86. *The Reaction of Hexachlorobicyclo*[2,2,1]*heptadiene with Potassium Ethoxide.*

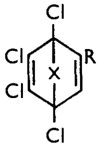
By K. Mackenzie.

Contrary to a previous report, 1,2,3,4,7,7-hexachlorobicyclo[2,2,1]hepta-2,5-diene reacts with potassium ethoxide to give 1,2,4,7,7-pentachloro-3-ethoxybicyclo[2,2,1]hepta-2,5-diene.

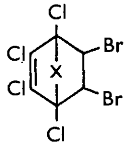
Hexachlorobicycloheptadiene (I) is reported[1] to react with alkoxide ion in the relevant alcohols to give various 7-alkoxy-1,2,3,4,7-pentachlorobicycloheptadienes (II). In a previous paper,[2] however, the reaction of the 5-phenyl derivative (III) with sodium methoxide under considerably less severe conditions was shown to give 2,3,4,5-tetrachlorobiphenyl, and not the ketal (IV) (whose instability was independently demonstrated, since phenylacetylene formed an adduct with tetrachlorodimethoxycyclopentadiene which decomposed to give the same tetrachlorobiphenyl).

The formation of the ketal (IV) could be rationalised on the basis of anchimeric assistance to nucleophilic displacement at the dichloromethano-bridge,[3] and similar considerations might be expected to apply to reaction of compound (I) with alkoxide ion, the chloro-ethers (II) reacting further to give ketals.

In the present work, an attempt to prepare the ketal (IVa) by reduction of the dibromo-compound (V) with zinc gave instead methyl 2,3,4-trichlorobenzoate, and in a reinvestigation of the reaction of compound (I) with alkoxide ion little evidence for the formation of 2,3,4-trichlorobenzoic acid (or incidentally 1,2,3,4-tetrachlorobenzene) could be found, these experimental facts suggesting that formulation of the products as (II) is erroneous.



(I) R = H; X = CCl_2
(II) R = H; X = $CCl{\cdot}OR'$
(III) R = Ph; X = CCl_2
(IV) R = Ph; X = $C(OMe)_2$
(IVa) R = H; X = $C(OMe)_2$



(V) X = $C(OMe)_2$

In fact the infrared light absorption of the product (denoted IIa) formed in the reaction of the bicycloheptadiene (I) with concentrated ethanolic potassium hydroxide is not consistent with the formulation (II; $R' = Et$). The highly characteristic *s*-dichloroethylene absorption near 1600 $cm.^{-1}$ is absent and instead a split maximum occurs in this region (1645vs, 1605ms $cm.^{-1}$) which persists in the dihydro- and the dibromo-derivative and in the cyclopentadiene adduct (VI) obtained from the product (IIa). Moreover, the product (IIa) and its dihydro-derivative are readily hydrolysed to ketones (IIb, IIc) whose stability to heat and infrared carbonyl absorption (1785vs, 1792vs $cm.^{-1}$) preclude bicyclo[2,2,1]-hepten-7-one structures.[4, 5]

However, the formation of the cyclopentadiene adduct (VI), which shows properties in accord with an *endo-endo*-fused 1,4 : 5,8-dimethanonaphthalene compound in analogy with the formation and reactions of isodrin,[6] indicates that the precursor (IIa) is a bicyclo-[2,2,1]hepta-2,5-diene compound and that the dichloromethano-bridge probably survives. For example, bromination of the adduct (VI) gives a saturated bromo-ketone (VII) whilst

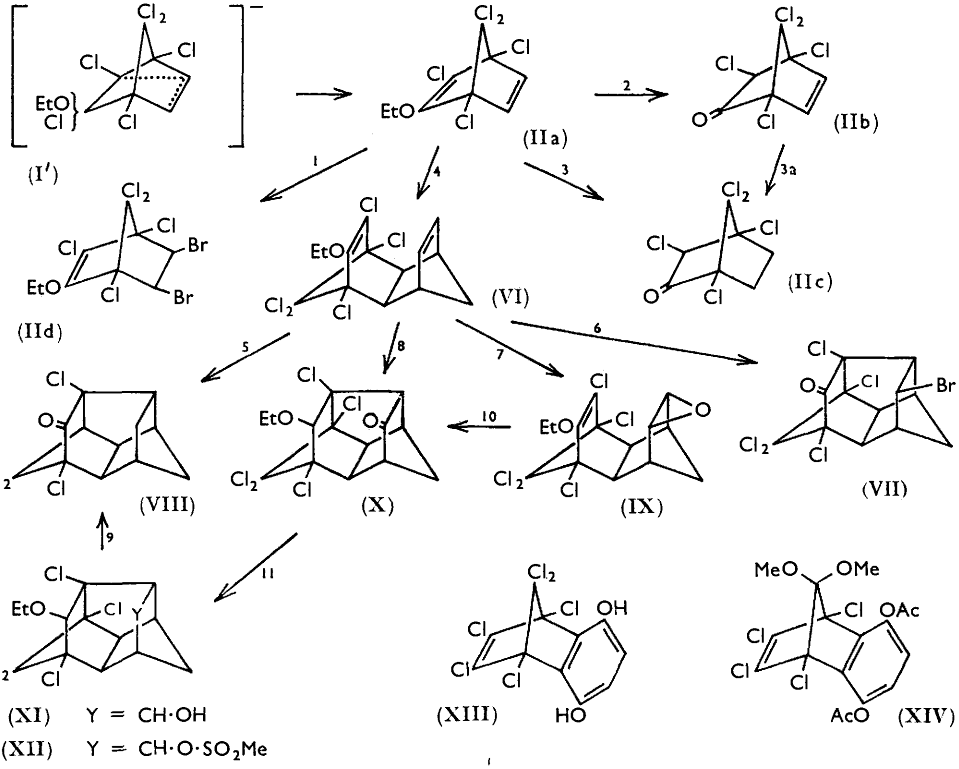
---

[1] Molotsky, U.S.P. 2,897,240/1959.
[2] McBee, Idol, and Roberts, *J. Amer. Chem. Soc.*, 1959, **77**, 6674.
[3] Winstein and Ordronneau, *J. Amer. Chem. Soc.*, 1960, **82**, 2084.
[4] Yates and Eaton, *Tetrahedron*, 1961, **12**, 13.
[5] Mackenzie, *J.*, 1960, 473.
[6] Soloway, Damiana, Sims, Bluestone, and Lidov, *J. Amer. Chem. Soc.*, 1960, **82**, 5377.

treatment with mineral acids gives a further saturated ketone (VIII), both compounds showing enhanced infrared carbonyl frequencies (1785vs, 1790vs cm.$^{-1}$) characteristic of α-chlorinated strained-ring ketones, the resistance to reduction and formation of derivatives in each case indicating considerable steric hindrance. Both ketones must have arisen by conjugate addition processes.

Epoxidation of the adduct (VI) gives either of two products, depending on the conditions. One is the expected unsaturated epoxide (IX) which slowly isomerises in polar solvents at 20° to the second product, a saturated ketone (X), the transformation being accelerated by heat. Under similar conditions, in non-polar solvents, the epoxide (IX) is almost completely stable but is rapidly converted into the ketone (X) in the presence of a trace of boron trifluoride. This conversion is also effected, slowly, by moderate heating of the solid epoxide. Unlike the compounds (VII and VIII), the ketone (X) can be reduced although with difficulty, and its infrared carbonyl absorption (1748vs cm.$^{-1}$) shows that there is no α-coplanar chlorine.

These reactions are summarised in the scheme annexed. The vinyl ether (IIa) must be formed[7] from the carbanion (I′) which is stabilised by homoconjugation with the 5,6-double bond and less significantly by the electronegative environment. The former effect is clearly the more important since only insignificant amounts of vinyl ether are present in the product of reaction of its dihydro-derivative with alkali under similar conditions.



Reagents: 1, Br$_2$. 2, H$_2$SO$_4$. 3, H$_2$–Pd, then H$_2$SO$_4$. 3a, H$_2$–Pd. 4, Cyclopentadiene at 165°. 5, HBr–AcOH or H$_2$SO$_4$. 6, Br$_2$–AcOH. 7, AcO$_2$H–C$_6$H$_6$. 8, AcO$_2$H–AcOH. 9, COMe$_2$–H$_2$O. 10, Heat or BF$_3$. 11, LiAlH$_4$, then Me·SO$_2$Cl–C$_5$H$_5$N.

The reaction sequence leading to (IIa), a novel mode in the bicycloheptadiene series,

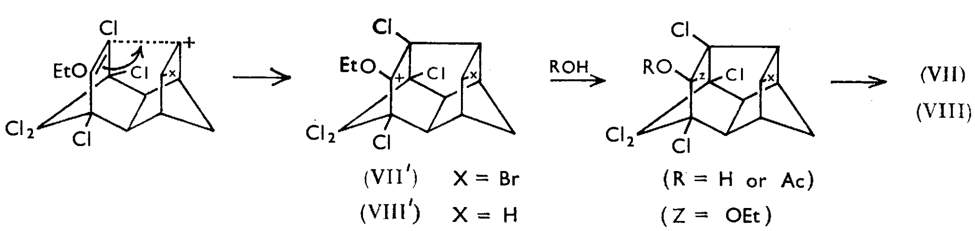
---

[7] Huett and Miller, *J. Amer. Chem. Soc.*, 1961, **83**, 408 and references therein.

rather than nucleophilic displacement of homoallylic chlorine contrasts with the behaviour of compound (III). Here the conjugated phenyl group must provide anchimeric assistance which, coupled with the more usual effect of adjacent halogen at a developing carbonium ion centre (*e.g.*, the solvolysis of benzylidene chloride), is sufficient to outweigh the effect of the electronegative environment in promoting displacement. The effect of the phenyl group in this connexion also recalls the great difference in reactivity of cinnamyl and allyl chloride in solvolysis.[8] On the other hand, the apparent inertness of the fused-ring compound (XIII) in basic media [9] resembles that of our compound (I), and the relation of benzyl and allyl chloride in their comparable reactivities is similar. Moreover, the fused-ring ketal (XIV) is readily isolated (unpublished work), unlike ketal (IV) or (IVa); attempts to trap the ketal (IVa) *in situ* with cyclopentadiene fail.

Bromination of the ether (IIa) to give predominantly 1,2-addition rather than rearranged product (*e.g.*, nortricyclenone derivatives) is surprising but finds a parallel in the case of similar reactions of substance (I), where rearranged products, characteristic of bicycloheptadiene,[10] have not so far been detected. Presumably π-orbital participation is reduced, rendering the intermediate carbonium ion less stable than that from the parent hydrocarbon.

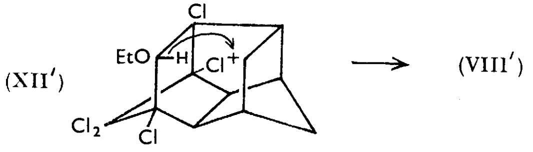
The ketones (VII and VIII) are formed by way of the intermediate carbonium ions (VII′, VIII′) (shown as classical forms for simplicity), which attack the solvent, the products decomposing to ketones.*



(VII′) X = Br
(VIII′) X = H

(R = H or Ac)
(Z = OEt)

The lability of the epoxide (IX) under acidic conditions, compared with endrin,[11] and its mode of cyclisation to the saturated ketone (X), must be determined by the $O(2p)$–π interaction of the vinyl ether system; the skeletal relationship of (X) to the half-cage structures (VII, VIII) is seen in the isolation of the latter ketone on solvolysis of the methanesulphonate (XII) of the alcohol (XI) obtained by reduction of the ketone (X).



The carbonium ion intermediate here (XII′) undergoes a 1,4-hydride shift with attack on solvent; subsequent decomposition of the semiketal formed leads to the product (VIII).

The ultraviolet light absorptions of the ketones (IIb and c) are of interest in that the former ketone shows a band at 303 mμ (ε 390), combining the effects of α-chlorination and homoconjugation, whilst the latter exhibits an ill-defined band near 303—306 mμ (ε ~50),

---

* The possibility of alkyl–oxygen fission as a route to these ketones in anhydrous inert media cannot, however, be overlooked, together with the possibility of competing processes such as cyclisation to full cage structures,[6] although no evidence for the latter has yet been found.

[8] Vernon, *J.*, 1954, 423, 4462.

[9] Segel, Lidov, and Hyman, U.S.P. 2,584,140/1948.

[10] Winstein and Shatavsky, *J. Amer. Chem. Soc.*, 1956, **78**, 592.

[11] Cookson and Crundwell, *Chem. and Ind.*, 1959, 703.

relating these compounds to dehydronorcamphor [12] (295 mμ; ε 315) and the stereoisomeric 2-chlorocamphors [13] (305, 306 mμ; ε 52·5, 56·2).

The infrared carbonyl frequency of the half-cage ketone (X) is somewhat lower than that of the analogue obtained from endrin [6] (1761 cm.$^{-1}$), but the proximity of the carbonyl-oxygen atom to the EtO·CH group raises the possibility of some degree of intramolecular hydrogen bonding.

EXPERIMENTAL

Infrared light absorptions were determined by using a Grubb-Parsons double-beam grating instrument for thin liquid films or paraffin mulls. M. p.s were determined on a gas-heated Kofler block.

5,6-*Dibromo*-1,2,3,4-*tetrachloro*-7,7-*dimethoxybicyclo*[2,2,1]-*hept*-2-*ene* (V).—Tetrachlorodimethoxycyclopentadiene (26·4 g., 0·1 mole) was heated with *cis*-dibromoethylene (18·6 g., 0·1 mole) in sealed tubes at 165° for 10 hr. The viscous oily product was recrystallised from methanol to give 5,6-dibromo-1,2,3,4-tetrachloro-7,7-dimethoxybicyclo[2,2,1]hept-2-ene (V) (20 g., 44%), m. p. 108—109°, $\nu_{max.}$ 1605ms cm.$^{-1}$ (ClC:CCl) (Found: C, 24·7; H, 1·8. $C_9H_8Br_2Cl_4O_2$ requires C, 24·0; H, 1·8%).

Debromination of the Adduct (V) *with Zinc*.—The adduct (7·2 g.) was heated with zinc dust (1·5 g.) in acetic acid (70 ml.) under reflux for 3 hr., the solvent then largely removed *in vacuo*, the residue taken up in ether, and the solution washed with 5% sodium hydrogen carbonate solution and water, dried (Na_2SO_4), and evaporated to give methyl 2,3,4-trichlorobenzoate (2·5 g., 65%) which, recrystallised from light petroleum (b. p. 60—80°), gave the pure ester, m. p. 67—68° (Found: C, 40·2; H, 2·25. Calc. for $C_8H_5Cl_3O_2$: C, 40·1; H, 2·2%). The ester was hydrolysed in 10% ethanolic sodium hydroxide solution in the usual manner to give 2,3,4-trichlorobenzoic acid, m. p. and mixed m. p. 195—197°.

In a similar experiment with methyl alcohol as solvent, distillation of the crude product gave methyl 2,3,4-trichlorobenzoate (1·2 g., 31%), b. p. 116—118°/0·1 mm., m. p. 67—68°. Using ethyl alcohol as solvent gave ethyl 2,3,4-trichlorobenzoate (30%), b. p. 120—124°/0·1 mm., n_D^{20} 1·5580, $\nu_{max.}$ 1715vs cm.$^{-1}$ (aromatic CO_2Et) (Found: C, 42·9; H, 2·8; Cl, 41·55. Calc. for $C_9H_7Cl_3O_2$: C, 42·6; H, 2·8; Cl, 41·9%).

Preparation of Authentic 2,3,4-*Trichlorobenzoic Acid*.—Vinyl chloride was passed through tetrachlorodimethoxycyclopentadiene [14] (50 g.) heated at 180—200° during 10—14 hr., and the mixture distilled to remove unchanged diene; 1,2,3,4,5-pentachloro-7,7-dimethoxybicyclo-[2,2,1]hept-2-ene (21·4 g., 35%), b. p. 138—140°/2 mm., n_D^{20} 1·5320, was then collected.

The pentachloro-ketal (30 g.) was added with stirring to sulphuric acid (100 ml.) and the mixture, which became hot, was stirred for 1 hr., then poured on ice; the solid product was filtered off, dissolved in 10% aqueous sodium hydroxide, filtered (kieselguhr pad) to remove a little oily matter, and acidified with hydrochloric acid; almost pure 2,3,4-trichlorobenzoic acid was precipitated (21 g., 72%). A sample, recrystallised from benzene-light petroleum, had m. p. 195—197°, $\lambda_{max.}$ 288, 296 (shoulder) mμ (ε 600, 490) [15] (Found: C, 37·45; H, 1·7; Cl, 47·9. Calc. for $C_7H_3Cl_3O_2$: C, 37·3; H, 1·3; Cl, 47·2%). Brimelow *et al.*[16] report m. p. 188—189°. The pure acid gave the methyl ester, m. p. 67—68°.

1,2,3,4,7,7-*Hexachlorobicyclo*[2,2,1]*hepta*-2,5-*diene* (I).—Hexachlorocyclopentadiene (1 kg.) was heated at 170—180° whilst vinyl chloride was passed through it for 14 hr.; unchanged diene (180 g.) was distilled off, leaving 1,2,3,4,5,7,7-heptachlorobicyclo[2,2,1]hept-2-ene (1004 g., 82%) which solidified. The crude product was used for the preparation of hexachlorobicycloheptadiene,[17] giving a fraction, b. p. 142—148°/10 mm., n_D^{25} 1·5473—1·5490 (600 g., 66%), a pale yellow oil which darkened on storage. The still residue, separately distilled, gave *ca.* 60 g. of the vinyl ether (IIa) (below).

1,2,4,7,7-*Pentachloro*-3-*ethoxybicyclo*[2,2,1]*hepta*-2,5-*diene* (IIa).—In a typical run [1] hexachlorobicycloheptadiene (119·6 g., 0·4 mole) was added to potassium hydroxide (40·2 g., 0·72 mole) in absolute ethanol (170 ml.), and the mixture heated, stirred under reflux for 4 hr., then

[12] Cookson and Wariyar, *J.*, 1956, 2302.
[13] Cookson, *J.*, 1954, 282.
[14] Cf. Ordas, U.S.P. 2,697,103/1954.
[15] Veldstra, *Rec. Trav. chim.*, 1952, **71**, 15.
[16] Brimelow, Jones, and Metcalfe, *J.*, 1951, 1208.
[17] Bluestone, U.S.P. 2,925,445/1960.

cooled and poured into water. The suspension was filtered (kieselguhr) to remove tar, and the organic product was extracted with ether and added to the washings of the filter pad. The combined ethereal solutions were washed, dried, and evaporated and the residual oil was distilled (9″ jacketed helix-packed column) to give the following fractions (b. p./1—1·5 mm., yield): 90—101°, 20 g.; 101—108°, 11·5 g.; 108—112°, 6·6 g.; 112—117°, 1 g.; 117°, 35 g.; 117—118°, 24 g.; n_D^{20} fell from 1·5525 to 1·5363. Infrared bands characteristic of compound (I) at 1150vs, 902vs, and 790 vs cm.$^{-1}$ declined through fractions 1—4, whilst new bands at 1645vs and 1261vs appeared and increased in intensity through fractions 4—6 (vinyl ether). Molotsky [1] reports b. p. 118°/1·5 mm., n_D^{20} 1·5330, for this product. Fractions 5 and 6 were combined as almost pure 1,2,4,7,7-*pentachloro*-3-*ethoxybicyclo*[2,2,1]*hept*-2,5-*diene* (IIa) (59 g., 48%). A sample redistilled for analysis had b. p. 124—126°/2—3 mm., n_D^{20} 1·5369, $\nu_{max.}$ 1645vs, 1605ms, 1261vs cm.$^{-1}$ (Found: C, 34·3; H, 2·4. $C_9H_7Cl_5O$ requires C, 34·9; H, 2·3%). The still residue was separately distilled and the fractions examined for the presence of 1,2,3,4-tetrachlorobenzene; but this was not found; the fractions consisted of the vinyl ether (IIa) (6 g.).

The aqueous phase was concentrated by boiling and the solution acidified (evolution of carbon dioxide); a black flocculent precipitate settled and was filtered off and dried *in vacuo* to give an unidentified solid (900 mg.).

Over palladium on chalk in methanol, the pentachloroethoxybicycloheptadiene absorbed 1 mol. of hydrogen, giving 1,2,4,7,7-*pentachloro*-3-*ethoxybicyclo*[2,2,1]*hept*-2-*ene*, b. p. 106—108°/0·75 mm., n_D^{20} 1·5344, $\nu_{max.}$ 1642vs, 1605ms, 1250ms cm.$^{-1}$ (vinyl ether) (Found: C, 34·5; H, 2·45. $C_9H_9Cl_5O$ requires C, 34·8; H, 2·9%).

The vinyl ether (IIa) (10 g.) was treated with bromine (5·8 g., 1·1 mol.) in carbon tetrachloride (30 ml.) at 60°, and the solution was washed with water, dried, and evaporated; the residual oil was distilled, to give 5,6-*dibromo*-1,2,4,7,7-*pentachloro*-3-*ethoxybicyclo*[2,2,1]*hept*-2-*ene* (IId) (13·2 g.) which, redistilled, had b. p. 154—158°/0·1 mm., $\nu_{max.}$ 1645vs, 1605ms, 1258 ms cm.$^{-1}$ (Found: C, 22·9; H, 1·6. $C_9H_7Br_2Cl_5O$ requires C, 23·2; H, 1·5%). The crude dibromo-adduct also showed $\nu_{max.}$ 1792w cm.$^{-1}$.

Hydrolysis of the Vinyl Ether (IIa).—The pentachloroethoxybicycloheptadiene (10 g.) was added to sulphuric acid (25 ml.), and the mixture shaken; a transient blue-green colour developed and the mixture became warm, depositing a sticky solid. After 1 hr. the mixture was poured on ice, the viscous oil was extracted with ether, the extracts were washed, dried, and evaporated, and the residue was dissolved in warm light petroleum (b. p. 60—80°) which, on cooling, deposited crystals; these (5 g., 54%) were filtered off, to give 1,3,4,7,7-*pentachlorobicyclo*[2,2,1]*hept*-5-*en*-2-*one* (IIb), m. p. 120—123°, raised to 123° by further crystallisation, $\nu_{max.}$ 1785vs cm.$^{-1}$ (CCl·CO in a strained ring), $\lambda_{max.}$ 303 mμ (ε 390) (Found: C, 30·6; H, 1·1. $C_7H_3Cl_5O$ requires C, 30·0; H, 1·1%). Hydrolysis was also effected in 50% ethanolic sulphuric acid, the ketone slowly crystallising (60% yield). This ketone (1·4 g., 0·005 mole) absorbed hydrogen (1 mol.) over palladium on chalk in methanol to give 1,3,4,7,7-*pentachlorobicyclo*[2,2,1]*heptan*-2-*one* (IIc) (1 g.), m. p. 154° (from light petroleum), $\nu_{max.}$ 1792vs cm.$^{-1}$, $\lambda_{max.}$ 303—306 mμ (ε ~50) (Found: C, 30·2; H, 1·7. $C_7H_5Cl_5O$ requires C, 29·8; H, 1·8%). The pentachlorobicycloheptanone (IIc) was also obtained when 1,2,4,7,7-pentachloro-3-ethoxybicyclohept-2-ene (6 g.) was kept in sulphuric acid (20 ml.) at 20°; similar changes to those observed with (IIa) occurred; working up was as above, giving, on distillation, the ketone, b. p. 104—108°/0·1 mm. (3·3 g., 60%), m. p. and mixed m. p. 154° (from light petroleum) (b. p. 60—80°).

Zinc Reduction of the Pentachlorobicycloheptanone (IIc).—The pentachlorobicycloheptanone (1·8 g.) was heated with zinc dust (800 mg.) in acetic acid (20 ml.) for 3 hr., then poured into water, and the product was filtered off, washed with water, and recrystallised from light petroleum (b. p. 60—80°), to give 1,4,7,7-*tetrachlorobicyclo*[2,2,1]*heptan*-2-*one* (700 mg.), m. p. 232—233°, $\nu_{max.}$ 1786vs cm.$^{-1}$ (CCl·CO in a strained ring) (Found: C, 33·6; H, 2·5. $C_7H_6Cl_4O$ requires C, 33·9; H, 2·4%).

Reaction of 1,2,3,4,7,7-*Hexachlorobicyclo*[2,2,1]*hept*-2-*ene with Concentrated Alkali*.—Hexachlorobicycloheptadiene (I) (30 g.) was hydrogenated over palladium–chalk in absolute ethanol (300 ml.) until 1 mol. was absorbed. The mixture was filtered and concentrated to 60 ml. (column), potassium hydroxide (10·3 g.) added, and the whole heated under reflux with stirring for 4 hr. After working up as before, the product was distilled, giving hexachlorobicyclohept-2-ene (18 g.), b. p. 104—108°/2 mm., n_D^{20} 1·5510—1·5520, identical (spectrum) with the compound separately prepared. The still residue, fractionally distilled, gave 1 g. of a product, b. p. 114—120°/2 mm., which contained vinyl ether, probably 1,2,4,7,7-pentachloro-3-ethoxybicyclohept-2-ene (spectral comparison).

Bromination of Hexachlorobicycloheptadiene.—The diene (3·35 g.) was dissolved in chloroform (25 ml.), and bromine (1·8 g., 1 mol.) added; the solution was slowly decolorised. Solvent was then removed *in vacuo*. The residual semi-solid product was distilled and after a forerun (1·2 g.) the dibromide (2·9 g.), b. p. 140—144°/0·1 mm., was obtained; it solidified. Infrared spectral comparison of the forerun and the main fraction showed the product to be homogeneous ($\nu_{\max.}$ 1603vs cm.$^{-1}$). On a larger scale the dibromide from hexachlorobicycloheptadiene (9 g.) and bromine (4·8 g.), prepared in acetic acid and worked up as before, was treated with zinc dust (2 g.) in ethanol (70 ml.); the mixture rapidly became warm and after 1 hour's shaking the mixture was poured into water, and the product extracted with ether. Evaporation and distillation of the residual oil gave hexachlorobicycloheptadiene (I) (6 g.), b. p. 144—150°/10—11 mm., identical with the authentic material.

1,2,4,10,10-*Pentachloro*-3-*ethoxy*-1,4,4a,5,8,8a-*hexahydro*-exo-exo-1,4 : 5,8-*dimethanonaphthalene* (VI).—The vinyl ether (IIa) (30·8 g., 0·1 mole) was heated in sealed tubes with freshly cracked cyclopentadiene (7·2 g., 0·11 mole) for 3—5 hr. at 165°. A small sample of the viscous oily product was distilled, to give a solid adduct, b. p. 137—142°/0·1 mm. This was used to seed a solution of the remainder of the material in ethanol; the *product* (22 g., 62%) had m. p. 108°, $\nu_{\max.}$ 1642vs, 1605ms, 1252vs cm.$^{-1}$ (vinyl ether) (Found: C, 44·6; H, 3·5. $C_{14}H_{13}Cl_5O$ requires C, 44·9; H, 3·5%), and gave a *nitrosochloride*, m. p. 200° (decomp.) (from benzene) (Found, C, 38·2; H, 2·9. $C_{14}H_{13}Cl_6NO_2$ requires C, 38·2; H, 3·0%).

The adduct (VI) (930 mg., 0·0025 mole) rapidly absorbed hydrogen (1 mol.) over palladium–chalk in methanol to give endo-endo-1,2,4,10,10-*pentachloro*-3-*ethoxy*-1,4,4*a*,5,6,7,8,8*a*-*octahydro*-1,4 : 5,8-*dimethanonaphthalene* (800 mg.), b. p. 160°/0·4 mm., m. p. 76—77° (Found: C, 44·6; H, 4·1. $C_{14}H_{15}Cl_5O$ requires C, 44·65; H, 4·0%).

Bromination of the Adduct (VI).—The adduct (3·74 g., 0·01 mole) was treated in warm acetic acid (40 ml.) with bromine (1·6 g., 1 mol.). On evaporation hydrogen bromide was evolved and, on cooling, the concentrated solution deposited crystals. These were recrystallised from ethanol, to give exo-12-*bromo*-2,4,5,5,6-*pentachloropentacyclo*[7,2,1,$0^{2,6}$,$0^{4,8}$,$0^{7,11}$]*dodecan*-3-*one* (VII) (3·8 g., 89%), m. p. 183°, $\nu_{\max.}$ 1785vs cm.$^{-1}$, no absorption in the 1600 cm.$^{-1}$ region (Found: C, 34·2; H, 1·75. $C_{12}H_8BrCl_5O$ requires C, 33·9; H, 1·9%). The same ketone was obtained, but more slowly, from the adduct (VI) by treatment with bromine in an excess in carbon tetrachloride. No semicarbazone (sealed tube, pyridine) or 2,4-dinitrophenylhydrazone (ethoxyethanol) could be isolated; in each case the ketone was recovered unchanged, as it was also on attempted reduction with lithium aluminium hydride in di-n-butyl ether.

Reaction of the Adduct (VI) *with Mineral Acids.*—(*a*) The adduct (3·74 g., 0·01 mole) was warmed in a saturated solution of hydrogen bromide in *ca.* 90% aqueous acetic acid at 80—90° for 1·5 hr., the solution evaporated *in vacuo*, and the residual solid recrystallised from ethanol, to give 2,4,5,5,6-*pentachloropentacyclo*[7,2,0,$1^{2,6}$,$0^{4,8}$,$0^{7,11}$]*dodecan*-3-*one* (VIII) (2·2 g., 65%), m. p. 228°, $\nu_{\max.}$ 1790vs cm.$^{-1}$, no absorption in the 1600 cm.$^{-1}$ region (Found: C, 42·0; H, 2·6. $C_{12}H_9Cl_5O$ requires C, 41·6; H, 2·6%). Attempted reduction with lithium aluminium hydride, (and preparation of carbonyl derivatives as described above), gave only recovered ketone. (*b*) A suspension of the adduct (3·74 g.) in sulphuric acid (50 ml.) was left overnight at 20°, then poured on ice, and the solid filtered off, washed with water, and recrystallised from ethanol to give the ketone (VIII) (2·74 g., 80%) of the above m. p. and mixed m. p. The ketone was also obtained by heating of the adduct (VI) in solutions of sulphuric acid in acetic acid.

Epoxidation of the Adduct (VI).—The adduct (3 g.) was dissolved in benzene (30 ml.), and 30—40% w/v peracetic acid (3 ml.) added; the mixture was left for 2 days at 20° with occasional shaking, then washed with dilute sodium hydroxide solution and water, dried, and cautiously evaporated *in vacuo*. The residue was recrystallised from ethanol to give 1,2,4,10,10-*pentachloro*-3-*ethoxy*-exo-6,7-*epoxy*-1,4,4*a*,5,6,7,8,8*a*-*octahydro*-exo-exo-1,4 : 5,8-*dimethanonaphthalene* (IX) (2·3 g., 72%), m. p. 113—115°, raised to 121° by repeated crystallisation, $\nu_{\max.}$ 1642vs, 1605m (shoulder), 1261vs (vinyl ether), 871vs, 846vs cm.$^{-1}$ (epoxide) (Found: C, 43·4; H, 3·4. $C_{14}H_{13}Cl_5O_2$ requires C, 43·05; H, 3·35%).

In a second preparation the adduct (1 g.) was dissolved in warm acetic acid (10 ml.), the solution cooled to 0°, and peracetic acid (5 ml.) added; after 2 days at 20° the mixture was poured into water and the crystalline product filtered off, thoroughly washed with water, and recrystallised from ethanol, to give 1,9,10,10,11-*pentachloro*-exo-12-*ethoxypentacyclo*-[7,2,1,$0^{2,6}$,$0^{4,8}$,$0^{7,11}$]*dodecan*-3-*one* (X) (700 mg., 67%), m. p. 137—138°, $\nu_{max.}$ 1748vs cm.$^{-1}$, no absorption in the 1600 or 871 cm.$^{-1}$ region (Found: C, 43·5; H, 3·2. $C_{14}H_{13}Cl_5O_2$ requires C, 43·05; H, 3·35%).

The epoxide (IX) was converted into the ketone (X) by the following methods. (*a*) The epoxide (100 mg.) was dissolved in acetic acid (3 ml.), and boron trifluoride–acetic acid complex (40%) (5 drops) added; the mixture which became warm was set aside for 1 hr., then poured into water, and the solid product filtered off and recrystallised from ethanol to give the ketone (X) (50 mg.) (mixed m. p., infrared spectrum). (*b*) A similar solution of the epoxide in acetic acid only was heated at 80—90° for 1 hr. and worked up as in (*a*); the infrared spectrum of the product showed that it consisted of a mixture of the epoxide and the ketone (X), the ketone predominating. (*c*) A solution of the epoxide (700 mg.) in benzene (7—10 ml.) was treated with boron trifluoride–acetic acid (4—5 mg.); the mixture immediately became warm and after 1 hr. was washed with water, dried, and evaporated; the residue recrystallised from ethanol to give the ketone (X) (350 mg.), m. p. 133—136°, raised to 137—138° by a further crystallisation. (*d*) The epoxide (300 mg.) was heated at 200—220° for 1 hr. and the product recrystallised from ethanol to give substantially pure ketone (X) (100 mg., 33%), m. p. 125—130°; recrystallised from ethanol once more it had m. p. and mixed m. p. 137—138° and the correct infrared spectrum; 50 mg. of the epoxide (IX) were recovered from the liquors.

Reduction of the Half-cage Ketone (X).—The ketone (2·2 g.) was dissolved in sodium-dried dibutyl ether (10 ml.), and lithium aluminium hydride (92 mg., 2 mol.) added. The solution was heated under reflux for 3 hr., poured into water, and acidified with hydrochloric acid. The organic phase was separated and bulked with several butyl ether extracts of the aqueous phase; the combined solutions were washed with aqueous sodium hydrogen carbonate and water, dried (Na_2SO_4) and evaporated *in vacuo*; the residual viscous oil, which did not solidify immediately, was thoroughly dried and used without further purification for the preparation of the methanesulphonate as follows. The alcoholic product was dissolved in pyridine (10 ml.) and an excess of methanesulphonyl chloride (2 ml.) added; the mixture was left for 2—3 hr., then poured into water, and the oily precipitate stirred until solid; the product was filtered off and recrystallised from ethanol to give 1,9,10,10,11-*pentachloro*-exo-12-*ethoxypentacyclo*[7,2,1,$0^{2,6}$,$0^{4,8}$,$0^{7,11}$]-*dodecan*-exo-3-*yl methanesulphonate* (XII) (850 mg., 31%), m. p. 155—157°, $\nu_{max.}$ 1346vs cm.$^{-1}$ (SO_3) (Found: C, 38·4; H, 3·55. $C_{15}H_{17}Cl_5O_4S$ requires C, 38·3; H, 3·6%). Unchanged ketone (350 mg.) was isolated from the concentrated liquors.

Solvolysis of the Methanesulphonate (XII).—The pure ester (800 mg.) was heated with calcium carbonate (100 mg.) in 80% aqueous acetone (50 ml.) under reflux for 6 days, filtered, evaporated until solid began to separate, and then cooled; filtration afforded the ketone (VIII) (400 mg., 68%), m. p. 225°, raised to 228° by recrystallisation from ethanol (mixed m. p.; infrared spectrum).

In a similar experiment, the methanesulphonate (500 mg.) was similarly heated in 80% aqueous dioxan (50 ml.) in the presence of calcium carbonate (50 mg.) for 3 days only and worked up as before; it gave the ketone (VIII) (250 mg., 68%), m. p. and mixed m. p. 228° without further purification.

The author expresses his appreciation of the kindly interest and encouragement given by Professor E. E. Turner, F.R.S., and Professor P. B. D. de la Mare, F.R.I.C.

BEDFORD COLLEGE, LONDON, N.W.1.

[*Received, July* 19*th*, 1961.]