415. cyclo*Octatetraene Derivatives. Part I. Dimers of* cyclo*Octatetraene.*

By William O. Jones.

A new solid *cyclo*octatetraene dimer, $C_{16}H_{16}$, m. p. 38·5°, has been isolated. It has two double bonds and yields a compound, $C_{16}H_{20}$, m. p. 44·5°, on complete hydrogenation. The previously known solid dimer has been partially reduced to an unsaturated liquid hydrocarbon, $C_{16}H_{20}$. Possible structures are suggested. The dimers form crystalline adducts with silver nitrate.

Two dimers of *cyclo*octatetraene have been described by Reppe and his co-workers (*Annalen*, 1948, **560**, 1; B.I.O.S. Final Report No. 137, Appendix). By prolonged boiling under reflux in an atmosphere of nitrogen, a viscous liquid dimer was obtained, of b. p. 150°/4 mm., n_D^{20} 1·5856, which gave a solid, saturated hydrocarbon, $C_{16}H_{20}$, m. p. 33—35°, on hydrogenation. When *cyclo*octatetraene was boiled under reflux in air, either alone or in solution in *o*-dichlorobenzene, a mixture of two dimers was produced, one of which was a solid, m. p. 43°, whilst the other was regarded as identical with the liquid dimer obtained in nitrogen. The solid dimer absorbed three molecular proportions of hydrogen to give a liquid, $C_{16}H_{22}$, b. p. 127°/0·2 mm.

On repetition of the preparation in *o*-dichlorobenzene, dimeric products were obtained in slightly better yield. The melting point of the principal solid dimer however could not be raised above 41·5°. The liquid dimer had n_D^{20} 1·6030, appreciably higher than the value given by Reppe, and has now been shown to be a mixture of at least four substances.

We have also repeated the dimerisation of *cyclo*octatetraene in the absence of a solvent in a nitrogen atmosphere, and in this case obtained a product (f. p. 13°) with the lower refractive index, n_D^{20} 1·5890. This material consists almost entirely of a new solid dimer, m. p. 38·5°, which we had previously prepared by boiling *cyclo*octatetraene with diethylaniline. It contains two double bonds and on catalytic hydrogenation yields a solid hydrocarbon, $C_{16}H_{20}$, m. p. 44·5°.

The dimer, m. p. 41·5°, was known to absorb three mols. of hydrogen when reduced in the presence of palladium–charcoal (Reppe, *loc. cit.*), the third mol. being taken up more slowly than the first two. We now find that with a palladium–barium carbonate catalyst, hydrogenation ceases after the absorption of two mols. of hydrogen, and a new compound, $C_{16}H_{20}$, can be isolated. This is still unsaturated, and, by use of a platinum oxide catalyst, can be converted into a fully saturated hydrocarbon, $C_{16}H_{22}$, identical with that described by Reppe.

The ultra-violet absorption spectra of the solid dimers, m. p. 41·5° and 38·5°, merely showed end-absorption beyond 2550 and 2240 Å respectively.

The dimers give high yields of fairly stable crystalline adducts with silver nitrate, and through their agency the original liquid dimers have been shown to be mixtures, and the individual dimers have been regenerated in a high state of purity by treatment of the adducts with ammonia.

The dimer of m. p. 41·5° forms two adducts, with 1 and 2 mols. respectively of silver nitrate, of m. p. 153° and 176° respectively (both explode at 192°). The 1 : 1 adduct can be converted into the 1 : 2 adduct by recrystallisation from glacial acetic acid or from aqueous 50% silver nitrate.

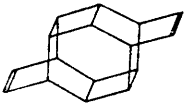
The new dimer (m. p. 38·5°) forms a 1 : 1 adduct with silver nitrate which melts at 196° and does not explode at temperatures up to 240°.

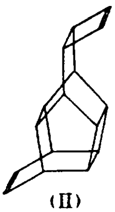
The apparent liquid dimer from the diethylaniline route is in fact the slightly impure 38·5° dimer since it gives over 90% of the calculated yield of a silver nitrate adduct, m. p. 194°, identical with that obtained from the solid dimer, and from which solid dimer of m. p. 36—38° can be recovered. We have not been able to isolate and purify the small amount of accompanying dimeric material which depresses the melting point. The same can be said of the liquid dimer obtained by heating *cyclo*octatetraene in a nitrogen atmosphere, which gave over 85% yields of the adduct, m. p. 194°.

The liquid portion of the dimer formed in *o*-dichlorobenzene is complex and has not been fully resolved. Both the solid dimers are present and, surprisingly, the hydride of the new solid dimer in small amount. Another dimer which gives an adduct, $C_{16}H_{16},2AgNO_3$, m. p. 154—156°, is also probably present.

The dimer obtained by the diethylaniline route is the only one which appears to form an adduct with cuprous chloride–ammonium chloride, but this addition has not been examined closely.

Thus, the dimerisation of *cyclo*octatetraene can give two dimers each containing two double bonds and one dimer containing three double bonds. Reppe regards the dimerisation as a diene synthesis, and for the dimers containing two double bonds he put forward structures such as (I) or (II). He made no suggestion in regard to a dimer with three double bonds.


(I)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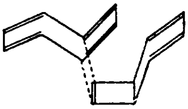

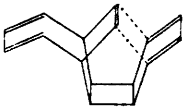
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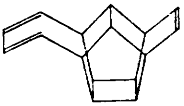
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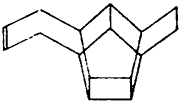
(V)

A dimer with three double bonds could be conceived as arising from a diene synthesis between one molecule of *cyclo*octatetraene as such and one molecule of the isomeric *bicyclo*[4 : 2 : 0]octa-2 : 4 : 7-triene. This would first give a product (III) with five double bonds, and a second intramolecular diene synthesis would then give a product (IV) with three double bonds. Further, two of these double bonds are conjugated (in the eight-membered ring), and, possibly, on hydrogenation 1 : 4-addition occurs first, as well as hydrogenation of the isolated double bond in the six-membered ring. Thus the partially saturated hydride is formulated as (V). The ability of an eight-membered ring to hydrogenate and retain one double bond is shown by *cyclo*octatetraene which can be converted into *cyclo*octene in virtually quantitative yield (Reppe, *loc. cit.*).

It is also possible that dimers containing three double bonds can have been formed by a doubling of the molecule through hydrogen transfer, followed by an intra-molecular Diels–Alder reaction.

EXPERIMENTAL

cyclo*Octatetraene in Boiling* o-*Dichlorobenzene*.—Freshly distilled *cyclo*octatetraene (300 g.; f. p. $-5{\cdot}0°$) and freshly distilled *o*-dichlorobenzene (750 g.) were boiled together under reflux for 48 hr., then fractionated *in vacuo*, yielding unchanged *cyclo*octatetraene (75 g.), mixed dimers, b. p. 80—108°/0·15 mm., n_D^{20} 1·6030 (190 g., 63% conversion), and residue (34 g.). The mixed dimers were refractionated through a Vigreux column. The main fraction (105 g.), b. p. 115—125°/0·7 mm., n_D^{17} 1·6060, formed laths, m. p. 41·5°, after several crystallisations from ether and from ethanol (Found: C, 92·1; H, 7·8. Calc. for $C_{16}H_{16}$: C, 92·3; H, 7·7%). The forerun in the distillation (76 g.; n_D^{17} 1·5983) could not be obtained solid.

Boiling cyclo*Octatetraene in a Nitrogen Atmosphere*.—*cyclo*Octatetraene (20 g.) was heated at 150—160° for 48 hr., during which a slow current of nitrogen was passed into the liquid. The product, on vacuum distillation, yielded unchanged *cyclo*octatetraene (4 g.), dimer (7 g.), b. p. 95—100°/0·5 mm., f. p. +13°, n_D^{20} 1·5890, and an orange resin which was not distilled.

cyclo*Octatetraene in Boiling Nitrobenzene*.—*cyclo*Octatetraene (100 ml.) and freshly distilled nitrobenzene (200 ml.) were refluxed on a sand-bath for 64 hr. A small amount of water was formed. *cyclo*Octatetraene (15 ml.) and nitrobenzene (165 ml.) were then recovered by distillation *in vacuo*. The recovered nitrobenzene gave positive tests for aniline. The residue was a black pitch, which hardened to a brittle solid, readily soluble in hot benzene, moderately in acetone and sparingly in ethanol.

cyclo*Octatetraene in Boiling Diethylaniline*.—*cyclo*Octatetraene (253 g.) and diethylaniline (550 ml.) were boiled under reflux for 24 hr. Distillation then gave *cyclo*octatetraene (29 g.), dimers, b. p. 90—105°/0·5 mm. (158 g.), and residue (45 g.). Fractional distillation of the crude dimers yielded 120 g., of n_D^{20} 1·5866, b. p. 85—95°/0·2 mm., most of which solidified (m. p. 28°) after about an hr. The m. p. of this *dimer* was raised to 36° after five crystallisations from ethanol (Found: C, 92·2; H, 7·6. $C_{16}H_{16}$ requires C, 92·3; H, 7·7%). The new dimer is readily soluble in light petroleum, benzene, chloroform, and *iso*amyl alcohol, and moderately soluble in methanol, ethanol, and acetic acid. The m. p. was depressed to below 15° on admixture with the dimer of m. p. 41·5°.

In another preparation wherein heating was for 64 hr., there was no unchanged *cyclo*octatetraene, the yield of dimers was 71%, and there was an increased amount of high-boiling residue.

Hydrogenation of Dimer, m. p. 41·5°.—The dimer (30 g.) was hydrogenated in a stainless steel rotating autoclave with 1·2% palladium–barium carbonate (6 g.), benzene (70 ml.), and methanol (130 ml.) at 106°/100 atm. for 28 hr. The catalyst and solvents were removed, and the residue distilled at 88°/0·05 mm. After redistillation at 99—100°/0·15 mm. and 130—133°/2 mm., the *hydride* had n_D^{21} 1·5725 (Found: C, 90·8, 90·7; H, 9·5, 9·6. $C_{16}H_{20}$ requires C, 90·5; H, 9·5%).

This hydrocarbon decolorized bromine in carbon tetrachloride, and a sample (2·942 g.) absorbed 280 ml. (0·90 mol.) of hydrogen in 50 min. at room temperature in the presence of pre-reduced platinum oxide (0·046 g.) in *cyclo*hexane (50 ml.). After distillation *in vacuo* (b. p. 171—172°/10 mm.), a colourless liquid (2·5 g.) was obtained, having f. p. $-15°$, n_D^{17} 1·5665 (Found: C, 89·7; H, 10·1. Calc. for $C_{16}H_{22}$: C, 89·7; H, 10·3%).

Hydrogenation of Dimer, m. p. 38·5°.—The dimer (6·57 g.) was shaken in methanol (100 ml.) with hydrogen in the presence of platinum oxide (0·2 g.). A white crystalline material soon separated and caused the catalyst to coagulate. Ethanol (50 ml.) was then added, and the mixture warmed to 55°, complete solution being obtained. A further 0·2 g. of catalyst was added and hydrogenation continued at 50°. Absorption ceased after 1130 ml. (1·6 mols.) of hydrogen had been taken up. On cooling, the saturated *hydrocarbon* crystallised in prisms, which melted at 44·5° after repeated recrystallisation from alcohol and then from acetone (Found: C, 90·8, 90·7; H, 9·4, 9·4. $C_{16}H_{20}$ requires C, 90·5; H, 9·5%).

Silver Nitrate Adduct from Dimer, m. p. 41·5°.—Silver nitrate (1·71 g.) in ethylene glycol (5 ml.) was added to the dimer (2·08 g.) in absolute ethanol (50 ml.) and the mixture boiled for 2 min. The *adduct* (2·74 g.), obtained on cooling, crystallised from ethanol in prisms, m. p. 153° (Found: Ag, 28·1. $C_{16}H_{16},AgNO_3$ requires Ag, 28·5%). Silver was determined by warming the adduct with concentrated nitric acid, dilution with water, and titration with potassium thiocyanate. Carbon and hydrogen values could not be obtained on any of the silver nitrate adducts because of violent decomposition on heating. The present adduct exploded in a capillary m. p. tube when the temperature reached 192°. On recrystallisation from glacial acetic acid or 50% aqueous silver nitrate, a new *adduct* was obtained, having m. p. 176° (explodes at 190°) (Found: Ag, 39·2. $C_{16}H_{16},2AgNO_3$ requires Ag, 39·4%). The dimer was regenerated by warming the 1 : 2 adduct (28 g.) slightly with concentrated aqueous ammonia (100 ml.). The liberated oil, when taken up in ether, washed, dried, and distilled, had b. p. 115—118°/0·7 mm., m. p. 41·0°, n_D^{22} 1·6075.

A homogeneous solution was obtained when the dimer was warmed with 25—50% aqueous silver nitrate, and one or other of the above adducts separated on cooling, depending on the amount of silver nitrate employed. In the first experiment, with excess of silver nitrate, colourless, feathery needles, m. p. 182°, were obtained, but all subsequent experiments yielded the modification melting at 176°.

Silver Nitrate Adduct from Dimer, M. P. 38·5°.—When a solution of silver nitrate (0·7 g. in 35 ml. of ethanol) was added to the dimer (0·8 g. in 10 ml. of ethanol) a white powder was immediately precipitated. After boiling for 5 min., the mixture was cooled and filtered, and the solid was washed with ethanol and with ether and air-dried. The *adduct* (1·05 g.) had m. p. 196° (Found: Ag, 28·4%). The melted specimen did not decompose explosively at temperatures up to 230°. There was a gradual loss of dimer on prolonged heating at 110°, the silver content being 30% after 18 hr. at this temperature.

The same adduct was formed in quantitative yield when the dimer was treated with aqueous silver nitrate (25%). Variation of the silver nitrate : dimer ratio from 3 : 1 to 1 : 1 always resulted in the formation of the 1 : 1 adduct.

By treatment of the adduct with ammonia, the dimer was recovered in a very pure form, b. p. 101—103°/0·25 mm., m. p. 38·5°.

Silver Nitrate Adduct from the Liquid Dimer from the Diethylaniline Route.—The liquid (n_D^{22} 1·5828) employed was a mixture of the fore-run obtained on re-distillation of the crude dimer, and the oil obtained when the solid was filtered off from the main fraction. The dimer (17·9 g.) was warmed on the steam-bath for 10 min. with 3 mols. of aqueous silver nitrate (50%). The grey precipitate was washed with ethanol and with ether, and dried (29 g.; m. p. 191—192°). The m. p. was raised to 193° by one crystallisation from 50% silver nitrate and a mixture with the above 196° adduct melted at 193—195°. Reaction in ethanol–ethylene glycol gave a purer product in a somewhat smaller yield (81%; m. p. 195°).

Regeneration of the dimer by means of ammonia gave an 85% recovery of material, m. p. 28—29°, from which the dimer, m. p. 38·5°, could be obtained by redistillation.

Silver Nitrate Adduct from the Liquid Dimer obtained by heating cyclo*Octatetraene in Nitrogen.*—The dimer (1·0 g.) was warmed at 90° for 2 min. with silver nitrate (2·5 g.) and water (2·5 g.). The white powder produced (1·6 g., 88%) had m. p. 191°, raised to 196° on extraction with hot ethanol, not depressed on mixing with the adduct obtained from the dimer of m. p. 38·5°.

Silver Nitrate Adduct from the Liquid Dimer from the o-*Dichlorobenzene Route.*—This dimeric material behaved very differently from those hitherto described in that there was no separation of adduct when the reaction was carried out in alcohol. (i) When a fraction, b. p. 90—100°/0·7 mm., n_D^{17} 1·6008 (23·9 g.), was added to 3 mols. of 50% aqueous silver nitrate at room temperature there was an immediate formation of an extremely viscous oil. After being kept overnight the major portion had formed colourless crystals, but there still remained a lump of pale brown gum. The crude adduct (58 g., 92%) was boiled with chloroform (200 ml.) and filtered. The residue (2 g.; m. p. 38—40°) obtained after removal of the solvent did not absorb bromine or hydrogen and its m. p. was not depressed on admixture with the hydride obtained from the dimer of m. p. 38·5° (Found: C, 90·3; H, 9·8. Calc. for $C_{16}H_{20}$: C, 90·5; H, 9·5%). The solid adduct remaining after the chloroform treatment was heated to the b. p. with

25% silver nitrate solution (400 ml.) and filtered hot. The undissolved portion (4 g.; m. p. 194°) was shown to be identical (by mixed m. p. of the adduct and of the regenerated dimer) with the adduct obtained from the dimer of m. p. 38·5°. Large, colourless plates (23 g.; m. p. 154°, explodes at 190°) separated when the aqueous silver nitrate extract was cooled. The m. p. was depressed slightly (146—148°) after admixture with the previously described adduct of m. p. 153°, and the non-identity of the two adducts was confirmed by the much higher silver content of the present adduct (Found: Ag, 38·8. $C_{16}H_{16},2AgNO_3$ requires Ag, 39·4%). (ii) In another preparation, with the dimer fraction of b. p. 85—90°/0·7 mm., n_D^{17} 1·5958 (18·8 g.), the crude adduct (33·1 g.) by tedious fractional crystallisation from ethanol and from 50% aqueous silver nitrate gave the adduct of m. p. 195° (21·6 g.), the adduct of m. p. 176° (6 g.), several fractions in the melting range 153—163° (Ag values about 33%), and an oil (0·3 g., n_D^{24} 1·590) which had not combined with silver nitrate.

Cuprous Chloride–Ammonium Chloride Addition Compound with cyclo*Octatetraene Dimer.*—The only dimer which appeared to react was that produced by the diethylaniline route, and this formed a bulky yellowish-green solid when shaken with the reagent. The adduct was insoluble in boiling ethanol and in toluene; it was not stable in boiling acetic acid. It does not possess a definite m. p.; it darkens at about 160—170° in a capillary tube, and dimer refluxes at about 250°.

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