cycloOctatetraene Derivatives. Part IV.* Reduction of cycloOctatetraene by Sodium and Alcohols.

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[Reprint Order No. 4565.]

*cyclo*Octatetraene is reduced by sodium and alcohols to a mixture of, principally, 1 : 3-, 1 : 4-, and 1 : 5-*cyclo*octadiene together with a very small quantity of *cyclo*octene. The individual dienes were isolated by selective extraction with aqueous silver nitrate. The relative amounts of the dienes formed depend upon the temperature and duration of heating, which suggests that isomerisation of the primary reduction products occurs. 1 : 3- and 1 : 5-*cyclo*Octadiene both gave mixtures of stereoisomeric tetrabromides, but only one mol. of bromine could be added to the 1 : 4-isomer.

*cyclo*OCTATETRAENE is readily hydrogenated to *cyclo*octane over nickel, palladium, or platinum (Reppe, Schlichting, Klager, and Toepel, *Annalen*, 1948, **560**, 1; Willstätter and Waser, *Ber.*, 1911, **44**, 3423). In solvents such as methanol and with a palladium catalyst, the rate of reaction diminishes suddenly after the absorption of three molar equivalents of hydrogen, and essentially pure *cis-cyclo*octene can be isolated at this stage in good yield. There has however been no indication that dienes or trienes can be isolated after catalytic hydrogenation.

Addition of one equivalent of hydrogen has been accomplished by non-catalytic methods, using sodium in liquid ammonia (Cope and Hochstein, *J. Amer. Chem. Soc.*, 1950, **72**, 2515), sodium in ether, followed by methanol (Reppe *et al.*, *loc. cit.*), and sodium with monomethylaniline (Ziegler and Wilms, *Annalen*, 1950, **567**, 1). In the last case, a *bicyclo*octadiene was initially formed, which readily isomerised to *cyclo*octa-1 : 3 : 5-triene.

When *cyclo*octatetraene is reduced by sodium in boiling alcohols two double bonds become saturated. The product, at first regarded as *cyclo*octa-1 : 5-diene (Elofson, U.S.P. 2,594,889), has been shown to be a mixture of at least three components, two of which have been identified as *cyclo*octa-1 : 4-diene and -1 : 5-diene (Craig, Elofson, and Ressa, *J. Amer. Chem. Soc.*, 1953, **75**, 480). This reaction had been examined independently by us and we confirm that the product consists almost entirely of *cyclo*octadienes, and have proved that the third main constituent is *cyclo*octa-1 : 3-diene. The presence of the 1 : 4- and the 1 : 5-isomer was demonstrated by nitric acid oxidation, which yielded glutaric acid and succinic acid together with larger quantities of unidentified nitrogen-containing acidic substances. Ozonolysis of the reduction product (after a preliminary treatment with silver nitrate to remove *cyclo*octa-1 : 5-diene) gave adipic, glutaric, and malonic acids, thus showing the presence of *cyclo*octa-1 : 3- and -1 : 4-diene.

Finally the three pure isomers were isolated through the agency of their adducts with silver nitrate. The silver nitrate adduct ($C_8H_{12},AgNO_3$) of *cyclo*octa-1 : 5-diene has been described by Cope, Stevens, and Hochstein (*J. Amer. Chem. Soc.*, 1950, **72**, 2510), and the adduct (not purified and analysed) of the 1 : 3-diene by Cope and Estes (*ibid.*, p. 1128). We have now obtained pure adducts from *cyclo*octa-1 : 3- and -1 : 4-diene, both of which have the composition $C_8H_{12},2AgNO_3$. The three adducts differ greatly in their stability in aqueous silver nitrate: at 0—5° all three are stable; above about 30° the adduct from *cyclo*octa-1 : 3-diene reverts to its two components; that from the 1 : 4-diene is largely dissociated at about 60°; and that from the 1 : 5-isomer is stable at 90—100°. It was thus possible to effect a rough separation of the products obtained by reducing *cyclo*octatetraene. The individual adducts were then readily obtained pure by recrystallisation, and the pure isomeric dienes were recovered from them by distillation in steam.

On addition of bromine to the mixed *cyclo*octadienes obtained by reduction of *cyclo*octatetraene, Craig, Elofson, and Ressa (*loc. cit.*) isolated a small yield of a tetrabromide, m. p. 127—128°. A mixture of stereoisomeric tetrabromides, m. p. 105—124°, was obtained by Ziegler and Wilms (*loc. cit.*) from the 1 : 5-diene. We have obtained three tetrabromides

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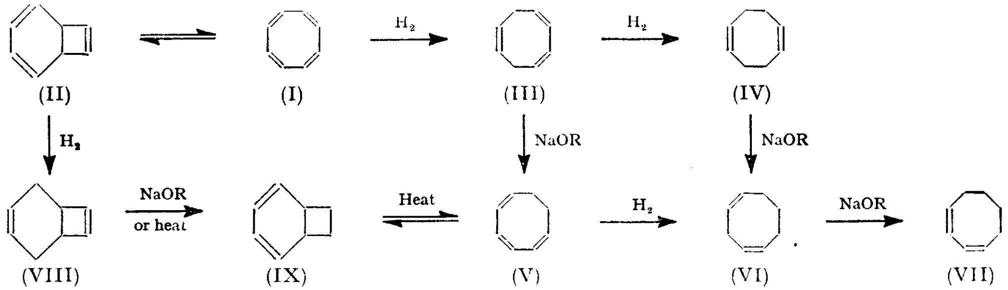
* Part III, *J.*, 1953, 4156.

(m. p. 139°, 135°, and 100°) from the *cyclo*octatetraene reduction mixture. The individual dienes differ markedly in behaviour, and the high-melting derivatives are stereoisomeric forms of 1 : 2 : 5 : 6-tetrabromo*cyclo*octane. *cyclo*Octa-1 : 5-diene with 2 mols. of bromine at −20° rapidly yielded a mixture, m. p. 110—120°. An unstable isomer, m. p. 133—134°, was obtainable by recrystallisation without delay, and this changed to a mixture, m. p. 103—110°, after about 24 hours at room temperature. The latter was separated by chromatography on alumina into two isomers, m. p. 135° and 139°.

A solid dibromide (m. p. 65°) was readily obtained from *cyclo*octa-1 : 4-diene. The further action of bromine resulted in the evolution of hydrogen bromide and it has not been possible to obtain a tetrabromide. This behaviour raised the question of whether rearrangement to a dibromo*bicyclo*[4 : 2 : 0]octane had occurred, as is known to be the case on addition of halogens to *cyclo*octatetraene, but catalytic hydrogenation showed that the dibromide contained one double bond so that the monocyclic ring was still intact.

The addition of 1 mol. of bromine to *cyclo*octa-1 : 3-diene at −20° was extremely rapid, and a liquid dibromide (m. p. approx. −12°) was isolated. This is presumably 3 : 8-dibromo*cyclo*octene, and is probably identical with the material obtained by Cope and Estes (*loc. cit.*) from *cyclo*octa-1 : 3-diene containing an undetermined amount of a less stable stereoisomer. The dibromide reacted slowly with more bromine at 0—10° to form a mixture from which 1 : 2 : 3 : 4-tetrabromo*cyclo*octane (m. p. 100°) was isolated. The identity of this derivative was established by its preparation from the diene obtained by the action of ammonia on 3-bromo*cyclo*octene.

The presence of *cyclo*octa-1 : 3-diene in the reduction product was not expected, since sodium in boiling alcohols normally reduces conjugated double bonds but does not affect isolated double bonds. We have, in fact, shown that *cyclo*octa-1 : 3-diene is no exception, for it was reduced to *cyclo*octene under such conditions. It is concluded therefore that the 1 : 3-diene present in the reduction product of *cyclo*octatetraene has been formed mainly by rearrangement of the 1 : 4- or the 1 : 5-isomer under the influence of the hot alcoholic sodium alkoxide [Cope and Hochstein (*loc. cit.*) described the analogous conversion of *cyclo*octa-1 : 3 : 6-triene (III) into *cyclo*octa-1 : 3 : 5-triene (V) by means of potassium *tert.*-butoxide]. This view is supported by the variability in the proportions of dienes obtained under different conditions. Judged by the results of silver nitrate experiments, the product contained 50% of *cyclo*octa-1 : 5-diene when the alcohol employed was ethanol, and 30—40% when *sec.*-butanol was used. This could be accounted for if either of the reactions (IV) ⟶ (VI), or (III) ⟶ (V) was more rapid in boiling *sec.*-butanol than in boiling ethanol. Our attempts to isomerise (IV) were not successful, but evidence for the change of (VI) to (VII) was obtained.



The annexed scheme is put forward to account for the formation of the three isomeric *cyclo*octadienes. It involves 1 : 4-addition of hydrogen to a conjugated system, and rearrangement of a pair of isolated double bonds to a conjugated pair under the influence of heat or of sodium alkoxide. In the reduction of (I) at low temperatures by means of sodium and *N*-methylaniline in ether, Ziegler and Wilms (*loc. cit.*) consider that the first product is *bicyclo*[4 : 2 : 0]octa-3 : 7-diene (VIII). We have confirmed Ziegler and Wilms's observation that only one double bond can be reduced under these conditions even in the presence of excess of sodium. Craig, Elofson, and Ressa (*loc. cit.*) did not obtain evidence for the formation of bicyclic products on repeating Ziegler and Wilms's work at room temperature, whilst Cope, Haven, Ramp, and Trumbull (*J. Amer. Chem. Soc.*, 1952, **74**, 4867), as a result of reducing (I) with sodium in a mixture of ether and liquid ammonia, suggested that *bicyclo*[4 : 2 : 0]octa-2 : 4-diene (IX) as well as (V) was present in Ziegler and Wilms's product. All these results can be accommodated by taking the view that *cyclo*octatetraene behaves as a mixture of the monocyclic (I) and the bicyclic (II) forms. Thus, in the work of Cope *et al.* (*loc. cit.*), the primary product would be a mixture of the observed triene (III), with Ziegler and Wilms's diene (VIII). During the subsequent working up, which involved heating with alcoholic potassium *tert.*-butoxide, (VIII) would be converted into (IX) (and thence V).

The complex formed from calcium and ammonia, $Ca(NH_3)_6$, readily attacks conjugated double bonds but has no action on isolated double bonds, *e.g.*, it reduces benzene to *cyclo*hexene (Dumanskii and Zvyereva, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 994; Kazanskii and Gostunskaya, *Doklady Akad. Nauk, S.S.S.R.*, 1950, **71**, 295.) Our preliminary results on the reduction of *cyclo*octatetraene with this reagent show that the products are *cyclo*octatrienes. Since these contain conjugated double bonds it seems probable that the primary reduction product was (VIII), and that the trienes arose through isomerisation during working up.

EXPERIMENTAL

Reduction of cyclo*Octatetraene with Sodium and Alcohol.*—Reductions were carried out essentially as described by Craig, Elofson, and Ressa (*loc. cit.*), the alcohols employed being ethanol or *sec.*-butanol. The latter forms an azeotrope (b. p. approx. 99°) with the *cyclo*octadienes and it was therefore removed from the product by repeated extraction with cold water. Analysis of a freshly distilled sample (n_D^{20} 1·4848) indicated that it consisted of *cyclo*octadienes (Found: C, 88·9; H, 11·2. Calc. for C_8H_{12}: C, 88·8; H, 11·2%). On catalytic hydrogenation 1·94 mols. of hydrogen were absorbed to give *cyclo*octane (f. p. 11·5°, n_D^{20} 1·4579). After 6 months' storage in the dark, the refractive index of the unsaturated hydrocarbons had risen to 1·4957 (at 20°), and material was now present which imparted a deep orange colour to aqueous sodium hydroxide.

Oxidation of the Reduction Product by Nitric Acid.—The dienes (22 c.c.) were added gradually at 90° to a mixture of nitric acid (75 c.c.; *d* 1·42), water (65 c.c.), and ammonium vanadate (0·5 g.). After 30 hr. at the boil, the clear lemon-yellow liquid was removed from a trace of dark brown oil and evaporated to dryness (16 g.). Glutaric acid (m. p. 82—84°) was obtained by extraction with benzene and characterised through its dianilide (m. p. and mixed m. p. 217—220°). The material which was not soluble in benzene was dissolved in acetone, and from this solution succinic acid (m. p. and mixed m. p. 183—184°) was obtained. The isolated glutaric and succinic acids in each case represented about 8% of the total acidic material (which gave a positive test for nitrogen).

Ozonolysis of the Diene Fraction remaining after Removal of cyclo*Octa*-1 : 5-*diene.*—The crude reduction product was extracted with 50% aqueous silver nitrate solution at 70—90° to remove *cyclo*octa-1 : 5-diene (as described later). A sample (6·3 g.) of the remaining hydrocarbon dissolved in chloroform (200 c.c.) was ozonised at −30°. The ozonide (12 g.; white powder; m. p. *ca.* 0°) was heated on the steam-bath for 12 hr. with acetic acid (150 c.c.) and hydrogen peroxide (94·5 c.c., 32·6%). After removal of the solvents *in vacuo* at 50°, a white crystalline solid (13 g.; m. p. 115—125°) was obtained. Trituration with chloroform (60 c.c.) left 3·4 g. undissolved, and this material was shown to be adipic acid by mixed m. p.s of the free acid (m. p. 150°) and its dianilide (m. p. 237—239°). The acids soluble in chloroform formed a viscous oil from which an unidentified solid (2 g.; m. p. 130—131°, depressed by malonic acid) separated during 2 days. The substance was highly soluble in water and in methanol (Found: C, 51·7; H, 7·2%). A portion (3·95 g.) of the residual oil was heated under reflux at 150° for 2 hr. to decompose any malonic acid present. Carbon dioxide was evolved, and the acetic acid which was also formed was subsequently distilled into standard sodium hydroxide, the amount obtained being equivalent to 1·6 g. of malonic acid. The residue in the flask was boiled for 1 hr. with acetic anhydride (10 c.c.) to complete the formation of glutaric anhydride, which was then distilled (2 g.; b. p. 90°/0·2 mm.) and characterised (mixed m. p.) by conversion into glutaric acid (m. p. 94°) and its dianilide (m. p. 222°).

Action of Silver Nitrate on the Crude Diene Mixture.—(*a*) The mixed dienes (105 c.c.; n_D^{20} 1·4895) obtained by reduction of *cyclo*octatetraene with sodium and ethanol during 4·5 hr. were shaken at 70° with 50% (w/w) aqueous silver nitrate (3 × 50 c.c.; 4 × 40 c.c.), the mixture being placed each time in a bath at 70° for about 20 min. to obtain a good separation of the layers. The lower layers were stored separately in the dark at room temperature. The oil (25 c.c.) remaining at this stage was then extracted at 40° (2 × 20 c.c.). The first two extractions at 70° removed 19 c.c. of the original hydrocarbon mixture, and they yielded colourless needles of the silver nitrate adduct of *cyclo*octa-1 : 5-diene on cooling. A second crop of needles was contaminated by a few colourless spherical aggregates. The adduct was exceedingly soluble (at least 1 g. in 1 c.c.) in boiling methanol, and formed long needles (6—8 cm.; m. p. 135—136°) on cooling (Found: C, 34·9; H, 4·3; Ag, 38·8. Calc. for $C_8H_{12},AgNO_3$: C, 34·6; H, 4·3; Ag, 38·8%). Cope, Stevens, and Hochstein (*loc. cit.*) recorded m. p. 128·5—131°. The third and fourth extractions removed appreciably less hydrocarbon (23 c.c., jointly) and the solid which separated on cooling was a mixture. The remaining extractions (5—9th) slowly removed almost pure *cyclo*octa-1 : 4-diene (17 c.c. in all) from the hydrocarbon layer. Only the first of these extracts deposited a solid adduct, which originally appeared as small colourless spheres, but these slowly changed (during 4 weeks) into large, flat, hexagonal crystals. This cyclo*octa*-1 : 4-*diene–silver nitrate* adduct was only moderately soluble in boiling methanol from which it crystallised in tablets, m. p. 110—111° (Found: C, 21·9; H, 2·7; Ag, 47·7. $C_8H_{12},2AgNO_3$ requires C, 21·5; H, 2·7; Ag, 48·2%).

The oil (21 c.c.; n_D^{25} 1·4835, f. p. −58°) remaining after the above extractions was treated with an excess of silver nitrate solution at 0—5°. The cyclo*octa*-1 : 3-*diene–silver nitrate* adduct which appeared after about 30 min. was collected and recrystallised from methanol. It formed clusters of colourless needles which did not melt in a capillary tube below 150°, at which point the hydrocarbon could be seen to have distilled away from the silver nitrate (Found: C, 21·5; H, 2·7; Ag, 48·1%). Cope and Estes (*loc. cit.*) obtained an unstable adduct which was not analysed. The aqueous mother-liquor from the formation of this adduct was steam-distilled and yielded a product (2 g.; n_D^{20} 1·4845, f. p. −50°) which was shown by elementary analysis (C, 89·0; H, 11·3%) and by catalytic hydrogenation (1·6 mols. absorbed; product f. p. 6—7°) to contain approx. 80% of a diene and 20% of a monoene (probably *cyclo*octene).

(*b*) In the case of mixed *cyclo*octadienes (168 g.) which had been prepared in *sec.*-butanol (4½ hr.) the loss in weight to 50% silver nitrate at 70° was only 30%. The product (b. p. 144—145°, f. p. −57°, n_D^{20} 1·4882) was shown by ozonolysis to contain *cyclo*octa-1 : 3- and -1 : 4-diene (see p. 314).

Regeneration of cyclo*Octadienes from their Silver Nitrate Adducts.*—The dienes were readily recovered from the adducts by steam-distillation. *cyclo*Octa-1 : 3-diene had n_D^{20} 1·4930, f. p. −35° (Ziegler and Wilms, *loc. cit.*, give n_{He}^{20} 1·4930, f. p. −53°; Cope and Estes, *loc. cit.*, give n_D^{25} 1·4908, f. p. −50°). *cyclo*Octa-1 : 4-diene (n_D^{20} 1·4884, f. p. −35°) also had a much higher f. p. than the recorded value (Ziegler and Wilms, *loc. cit.*, give n_{He}^{20} 1·4896, f. p. −53°). Our regenerated *cyclo*octa-1 : 5-diene had n_D^{20} 1·4935, f. p. −65° (Ziegler and Wilms, *loc. cit.*, give n_{He}^{20} 1·4936, f. p. −70°; Cope, Stevens, and Hochstein, *loc. cit.*, give n_D^{20} 1·4910, f. p. −69°).

Addition of Bromine to cyclo*Octa*-1 : 5-*diene.*—The diene (1·03 g.) in carbon tetrachloride (25 c.c.) was treated at −20° with 32 c.c. of a solution of bromine (10 g.) in carbon tetrachloride (100 c.c.). The mixture was colourless after 3 min. and was washed with water, and dried ($CaCl_2$), and the solvent was removed *in vacuo*. The product (4·1 g.; m. p. 90—115°) crystallised from light petroleum (60—80°), and then from methanol, at which stage it had m. p. 133—134°, but this m. p. had changed to 106—114° after 24 hr. The mixture was separated into two isomeric 1 : 2 : 5 : 6-*tetrabromo*cyclo*octane*, by chromatography on alumina with light petroleum (b. p. 60—80°)–benzene (9 : 1) as solvent. The solid obtained from the earlier eluates formed colourless needles, m. p. 135°, from light petroleum (b. p. 100—120°) (Found: C, 22·7; H, 2·9; Br, 75·0. $C_8H_{12}Br_4$ requires C, 22·5; H, 2·8; Br, 74·7%). The second isomer, from the later eluates, formed colourless rhombs, m. p. 139°, from the same solvent (Found: C, 22·7; H, 2·8; Br, 75·0%). A mixture melted at 97—110°. The m. p. of the unstable tetrabromide originally isolated was depressed to 112—114° by either of the stable forms.

Addition of Bromine to cyclo*Octa*-1 : 4-*diene.*—The diene (1·5 g.) in carbon tetrachloride (25 c.c.) was treated at −20° with the same solution of bromine (22·5 c.c.) as above. Decolorisation was instantaneous until 22 c.c. had been added, after which there appeared to be no change in 2 hr. The product, presumably 4 : 5-*dibromo*cyclo*octene*, was worked up in the usual manner and yielded colourless rhombs, m. p. 65°, from light petroleum (b. p. 60—80°) (Found: C, 35·7; H, 4·6: $C_8H_{12}Br_2$ requires C, 35·9; H, 4·5%). The dibromide darkened and liquefied after a few days in air. On treatment of the dibromide with a further mol. of bromine at 0—10°

hydrogen bromide was evolved and all the bromine was consumed in 1 hr. On working up of the product, some dibromide was recovered, together with a lachrymatory oil, b. p. 90—95°/0·3 mm., n_D^{14} 1·5606 (Found: Br, 55·3%). The dibromide (0·773 g.) on hydrogenation at 20° in ethanol in presence of 5% palladium–charcoal (1 g.) absorbed 173 ml. (2·7 mol.) of hydrogen in 115 min. (Found: Br^-, 0·35 g. Calc. for $2Br^-$: 0·46 g.).

Addition of Bromine to cyclo*Octa*-1 : 3-*diene*.—At −20° addition of bromine ceased after the absorption of 1 mol., and a colourless oil, b. p. 93°/1·2 mm., n_D^{17} 1·5660, was isolated, presumably 3 : 8-dibromo*cyclo*octene (Found: C, 36·5; H, 4·8; Br, 59·9. Calc. for $C_8H_{12}Br_2$: C, 35·9; H, 4·5; Br, 59·6%). Cope and Estes (*loc. cit.*) obtained a similar compound, b. p. 73—76°/0·3 mm., n_D^{25} 1·5648—1·5687, from *cyclo*octa-1 : 3-diene containing some stereoisomeric material. At 5—10°, two mols. of bromine were absorbed rapidly; from the oily product a solid modification of 1 : 2 : 3 : 4-*tetrabromo*cyclo*octane*, m. p. 100°, was obtainable by trituration with methanol or light petroleum, followed by recrystallisation from methanol (Found: C, 22·6; H, 2·9; Br, 74·4. $C_8H_{12}Br_4$ requires C, 22·5; H, 2·8; Br, 74·7%). The same tetrabromide (m. p. 100°) was obtained from a *cyclo*octa-1 : 3-diene (n_D^{20} 1·4865) obtained as a by-product in the reaction between 3-bromo*cyclo*octene and ammonia.

Addition of Bromine to the Reduction Product of cyclo*Octatetraene*.—The mixed *cyclo*octadienes (10 g.) were brominated in chloroform at −20° to 0°, 1·7 mols. of bromine being absorbed. The crude oily product (30·9 g.) was triturated with light petroleum and stored overnight at 0°. A white solid (11·6 g., m. p. 110—120°) was obtained which was separated by chromatography into the isomeric 1 : 2 : 5 : 6-tetrabromo*cyclo*octanes, m. p. 135° and 139°. The light petroleum mother-liquor afforded a white solid at −80°, and as this became oily at about −10° the supernatant liquid was poured away at −80° and the solid was dissolved in ethyl ether. The ethereal solution, on strong cooling, gave 1 : 2 : 3 : 4-tetrabromo*cyclo*octane (2 g., m. p. 100°).

Reduction of cyclo*Octa*-1 : 3-*diene by Sodium and Ethanol*.—The diene (0·4 g.; n_D^{20} 1·4930) was treated in boiling ethanol (10 c.c.) with sodium (1 g.). The product was isolated by distillation in steam and dried ($CaCl_2$). The crude *cyclo*octene obtained had n_D^{20} 1·4740, and absorbed 1·12 mols. of hydrogen on catalytic hydrogenation.

Attempts to Isomerise cyclo*Octa*-1 : 5- and -1 : 4-*diene by Means of Sodium* sec.-*Butoxide*.—(*a*) *cyclo*Octa-1 : 5-diene (1 g.; n_D^{20} 1·4935) was heated on the steam-bath in nitrogen for 16 hr. with sodium *sec.*-butoxide (0·5 g. of sodium dissolved in 10 c.c. of *sec.*-butanol). The recovered hydrocarbon had n_D^{20} 1·4880, f. p. −69°, and gave the same silver nitrate adduct (m. p. and mixed m. p. 132—134°) as the starting material. (*b*) When *cyclo*octa-1 : 4-diene (1 g.; n_D^{20} 1·4885) was treated similarly, the recovered hydrocarbon had n_D^{20} 1·4853, absorbed 1·92 mols. of hydrogen, and slowly formed an adduct at 0° with 50% aqueous silver nitrate. The adduct did not possess a m. p. and was probably derived from *cyclo*octa-1 : 3-diene.

Attempts to Demonstrate the Presence of Bicyclic Hydrocarbons during Reduction.—*cyclo*Octatetraene was reduced (*a*) at 0° by Ziegler and Wilms's method (*loc. cit.*) (titration showed that only two atoms of sodium would react), (*b*) at −30° by sodium and ethanol in liquid ammonia, and (*c*) at −30° by sodium in liquid ammonia (Cope and Hochstein, *loc. cit.*). The solvents were removed at low temperature, and the products washed with water at 0°, dried, and perhydrogenated at 0—10° in the presence of palladium–charcoal or platinum oxide. In each case the final product was *cyclo*octane, f. p. 9·5° to 11·5°, so that no direct evidence for the formation of bicyclic compounds was obtained.

Reduction of cyclo*Octatetraene with Calcium–Ammonia Complex*.—*cyclo*Octatetraene (5 g.) was mixed with dry *cyclo*hexane (50 c.c.) and calcium turnings (20 g.), and dry ammonia gas passed in at 0—5° until the formation of the reddish-brown powdery complex was complete. The mixture was stirred at room temperature for 36 hr., and the unused calcium compound was decomposed in a nitrogen atmosphere by the addition of water through a capillary tube. The product obtained after distillation and fractionation had b. p. 136—146°, n_D^{16} 1·5077—1·5113. About 30% of the product absorbed oxygen from the air in a few days to form a yellow gel which was soluble in hot dilute sodium hydroxide solution. The remainder of the product was more stable and appeared to be mainly *cyclo*octatrienes (probably 1 : 3 : 6 as judged by the low refractive index), which absorbed 2·7 mols. of hydrogen and formed a silver nitrate adduct which melted with decomposition at 120°.

The author thanks Dr. S. A. Miller for his advice, Mr. E. S. Norton for technical assistance, and the Directors of The British Oxygen Co. Ltd., for permission to publish these results.

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[*Received, August* 7*th*, 1953.]