

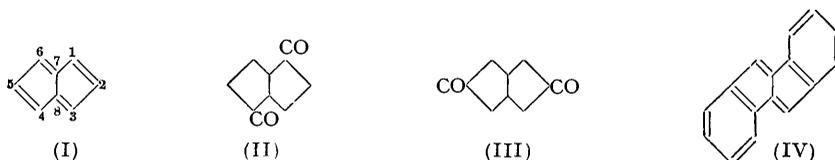
421. Fused Carbon Rings. Part XX.* Experiments directed towards the Synthesis of Simple Pentalenes.

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Experiments have been made on the preparation of pentalene (I) and various simple derivatives from *cis*-octahydro-1:4-diketopentalene (II), the preparation of which has been improved. 2:5-Dibenzylideneoctahydro-1:4-diketopentalene (X) showed no tendency to isomerise to dibenzylidihydroxypentalene. Dibromo-octahydrodiketopentalene could not be dehydrobrominated to dihydroxypentalene. Octahydrodiketopentalene was converted by a double Grignard reaction into 3:6:7:8-tetrahydro-1:4-dimethylpentalene (XV), which has an unconjugated arrangement of double bonds. Various attempts to introduce two more double bonds into (XV) failed; these included disproportionation, dehydrogenation, and transfer dehydrogenation over catalysts. Negative results were also obtained from the route, (II) \longrightarrow octahydro-1:4-dihydroxypentalene \longrightarrow tetrahydro-pentalene \longrightarrow pentalene.

INTEREST has recently increased in pentalene (I), the unknown counterpart of naphthalene, composed of two five-membered rings. In 1936, Barrett and Linstead reported (*J.*, 1936, 611) that pentalene was not formed by treatment of *cis*-bicyclo[3:3:0]octane (*cis*-octahydropentalene) under conventional dehydrogenating conditions. Neither could a benzylidenebicyclooctane be converted into benzylpentalene. The pentalene system thus showed a reluctance of formation in comparison with naphthalene. Since that time there has been a great expansion of "non-benzenoid aromatic" chemistry, particularly in the azulene and tropolone fields (see, *e.g.*, Wilson Baker, *J.*, 1945, 258; J. W. Cook and Loudon, *Quart. Reviews*, 1951, 5, 99, for reviews).

Theoretical arguments have been advanced (Craig and Maccoll, *J.*, 1949, 964; Brown, *Trans. Faraday Soc.*, 1949, 45, 296; 1950, 46, 146) which predict a rather high resonance energy and a reasonable stability for pentalene.†



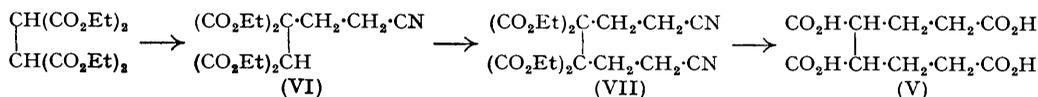
The present paper, and that which follows it, describe new attacks on the experimental problem. Three routes have been explored for the preparation of pentalene and its derivatives. The first started with octahydro-1:4-diketopentalene (II) and the second from its 2:5-diketo-isomeride (III). The third, the only one to be fully successful, was aimed at the preparation of 1:2-4:5-dibenzopentalene (IV). This is described in the following paper. Of the two diketone routes, that from the 1:4-isomeride forms the subject of the present paper. The necessary intermediates for the 2:5-diketone proved far harder to prepare in quantity. The experiments in this direction are described separately (Blood, Cartwright, and Linstead, *J.*, 1952, p. 2268).

Octahydro-1:4-diketopentalene has been synthesised by Ruzicka, de Almeida, and Brack (*Helv. Chim. Acta*, 1934, 17, 183) from hexane-1:3:4:6-tetracarboxylic acid (V). Before examining their process, we studied three possible alternatives. Silberrad (*J.*, 1904, 85, 611) obtained (V) in very small yield from the product of the reaction of β -iodopropionic ester with the sodio-compound of ethanetetracarboxylic ester. The difficulty in this process lies in the introduction of the second propionic residue and we have not been

* Part XIX, *J.*, 1940, 727.

† But see Part XXI, p. 2266, footnote.

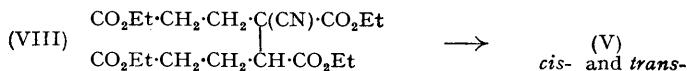
able to improve on Silberrad's results. However, a possible new reagent for the conversion of ethanetetra-carboxylic ester into the desired hexanetetra-carboxylic acid was available in acrylonitrile, the route being :



In practice, ethanetetra-carboxylic ester reacted smoothly with only one mole of acrylonitrile in the presence of benzyltrimethylammonium hydroxide to give a compound, $\text{C}_{17}\text{H}_{25}\text{O}_8\text{N}$, the most obvious formulation for which is (VI). Attempts to obtain the further condensation product (VII) were fruitless. As Bruson has shown ("Organic Reactions," Vol. V, p. 79) that acrylonitrile usually reacts with every carbon atom which holds an active hydrogen, the formation of (VI) is unexpected; it is possible that the substance may have an isomeric, perhaps carbocyclic, structure.

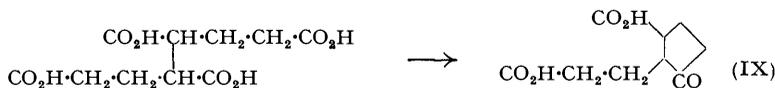
The addition of acrylonitrile to acetosuccinic ester was also examined as a route to (V). This failed, because with the use of a quaternary hydroxide as catalyst no addition occurred, whilst sodium ethoxide led to the production of α -acetyl- β -carbethoxy- γ -methyl- Δ^{β} -butenolide identical with that prepared by Knorr's method (*Ber.*, 1889, **22**, 158.) Finally, the elimination of halogen between two molecules of α -bromoglutaric ester was examined. The use of silver powder (cf. Hudson and Robinson, *J.*, 1942, 691) on this gave largely a low-boiling mixture containing ethyl glutaconate together with a small yield of tetra-ester which was hydrolysed to *trans*-hexane-1 : 3 : 4 : 6-tetra-carboxylic acid.

In view of these unpromising results we returned to the method of Ruzicka, de Almeida, and Brack (*loc. cit.*), which consists in the condensation of α -bromoglutaric ester with sodio- α -cyanoglutaric ester to 3-cyano-hexane-1 : 3 : 4 : 6-tetra-carboxylic ester (VIII).



The formation of (VIII) and its intermediates has been considerably improved in detail by methods described in the Experimental section. An attempt was made to cause acrylonitrile to react with one mole of cyanoacetic ester and thus obtain carbethoxy-glutaronitrile which could have been used in the place of cyanoglutaric ester in the Ruzicka synthesis. However, even in the presence of a large excess of cyanoacetic ester, two mols. of acrylonitrile reacted with the production of ethyl 1 : 3 : 5-tricyanopentane-3-carboxylate.

Ruzicka *et al.* found that the cyanotetra-ester (VIII) on acid hydrolysis gave a mixture of a "*trans*"-hexane-1 : 3 : 4 : 6-tetra-carboxylic acid, m. p. 202—203°, and a "*cis*"-isomeride, isolated as a mixture with its anhydride. In our hands the *trans*-acid (to retain Ruzicka's nomenclature—the configurations are not known with certainty) melted at 216—217° and the *cis*-acid was obtained in a homogeneous form, m. p. 167°. The lower-melting acid is readily converted into the *trans*-isomeride by boiling hydrochloric acid. Both isomerides give crystalline tetramethyl esters, m. p.s 60° (*cis*) and 73° (*trans*). The *cis*- is inverted to the *trans*-ester by boiling methanolic sodium methoxide (cf. Hüchel and Goth, *Ber.*, 1925, **58**, 447; Linstead and Doering, *J. Amer. Chem. Soc.*, 1942, **64**, 1992). No anhydride was obtained by the action of acetyl chloride, which inverted the *cis*- to the *trans*-acid.



A number of methods were examined for the conversion of the hexane-1 : 3 : 4 : 6-tetra-carboxylic acids or esters into bicyclooctane derivatives. When the *cis*-acid was heated with a little baryta it decomposed smoothly into β -2-carboxy-5-ketocyclopentylpropionic acid (IX). The *trans*-acid gave the same product, but at a rather higher temperature.

Various attempts to close the second ring at higher temperatures were unsuccessful. This was a little surprising as both stereoisomeric forms of the deoxo-compound corresponding to (IX) yield octahydro-1-ketopentalene without difficulty (A. H. Cook and Linstead, *J.*, 1934, 946). The dimethyl ester of (IX) gave complex products under the Dieckmann conditions. In spite of this the solid tetramethyl esters of both the acids (V) gave the same crystalline octahydrodiketopentalenedicarboxylic ester by a double Dieckmann condensation. The yield of bicyclic material (60%) was the same from both the *cis*- and the *trans*-ester, and better than that obtained by the previous workers using the ethyl esters. On hydrolysis, the diketo-diester gave octahydro-1:4-diketopentalene (II), m. p. 46°, identical with that reported by Ruzicka *et al.*

The structure of the diketone (II) has been clearly shown by Ruzicka *et al.*; we can add the following supporting evidence: (a) There is no ultra-violet absorption band in the spectrum above 200 m μ ; (b) no hydrogenation occurs over palladised charcoal; (c) there is no colour with ferric chloride. Hence there is no tendency for the formation of a conjugated di-enol. Cook and Linstead (*loc. cit.*) have shown that the octahydro-1-ketopentalene made through the Dieckmann procedure from both *cis*- and *trans*- β -2-carboxycyclopentylpropionic esters has the stable *cis*-locking of the rings. There is no reason to suppose that the present diketone will not have the same steric arrangement. It follows that all the hydropentalene derivatives described in the present paper (with the obvious exception of those with bridgehead double bonds) will have the *cis*-configuration.

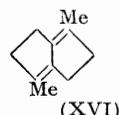
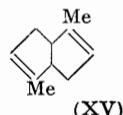
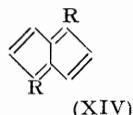
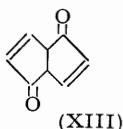
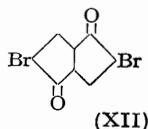
As observed by Ruzicka *et al.*, the diketone gives a dibenzylidene derivative. The light absorption of this compound (λ_{max} , 320 m μ ; ϵ 43,000) is more intense and at longer wave-length than might have been expected for the straight-forward structure (X).



Nevertheless, the other properties of the substance agree with formula (X) rather than with a more conjugated dienolic structure such as (XI). Thus, the light absorption is independent of the solvent used; no reaction occurs with phenyl isocyanate; two ethylenic double bonds are indicated by catalytic hydrogenation, and two ketone groups by the formation of a dioxime. The dibenzylidene compound thus shows no apparent tendency to isomerise, for example into a dibenzylidihydroxypentalene.

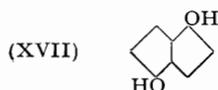
Experiments on the Formation of Pentalenes from the Diketone (II).—(a) *Approaches to dihydroxypentalene.* Octahydro-1:4-diketopentalene (II) reacted smoothly at room temperature with bromine in acetic acid to yield a dibromo-derivative, presumably (XII). Dehydrobromination of this to the corresponding unsaturated diketone (XIII) was examined in some detail, because this product would have been the keto-form of 1:4-dihydroxypentalene (XIV; R = OH). The dibromo-ketone melted with decomposition at 144° but was stable below that temperature: its solution in boiling xylene did not evolve hydrogen bromide and it could be sublimed without decomposition at 130–140°/0.2 mm. Thermal decomposition at 145°/760 mm. yielded hydrogen bromide and an unsaturated product which at once polymerised to a dark non-volatile material. Bromide ion was immediately liberated by the action of dilute alkali on the bromo-ketone and by its interaction with triethylamine in dry organic solvents. Again, only polymeric products could be recovered from the dehydrobrominated material and these failed to yield semi-carbazones. Somewhat more promising results were obtained by reaction of the bromo-ketone with silver acetate, as the dehydrobrominated material was then partly volatile in a high vacuum. The oil so obtained was unsaturated and ketonic but the yield was very poor and the product was so unstable that further experiments on it were abandoned. It may well have contained the desired unsaturated diketone (XIII). Corresponding experiments using *N*-bromosuccinimide as the brominating agent led to a ready reaction, but in this case the dibromo-ketone could not be isolated. It lost hydrogen bromide spontaneously leaving a dark viscous mass.

(b) *Tetrahydrodimethylpentalene*. Reaction of octahydro-1 : 4-diketopentalene (II) with Grignard reagents yielded ditertiary alcohols which were easily dehydrated to the corresponding substituted tetrahydropentalenes. Preliminary experiments with methylmagnesium iodide and phenylmagnesium bromide showed that the former was the preferable reagent; it yielded 3 : 6 : 7 : 8-tetrahydro-1 : 4-dimethylpentalene (XV). The structure of this was shown by analysis and by catalytic hydrogenation. The two double bonds were placed in the unconjugated (1 : 4) position rather than between the 1—7 and 4—8 carbon atoms because there was no ultra-violet light absorption at above 200 $m\mu$ and no exaltation of the molecular refractivity. The non-formation of the conjugated $\Delta^{1(7):4(8)}$ -hydrocarbon is understandable, as the bridgehead double bonds would strain the molecule and this might well outweigh the stabilisation by conjugation.



A study was next made of the possible disproportionation and dehydrogenation of tetrahydro-1 : 4-dimethylpentalene to 1 : 4-dimethylpentalene (XIV; R = Me), control experiments being carried out on tetralin and *cyclohexene*. These are summarised below in the order of increasing severity of the conditions.

(i) *cyclohexene* disproportionates smoothly into benzene and *cyclohexane* over palladium black in boiling tetrahydrofuran (Linstead, Braude, and Mitchell, unpublished). Tetrahydrodimethylpentalene was unchanged under the same conditions. (ii) Tetralin transfers its four surplus hydrogen atoms to *p*-nitrotoluene over palladium (Linstead, Braude, and Wooldridge, unpublished). This reaction is appreciable in boiling anisole (154°) and fast in boiling decalin (186°), *p*-toluidine being produced. No detectable amount of *p*-toluidine was formed in either solvent when tetrahydrodimethylpentalene was tried as hydrogen donor. (iii) No measurable amount of hydrogen was evolved when tetrahydrodimethylpentalene was boiled over palladised charcoal under atmospheric pressure (160°) in a stream of carbon dioxide; the diene was recovered unchanged. The general technique of Linstead, Millidge, Thomas, and Walpole (*J.*, 1937, 1146) was used and it was shown that boiling tetralin was readily dehydrogenated over the same catalyst. (iv) Tetrahydrodimethylpentalene was recovered unchanged when it was passed in a stream of nitrogen over palladised charcoal at 350°. Tetralin yielded naphthalene under the same conditions.



(c) *Tetrahydropentalene*. Octahydro-1 : 4-diketopentalene readily took up 2 mols. of hydrogen over Raney nickel. The dihydroxy-compound (XVII) was isolated as a non-crystalline glass and was presumably a mixture of stereoisomerides. A similar product was obtained by means of lithium aluminium hydride. It yielded an amorphous mixture of ditoluene-*p*-sulphonyl derivatives, only one stereoisomeride being obtained crystalline by an indirect method (see Experimental). Reaction of the crude toluene-*p*-sulphonyl derivative with aqueous alkali yielded a steam-volatile oil which was largely composed of tetrahydropentalene (XVIII or isomeride). The material distilled at room temperature under 0.2 mm. but was not analytically pure, and refractionation over sodium led to much decomposition. Its general properties were those of a rather unstable diene and it showed a distinct band at 242 $m\mu$. From this it is concluded that it contained some of the strained conjugated $\Delta^{1(7):4(8)}$ diene (XVIII). An attempt was made to convert the diene into pentalene by bromination (at the 2 and 5 carbon atoms) with *N*-bromosuccinimide followed by Hofmann degradation. Distillation of the bis-quaternary hydroxide obtained in this series of reactions gave a tar and no volatile hydrocarbon.

These results indicate that it is difficult (or perhaps impossible) to prepare simple pentalenes under conditions which permit of their continued existence. The significance of this is discussed in the next paper.

EXPERIMENTAL

Miscellaneous Attempts to synthesise Hexane-1 : 3 : 4 : 6-tetracarboxylic Acid.—(a) A solution of tetraethyl ethanetetra-carboxylate (10 g.) in dioxan (25 ml.) was treated successively with 2 ml. of "Triton B" (30% w/w benzyltrimethylammonium hydroxide in water) and acrylonitrile (5 ml.). The mixture was warmed to 55–60° and shaken at intervals. After 5 hours, the mixture was acidified, the solvent removed under reduced pressure, and the product isolated by means of ether. Vacuum-distillation yielded 9 g. (77%) of tetraethyl 4-cyanobutane-1 : 1 : 2 : 2-tetracarboxylate (VI), b. p. 165–170°/0.01 mm., n_D^{20} 1.4531 (Found : C, 55.1; H, 6.8; N, 4.1. $C_{17}H_{25}O_8N$ requires C, 55.0; H, 6.8; N, 3.8%). The compound was recovered unchanged after 4 hours' heating at 100° with more acrylonitrile and catalyst.

(b) Diethyl diacetosuccinate was warmed with acrylonitrile (2 mols.) and sodium ethoxide in a similar manner to the above. The crystalline product was identified as α -acetyl- β -carbethoxy- γ -methyl- Δ^{β} -butenolide by m. p. (106°) and mixed m. p. "Triton B" was ineffective as catalyst.

(c) A mixture of diethyl α -bromoglutarate (50 g.) and silver powder (25 g.) was stirred vigorously at 150–160° for 3 hours. The cold product was filtered and the solid washed with ether. The combined filtrates, freed from ether and distilled, yielded a mixture containing diethyl glutaconate (10 g.), unchanged bromoglutaric ester (19 g.), and 8 g. of a fraction, b. p. 170–200°/0.15 mm. Redistillation followed by acid hydrolysis gave a small quantity of *trans*-hexane-1 : 3 : 4 : 6-tetracarboxylic acid, m. p. 214–216°.

Octahydro-1 : 4-diketopentalene.—Condensation of diethyl α -cyanoglutarate and diethyl α -bromoglutarate. Diethyl α -cyanoglutarate (230 g.; Koelsch, *J. Amer. Chem. Soc.*, 1943, **65**, 2458) was added to a solution of sodium (26 g.) in dry ethanol (600 ml.); the resulting solution of sodio-derivative was evaporated in a vacuum, leaving a yellow-brown syrup. Diethyl α -bromoglutarate (314 g.; Schwenk and Papa, *ibid.*, 1949, **70**, 3626) was added to the residue, and the mixture was warmed until it became homogeneous. Sodium bromide soon separated; the suspension was heated on the steam-bath for a further 3 hours. The mixture was diluted with water, the liquid was made just acid with sulphuric acid, and the oil taken up in ether. The ethereal solution was washed with water, dried ($CaCl_2$), and distilled. The yield of tetraethyl 3-cyano-hexane-1 : 3 : 4 : 6-tetracarboxylate was 74% (320 g.), and the b. p. 205–210°/0.05 mm.

cis- and trans-Hexane-1 : 3 : 4 : 6-tetracarboxylic acids. Tetraethyl 3-cyano-hexane-1 : 3 : 4 : 6-tetracarboxylate (320 g.) was hydrolysed by boiling it under reflux with hydrochloric acid (600 ml. of *d* 1.18 and 350 ml. of water) for about 18 hours (Ruzicka *et al.*, *loc. cit.*). The solution obtained was concentrated to a small bulk, and the solid which separated was crystallised from water to give *trans*-hexane-1 : 3 : 4 : 6-tetracarboxylic acid, m. p. 216–217° (Found : C, 46.1; H, 5.4%; equiv., 67.4. $C_{10}H_{14}O_8$ requires C, 46.15; H, 5.4%; equiv., 65.5). The combined mother-liquors were continuously extracted with ether, and the extract was crystallised from acetic acid-chloroform, giving the *cis*-acid, m. p. 167° (Found : C, 46.0; H, 5.6%; equiv., 68.6). The total yield was 48% (40 g. of *trans*- and 60 g. of *cis*-acid).

The *cis*-acid (0.3 g.) was boiled under reflux with hydrochloric acid (10 ml. of *d* 1.18 and 10 ml. of water) for 24 hours. The solution was evaporated to dryness, and the residue crystallised from water, yielding the *trans*-acid, m. p. and mixed m. p. 216° (50%, 0.15 g.).

The *trans*-acid (40 g.), methanol (90 ml.), benzene (225 ml.), and concentrated sulphuric acid (30 ml.) were heated under reflux on the steam-bath for 24 hours. The mixture was diluted with water, the aqueous layer extracted with ether, and the extract added to the benzene solution. The combined solution was washed with water, dried ($CaCl_2$), and evaporated. The solid ester produced upon scratching of the residual oil was crystallised from light petroleum (b. p. 60–80°), giving *trans*-tetramethyl hexane-1 : 3 : 4 : 6-tetracarboxylate, m. p. 73° (91%, 44 g.) (Found : C, 52.9; H, 6.9. $C_{14}H_{22}O_8$ requires C, 52.8; H, 7.0%). The *cis*-ester, m. p. 60°, was obtained in identical yield in the same way (Found : C, 52.5; H, 7.0%).

cis-Octahydro-1 : 4-diketopentalene (cf. Ruzicka *et al.*, *loc. cit.*).—A solution of the foregoing *cis*-tetramethyl ester (65 g.) in warm benzene (75 ml.) was added to molecular sodium (13.5 g.) covered with benzene (25 ml.). Dry methanol (0.5 ml.) was added, and the mixture was warmed under reflux until the sodium began to dissolve vigorously; cooling was sometimes necessary

to control the reaction, but a rapid and vigorous dissolution of the sodium was essential for a high yield. After a further 1.5 hours under reflux the mixture was treated with excess of ice and dilute sulphuric acid under nitrogen and shaken vigorously until all the sodium had been destroyed. The aqueous layer was separated and extracted with ether; the combined extracts and the benzene solution were washed once with sodium hydrogen carbonate solution. The solution was extracted with successive small portions of 2N-sodium carbonate solution (15 × 100 ml.); the alkaline extracts were acidified immediately, and the precipitated keto-ester was taken up in ether again. The keto-ester solution was washed once with sodium hydrogen carbonate solution, and then dried (CaCl₂); on evaporation the solution yielded nearly pure *dimethyl cis-octahydro-1 : 4-diketopentalene-2 : 5-dicarboxylate* (31 g., 60%). It crystallised from methanol in white needles, m. p. 91° (Found : C, 56.4; H, 5.6. C₁₂H₁₄O₆ requires C, 56.7%; H, 5.6%).

The keto-ester was warmed with hydrochloric acid (75 ml. of *d* 1.18 and 45 ml. of water) until dissolved. The warm solution of keto-acid was shaken vigorously until decarboxylation had ceased (about 1 hour). The pH of the liquid was brought to 9, and the diketone was extracted continuously with ether. Distillation of the extract yielded *cis*-octahydro-1 : 4-diketopentalene (12.6 g., 75% based upon keto-ester), b. p. 86—88°/0.2 mm., m. p. 46—46.5°. Ruzicka *et al.* (*loc. cit.*) quote b. p. 86—88°/0.2 mm. and m. p. 45° (Found : C, 69.7; H, 7.1. Calc. for C₈H₁₀O₂ : C, 69.5; H, 7.2%).

An identical yield of diketone was obtained from the *trans*-tetramethyl ester of (V).

A solution of diketone in ethanol showed no appreciable ultra-violet absorption at λ greater than 200 m μ . No colour was given by the compound with ferric chloride solution. The diketone was not reduced over a 20% palladium-charcoal catalyst which was active for double bonds, but not keto-groups.

Bromine (1.9 g., 2 mols.) was added in acetic acid solution (3 ml.) to a solution of octahydro-1 : 4-diketopentalene (0.8 g.) in acetic acid (8 ml.). The solution was kept under a strong light for 15 minutes; the crystalline precipitate was filtered off, and washed with benzene; further material was obtained from the mother-liquor on concentration in vacuum. 2 : 5-Dibromo-octahydro-1 : 4-diketopentalene was crystallised from glacial acetic acid, then having m. p. 144° (decomp.) (yield : 1.2 g.) (Found : C, 32.5; H, 2.9; Br, 54.1. C₈H₈O₂Br₂ requires C, 32.4; H, 2.7; Br, 54.1%).

The dibromo-diketone was stable in boiling xylene solution; it could be sublimed unchanged in a vacuum at temperatures below the m. p. (*e.g.*, 130—140°/0.2 mm.). It dissolved rapidly in sodium hydroxide solution giving a deep brown solution containing bromide ion; no semi-carbazone was given by this solution after neutralisation with acetic acid.

Attempted Dehydrobromination of 2 : 5-Dibromo-octahydro-1 : 4-diketopentalene.—With triethylamine. The dibromo-diketone (100 mg.) was added to a solution of triethylamine (200 mg.) in dry benzene (3 ml.) and ether (2 ml.); the mixture was warmed to 40°. The bromo-compound dissolved and a brown precipitate then separated rapidly. The mixture was heated on the steam-bath for $\frac{1}{2}$ hour, and the precipitate filtered off. Evaporation of the filtrate left no residue. The precipitate was insoluble in sodium acetate solution, 40% sodium hydroxide solution, and organic solvents, and was not volatile in high vacuum.

With silver acetate. A solution of 2 : 5-dibromo-ketone (0.9 g.) in dry benzene (25 ml.) was boiled under reflux in the dark for 2 hours with silver acetate (2.0 g.). The mixture was filtered hot, and the residue of silver bromide and silver acetate washed with hot acetone. Upon evaporation of the combined washings and mother-liquor in a vacuum a brown gum was obtained; it did not decolorise a solution of bromine in chloroform.

The product was distilled slowly at 100°/10⁻⁴ mm.; a small quantity of colourless sticky crystals was obtained. These softened at 90—95° and melted with decomposition at 115—116°. This substance rapidly reduced alkaline permanganate solution, but did not decolorise a solution of bromine in chloroform; it gave a very insoluble, dark red-brown 2 : 4-dinitrophenylhydrazone. The sticky product rapidly decomposed to a brown gum.

cis-3 : 6 : 7 : 8-Tetrahydro-1 : 4-dimethylpentalene.—Octahydro-1 : 4-diketopentalene (11 g.), dissolved in ether (150 ml.), was added to a stirred solution of methylmagnesium iodide (78 g.) in ether (200 ml.). After 1 hour the mixture was poured into ice and dilute hydrochloric acid, and the traces of magnesium remaining were filtered off. The ethereal layer was separated, and the aqueous layer was extracted continuously with ether. Oxalic acid (25 g.) was added to the ethereal extracts, and the solvent was distilled away in steam (carrying some diene with it). Steam-distillation of the residue was continued, the concentration of oxalic acid in the solution being maintained at 40—50%, until no more volatile oil distilled. The combined distillates were continuously extracted with a small quantity of ether (20 ml.). The ether was distilled

from the dried extract through a column, and the residual oil was distilled in vacuum, yielding 2.7 g. of pale yellow oil with a terpene-like odour, b. p. 94—102°/65 mm., n_D^{20} 1.482. The product was found to contain a trace of ether by elementary analysis. Pure 3 : 6 : 7 : 8-tetrahydro-1 : 4-dimethylpentalene was obtained by redistillation at atmospheric pressure over sodium, but considerable loss was incurred during this process; it had b. p. 160°/760 mm., n_D^{20} 1.490, d_4^{20} 0.9280, $[R_L]_D$ 41.8 (Calc. : 43.0) (Found : C, 89.0; H, 10.4. $C_{10}H_{14}$ requires C, 89.5; H, 10.5%). The diene (48 mg.) in ethanol (5 ml.) was hydrogenated in the presence of 20% palladium-charcoal; 2.0 mols. of hydrogen (16.3 ml.) were absorbed.

Attempted Disproportionation of Tetrahydrodimethylpentalene.—The diene (330 mg.) was boiled under reflux with palladium-black catalyst (10 mg.; Wieland, *Ber.*, 1912, **45**, 484) in tetrahydrofuran (25 ml.). Aliquot parts (5 ml.) were removed at intervals, and unchanged diene was estimated by hydrogenation as described above. No change in hydrogen uptake was found after 24 hours' heating. A sample of the mixture was also examined spectroscopically : no appreciable ultra-violet light absorption was detected. A control experiment was carried out with the same catalyst and solvent and cyclohexene instead of tetrahydrodimethylpentalene; disproportionation to cyclohexane and benzene was almost complete after 6 hours.

Attempted Dehydrogenation.—(a) (i) The apparatus and procedure followed that used by Linstead, Millidge, Thomas, and Walpole (*loc. cit.*, p. 1153). The catalyst used was 20% palladised charcoal made by reduction of palladium chloride with hydrazine at -5° (Cheronis and Levin, *J. Chem. Educ.*, 1944, **21**, 606) which was shown to bring about the dehydrogenation of boiling tetralin.

(ii) *With tetrahydrodimethylpentalene.* 130 Mg. of the diene evolved no significant volume of gas during 3 hours' heating at 170° with 10 mg. of palladised charcoal. The product was slightly brown, but the dimethyldiene was recovered unchanged with small loss on redistillation.

(b) *Vapour-phase method.* (i) The reaction tube, 25 cm. long and of 1.2 cm. internal diameter, was packed with 20% palladised charcoal supported on asbestos. Clumps of catalyst were separated by glass tubing to prevent choking. After being packed, the tube was sealed to a volatilization tube fitted with a fused-on capillary and dropping funnel. The reaction tube was heated to 350° ($\pm 10^\circ$) by means of a tubular electric furnace. The other end of the reaction tube was fused to a receiving U-tube. The catalyst was first dried in the furnace in a stream of nitrogen under 20 mm. pressure. The receiver was then cooled in solid carbon dioxide-alcohol and a weighed quantity of the material to be dehydrogenated was drawn into the volatilization vessel through the funnel and capillary. The substance was then vaporized in a stream of nitrogen at 20 mm.

In this apparatus tetralin at 350° gave in one pass a mixture from which naphthalene picrate (m. p. 150°) could be isolated in an overall yield of 60%.

(ii) *With tetrahydrodimethylpentalene.* The product in the receiver was a pale yellow oil; after one distillation it had the refractive index and other properties of the dimethyldiene. Recovery of unchanged material was almost quantitative. After use with tetrahydrodimethylpentalene the catalyst was still active towards tetralin.

(c) *Attempted hydrogen transfer.* The general technique of Linstead, Braude, Mitchell, Wooldridge, and Jackman was used (*Nature*, 1952, **169**, 100). Tetrahydrodimethylpentalene was boiled under reflux with *p*-nitrotoluene (as hydrogen acceptor) and palladium black, anisole and decalin being used as solvents. No *p*-toluidine (azo-dye formation) was formed in either solvent. Tetralin readily transferred hydrogen to *p*-nitrotoluene under the same conditions.

Octahydro-1 : 4-dihydroxypentalene.—Octahydro-1 : 4-diketopentalene (6.1 g.) in ethanol (100 ml.) containing 2 drops of 25% sodium hydroxide solution was hydrogenated at atmospheric pressure with freshly prepared Raney nickel catalyst (400 mg.). The theoretical volume of hydrogen (2 mols., 2 l.) was absorbed during 24 hours. The solution, filtered from catalyst, was acidified with hydrochloric acid and evaporated in a vacuum. The product was a glassy solid which could not be crystallised.

Ditoluene-p-sulphonyl derivative. The crude product from the previous experiment in pyridine (10 ml.) was left overnight at 0° with toluene-*p*-sulphonyl chloride (17 g.). Ice was added to the mixture, which was then extracted with chloroform. The extract was washed with dilute sulphuric acid and dried ($CaCl_2$); on evaporation the solution left a brown gum which did not crystallise. The crude material was distilled in steam with 30% (w/w) potassium hydroxide solution (45 g.), the concentration of alkali being maintained. During 3 hours traces of volatile oil were carried over. The steam-distillate was extracted continuously with ether (20 ml.). The extract was dried ($CaCl_2$), and the ether distilled off through a column. The residual strong-smelling oil decomposed upon boiling under atmospheric pressure, but could be

distilled at room temperature and 0.2 mm. pressure, the distillate being collected in a U-tube surrounded by a bath of solid carbon dioxide-alcohol. The colourless distillate was redistilled in the same way over sodium, but much decomposition took place. The product reduced alkaline permanganate solution and decolorised bromine solution in chloroform. Both catalytic hydrogenation and elementary analysis indicated the presence of some oxygenated impurity, probably ether. The yield of redistilled material was 0.7 g.

The residue from the steam-distillation was diluted with water, and organic matter was extracted with ether. The extract gave a sticky solid upon evaporation; this slowly solidified. The product, which contained sulphur, crystallised from ethanol as colourless leaflets, m. p. 110° (Found: C, 59.0; H, 5.9. $C_{22}H_{26}O_6S_2$ requires C, 58.7; H, 5.8%). The substance was apparently unreacted *octahydro-1:4-dihydroxypentalene ditoluene-p-sulphonate*.

A small quantity of unsaturated oil, apparently identical with the product from the toluene-sulphonate and potassium hydroxide, was obtained by heating the diol with oxalic acid.

Attempted Formation of Pentalene from Tetrahydropentalene.—Impure tetrahydropentalene (0.6 g.), prepared from the toluenesulphonate, was boiled under reflux with *N*-bromosuccinimide (3.0 g.) and a trace of benzoyl peroxide in carbon tetrachloride (20 ml.). After 3 hours reaction appeared to be complete; the mixture was cooled, and the solution was filtered from succinimide and evaporated in a vacuum at 40°. The crude bromo-compound was dissolved in 20% dimethylamine-benzene solution (20 ml.) and the solution was kept at 5° for 3 days. The deep brown product was concentrated in a vacuum; ether was added, and the solution was extracted with dilute hydrochloric acid. The acid extract was made alkaline, and the basic material taken up in ether again. The ethereal solution was evaporated, and the residue dried in a vacuum. The crude tertiary base was boiled under reflux with methyl iodide (2 ml.) for 20 min., and the excess of iodide was then distilled off in vacuum. The residue was dissolved in water (5 ml.); the solution was warmed with silver oxide (2 g.) for 1 hour on the steam-bath whilst being shaken at intervals. The suspension was filtered, and the filtrate was evaporated in a vacuum. The residue was distilled as completely as possible at 15 mm. pressure. A colourless liquid with a strong basic odour distilled over, leaving a dark tarry residue. The distillate was miscible with water, and yielded trimethylamine picrate, m. p. 215° (lit., m. p. 215°), alone or mixed m. p. with authentic trimethylamine picrate.

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