complete after 15—20 hours' boiling. From the product there have been isolated s-*dibenz*cyclo*octadiene* (I), m. p. 108·5°, in *ca.* 6% yield, and much smaller quantities of αβ-di-o-tolylethane, $C_6H_4Me \cdot CH_2 \cdot CH_2 \cdot C_6H_4Me$, m. p. 65°, and s-*tribenz*cyclo*dodecatriene* (II), m. p. 184·5°. The structures of (I) and (II) are discussed below.

When, however, a solution of o-xylylene dibromide in ether was boiled with an excess of sodium, no apparent reaction occurred even after many hours' boiling. The addition of a small quantity of ethyl acetate induced a moderately rapid reaction, with the separation of much amorphous organic material. From the solution, however, there have been isolated o-xylene (*ca.* 5%), αβ-di-o-tolylethane (*ca.* 6%), and smaller quantities of
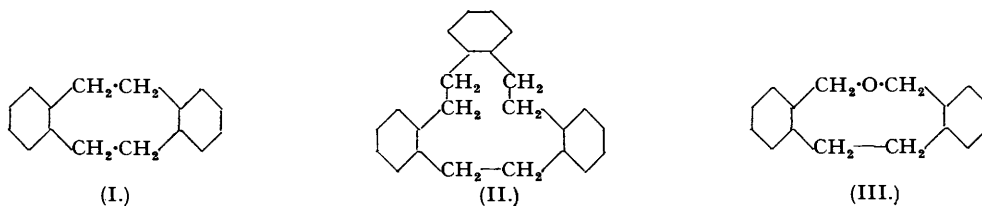
(I.) (II.) (III.)

the cyclo*dodecatriene* (II) and of a compound $C_{16}H_{16}O$, m. p. 97·5—98·5°, whose properties indicate that it is probably 3 : 4 : 7 : 8-*dibenzoxa*cyclo-$\Delta^{3:7}$-*nonadiene* (III). It is noteworthy that, although the yields of the ditolylethane and the hydrocarbon (II) were greater in the ether than in the dioxan experiments, the cyclooctadiene (I) was not isolated from the former reaction product, although there were indications of its presence in minute quantity.

The amorphous product which separated from the ether experiments was soluble in other organic liquids, but it has not been obtained crystalline. It is an extremely stable product, with the same empirical formula as the crystalline ether (III); molecular-weight determinations indicate a formula $(C_{16}H_{16}O)_{8-9}$, but owing to experimental difficulties, the number of $C_{16}H_{16}O$ units in the molecule is still uncertain (p. 29).

The formation of o-xylene and the ditolylethane in the ether experiments can be readily explained : the interaction of the sodium and the ethyl acetate would generate nascent hydrogen, which would in turn reduce small quantities of o-xylylene dibromide and also of the first product of the Wurtz condensation, *viz.*, αβ-di-o-ω-bromotolylethane, $C_6H_4(CH_2Br) \cdot CH_2 \cdot CH_2 \cdot C_6H_4 \cdot CH_2Br$. o-Xylene was not detected in the dioxan experiments where no ethyl acetate was present, and the minute yield of ditolylethane in these experiments may have originated from traces of water unavoidably present. In the ether experiments, the presence of a trace of water in conjunction with the sodium could account for the formation of the cyclic ether (III) from the above dibromotolylethane.

The structure and stereochemistry of the two cyclic hydrocarbons (I) and (II) are of great interest.

The identification of the former as s-*dibenz*cyclo*octadiene* (I) rests on the following evidence. (*a*) Although

a Wurtz reaction to give (I) or similar compounds of higher molecular weight is the most probable condens-ation, it is not impossible that, by a Friedel–Crafts type of reaction in the presence of a reducing agent, a compound such as 2 : 3-dimethyl-9 : 10-dihydroanthracene might be formed. The hydrocarbon (I) has, however, considerable stability towards oxidising agents, whereas 2 : 3-*dimethyl-9 : 10-dihydroanthracene* is very readily oxidised. This property of ready oxidation would also apply to other similar isomerides of even more improbable occurrence. (b) Dr. Edna M. Davidson, of Bedford College (University of London), working in the Cavendish Laboratory of the University of Cambridge, has investigated the hydrocarbon (I) crystallographically. She finds that the molecule has a centre of symmetry. (c) Dr. G. B. B. McI. Sutherland has subjected both the hydrocarbons $C_{16}H_{16}$ (I) and $C_{24}H_{24}$ (II) to infra-red spectroscopic examination, and finds that neither possesses a methyl group. This cumulative evidence proves that the hydrocarbon of formula $C_{16}H_{16}$ must have the structure (I).

It should be noted, however, that s-dibenz*cyclo*octadiene (I) is probably capable of existing in two stereo-isomeric forms. If models are constructed in which the correct intervalency angles are fixed, but in which the methylene carbon atoms can (when the structure permits) twist about their valency bonds, the possible existence of two distinct forms (Figs. 1 and 1A) * becomes apparent. In the first form (Fig. 1), the molecule is rigid, and possesses a plane and a centre of symmetry. In the second form (Fig. 1A) the central ring system is mobile, and a gentle twisting pressure, applied, for instance, to the right-hand benzene ring, causes the latter to fold over until it reaches the extreme position above the former left-hand ring (Fig. 1B). If this pressure is now reversed, the upper ring twists back until the former position (Fig. 1A) is attained, and may then continue twisting until it occupies the same relative position below the left-hand ring as it formerly occupied above, *i.e.*, its structure is now again identical with that shown in Fig. 1B. It is important to note that, whereas the structure acquired at each extreme of this twisting process (Fig. 1B) has two planes of symmetry, neither this nor any intermediate structure (such as Fig. 1A) has a centre of symmetry. It follows that the hydrocarbon isolated must be the form (Fig. 1) having the rigid configuration. A search for the second form of the hydrocarbon (I) in the original reaction product has so far proved unsuccessful. Höhn (Richter–Anschütz, " Chemie der Kohlenstoff-Verbindungen," 1935, II, 2, 392) has suggested for the two known forms of disalicylide " chair ," and " trough " structures, presumably similar in type to those shown in Fig. 1 and Fig. 1A : in the disalicylides, however, the central ring contains two oxygen atoms.

A model of s-tribenz*cyclo*dodecatriene (II), similarly constructed, shows that the central ring system possesses considerable mobility, and a large number of strainless phases is possible : four of these are shown in Figs. 2A—2D. There is one form (Fig. 2A) in which the molecule is planar, but the three central methylene groups are almost certainly too near together for this form to exist. Gentle manipulation of the ring system, how-ever, readily converts this form into that shown in Fig. 2B, in which the top and the right-hand $CH_2 \cdot C_6H_4 \cdot CH_2$ units are parallel, the plane of the latter unit being below that of the top unit ; the left-hand unit is neces-sarily obliquely inclined to these planes, having its top CH_2 group in the plane of the right-hand unit and its right-hand CH_2 group in the plane of the top unit. This form (Fig. 2B) is therefore strictly asymmetric. Further rotational pressure converts this form into that shown in Fig. 2c, in which the plane of the paper is a plane of symmetry. The left-hand $CH_2 \cdot C_6H_4 \cdot CH_2$ unit in this form can be readily folded downwards below the other two units to give the fourth form (Fig. 2D), in the photograph of which, however, the model has been realigned to show its character more clearly. It will be seen that this form possesses three planes of symmetry and also, running vertically through the centre of the molecule, a direct 3-fold axis of symmetry.

It must be emphasised that the model allows ready interconversion of all these forms without rupture of the central ring, or change of the valency angles or interatomic distances. The compound (II) is therefore of particular interest and it is hoped later to determine by *X*-ray analysis the particular form adopted by the molecule in the crystalline state. The minute size of the crystals makes such an analysis difficult. Pre-liminary optical examination, kindly undertaken by Dr. M. Perutz, shows that the crystals are either ortho-rhombic or monoclinic. It is very unlikely, therefore, that the molecules can have trigonal symmetry, and consequently the forms shown in Fig. 2A and Fig. 2D are of improbable occurrence in the crystalline state.

<div align="center">EXPERIMENTAL.</div>

The o-xylylene dibromide was prepared by Perkin's method (J., 1888, **53**, 5) and recrystallised until pure.

Condensation of o-Xylylene Dibromide with Sodium.—(A) *In dioxan.* The dibromide (20 g., 1 mol.), dissolved in pure dioxan (175 c.c., previously refluxed and distilled over sodium), was added to sodium (6·5 g., 3·7 atoms, previously " powdered " under toluene), and the mixture heated on the water-bath (15—20 hours) until the supernatant liquid ceased to give the Beilstein halogen test. Alcohol was first added to the cold mixture to remove unchanged sodium, and then water. The sticky, cream-coloured precipitate was extracted with warm benzene, the extract dried, and the solvent removed by distillation. The residue was worked up by either (a) steam-distillation or (b) extraction with alcohol.

(a) Steam-distillation yielded a colourless solid (0·4—0·6 g., ca. 6%), m. p. 105—107°, which after several crystal-lisations from alcohol furnished s-*dibenzcyclo*octadiene (I), hexagonal plates, m. p. 108·5° (Found : C, 92·4, 92·1 ; H, 7·9, 7·8 ; *M*, by Rast's method in 10% camphor solution, 212, 222. $C_{16}H_{16}$ requires C, 92·3 ; H, 7·7% ; *M*, 208). Con-centration of the mother-liquor from the first recrystallisation yielded a very small amount of αβ-di-o-tolylethane, m. p. 56—58°, which when mixed with an authentic sample, prepared by the method of Moritz and Wolffenstein (*Ber.*, 1899, **32**, 2531) or by that of Carré (*Compt. rend.*, 1909, **148**, 1109 ; *Bull. Soc. chim.*, 1909, **5**, 489), had m. p. 57—59°.

(b) The residue was refluxed for 12 hours with alcohol (500 c.c.), filtered hot, and concentrated (charcoal). The filtrate deposited a colourless solid mixture (this softened at ca. 100° and melted at 177—179°) which was distilled in

* In all the models shown in the photographs, the hydrogen atoms have been omitted for simplicity.

Fig. 1

Fig. 1 A

Fig. 1 B.

Fig 2 A

Fig. 2 B

Fig. 2 C

Fig 2 D
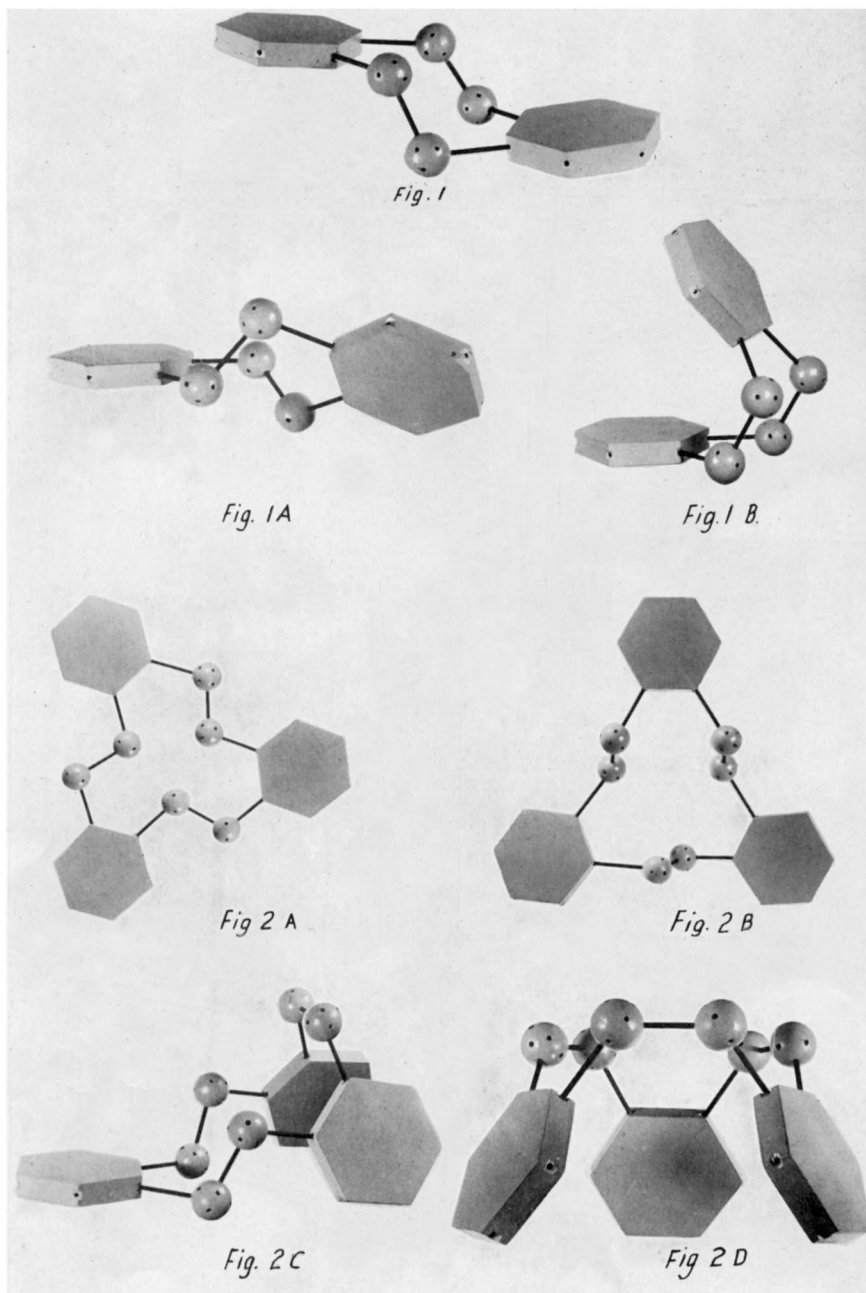
steam. The distillate deposited the compound (I), m. p. 107—108°, identical with that isolated in (*a*) above. The non-volatile residue, when recrystallised from alcohol, gave impure s-*tribenz*cyclo*dodecatriene* (II), which softened at *ca.* 160° and melted at 177—179° [Found : C, 92·2; H, 7·9; *M* (Rast) 305, 322. $C_{24}H_{24}$ requires C, 92·3; H, 7·7%; *M*, 312]. The yield of (II) was small and complete purification could not be achieved; the higher yield obtained in ether (see below) enabled the pure hydrocarbon to be isolated.

s-Dibenz*cyclo*octadiene (I) is very stable towards oxidising agents; it is unaffected by a boiling acetone solution of potassium permanganate, and is scarcely attacked by a cold chromic acid–acetic acid mixture (cf. 2 : 3-dimethyl-9 : 10-dihydroanthracene below). It is not attacked under the usual Kuhn–Roth conditions for estimation of *C*-methyl groups (*Z. angew. Chem.*, 1931, **44**, 847; *Ber.*, 1933, **66**, 1274).

(B) *In ether.* Fine sodium wire (40 g., 4·4 atoms) was added to a solution of the dibromide (105·6 g., 1 mol.) in dry ether (600 c.c.), and the mixture refluxed. Ethyl acetate (2 c.c.) was added to the boiling mixture, and the refluxing was then continued for 24 hours, further additions of ethyl acetate (each of 2 c.c.) being made at the end of the 5th, 15th, and 20th hour of heating; even after 5 hours' heating much of the sodium had disintegrated and a considerable amount of amorphous solid had separated, and this change appeared to be complete after the 24 hours' heating. The liquid was now filtered, and the cream-coloured amorphous residue washed on the filter with ether. The united filtrate and washings were distilled. After the ether had thus been removed, the liquid residue was separated into the following four fractions, the last three being selected arbitrarily, as no sharp separation at this stage appeared possible : (i) b. p 38—48°/15 mm., 2 g.; (ii) b. p. 100—140°/0·05 mm., 3 g.; (iii) b. p. 140—210°/0·05 mm., 4 g.; (iv) b. p. 210—260°/0·05 mm., 2 g.

Fraction (i), a clear mobile liquid, on refractionation gave *o*-xylene, b. p. 141—143° (Found : C, 90·25; H, 9·8. Calc. for C_8H_{10} : C, 90·5; H, 9·5%); 5%.

Fraction (ii) readily crystallised when set aside. On refractionation, the main bulk distilled at 110—120°/0·03 mm., and again solidified. Recrystallisation from alcohol furnished *αβ*-di-*o*-tolylethane, m. p. 65—66°, alone and when mixed with an authentic sample (Found : C, 91·6; H, 8·4; *M*, ebullioscopic in 1·47% benzene solution, 210; in 0·88% acetone solution, 201. Calc. for $C_{16}H_{18}$: C, 91·4; H, 8·6%; *M*, 210); 2·5 g., 6%.

Fraction (iii), a thick viscous oil, could not be obtained crystalline and was consequently redistilled, the following fractions being arbitrarily selected : (iii*a*) b. p. 140—143°/0·03 mm.; (iii*b*) b. p. 148—150°/0·01 mm.; (iii*c*) b. p. 150—175°/0·03 mm.; (iii*d*) b. p. 175—210°/0·03 mm. Fractions (iii*a*) and (iii*c*) were pale yellow, viscous liquids which did not crystallise even when set aside for many months, or when subjected to various treatments. Fraction (iii*b*), a thick viscous liquid, also remained liquid for many months. Ultimately, however, it was mixed with a small volume of alcohol and seeded with the *cyclo*octadiene (I), whereupon crystallisation rapidly occurred. The colourless crystals so obtained were bromine-free, and when twice recrystallised from alcohol furnished 3 : 4 : 7 : 8-*dibenzoxacyclo*-Δ³ ⁷-*non*-*adiene* (III), m. p. 97·5—98·5° (Found : C, 85·7; H, 7·2; *M*, ebullioscopic in 0·53% benzene solution, 225; in 1·13% solution, 225. $C_{16}H_{16}O$ requires C, 85·7; H, 7·2%; *M*, 224). A mixture of this compound with the *cyclo*octadiene (I) of m. p. 108·5° had m. p. 75—104°. The structure (III) assigned to this compound was suggested by the facts that (*a*) the compound was recovered unchanged after 30 minutes' boiling in acetic anhydride solution, and after 20 minutes' boiling in an acetic acid–phenylhydrazine mixture, (*b*) its alcoholic solution gave no coloration with ferric chloride. Fraction (iii*d*), a brown viscous liquid, slowly crystallised when set aside. Vigorous stirring with a small amount of alcohol and petrol gave a clear separation of colourless crystals, which when collected and recrystallised from alcohol, gave s-tribenz*cyclo*dodecatriene (II), m. p. 184·5° (Found : C, 92·3; H, 7·9%; *M*, ebullioscopic in 1·53% benzene solution, 321; in 1·00% acetone solution, 295).

Fraction (iv) also crystallised when set aside. When treated precisely as (iii*d*) above, it furnished a further crop of the *cyclo*dodecatriene (II), m. p. 184·5° (Found : C, 91·95; H, 7·8%).

The original condensation in ether was repeated, but the residue obtained after the evaporation of the ether from the united filtrate and washings was now distilled in steam. The following separated in turn from the distillate; (i) *o*-xylene; (ii) colourless crystals, m. p. 45—55°, 2·5 g.; (iii) a very small quantity of an oil which partly crystallised. Alcoholic recrystallisation of (ii) gave crystals, m. p. 57—59°, unaffected by two more recrystallisations, or by admixture with authentic *αβ*-di-*o*-tolylethane of m. p. 66·5°; concentration of the first mother-liquor gave a further small crop, m. p. 63—65°, similarly unaffected.

Fraction (iii) when triturated with alcohol gave colourless crystals, m. p. 57—59°, also unaffected by admixture with the ditolylethane. It is clear from these results that the crystalline product in the aqueous distillate must have been the ditolylethane containing a trace of some impurity, presumably the *cyclo*octadiene (I), which could not be removed by alcoholic crystallisation.

The cream-coloured amorphous powder which separated during the original condensation in ether clearly represented the main product of the reaction. After it had been washed with ether, and traces of unchanged sodium removed by hand, the powder was thoroughly extracted with cold water and dried : the residue (20 g.) was now bromine-free. This product had no definite m. p.; on being heated, it slowly became viscous above 50° and ultimately formed a mobile liquid. It was freely soluble in cold benzene, toluene, xylene, chloroform, and ethylene dibromide, and almost insoluble in cold alcohol, acetone, ethyl acetate, and ether. All attempts to crystallise this compound failed : contact with organic solvents in which it was not freely soluble usually gave either a sticky semi-solid mass or a viscous suspension. In an attempted purification, two samples, obtained in different preparations, were thoroughly washed with cold alcohol and then dried in a vacuum over phosphoric anhydride. A third sample was mixed with acetone and set aside for several days : it became sticky on immediate contact with the acetone but later resolidified, and was then collected, washed with alcohol, and dried as before. The three samples were analysed [Found : C, 85·4, 85·8, 85·7; H, 7·3, 7·4, 7·1; *M*, determined with the first sample ebullioscopically in 2·10% benzene solution, 1830; in 1·99% solution, 1870; in 2·91% solution, 1860; cryoscopically in 1·22% ethylene dibromide solution, 2010. $(C_{16}H_{16}O)_8$ requires C, 85·7; H, 7·2%; *M*, 1792. $(C_{16}H_{16}O)_9$ requires *M*, 2016]. The above data indicate that the product is probably homogeneous because the very small temperature differences involved in the molecular-weight determinations do not distinguish decisively between the above two alternative values.

This product was recovered apparently unchanged after it had been (*a*) precipitated from benzene solution by addition of alcohol, collected, and washed in turn with alcohol and acetone, (*b*) boiled with a mixture of constant b. p. hydriodic acid and acetic anhydride for 5 hours, (*c*) boiled for several hours with either dilute hydrochloric acid or 10% aqueous sodium hydroxide. When heated at 14 mm. pressure, it melted readily, but even on strong heating it furnished only a very small amount of a viscous distillate which could not be obtained crystalline.

The following hydrocarbons were prepared for direct comparison with (I) before the structure of the latter had been determined by other means.

2 : 3-*Dimethyl*-9 : 10-*dihydroanthracene.* 2 : 3-Dimethylanthracene (1 g.; Elbs and Eurich, *J. pr. Chem.*, 1890, **41**, 5; Fairbourne, *J.*, 1921, **119**, 1573) was refluxed in alcohol (30 c.c.), and 2% sodium amalgam added occasionally in small portions until a test portion of the solution gave no orange coloration when added to a benzene solution of picric acid (12 hours); during this period, a few drops of acetic acid were added at hourly intervals. The solution was

then poured into water, and the precipitated 2 : 3-*dimethyl*-9 : 10-*dihydroanthracene* collected and recrystallised from alcohol; plates, m. p. 122° (Found : C, 92·4; H, 7·8. $C_{16}H_{16}$ requires C, 92·3; H, 7·7%). This compound, unlike (I), rapidly reduces a boiling acetone solution of potassium permanganate, and a cold chromic acid–acetic acid mixture.

2 : 3′ : 4′-*Trimethyldiphenylmethane*. Anhydrous aluminium chloride (10 g.) was slowly added to a mixture of *o*-xylene (20 g.) and *o*-toluoyl chloride, the latter having been prepared from *o*-toluic acid (10 g.) and thionyl chloride (25 c.c.). When the vigorous initial reaction had subsided, the mixture was heated on a water-bath for 6 hours, and then poured into water and extracted with ether. Distillation of the extract gave 2 : 3′ : 4′-*trimethylbenzophenone*, b. p. 192—197°/15 mm., which readily solidified (11 g.) and after draining and repeated crystallisation from petrol (b. p. 40—60°) was ultimately obtained as colourless crystals, m. p. 55—58° (Found : C, 85·1; H, 7·5. $C_{16}H_{16}O$ requires C, 85·7; H, 7·2%). A solution of this ketone (5 g.) in toluene (10 c.c.) was refluxed for 24 hours with amalgamated zinc (10 g.), concentrated hydrochloric acid (8 c.c.), and water (17·5 c.c.), a further addition of the acid (5 c.c.) being made every 6 hours. Extraction with ether, followed by distillation, gave 2 : 3′ : 4′-*trimethyldiphenylmethane* as a colourless oil (4 g.), b. p. 173°/21 mm. (Found : C, 91·4; H, 8·6. $C_{16}H_{18}$ requires C, 91·4; H, 8·6%). This compound was slowly oxidised by a boiling acetone solution of potassium permanganate and by a cold chromic acid–acetic acid mixture.

Dr. Davidson reports on the hydrocarbon (I) as follows :

"The specimen consisted of small colourless highly birefringent crystals, in the form of thick irregular tablets, having the sign of the birefringent positive and the dominant face of the tablet (100).

"The unit cell dimensions and the space-group were determined by single-crystal *X*-ray oscillation and Weissenberg photographs, and gave $a = 6·80$ A., $b = 6·84$ A., $c = 13·63$ A., $\beta = 100°$; the space-group was monoclinic $P2_1/c$.

"The density determined by flotation in aqueous acetone was 0·986 g./c.c., giving the number of molecules in the unit cell as two. Since there are four general positions in the space group $P2_1/c$, it follows that the molecules cannot lie in general positions, but must lie in special positions, *i.e.*, they must lie on the centres of symmetry in the unit cell, and therefore the molecules themselves must possess centres of symmetry. On cooling in liquid air, the crystals showed no pyroelectric effect, which also indicates the absence of a polar structure."

Dr. M. Perutz reports on the hydrocarbon (II) as follows :

"The compound forms lath-shaped needles with straight extinction parallel to the needle axis and strong negative birefringence. There are only two faces parallel to the needle axis, and the angle between them is 87°; this angle excludes the trigonal and hexagonal systems and indicates that the crystals are either orthorhombic or monoclinic. In these circumstances it is unlikely that the molecule itself has trigonal symmetry, and therefore the forms shown in Fig. 2A and 2D are unlikely to occur in the crystalline state. The form shown in Fig. 2A is improbable for structural reasons (because of the close approach of the central methylene groups), while that shown in Fig. 2D would hardly give rise to needle-shaped crystals with such strong negative birefringence."