# *Reactions of* cyclo*Octatetraene. Part V.* Selective Reduction by Metals and Alkalis or Acids.*

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*cyclo*Octatetraene has been reduced to *cyclo*octene by treatment with Raney nickel alloy in dilute sodium hydroxide. Reduction by zinc dust in sodium hydroxide or in aqueous-alcoholic sulphuric acid gave good yields of *cyclo*octatrienes, principally the 1 : 3 : 6-triene. With alcoholic potassium hydroxide and zinc dust, however, the main constituent was *cyclo*octa-1 : 3 : 5-triene. Addition of halogens to the *cyclo*octatrienes has been examined, and the silver nitrate adducts of *cis-cyclo*octene and of *cyclo*octa-1 : 3 : 6-triene have been prepared.

After our studies * on the reduction of *cyclo*octatetraene with sodium and alcohol, we examined its behaviour on treatment with Raney nickel alloy in hot aqueous alkali without the addition of external hydrogen (cf. Papa, Schwenk, and Breiger, *J. Org. Chem.*, 1949, **14**, 366). This might be expected to be equivalent to hydrogenation with a Raney nickel catalyst, since the latter, together with hydrogen, is produced *in situ*. Reppe (FIAT Final

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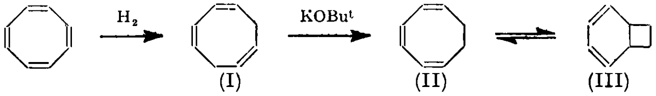
* Part IV, *J.*, 1954, 312.

Report No. 967, p. 85) found catalytic reduction of *cyclo*octatetraene with Raney nickel to give *cyclo*octane even more rapidly than with platinum catalysts, there being presumably no sign of selective reduction to *cyclo*octene as is the case with palladium catalysts. However, with Raney alloy and alkali, without added hydrogen, reduction does not proceed beyond *cyclo*octene. The product ($n_D^{20}$ 1·4730, f. p. −25°), after one treatment, contained 90—95% of *cyclo*octene, 4—9% of *cyclo*octadienes, and (probably) about 1% of *bicyclo*-[4 : 2 : 0]octane. By extraction with 50% aqueous silver nitrate, most of the dienes were removed at 70° and the bulk of the *cis-cyclo*octene at 40—45°, the bicyclic hydrocarbon remaining in the residue. A crystalline adduct, $2C_8H_{14},AgNO_3$ (m. p. 51°), of *cis-cyclo*-octene was isolated. Cope, Pike, and Spencer (*J. Amer. Chem. Soc.*, 1953, **75**, 3212) reported that *trans-cyclo*octene can be extracted from pentane solution by 20% aqueous silver nitrate, but the *cis*-isomer did not react under these conditions.

The *cyclo*octadienes produced in the Raney alloy reduction were only slowly reduced to *cyclo*octene by further reaction with Raney alloy and sodium hydroxide (3 or 4 more treatments required). This is in marked contrast to the behaviour of the *cyclo*octadienes which are formed *en route* to *cyclo*octene by the normal catalytic process, *e.g.*, with palladium on barium sulphate in methanol; these dienes are readily reduced to *cyclo*octene by one treatment with Raney alloy and sodium hydroxide. This suggests that different stereoisomeric dienes are present in the two cases. In this connection, Ziegler and Wilms (*Annalen*, 1950, **567**, 14) have reported that the labile isomer of *cyclo*octa-1 : 5-diene is hydrogenated to *cyclo*octene twice as fast as the stable isomer.

In aqueous sodium hydroxide *cyclo*octatetraene was not reduced when aluminium powder was employed instead of Raney alloy, although reduction to *cyclo*octatrienes occurred in alcoholic alkali. It is evident therefore that the presence of the nickel in the Raney alloy is necessary for reduction beyond the *cyclo*octatriene stage.

Reduction of *cyclo*octatetraene to *cyclo*octatrienes was first effected by Reppe, Schlichting, Klager, and Toepel (*Annalen*, 1948, **560**, 1) by treating its dilithium adduct with methanol. The complex nature of the products of this reaction was demonstrated by Cope *et al.* (*J. Amer. Chem. Soc.*, 1950, **72**, 2515; 1952, **74**, 4867) who also described improved methods of reduction in which *cyclo*octatetraene was treated in liquid ammonia with sodium and then with ammonium chloride. Cope and his co-workers also showed that the partly unconjugated 1 : 3 : 6-isomer (I) rearranges to the fully conjugated 1 : 3 : 5-isomer (II) when heated with potassium *tert.*-butoxide, and that *cyclo*octa-1 : 3 : 5-triene is normally in mobile equilibrium with the bridged isomer, *bicyclo*[4 : 2 : 0]octa-2 : 4-diene (III) [85% of (II) and 15% of (III) at equilibrium].



We now find that reduction of *cyclo*octatetraene with zinc dust in aqueous-alcoholic caustic alkali does not proceed beyond the *cyclo*octatriene stage, the main constituent being (I) when sodium hydroxide was used and (II) [in equilibrium with (III)] when potassium hydroxide was used. Since (I) is readily isomerised to (II) by alcoholic potassium hydroxide it is probable that the former is the primary product with either alkali. The silver nitrate adduct of (I), $C_8H_{10},3AgNO_3$, m. p. 139°, was formed from the trienes obtained by use of sodium hydroxide. Pure (I) was obtained by treating the adduct with aqueous ammonia. Cope and Hochstein (*J. Amer. Chem. Soc.*, 1950, **72**, 2515) have described material which was contaminated with 4—6% of (II).

The product ($n_D^{25}$ 1·5110) initially isolated on use of sodium hydroxide was easily converted into the equilibrium mixture of (II) and (III) ($n_D^{25}$ 1·5223) by hot alcoholic potassium hydroxide. Alternatively, *cyclo*octatetraene was converted in one step into the same equilibrium mixture, simply by heating it for a short time on the steam-bath with zinc dust and alcoholic potassium hydroxide.

In view of the above results we examined the reduction with zinc in an acid medium. Craig, Elofson, and Ressa (*ibid.*, 1953, **75**, 481) reported that reduction proceeds to a limited extent with zinc and acetic acid, but the products were not isolated, ultra-violet absorption curves suggesting that *cyclo*octatrienes were present. It has now been found that with zinc and sulphuric acid in 75% ethanol reduction proceeds only as far as *cyclo*octatriene, the principal constituent of the product ($n_{\mathrm{D}}^{25}$ 1·5088) being (I).

An adduct, m. p. 140—142°, was formed when *cyclo*octa-1 : 3 : 6-triene was heated with maleic anhydride at 140—150° and was shown (by mixed m. p. determinations) to be identical with the known adduct from (II) or from (III) (Reppe *et al.*, *loc. cit.*; Cope *et al.*, *loc. cit.*, 1952). It follows that isomerisation of (I) to (II) and/or (III) must have taken place. This was confirmed by heating (I) ($n_{\mathrm{D}}^{25}$ 1·5050) at 140—150° for one hour, which caused a change in refractive index to $n_{\mathrm{D}}^{25}$ 1·5240, and from which the silver nitrate adduct of (II) was readily obtained. There was no detectable isomerisation of (I) at 100° (1 hr.).

Unlike *cyclo*octatetraene, which rearranges to a bicyclic system on halogenation (Reppe *et al.*, *loc. cit.*) the *cyclo*octatrienes maintained their eight-membered ring, at least to a very large extent. Both trienes yielded a mixture of tetra- and hexa-chlorides (in a molar ratio of 1 : 3) on treatment with an excess of chlorine at —20°. At higher temperatures (20°) and with a larger excess of chlorine, substitution also occurred, to give heptachlorides. On bromination at 0°, a mixture of tetra- and hexa-bromides could be obtained from (II), whereas (I) gave only tetrabromides. The latter, however, added chlorine slowly, which indicates that the tetrabromides are tetrabromo*cyclo*octenes rather than *bicyclo*[4 : 2 : 0]-octane derivatives. The halogenation products are believed to consist of mixtures of stereoisomers, and from the various halogenations a number of individual isomers have been isolated in crystalline form.

## EXPERIMENTAL

*Reduction of* cyclo*Octatetraene with Raney Nickel Alloy and Sodium Hydroxide.*—(*a*) *cyclo*-Octatetraene (15 g.) and 10% aqueous sodium hydroxide (500 ml.) were stirred rapidly in a 2-l. flask at 80—90°, and Raney alloy (50 g.) was added during 2 hr. The crude *cyclo*octene (15 g.; $n_{\mathrm{D}}^{20}$ 1·4751, f. p. −23°) was recovered by steam-distillation.

(*b*) *cyclo*Octatetraene (104 g.), ethanol (1 l.), and Raney alloy (162 g.) were stirred at the b. p., and 20% sodium hydroxide solution (900 ml.) was added at such a rate that the heat of reaction maintained the mixture at the boil. The product (b. p. 54—55°/50 mm., f. p. −30°, $n_{\mathrm{D}}^{20}$ 1·4740) was isolated by addition of water (2 l.), washed until alkali-free, dried ($CaCl_2$), and distilled.

(*c*) A 1-l. stainless-steel rotating autoclave was charged with Raney alloy (37 g.), *cyclo*-octatetraene (33 g.), and 10% aqueous sodium hydroxide (350 ml.), the latter being contained in a glass liner to avoid mixing until after closure. The autoclave was rolled for 3 hr., no external heat being applied. The temperature reached 46° and the pressure 220 lb./sq. in. in 10 min. and then decreased slowly (33°/15 lb. after 1·5 hr.). The product ($n_{\mathrm{D}}^{20}$ 1·4730, f. p. −24°) was isolated as in (*a*). Catalytic hydrogenation (Adams catalyst in acetic acid) showed the presence of 5% of *cyclo*octadienes and yielded *cyclo*octane, m. p. 11·5°, $n_{\mathrm{D}}^{20}$ 1·4568, of approx. 98% purity (cf. Cope and Hochstein, *loc. cit.*).

The f. p.s of crude *cis-cyclo*octene (−23° to −30°) prepared by the above methods compare with −12° for the pure compound (Ziegler and Wilms, *loc. cit.*). By subjecting a material of f. p. −30°, $n_{\mathrm{D}}^{20}$ 1·4750, to four further treatments with Raney alloy and sodium hydroxide its f. p. was raised only to −22° ($n_{\mathrm{D}}^{20}$ 1·4705; 0·97 mol. of hydrogen absorbed on catalytic hydrogenation). On the contrary, crude *cis-cyclo*octene (20 g.; f. p. −22°; containing 10% of *cyclo*octadienes) which had been prepared by catalytic hydrogenation of *cyclo*octatetraene (Pd–$BaSO_4$ catalyst; no diluent) had f. p. −14° after one treatment with Raney alloy (50 g.) and 10% aqueous sodium hydroxide (500 ml.).

*Preparation of the Silver Nitrate Adduct of* cis-cyclo*Octene.*—Crude *cyclo*octene [40 ml.; obtained by catalytic hydrogenation (Pd–$BaSO_4$) of *cyclo*octatetraene in the absence of a diluent] was shaken at 70—80° with 50% (w/w) silver nitrate solution (2 × 15 ml.) to remove *cyclo*-octadienes (aqueous layer). Extraction was continued at 40° (4 × 20 ml.), three layers now being formed each time, the middle layer being the silver nitrate adduct of *cis-cyclo*octene, which crystallised (m. p. 38°) on separation and cooling to room temperature. The *adduct* was highly soluble in methanol (at least 1 g. in 1 ml.), from which it crystallised (at 0°) in large flat needles which were dried during one week under a slight vacuum over calcium chloride and *cyclo*octene saturated with paraffin wax. The product (m. p. 51°) lost hydrocarbon rapidly on exposure to air (Found: C, 48·8; H, 7·2; Ag, 27·4. $2C_8H_{14},AgNO_3$ requires C, 49·2; H, 7·2; Ag, 27·7%).

*Approximate Separation of Components of Crude* cyclo*Octene by Means of Silver Nitrate.*—When crude *cyclo*octene (35 ml.) from a Raney alloy reduction [sample from (*b*) above] was subjected to a similar treatment with silver nitrate, an oil (1·7 ml.; $n_D^{20}$ 1·4675) remained after the *cyclo*octadienes (2·5 ml.) and most of the *cyclo*octene had been removed. It absorbed 0·72 mol. of hydrogen to give an impure *cyclo*octane ($n_D^{20}$ 1·4582, f. p. −15°). These results suggest that the oil was a mixture of *cyclo*octene (72%) and *bicyclo*octane (28%), the estimated refractive indices (20°) of such a mixture before and after hydrogenation being 1·4671 and 1·4589 respectively.

*Reduction of* cyclo*Octatetraene to* cyclo*Octatrienes by Means of Sodium Hydroxide and Zinc Dust.*—(*a*) The following materials were charged into a 1-l. stainless steel rocking autoclave: *cyclo*octatetraene (104 g.), zinc dust (130 g.), sodium hydroxide (160 g. in 320 g. of water), ethanol (200 ml.), and platinum chloride (4 drops of a 2% aqueous solution, for activating the zinc). The contents were heated at 90—100° for 3 hr. The product consisted of a grey mass of needles and an orange liquid and was steam-distilled, yielding a very pale yellow oil (principally *cyclo*octa-1 : 3 : 6-triene; 92 g.; $n_D^{25}$ 1·5150; 0·12% of *cyclo*octatetraene by polarography).

(*b*) *cyclo*Octatetraene (50 g.), zinc dust (130 g.), ethanol (600 ml.), and water (60 ml.) were stirred rapidly on the steam-bath, and sodium hydroxide solution (160 g. in 640 ml. of water) was added dropwise during 1 hr. After a further 2½ hr. the product was isolated by steam-distillation. The bulk of the product was colourless (39 g.; $n_D^{25}$ 1·5107), but towards the end of the distillation the product was very pale yellow and this portion was discarded. On hydrogenation (Pd–$CaCO_3$ in methanol) 2·85 mols. of hydrogen were absorbed (a sharp break occurring at 1·96 mols.), and *cyclo*octane, m. p. 8—9°, $n_D^{25}$ 1·4568 (97·5% purity), was produced.

*Isomerisation of the* cyclo*Octa*-1 : 3 : 6-*triene Component of the Mixed Trienes.*—(*a*) A mixture of trienes (5 g.; $n_D^{25}$ 1·5120) was treated with potassium (0·1 g.) and *tert.*-butanol (20 ml.) on the steam-bath for 2 hr. A dark brown colour was produced immediately on mixing and a small quantity of resin separated. The oil obtained on steam-distillation had $n_D^{25}$ 1·5175. (*b*) By heating the mixed trienes (50 g.; $n_D^{25}$ 1·5150) with alcoholic potassium hydroxide (66 g. of alkali in 300 ml. of ethanol) in an autoclave at 90—100° for 4 hr. a product with $n_D^{25}$ 1·5223 was obtained (2·76 mols. of hydrogen absorbed over Pd–$CaCO_3$ in methanol), which yielded the adduct (m. p. 123—125°) of (II) with 50% silver nitrate solution.

*Reduction of* cyclo*Octatetraene to* cyclo*Octa*-1 : 3 : 5-*triene* (II).—A mixture of *cyclo*octatetraene (5 g.), ethanol (40 ml.), zinc dust (10 g.), and potassium hydroxide (10 g.) was heated on the steam-bath in nitrogen. There was no appreciable reaction until 2—3 drops of aqueous platinum chloride (4% solution) were introduced. Heating was continued for 3 hr. with occasional shaking, and the mixture was then steam-distilled. The product (5 g.) consisted of a colourless oil, $n_D^{25}$ 1·5220, which gave an 85% yield of the silver nitrate adduct (m. p. 123—125°) of (II) and absorbed 2·8 mols. of hydrogen on catalytic hydrogenation (Pd–$CaCO_3$ in acetic acid), the resulting *cyclo*octane having m. p. 7—8°, $n_D^{25}$ 1·4568, purity 97%.

The product was yellow when nitrogen had been omitted, and towards the end of the steam-distillation a viscous yellow oil and a pale yellow solid appeared, the latter probably the oxygen addition compound of (II) (Cope and Hochstein, *loc. cit.*, 1950). This solid decomposed vigorously on being heated, and was insoluble in ether and in benzene, and soluble in hot aqueous sodium hydroxide [Found: C, 67·9; H, 6·7. Calc. for $(C_8H_{10}O_2)_x$: C, 69·5; H, 7·3%].

When the experiment was carried out with aqueous potassium hydroxide, *cyclo*octatetraene was converted in 3 hr. into a product with $n_D^{25}$ 1·5187. After a further 8 hr. the pale yellow product had $n_D^{25}$ 1·5215, which suggested that its composition was close to that of the equilibrium mixture of (II) and (III). Treatment with 50% aqueous silver nitrate, however, gave only a small yield of the adduct of (II), whereas a high yield was obtained from an authentic equilibrium mixture.

Presence of Raney nickel (1 g.) during the reaction in alcoholic potassium hydroxide enabled the reduction to proceed beyond the *cyclo*octatriene stage, the product having $n_D^{25}$ 1·5025 and 1·4705 after 3 and 9 hr., respectively.

Aluminium powder was not as effective in the formation of trienes as zinc dust, no reduction being observed in aqueous-alcoholic sodium hydroxide, whilst the product ($n_D^{25}$ 1·5208) formed (in 2 hr.) in alcoholic potassium hydroxide remained pale yellow and gave only a small yield of the adduct of (II) with 50% silver nitrate solution. *cyclo*Octatetraene was not affected by pin dust and hydrochloric acid in boiling ethanol.

*Reduction of* cyclo*Octatetraene by Means of Zinc Dust and Aqueous-alcoholic Sulphuric Acid.*—A mixture of zinc dust (30 g.), *cyclo*octatetraene (20 ml.), and ethanol (250 ml.) was boiled on the steam-bath, and 50% (w/w) sulphuric acid (100 ml.) containing 3 drops of 4% platinum chloride was added dropwise during 0·5 hr. A sample isolated after 4 hours' heating had a pale yellow colour and $n_D^{25}$ 1·5150. After the addition of more zinc dust (30 g.), ethanol (250 ml.), and sulphuric acid (100 ml.; 50% w/w) the main portion was heated again for 6 hr. The supernatant liquid was poured into water (2 l.), and the pale yellow oil was separated, washed, and dried ($CaCl_2$). Distillation yielded a colourless product ($n_D^{25}$ 1·5088; f. p. $< -70°$), which gave the adduct (m. p. 139°) of *cyclo*octa-1 : 3 : 6-triene with silver nitrate in ethanol. On catalytic hydrogenation, 2·7 mols. of hydrogen were absorbed by the crude triene, to yield *cyclo*octane of f. p. 1—2° (95% purity).

*Purification of* cyclo*Octa*-1 : 3 : 6-*triene* (I) *through its Silver Nitrate Adduct.*—The mixed hydrocarbons (12 g.; $n_D^{25}$ 1·5150) obtained by the action of zinc dust and aqueous-alcoholic sodium hydroxide on *cyclo*octatetraene were boiled with ethanol (150 ml.) and powdered silver nitrate (58 g.) and filtered hot. The *adduct* (25 g.) obtained on cooling formed flat needles, m. p. 138—139°, from methanol (Found: C, 15·8; H, 1·6. $C_8H_{10},3AgNO_3$ requires C, 15·6; H, 1·6%). The original mother-liquor very slowly deposited a second crop of crystals, the majority of which were small needles but which also contained a few large rectangular crystals shown (after hand-separation and recrystallisation, mixed m. p.) to be the adduct of (II).

The complex from (I) was decomposed by adding it to an excess of dilute aqueous ammonia at room temperature. The liberated oil was washed, and dried ($CaCl_2$). Pure *cyclo*octa-1 : 3 : 6-triene obtained in this way had $n_D^{25}$ 1·5050, f. p. −52° (Found: C, 90·8; H, 9·4. Calc. for $C_8H_{10}$: C, 90·5; H, 9·5%). Cope and Hochstein (*loc. cit.*) gave $n_D^{25}$ 1·5046, f. p. −56° to −62° for slightly impure material. On hydrogenation in methanol (Pd–$CaCO_3$), 1·96 mols. were absorbed very rapidly, and hydrogen uptake ceased at 2·94 mols. The refractive index of (I) was unchanged after 1 hr. on the steam-bath, but heating for 1 hr. at 150° caused its value to rise to 1·5240 (25°). The resulting product gave a high yield of the adduct of (II) on treatment with aqueous silver nitrate (m. p. and mixed m. p. 123—125°). (I) did not form an adduct with maleic anhydride in benzene at room temperature (in presence of a trace of trichloroacetic acid), but at 140—150° in the absence of a solvent an adduct, m. p. 145—146°, was obtained, identical with the maleic anhydride adduct of (II) (mixed m. p.).

The isomeric trienes (I) and (II) differ appreciably in their behaviour with silver nitrate. With an aqueous solution of the reagent (50% w/w), the complex with *cyclo*octa-1 : 3 : 5-triene was precipitated immediately in excellent yield, whilst that from (II) did not separate even after several hours at 0° (an exothermic reaction on mixing, and the formation of a homogeneous solution showed that adduct formation had occurred). When the aqueous silver nitrate mixtures were warmed the adduct from (III) appeared to be stable up to 70—75° at which point the solid disappeared and a hydrocarbon layer was formed on the surface; the solution containing (II) became milky at 40°. Both trienes form beautifully crystalline adducts with powdered silver nitrate in ethanol. The complex from (III) lost hydrocarbon on exposure to air much more quickly than did that from (II). Pure *cyclo*octa-1 : 3 : 5-triene regenerated from its adduct by means of cold aqueous ammonia had $n_D^{25}$ 1·5245 (f. p. $< -70°$). in good agreement with the value recorded by Cope *et al., loc. cit.*, 1952).

*Addition of Bromine to* cyclo*Octa*-1 : 3 : 5-*triene.*—(*a*) The triene (2·84 g.) in carbon tetrachloride (100 ml.) was treated at 0° with bromine (2·5 mols.) in the same solvent (110 ml.). The first mol. of bromine was absorbed instantly, but after one week the total uptake was only 1·9 mols. The excess of bromine was removed with aqueous sodium hydrogen sulphite, and the solution was washed and dried ($Na_2SO_4$). A colourless oil (10·7 g., 94% yield as tetrabromides) was left after removal of the solvent. A portion (1·0 g.) of the product was obtained in a solid form by keeping a solution in light petroleum (b. p. 60—80°) at 0—10° for 2—3 hr. The *tetrabromide* (possibly 3 : 4 : 7 : 8-tetrabromo*cyclo*octene), recrystallised from methanol, had m. p. 169—170° (Found: C, 22·6; H, 2·3; Br, 75·2. $C_8H_{10}Br_4$ requires C, 22·6; H, 2·4; Br, 75·1%).

(*b*) By employing twice as much bromine, a semisolid mixture of tetra- and hexa-bromides (21 g. from 5 g. of triene) was obtained, which yielded 1 : 2 : 3 : 4 : 5 : 6-*hexabromo*cyclo*octane* (9·9 g.) on trituration with methanol; this formed colourless prisms, m. p. 149°, from *iso*propanol or from benzene–light petroleum (Found: C, 16·0; H, 1·8; Br, 82·5. $C_8H_{10}Br_6$ requires C, 16·4; H, 1·7; Br, 81·9%).

*Addition of Bromine to* cyclo*Octa*-1 : 3 : 6-*triene.*—This hydrocarbon (1·59 g.) was treated with bromine as in (*a*), 1 mol. of bromine being absorbed immediately and a second in 3 days. The viscous oily product (6·5 g.) consisted of tetrabromides (Found: C, 22·6; H, 2·4%) from which one *isomer* (0·9 g.) was obtained in a crystalline form from ethyl acetate. It formed colourless prisms (m. p. 121°) from benzene (Found: C, 22·6; H, 2·4; Br, 75·1%). The remainder of the material was chromatographed (light petroleum–alumina), but no other solid isomer could be isolated.

On use of a large excess of bromine [as in (*b*) above], the product was again essentially tetrabromide (Found : C, 21·8; H, 2·3%). Treatment with a large excess of chlorine in carbon tetrachloride for one week at 20° resulted in addition and some substitution (Found : C, 17·7; H, 1·9. Calc. for $C_8H_9Cl_3Br_4$ : C, 18·1; H, 1·7%).

*Addition of Chlorine to* cyclo*Octa*-1 : 3 : 5-*triene*.—(*a*) The pure triene (6 g.) was treated in chloroform (75 ml.) at −20° with chlorine until the increase in weight was 14 g. The excess of chlorine and the solvent were removed after 16 hr. at 0° (14·5 g.) (Found : C, 31·9; H, 3·2; Cl, 64·6%). The oily mixture of hexa- and tetra-chlorides on chromatography [alumina; light petroleum (b. p. 60—80°) containing 1% of benzene] yielded very small quantities of two isomeric *tetrachlorides*, (i) colourless needles (from methanol), m. p. 92—93° (Found : C, 37·7; H, 4·2; Cl, 57·9. $C_8H_{10}Cl_4$ requires C, 38·7; H, 4·1; Cl, 57·2%), and (ii) colourless needles (from methanol), m. p. 168° (Found : C, 38·7; H, 4·2%).

Some substitution occurred on chlorination at 20° (4 days), the colourless oil, $n_D^{17}$ 1·5600, approximating to a heptachloride (Found : C, 27·6; H, 2·6. Calc. for $C_8H_9Cl_7$ : C, 27·2; H, 2·6%).

(*b*) Addition of 2 mols. of chlorine to (II) yielded a colourless oil, b. p. 119—120°/1 mm., $n_D^{17}$ 1·5596 (Found : C, 38·5; H, 4·0%), but the only solid obtained on chromatography was the tetrachloride, m. p. 168° (approx. 1% of the original product).

*Addition of Chlorine to* cyclo*Octa*-1 : 3 : 6-*triene*.—*cyclo*Octa-1 : 3 : 6-triene (3·9 g.) gave a mixture (9 g.) of hexa- and tetra-chlorides (Found : C, 32·0; H, 3·3%) on chlorination at −20°. On chromatography, a very small yield of a crystalline *hexachloride* was obtained which formed bunches of colourless needles, m. p. 119—120°, from light petroleum (b. p. 60—80°) (Found : C, 29·8; H, 3·3. $C_8H_{10}Cl_6$ requires C, 30·1; H, 3·2%).

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