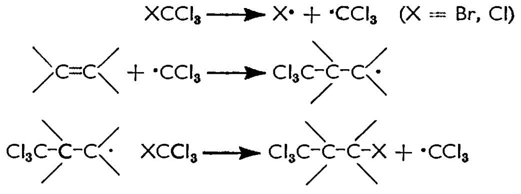
729. *The Addition of Bromotrichloromethane and Carbon Tetrachloride to Aldrin.*

By D. I. Davies.

The radical-catalysed addition of bromotrichloromethane and carbon tetrachloride to the 6,7-double bond of aldrin (I) has been studied, and evidence obtained indicating that it occurs in the *trans*-manner. A similar stereochemistry may be inferred for similar additions to norbornene.

In 1947 Kharasch and his colleagues[1] showed that bromotrichloromethane and carbon tetrachloride added to various olefins in the presence of free-radical initiators:



Kharasch and Friedlander[2] studied the addition of bromotrichloromethane to norbornene (bicyclo[2,2,1]hept-2-ene), and they found the product to be inert on mild treatment with ethanolic potassium hydroxide. Fawcett[3] then deduced that addition had occurred in a *trans*-manner, as the hydrogen and bromine would then be *cis* to one another and not readily eliminated. This deduction is now invalid as Cristol *et al.*[4] have shown that in the norbornane series, with its rigid geometry, the stereochemical requirement of *trans*-coplanarity for ready elimination cannot be met. Kwart and Rolleri[5] found

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[1] Kharasch, Jensen, and Urry, *J. Amer. Chem. Soc.*, 1947, **69**, 1100; Kharasch, Reinmuth, and Urry, *ibid.*, p. 1105.

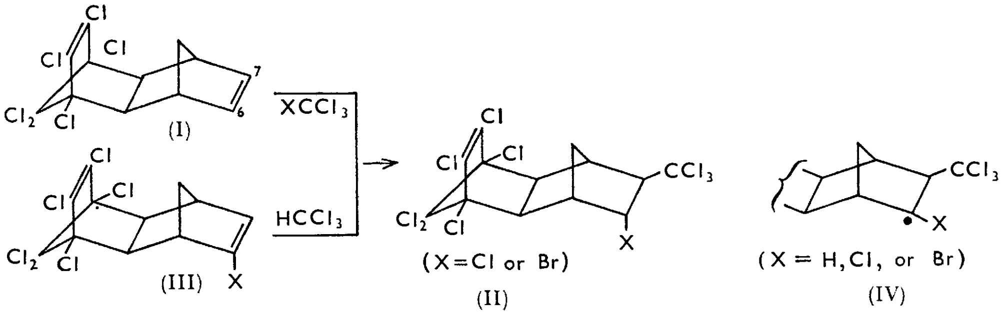
[2] Kharasch and Friedlander, *J. Org. Chem.*, 1949, **14**, 239.

[3] Fawcett, *Chem. Rev.*, 1950, **47**, 219.

[4] Cristol and Hoegger, *J. Amer. Chem. Soc.*, 1957, **79**, 3438; Cristol and Hause, *ibid.*, 1952, **74**, 2193.

[5] See Rolleri, *Diss. Abs.*, 1958, **19**, 960.

that the dipole moment of the addition product, although somewhat ambiguous, indicated *cis*-addition. Rearrangement during the addition is unlikely as the addition product of chloroform and norbornene gave norcamphor on dehydrochlorination with potassium t-butoxide, followed by oxidation, a clear chemical proof of simple, unrearranged addition to the 1,2-double bond.[5]



(I)

(III)

(X=Cl or Br)

(II)

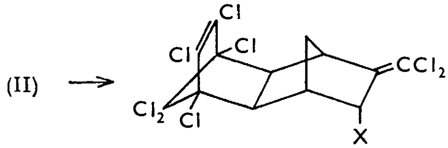
(X = H,Cl, or Br)

(IV)

Because of the varying opinions, we began a re-investigation, using aldrin (I) instead of norbornene since the products are crystalline.

Carbon tetrachloride added to the 6,7-double bond in aldrin in high yield, and the product was identical with that from chloroform and 6-chloroaldrin. Similarly bromotrichloromethane added to aldrin, to give a product identical with that from chloroform and 6-bromoaldrin. These results, although not conclusive, favour *trans*-addition of bromotrichloromethane and carbon tetrachloride to aldrin, and *cis*-addition of chloroform to 6-chloroaldrin and 6-bromoaldrin.

Alder and Stein[6] showed that *exo*- is more stable than *endo*-norborneol,* and this has been confirmed by the study of other *exo*- and *endo*-derivatives of the norbornane series; for example, Winstein and Trifan[7] found that solvolyses of both *endo*- and *exo*-norbornyl arylsulphonate gave *exo*-products with great stereospecificity. Later studies of ionic and free-radical additions to norbornene and related compounds[8] have all shown that the attacking entity approaches from the *exo*-side of the molecule, and thus it is assumed that the $\cdot CCl_3$ radical will attack aldrin, 6-chloroaldrin, and 6-bromoaldrin to give an intermediate of type (IV) in which the radical centre at position 7 will presumably have an approximately trigonal structure. In the reactions of carbon tetrachloride and bromotrichloromethane with aldrin, these large molecules cannot approach the intermediate (IV; X = H) from the *exo*-side of the molecule on account of the steric hindrance of the trichloromethyl group, and they consequently attack from the *endo*-side to give a *trans*-addition product. When chloroform reacts with 6-chloroaldrin and 6-bromoaldrin, the chloroform molecule, if correctly orientated, can attack the intermediate (IV; X = Cl or Br) to give products of *cis*-addition, in which the trichloromethyl and halogeno-groups



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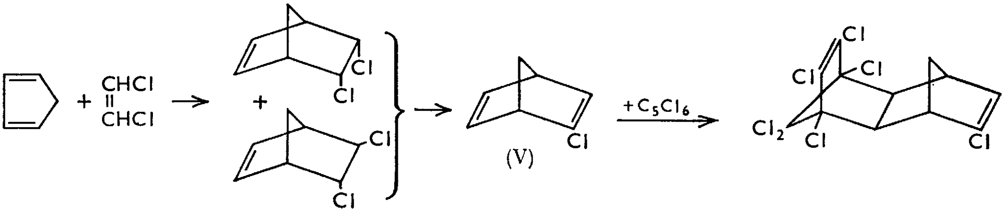
* In this paper the *exo*-side of aldrin is considered to be that on which the methylene bridge projects; the other side is termed *endo*-.

[6] Alder and Stein, *Annalen*, 1934, **514**, 211; 1936, **525**, 183.

[7] Winstein and Trifan, *J. Amer. Chem. Soc.*, 1952, **74**, 1147, 1154.

[8] Kwart and Kaplan, *J. Amer. Chem. Soc.*, 1954, **76**, 4072; Cristol, Arganbright, Brindell, and Heitz, *ibid.*, 1957, **79**, 6035; LeBel, *ibid.*, 1960, **82**, 623; Cristol and Brindell, *ibid.*, 1954, **76**, 5699; Cristol and Arganbright, *ibid.*, 1957, **79**, 6039; Berson, *ibid.*, 1954, **76**, 5748.

will be *trans*-related and which are consequently identical with the addition products of carbon tetrachloride and bromotrichloromethane to aldrin. The results could be explained by *cis*-addition of bromotrichloromethane and carbon tetrachloride to aldrin, and *trans*-addition of chloroform to 6-chloroaldrin and 6-bromoaldrin. This seems unlikely, however, as it implies that steric hindrance to the attack by the smaller chloroform molecule on the intermediate (IV) is greater than for the larger carbon tetrachloride and bromotrichloromethane. The *cis*-addition of chloroform to 6-chloroaldrin and 6-bromoaldrin renders unlikely a bridged-radical intermediate, which accords with studies by LeBel [8] and by Cristol *et al.*[8] on other additions of free radicals in the norbornene series. Aldrin is a substituted norbornene, and if the addition of bromotrichloromethane to aldrin is analogous to its addition to norbornene, then that addition must also give the *trans*-product.



The adducts (II) of carbon tetrachloride and bromotrichloromethane to aldrin both eliminated one mol. of hydrogen chloride when treated with potassium hydroxide in refluxing ethyl alcohol. If Bredt's rule is obeyed,[3] elimination must have occurred as illustrated. This is supported by the infrared spectra (KCl discs) where the elimination products showed bands at 6·09 μ. If elimination had given a 6,7-double bond, the bands would have been expected at 6·33 μ as in 6-chloro- and 6-bromo-aldrin. The following synthesis employed for 6-chloroaldrin is of interest as it involves the preparation of 2-chloronorbornadiene (V) as an intermediate.

A mixture of *endo-cis-* and *trans*-5,6-dichloronorbornene gave a moderate yield (28·5%) of 2-chloronorbornadiene (V) on treatment with potassium hydroxide in refluxing ethylene glycol. Roberts *et al.*[9] found that under milder conditions *endo-cis*-5,6-dichloronorbornene did not undergo significant dehydrohalogenation. Soloway [10] prepared 6-bromoaldrin by the action of alcoholic potassium hydroxide on a mixture of dibromides obtained on reaction of aldrin with bromine in carbon tetrachloride. A repetition of this experiment gave in high yield a single dibromide, which with potassium hydroxide in ethyl alcohol gave 6-bromoaldrin. In the related reaction of 1,2,3,4-tetrachloro-1,4,4a,5,8,8a-hexahydro-1,4-dimethoxymethano-5,8-methanonaphthalene with bromine in chloroform, Mackenzie [11] similarly obtained a single dibromide.

EXPERIMENTAL

Aldrin, obtained from the Shell Chemical Company melted at 60—80°. Recrystallised several times from methanol it gave pale yellow needles, m. p. 103—104·5°.

Reaction of Carbon tetrachloride with Aldrin.—To aldrin (5·0 g.) in carbon tetrachloride (50 ml.) benzoyl peroxide (0·1 g.) was added. The mixture was boiled for 40 hr., then the carbon tetrachloride was removed by distillation, finally under reduced pressure on the steam-bath. endo-6-*Chloro*-6,7-*dihydro*-exo-7-*trichloromethylaldrin* (6·5 g.), on recrystallisation from methanol, had m. p. 137—138° (Found: C, 30·05; H, 1·6. $C_{13}H_8Cl_{10}$ requires C, 30·1; H, 1·55%). The infrared spectra of the crude and the purified product showed no detectable differences, indicating that a single compound was formed.

Addition of cis-*Dichloroethylene to Cyclopentadiene.*—This was carried out by the method of

[9] Roberts, Johnson, and Carboni, *J. Amer. Chem. Soc.*, 1954, **76**, 5692.
[10] Soloway, U.S.P. 2,676,131. *Chem. Abs.*, 1954, **48**, 8473.
[11] Mackenzie, *J.*, 1960, 473.

Roberts *et al.*,[9] and a mixture of *endo-cis-* and *trans*-5,6-dichloronorbornene obtained. Most of the product solidified and thus consisted predominantly of the *cis*-isomer.

Dehydrochlorination of the Mixed Dichloronorbornenes.—The mixture (20 g.) was boiled with potassium hydroxide (10 g.) in ethylene glycol (40 ml), for 1·5 hr., and the product, b. p. 100—180°, was distilled off. It contained about 20% of water and was diluted with ether. The ether layer was dried ($CaCl_2$) and evaporated. 2-*Chloronorbornadiene*, b. p. 140° (5·6 g.), on redistillation, had b. p. 64°/70 mm., n_D^{22} 1·4960 (Found: C, 66·7; H, 5·9. C_7H_7Cl requires C, 66·4; H, 5·6%). It polymerised to a brown gum at room temperature during several months.

Addition of Hexachlorocyclopentadiene to 2-Chloronorbornadiene.—Hexachlorocyclopentadiene (10·6 g.) and 2-chloronorbornadiene (6·3 g.) were heated together in a sealed Pyrex tube at 140° for 12 hr. After removal of the unchanged reactants, 6-chloroaldrin (12·3 g.) was distilled off (b. p. 146°/0·1 mm.); it had m. p. 55—57° after several recrystallisations from methanol (Found: C, 36·1; H, 1·8. Calc. for $C_{12}H_7Cl_7$: C, 35·95; H, 1·75%). Lidov and Soloway [12] record m. p. 55—57°, and Cristol and Arganbright [8] record m. p. 62—64°.

Reaction of 6-Chloroaldrin with Chloroform.—A solution of 6-chloroaldrin (4 g.) and benzoyl peroxide (0·1 g.) in chloroform (50 ml.) was refluxed for 240 hr. The chloroform was removed and the product was distilled, giving two fractions: the first, b. p. 120—140°/0·05 mm. (2·7 g.), slowly solidified; its infrared spectrum indicated a mixture of 6-chloroaldrin with a trace of another material whose absorption bands could be correlated with those of the addition product of aldrin and carbon tetrachloride. The second, b. p. 160—180°/0·1 mm. (1·6 g.), solidified and after several recrystallisations had the m. p. and mixed m. p. of *endo*-6-chloro-6,7-dihydro-*exo*-7-trichloromethylaldrin 137—138° (Found: C, 30·1; H, 1·45. Calc. for $C_{13}H_8Cl_{10}$: C, 30·1; H, 1·45%) (identical infrared spectra). All bands in the infrared spectrum of the crude distillate could be correlated with those of these two substances.

Addition of Bromotrichloromethane to Aldrin.—Aldrin (5 g.), bromotrichloromethane (40 ml.), and benzoyl peroxide (0·1 g.) were heated at 100° under nitrogen for 40 hr. Bromotrichloromethane was removed by distillation, and then on the steam-bath, leaving endo-6-*bromo*-6,7-*dihydro*-exo-7-*trichloromethylaldrin* (7·5 g.). After several recrystallisations its m. p. was 153—154° (Found: C, 27·75; H, 1·35. $C_{13}H_8BrCl_9$ requires C, 27·7; H, 1·4%). The infrared spectra of the crude and the purified product indicated that a single product had been formed.

Addition of Bromine to Aldrin.—To a stirred solution of aldrin (10 g.) in carbon tetrachloride (100 ml.) at 0° bromine (4·4 g.) in carbon tetrachloride (100 ml.) was added during 2 hr. Stirring was continued for 24 hr. The excess of bromine and carbon tetrachloride was distilled off to leave *endo*-6-*exo*-7-dibromo-6,7-dihydroaldrin (13 g.), m. p. 174—175° (from 1 : 1 benzene–ethanol) (Found: C, 27·6; H, 1·5. Calc. for $C_{12}H_8Br_2Cl_6$: C, 27·5; H, 1·5%).

Dehydrobromination of endo-6-exo-7-*Dibromo*-6,7-*dihydroaldrin.*—Potassium hydroxide (5 g.) and *endo*-6-*exo*-7-dibromo-6,7-dihydroaldrin (10 g.) were refluxed in 95% ethanol (100 ml.) for 18 hr. Most of the ethanol was then removed by distillation, and water (100 ml.) was added to the residue to dissolve the inorganic materials. The resultant mixture was extracted with benzene (4 × 50 ml.) and the extracts were washed with water, dried ($CaSO_4$), and evaporated. The residue recrystallised to give a pale yellow solid, m. p. 84·5° (7·0 g.). Further recrystallisation gave white 6-bromoaldrin, m. p. 85—86° (Lidov and Soloway [12] report m. p. 84—85°) (Found: C, 32·4; H, 1·4. Calc. for $C_{12}H_7BrCl_6$: C, 32·45; H, 1·6%).

Addition of Chloroform to 6-Bromoaldrin.—6-Bromoaldrin (4 g.) and benzoyl peroxide (0·1 g.) were boiled in chloroform (50 ml.) for 200 hr. The excess of chloroform was removed and the product distilled. Fraction (i), b. p. 130—140°/0·03 mm. (3·0 g.), which solidified and gave the infrared spectrum of 6-bromoaldrin. Fraction (ii), b. p. 160—185°/0·04 mm. (1·13 g.), was a yellowish-white solid, the infrared spectrum of which indicated a mixture of 6-bromoaldrin and *endo*-6-bromo-6,7-dihydro-*exo*-7-trichloromethylaldrin. Recrystallisation from ethanol gave the latter with m. p. 151—152° and the correct infrared spectrum (Found: C, 28·05; H, 1·7. Calc. for $C_{13}H_8BrCl_9$: C, 27·7; H, 1·4%).

Dehydrohalogenation of the Addition Product of Carbon Tetrachloride and Aldrin.—The adduct (2 g.) was boiled with potassium hydroxide (2 g.) in absolute ethanol (100 ml.) for 4 hr., then worked up as in the case of 6-bromoaldrin. endo-6-*Chloro*-7-*dichloromethylene*-6,7-*dihydroaldrin* (1·4 g.) had m. p. 124—125° (Found: C, 32·3; H, 1·5. $C_{13}H_7Cl_9$ requires C, 32·4; H, 1·5%).

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[12] Lidov and Soloway, B.P. 692,546.

Dehydrohalogenation of the Addition Product of Bromotrichloromethane and Aldrin.—Reaction as in the preceding paragraph gave endo-6-*bromo*-7-*dichloromethylene*-6,7-*dihydroaldrin* (1·6 g. from 2 g.), m. p. 138—139° (Found: C, 29·5; H, 1·3. $C_{13}H_7BrCl_8$ requires C, 29·6; H, 1·3%).

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