Free-radical Reactions of Halogenated Bridged Polycyclic Compounds. Part XI.† Application of the Cristol–Firth Reaction to Some Carboxylic Acids containing a Chloronorbornene Ring System

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The Cristol-Firth reaction has been applied to a number of carboxylic acids containing a chloronorbornene ring system. 1,4,5,6,7,7-Hexachloronorborn-5-en-2-ylacetic acid affords, *via* the 1,4,5,6,7,7-hexachloronorborn-5-en-2-ylmethyl radical, the corresponding 1,4,5,6,7,7-hexachloronorborn-5-en-2-ylmethyl halides. 1,4,5,6,7,7-Hexachloronorborn-5-en-2-ylcarboxylic acid gives the 1,4,5,6,7,7-hexachloronorborn-5-en-2-yl radical, which may undergo chain transfer from both the *exo*- and *endo*-directions to afford the corresponding halides. If the halogen is bromine rearrangement to the 2,3,3,4,5,6-hexachloronorborn-5-en-2-yl radical competes with chain transfer, and this new radical can additionally afford products on chain transfer with bromine. Reactions with other chloronorborn-5-en-2-ylcarboxylic acids are similar. Evidence is presented that chloronorborn-5-en-2-yl radicals, with the *exo*-radical being favoured due to minimised nonbonded interactions.

THE Hunsdiecker reaction ¹ is a useful route for the conversion of carboxylic acids into halides by the reaction of the silver salt of a carboxylic acid with free halogen. A useful modification of this reaction, in which halogen is added to a boiling carbon tetrachloride solution of a carboxylic acid in the presence of red mercuric oxide, was discovered by Cristol and Firth.² The stoicheiometry of the reaction is given in the following equation:

$$\begin{array}{c} 2\text{RCO}_2\text{H} + \text{HgO} + 2\text{Br}_2 \longrightarrow \\ 2\text{RBr} + \text{HgBr}_2 + \text{H}_2\text{O} + 2\text{CO}_2 \end{array}$$

[†] Part X, D. I. Davies and M. J. Parrott, J. Chem. Soc. (C), 1970, 659.

¹ C. V. Wilson, Org. Reactions, 1957, 9, 335; R. G. Johnson and R. K. Ingham, Chem. Rev., 1956, 56, 219. ² S. J. Cristol and W. C. Firth, jun., J. Org. Chem., 1961, 26,

² S. J. Cristol and W. C. Firth, jun., *J. Org. Chem.*, 1961, 26, 280.

Like the Hunsdiecker reaction there is little doubt, following the application of the Cristol-Firth reaction to a variety of carboxylic acids,³ that the reaction involves the intermediacy of the free radical R[•]. The Cristol-Firth reaction is thus a convenient way of studying free radicals R[•] generated from carboxylic acids RCO_{2}H .

The Cristol-Firth reaction has now been applied to 1,4,5,6,7,7-hexachloronorborn-5-en-2-ylacetic acid (I), and affords 1,4,5,6,7,7-hexachloronorborn-5-en-2-yl-methyl bromide (IIa) and iodide (IIb) respectively,

³ (a) S. J. Cristol, J. R. Douglass, W. C. Firth, jun., and R. E. Krall, J. Org. Chem., 1962, 27, 2711; (b) F. W. Baker, H. D. Holtz, and L. M. Stock, J. Org. Chem., 1963, 28, 514; (c) J. A. Davis, J. Herynk, S. Carroll, J. Bunds, and D. Johnson, J. Org. Chem., 1965, 30, 415; (d) A. J. Solo and B. Singh, J. Org. Chem., 1967, 32, 567; (e) J. W. Wilt and J. A. Lundquist, J. Org. Chem., 1964, 29, 921. when bromine and iodine are used as halogen. Clearly the intermediate 1,4,5,6,7,7-hexachloronorborn-5-en-2ylmethyl radical has no tendency to rearrange. The products were identified from their n.m.r. data (see Table 2), which were consistent with literature compilations,⁴ and by the identity of products (IIa) and (IIb) with the Diels-Alder adducts of hexachlorocyclopentadiene to allyl bromide⁵ and allyl iodide⁶ respectively. Treatment of 1,4,5,6,7,7-hexachloronorborn-5-en-2-endo-vlcarboxvlic acid (IIIa) with mercuric oxide and bromine gave a 3:4:1 mixture of 5-exo-bromo-1,2,3,4,7,7-hexachloronorborn-2-ene (VIIa), its 5-endobromo-epimer (VIIIa) and the rearranged bromide 5-exo-bromo-1,2,3,5-endo,6,6-hexachloronorborn-2-ene

(XIIa). The products were identified from their n.m.r. data (see Table 2) by comparison with literature compilations,⁷⁻¹⁰ and additionally in the case of the 5-endobromide (VIIIa) by its identity with the Diels-Alder adduct of vinyl bromide and hexachlorocyclopentadiene.^{11a} Support that the Diels-Alder adduct is the endo-bromide is provided by the recent observation of Williamson¹¹^b that the Diels-Alder addition of vinyl bromide to pentachlorocyclopentadiene affords 5-endobromo-1,2,3,4,7-anti-pentachloronorborn-2-ene as one of the products, but not the corresponding epimeric 5-exo-bromide.

The formation of the products from the reaction of acid (IIIa) with mercuric oxide and bromine is best rationalised as involving the intermediacy of the 1,4,5,6,7,7-hexachloronorborn-5-en-2-yl radical (IVa), which can either abstract a bromine atom from molecular bromine to give the 5-exo- (VIIa) and 5-endo- (VIIIa) bromides, or alternatively undergo rearrangement via the nortricyclyl-type radical (Va) to give the chlorinesubstituted radical (VIa) from which the rearranged bromide (XIIa) is derived. This is analogous to those rearrangements observed in free-radical addition reactions of hexachloronorbornadiene and related compounds^{9,12} and probably has as its driving force the increased stabilisation occasioned by chlorine-substitution^{9,13} at the radical centre in (VIa) compared with hydrogen substitution at the radical centre in (IVa). Mercuric oxide and iodine gave a 4:3 mixture of 1,2,3,4,7,7-hexachloro-5-exo-iodonorborn-2-ene (IXa) and its 5-endo-iodo-epimer (Xa), but no rearranged iodide analogous to the rearranged bromide (XIIa) was formed. Clearly the 1,4,5,6,7,7-hexachloronorborn-5-en-2-yl radical (IVa) can abstract an iodine atom from

⁶ R. Riemschneider and H. J. Kolzsch, Monatsh., 1960, 91, **4**1.

⁷ K. L. Williamson, J. Amer. Chem. Soc., 1963, **85**, 516; K. L. Williamson, N. C. Jacobus, and K. T. Soucy, *ibid.*, 1964, **86**, 4021; K. L. Williamson, *ibid.*, 1964, **86**, 5712. ⁶ A. U. Stepanyants and V. F. Bystrov, *Izvest. Akad. Nauk*

S.S.S.R., Ser. khim., 1968, 1003.
Part I, J. A. Claisse, D. I. Davies, and C. K. Alden, J. Chem. Soc. (C), 1966, 1498, and subsequent papers in the series.

molecular iodine at a very much faster rate than rearrangement to the radical (VIa). This difference

CL CL CI ĊI ĊH2•CO2H ĊH₂X (II) a; X=Br, b; X=I (I) CI ĊO,H (田) (IV) (Y) R (⊻∏) (YI) х Cl4 cl Br (111) (IX)(X)CI Ċl CI (XI) (XII) (XIII) (XIV) (XV) (XVI) For (III) - (XIII) and (XIV) - (XVI) α ; $R \blacksquare H$, X = Cl, b; R = H, X = H;c; R = Me, X = Cl;

in the ease of abstraction of bromine and iodine by radical (IVa) may be due, in part, to the lower value of 36 kcal./mole for the dissociation energy of molecular

¹⁰ J. C. Davis, jun., and T. V. Van Auken, J. Amer. Chem. Soc., 1965, 87, 3900; P. Laszlo and P. von R. Schleyer, *ibid.*, 1964, 86, 1171; R. R. Fraser, Canad. J. Chem., 1962, 40, 78; E. W. C. Wong and C. C. Lee, *ibid.*, 1964, 42, 1245.
 ¹¹ (a) U.S.P. 2,912,356/1959 (Chem. Abs., 1960, 54, 3271); B. A. Arbuzov and A. N. Vereshchagin, Bull. Acad. Sci. U.S.S.R., 1965, 586: (b) K. L. Williamson, Yuan, Earg Li Hsu, R. Lacko

1965, 586; (b) K. L. Williamson, Yuan-Fang Li Hsu, R. Lacko,

and Chung He Youn, J. Amer. Chem. Soc., 1969, 91, 6129.
 ¹² E. N. Prilezhaeva, V. A. Azovskaya, and N. P. Petukova, Zhur. org. Khim., 1968, 4, 621; E. N. Prilezhaeva, 'Organo-sulfur Chemistry,' ed. M. J. Janssen, Interscience, 1967, p. 57.
 ¹³ A. N. Nesmeyanov, R. Kh. Friedlina, V. N. Kost, and

M. Ya. Khorlina, Tetrahedron, 1961, 16, 94.

⁴ R. G. Foster and M. C. McIvor, *Chem. Comm.*, 1967, 280; E. Pretsch, H. Immer, C. Pascual, K. Schaffner, and W. Simon, *Helv. Chim. Acta*, 1967, **50**, 105; J. A. Claisse and D. I. Davies, J. Chem. Soc. (B), 1967, 679.

E. K. Fields, J. Amer. Chem. Soc., 1954, 76, 2709.

iodine compared with 46 kcal./mole for molecular bromine. 14

The reactions with 1,4,5,6-tetrachloronorborn-5-en-2endo-ylcarboxylic acid (IIIb) afforded a 5.76:1 mixture of 5-exo-bromo-1,2,3,4-tetrachloronorborn-2-ene (VIIb) and its 5-endo-bromo-epimer (VIIIb) using mercuric oxide and bromine, and a 2.2:1 mixture of 1,2,3,4tetrachloro-5-exo-iodonorborn-2-ene (IXb) and its 5-endoiodo-epimer (Xb) using mercuric oxide and iodine. The failure to observe the rearranged bromide (XIIb) and analogous rearranged iodide indicates that in the 1,4,5,6,7,7-hexachloronorborn-5-en-2-yl radical (IVa) the bridge chlorines hinder abstraction by the radical centre, of a bromine atom from molecular bromine, and when these are absent, as in the 1,4,5,6-tetrachloronorborn-5-en-2-yl radical (IVb), bromine atom abstraction is facilitated and takes place exclusively at the expense of rearrangement of (IVb) to (VIb). 1,4,5,6-Tetrachloronorborn-5-en-2-exo-ylcarboxylic acid (XIII) gives the same product proportions, within experimental error, as the 2-endo-epimeric acid (IIIb). This suggests that both acids afford the same radical intermediate. This could be either the equilibrating tetrahedral (or pyramidal) exo- (XIVb) and endo- (XVb) radicals or an intermediate planar radical (XVIb). As in most experiments with norborn-2-yl radicals ¹⁵ no distinction between these possibilities can be made on the basis of these Theoretical predictions for the unexperiments. substituted norborn-2-yl radical suggest that it is pyramidal, at least 5° from planar and favouring the exo-configuration.16

The mercuric oxide-bromine reaction with 1,4,5,6,7,7hexachloro-2-exo-methylnorborn-5-en-2-endo-ylcarboxylic acid (IIIc) gave an 8:3:2:1 mixture of 5-exo-bromo-1,2,3,4,7,7-hexachloro-5-endo-methylnorborn-2-ene (VIIc), its 5-endo-bromo-epimer (VIIIc), 3-exo-bromo-1,2,3-endo,4,7,7-hexachloro-6-methyltricyclo[2,2,1,0^{2,6}]heptane (XIc) and 5-exo-bromo-1,2,3,5endo,6,6-hexachloro-4-methylnorborn-2-ene (XIIc). The isolation of the nortricyclyl-type halide (XIc) is important as it provides evidence for the participation of nortricyclyl-type radicals (V) in the rearrangement of (IV) to (VI). We had previously only isolated a nortricyclene-type product, derived from a nortricyclyl-type radical involved in radical rearrangements similar to the conversion of (IV) to (VI),⁹ in the respective additions of bromotrichloromethane and bromine to hexachloromethylenenorbornene.¹⁷ Less rearrangement of the intermediate radical (IVc) has taken place compared with intermediate radical (IVa) from acid (IIIa). This is likely to be a reflection of the greater stability of the methyl-substituted tertiary radical (IVc) compared with the hydrogen-substituted secondary radical (IVa). Reaction of the acid (IIIc) with mercuric oxide and iodine affords only 1,2,3,4,7,7-hexachloro-5-exo-iodo-5endo-methylnorborn-2-ene (IXc) and its 5-endo-iodoepimer (Xc) in the ratio 3:2. A very short reaction time was necessary (2 hr.) since the iodides readily lost hydrogen iodide to give hexachloromethylenenorbornene. If the reaction time was extended (to 18.5 hr.) this was the only product isolated from the reaction mixture.

When the results for acids (IIIa) and (IIIc) are compared, the relative amounts of products derived from chain transfer with halogen from the exo-direction are greater for radical (IVc) than (IVa) in spite of the presence of the methyl group in (IVc), even if it is assumed that the route to rearrangement products (XI) and (XII) involves reaction of radicals (IV) from the endo-direction. Models suggest that the 7-anti-bridge chlorine and the methyl group hydrogen are ca. 3.3 Å apart in the planar radical (XVIc), and in (XVIa) the 7-anti-chlorine and the hydrogen substituting the radical centre are a similar distance apart. Since the van der Waals radius of hydrogen is 1.2 Å and of chlorine 1.80 Å,¹⁸ this leaves only 0.3 Å for the attacking halogen molecule to approach the radical centre in (XVIa) and (XVIc). Therefore, steric effects for exo-chain transfer with planar radical (XVI) make such exo-chain transfer a virtual impossibility. It would therefore appear likely that the intermediates involved in the reactions of acids (III) are the equilibrating tetrahedral or pyramidal radicals (XIV) and (XV). The preference for exoproducts from the acid (IIIc) suggests that the presence of the methyl substituent at the radical centre causes the exo-radical (XIVc) to be favoured over the endoradical (XVc) rather more than in the case of (XIVa) and (XVa), where the radical centre is hydrogen substituted. This will be a function of the varying nonbonded interactions of the methyl group in (XIVc) and (XVc), compared with hydrogen in (XIVa) and (XVa), with other groups in the molecule. Examination of models shows that the C-2 substituent is also closer to the C-1 bridgehead chlorine for endo-radicals (XV) than for exo-radicals (XIV). This is more pronounced when the C-2 substituent is methyl than when it is hydrogen. A C-2 substituent in a planar radical (XVI) is even closer to a C-1 bridgehead chlorine than is the 2-exo-substituent in the endo-radical (XV), which is further evidence against the participation of the planar radical (XVI) in product formation. The variation in the exo/endo ratios of bromides and iodides in the products derived from the acids (IIIa---c) are likely to be a reflection of the different steric and electronic effects of chlorine and hydrogen at the bridge positions on the approach of bromine and iodine molecules respectively.

¹⁶ H. J. Fujimoto and K. Fukui, *Tetrahedron Letters*, 1966, 5551.
¹⁷ Part III, C. K. Alden and D. I. Davies, J. Chem. Soc. (C),

¹⁷ Part III, C. K. Alden and D. I. Davies, *J. Chem. Soc.* (C), 1967, 1017.

¹⁸ L. Pauling, 'The Nature of The Chemical Bond,' Oxford University Press, Oxford, 1940, 2nd edn., p. 189.

¹⁴ V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, 'Bond Energies, Ionisation Potentials, and Electron Affinities' (English Translation), Arnold, London, 1966.

¹⁵ See for example: H. Hart and F. D. Chloupek, J. Amer. Chem. Soc., 1963, **85**, 1155; E. C. Kooyman and G. C. Vegter, Tetrahedron, 1958, **4**, 382; S. J. Cristol, L. K. Gaston, and T. Tiedeman, J. Org. Chem., 1964, **29**, 1279.

The effect cannot be entirely steric since with acid (IIIa) there is a greater preference for reaction with mercuric oxide and iodine to give the *exo*-iodide (IXa), than for formation of the *exo*-bromide (VIIa) from the reaction with mercuric oxide and bromine. The product ratios are an accurate reflection of the reaction pathways of radicals (IV)—(VI) since we could observe no inter-conversion of products under the conditions of the reactions.

The Diels-Alder addition of 2-chloroacrylic acid to hexachlorocyclopentadiene gave a 2:1 mixture of 1,2-exo-4,5,6,7,7-heptachloronorborn-5-en-2-endo-ylcarboxylic acid (XVIIa) and its 2-endo-chloro-2-exo-ylcarboxylic acid epimer (XVIIIa). The individual isomers could not be distinguished from their n.m.r. data (see Table 1); however, their structures could be correlated by reaction with ethanolic potassium hydroxide, which occurs more readily with (XVIIa) since it has the correct stereochemistry for the exo-cis elimination of hydrogen chloride.¹⁹ Reaction of the mixture of acids (XVIIa)



For (XYII) - (XXIII) a; X = CI; b; X = Br.

and (XVIIIa) with mercuric oxide and bromine gave 5-exo-bromo-1,2,3,4,5-endo-7,7-heptachloronorborn-2-ene (XXIa), its 5-endo-bromo-5-exo-chloro-epimer (XXIIa) and the rearranged bromide 5-exo-bromo-1,2,3,5-endo,6,6heptachloronorborn-2-ene (XXIIIa) in the ratio 8:4:1. The rearranged bromide (XXIIIa) was recognised in the n.m.r. spectrum of the product mixture because the geminal 7,7-coupling in (XXIIIa) is, as expected,¹⁰ smaller than the 6,6-coupling in (XXIa), (XXIIa), and 3,3-coupling in (XVIIa) and (XVIIIa). The bromide (XXIa) was tentatively distinguished from the bromide (XXIIa) by its more ready reaction with alkali, which may be rationalised on the assumption of more ready exo-cis elimination of hydrogen bromide from (XXIa) than of hydrogen chloride from (XXIIa) since bromide ion is likely to be a better leaving group than chloride ion. The small proportion of rearranged bromide (XXIIIa) indicates that the initial chlorinesubstituted radical intermediate (XIXa) has less tendency to rearrange than the comparable hydrogen-substituted radical (IVa) from acid (IIIa). This is likely to be a consequence of the increased stability conferred by chlorine-substitution at a radical centre.^{9,13}

The Diels-Alder addition of 2-bromoacrylic acid to hexachlorocyclopentadiene gave a 4:1 mixture of 2-exo-bromo-1,4,5,6,7,7-hexachloronorborn-5-en-2-endovlcarboxylic acid (XVIIb) and 2-endo-bromo-1,4,5,6,7,7hexachloronorborn-5-en-2-exo-ylcarboxylic acid (XVIIIb), which on treatment with mercuric oxide and bromine gave a 10 : 1 mixture of 5,5-dibromo-1,2,3,4,7,7hexachloronorborn-2-ene [(XXIb) or (XXIIb)] and the rearranged bromide 4,5-exo-dibromo-1,2,3,5-endo-6,6hexachloronorborn-2-ene (XXIIIb). This result suggests that bromine-substitution of the radical centre in intermediate (XIXb) confers stability comparable with that due to chlorine-substitution in (XIXa). Consequently there is no great tendency for the rearrangement of radical (XIXb) to (XXb) leading to rearranged bromide (XXIIIb). Reactant and product identification were made in a similar manner as for acids (XVIIa) and (XVIIIa), and the products derived from them. Additionally bromide [(XXIb) or (XXIIb)] was identical with a product from the Diels-Alder addition of 1,1-dibromoethylene to hexachlorocyclopentadiene.

In products of type (XI), (XII), and (XXIII) derived from radicals (V), (VI), and (XX) respectively, the introduced bromine has been assumed to enter the *exo*position although it is not possible to prove this unambiguously from spectral or chemical data. However, the structural assumption is likely to be correct since



radicals (V), (VI), and (XX) are likely to have the exo-structures (XXIV)--(XXVI) as this will minimise

¹⁹ J. K. Stille and F. M. Sonnenberg, *Tetrahedron Letters*, 1966, 4587, and references cited therein.

nonbonded interactions of the chlorine-substituent at their radical centres. Additionally, this allows the preferred exo-chain transfer characteristic of norborn-2-vl radicals.²⁰

The Cristol-Firth reaction of norborn-5-en-2-endoylcarboxylic acid (XXVII) afforded, when mercuric oxide and iodine were used, a good yield of the iodolactone (XXVIII).^{3d} The crude products from reaction of the acids (IIIa) and (IIIb) with both mercuric oxide and bromine, and mercuric oxide and iodine, showed appreciable y-lactone absorption in the i.r. region at 1830 cm.⁻¹ suggesting that the lactones (XXIXa, b) and (XXXa, b) may be products. Unfortunately all attempts at isolation of such products failed.

EXPERIMENTAL

The n.m.r. spectra were recorded with a Perkin-Elmer R.10 instrument operating at 60 MHz, and the i.r. spectra with a Perkin-Elmer 257 grating i.r. spectrometer. G.l.c. analysis was carried out with a Griffin D6 Density Balance Chromatograph fitted with a 6 ft. $\times \frac{1}{2}$ in. column of 20% silicone oil SE 30 on Chromsorb W (80-100 mesh). Unless otherwise stated Woelm acid alumina, activity grade I, was used for column chromatography. Light petroleum had b.p. 40-60°. The n.m.r. data for starting acids are recorded in Table 1, and of product bromides in Table 2.

TABLE 1

N.m.r. data for starting acids

			J(Hz)				
	τ-ν	alues	2-exo.	2-exo.	3-exo.		
	H(3-exo)	H(3-endo)	3-endo	3-exo	3-endo		
(I)	*	8·27q	4	*	12.5		
(IIIa)	7∙31q	7∙59q	5	8	12.5		
(IIIb)	*	*	5	9.5	*		
(IIIc)	6·85d	7.55d			13		
(XVIIa)	6·45d	7.05d			13		
(XVIIb)	6.58d	7.04d			15		
(XVIIIa)	6·18d	7.85d			13		
(XVIIIb)	6·30d	7.34d			15		

* Not observable due to overlapping. Compound (XIII): 7·loctet, H(2-endo); J(2-endo, 3-endo) = 8.5; J(2-endo, 3-exo) = 5; J(2-endo, 7-syn) = 2.5. Other resonances: (IIIa) 6.38q, H(2-exo); (IIIb) 6.35q, H(2-exo); (IIIc) 8.2s, Me.

Preparation of Acids.-The following acids were prepared by literature procedures. 1,4,5,6,7,7-Hexachloronorborn-5-en-2-endo-ylacetic acid (I) by Diels-Alder addition of vinylacetic acid to hexachlorocyclopentadiene, m.p. 121.5-122.5° (lit.²¹ m.p. 121-123°); 1,4,5,6,7,7hexachloronorborn-5-en-2-endo-ylcarboxylic acid (IIIa) by the Diels-Alder addition of acrylic acid to hexachlorocyclopentadiene, m.p. 181.5-182° (lit.,²² m.p. 182-183°); 1,4,5,6-tetrachloronorborn-5-en-2-endo-ylcarboxylic acid (IIIb), m.p. 156-157° (lit.,²¹ m.p. 157-158°) and 1,4,5,6tetrachloronorborn-5-en-2-exo-ylcarboxylic acid (XIII), m.p. 139-140° (lit.,²¹ m.p. 138-140°) by Diels-Alder addition of acrylic acid to 1,2,3,4-tetrachlorocyclopentadiene (m.p. 62-63° prepared by the method of McBee, Meyers,

²⁰ P. von R. Schleyer, J. Amer. Chem. Soc., 1967, 89, 699, 701.
 ²¹ U.S.P. 2,758,918/1956 (Chem. Abs., 1956, 50, 17,307);
 U.S.P. 2,839,553/1958 (Chem. Abs., 1959, 53, 6114).
 ²² W. E. Noland and L. R. Smith, J. Amer. Chem. Soc., 1960,

82, 2021.

and Baranauckas²³) followed by separation of the product mixture by fractional crystallisation.

1,4,5,6,7,7-Hexachloro-2-exo-methylnorborn-5-en-2-endoylcarboxylic Acid (IIIc) .-- A mixture of hexachlorocyclopentadiene (137.5 g.) and 2-methylacrylic acid (43 g.) was heated at 160° for 5 hr. The solidified product was stirred with light petroleum $(4 \times 500 \text{ ml.})$ to leave an insoluble white polymeric material (28 g.), m.p. 239-240° (decomp.) (Found: C, 48.9; H, 5.4; Cl, 14.65%). A polymer of hexachlorocyclopentadiene (1 mol. proportion) and 2-methacrylic acid (12 mol. proportions) has formula (C53H72Cl6-O₂₄)_n (Calc.: C, 48.7; H, 5.61; Cl, 16.29%). Concentration of the light petroleum solution afforded 1,4,5,6,7,7-hexachloro-2-exo-methylnorborn-5-en-2-endo-ylcarboxylic acid (IIIc) (66.7 g.), m.p. 268-269° (from methylene chloridelight petroleum) (Found: C, 30.2; H, 1.65. C₈H₄Cl₆O₂ requires C, 30.1; H, 1.65%).

1,2-exo,4,5,6,7,7-Heptachloronorborn-5-en-2-endo-ylcarboxylic Acid (XVIIa) and 1,2-endo,4,5,6,7,7-Heptachloronorborn-5-en-2-exo-ylcarboxylic Acid (XVIIIa) .-- Hexachlorocyclopentadiene (60 g.) and 2-chloroacrylic acid 24 (24 g.) were mixed with p-t-butylcatechol (0.1 g.) and heated at 120-130° for 18 hr. The reaction product was extracted with carbon tetrachloride (5 \times 150 ml.) to leave a polymeric residue (55 g.). The carbon tetrachloride solution was washed with saturated aqueous sodium hydrogen carbonate (4 \times 50 ml.) and 2n-sodium hydroxide solution (4 \times 50 ml.) to give an aqueous solution of the sodium salts of carboxylic acids. This solution was acidified with 6Naqueous hydrochloric acid (250 ml.) and the precipitated acid was extracted into carbon tetrachloride (6×75 ml.). The carbon tetrachloride solution was dried $(MgSO_4)$, filtered, and the solvent removed to afford a 2:1 mixture (based on n.m.r. integrals) (12 g.), m.p. 212-215° on crystallisation from light petroleum, of 1,2-exo,4,5,6,7,7heptachloronorborn-5-en-2-endo-ylcarboxylic acid (XVIIa) and 1,2-endo,4,5,6,7,7-heptachloronorborn-5-en-2-exo-ylcarboxylic acid (XVIIIa) (Found: C, 25.8; H, 0.85; Cl, 64.9. C₈H₃Cl₇O₂ requires C, 25.35; H, 0.8; Cl, 65.45%). To distinguish the two acids a mixture (0.19 g.) was heated under reflux with a solution (3.7 ml.) of 0.4% ethanolic potassium hydroxide for 2 hr. The reaction mixture was cooled, acidified, and poured into water (15 ml.) and the precipitated acid was extracted into methylene chloride $(4 \times 15 \text{ ml.})$. The n.m.r. spectrum of the acid product obtained on evaporation of the solvent showed a decrease in the absorption at τ 6.45d and 7.05d of (XVIIa) compared with those at τ 6.18d and 7.85d due to (XVIIIa)

2-exo-Bromo-1,4,5,6,7,7-hexachloronorborn-5-en-2-endoylcarboxylic Acid (XVIIb) and 2-endo-Bromo-1,4,5,6,7,7-hexachloronorborn-5-en-2-exo-ylcarboxylic Acid (XVIIIb).-Hexachlorocyclopentadiene (27 g.), 2-bromoacrylic acid 24 (15 g.), and p-t-butylcatechol (0.1 g.) were heated at $150-160^{\circ}$ for 18 hr. Work-up as for the chloro-acids (XVIIa) and (XVIIIa) afforded polymeric residue (30 g.) and a 4:1 mixture (based on n.m.r. integrals) (5.2 g.), m.p. 252-253° on recrystallisation from light petroleum of 2-exobromo-1,4,5,6,7,7-hexachloronorborn-5-en-2-endo-ylcarboxylic acid (XVIIb) and 2-endo-bromo-1,4,5,6,7,7-hexachloronorborn-5-en-2-exo-ylcarboxylic acid (XVIIIb) (Found: C, 22.7; H, 0.75. C₈H₃BrCl₆O₂ requires C, 22.7; H, 0.7%).

²³ E. T. McBee, R. K. Meyers, and C. F. Baranauckas, J.

Amer. Chem. Soc., 1955, 77, 86. ²⁴ C. S. Marvel, J. Dec, H. G. Cooke, jun., and J. C. Cowan, J. Amer. Chem. Soc., 1940, **62**, 3495.

To distinguish the two acids a mixture (0.4 g.) was heated under reflux with a solution of potassium hydroxide (0.4 g)in ethanol (15 ml.) for 24 hr. The reaction mixture was cooled, acidified, and poured into water (30 ml.) and the precipitated acid was extracted into methylene chloride $(4 \times 40 \text{ ml.})$. The n.m.r. spectrum of the acid product actants and crude products are given in Table 3. The product ratios were obtained by g.l.c. and/or n.m.r. analysis of crude products. Frequently, repeated chromatography of the crude product was necessary to isolate pure specimens of individual compounds, and the amounts obtained often bear little relationship to the amounts present in the crude

T/TT->

TABLE 2

N.m.r. data for product halides

- (IIa): H(3-endo), $\tau 8.07q$; J(2-exo, 3-endo) = 4, J(3-exo, 3-endo) = 13(IIb): H(3-endo), $\tau 8.25q$; J(2-exo, 3-endo) = 4, J(3-exo, 3-endo) = 12(XIc): H(5-exo), $\tau 7.7d$; H(5-endo), 7.95d; $-CH_3$, 8.4s; J(5-exo, 5-endo) = 11.5(XIIa) †: H(7-anti), $\tau 7.12q$; H(7-syn), 7.37q; H(4), 6.15brt; J(7-anti, 7-syn) = 10; J(7-anti, 4) = 1.8; J(7-syn, 4) = 2.1(XIIc) †: H(7-anti), $\tau 6.87d$; H(7-syn), 7.39q; J(7-anti, 7-syn) = 12(XXIIIa) †: H(7-anti), $\tau 6.58d$; H(7-syn), 7.39d; J(7-anti, 7-syn) = 8(XXIIIb) †: H(7-anti), $\tau 6.13d$; H(7-syn), 6.88d; J(7-anti, 7-syn) = 12

	-Volues								
		۰۱-۷۵.			5-exo,	5-exo,	5-endo,	5-endo,	6-endo,
Compound	H(5-exo)	H(5-endo)	H(6-exo)	H(6-end o)	6 -endo	6-ex0	6-endo	6- <i>exo</i>	6- <i>exo</i>
(VIIa)		5∙87q	7∙28q	7.04q			8	6	13.5
(VIIb)		5.97octet	* -	*			6.7	4	*
(VIIc)			7	ls					0
(VIIIa)	5·36q		6∙9q	7·65q	3.2	8			13.5
(VIIIb)	5·45q		*	* -	3.9	8.3			*
(VIIIc)			6·8d	7.6d					13
(IXa)		5∙79q	7·40q	7·11q			8.3	5.5	14
(IXb)		5.93octet	*	*			6.25	5.25	*
(IXc)			6.99d	$7 \cdot 23 d$					13.5
(Xa)	5∙35q		6·91q	7·62q	4	9			14
(\mathbf{Xb})	5 ∙55q		*	*	5	9			*
(Xc)			6·9d	7.8d					13.5
(XXIa)			6.52d	6·87d					15
(XXIIa)			6.6d	7.1d					15
(XXIb)			6∙28d	6∙82d					15
or(X X Hh)									

* Not discernible due to overlapping peaks.

Additional information

- (VIIb) $J(5\text{-endo}, 7\text{-syn}) = 2\cdot 5$. (VIIc) CH_3 , $7\cdot 7s$, C-6 protons are equivalent. (VIIc) $-CH_3$, $8\cdot 2s$.

(IXb) J(5-endo, 7-syn) = 2.5.(IXc) $CH_3, 7.4s.$ (Xc) $CH_3, 7.91s.$

(

† In (XIIa) τ values for H(7-anti) and H(7-syn) assigned on the basis of the smaller 7-anti, 4 coupling than 7-syn, 4 coupling. The positions of these protons in (XIIc), (XXIIIa), coupling. The positions of these pr and (XXIIb) assigned by analogy.

		Weight	s of reactants	and products			
Acid	Wt. of acid (g.)	Wt. of bromine (g.)	Wt. of iodine (g.)	Wt. of mercuric oxide (g.)	Vol. CCl ₄ ‡ (ml.)	Wt. of product (g.)	Reaction time
(I)	5	2.3		$2 \cdot 3$	50	4	18·5 hr.
(I)	5		3 + 1	$2 \cdot 3$	50	6.2	4 days
(IIIa)	5	3		2.5	125	4.5	18.5 hr.
(IIIa)	5		4 + 2.5	2.5	125	5.5	6 days
(IIIb)	$2 \cdot 8$	1.7		1.7	400	3	18.5 hr.
(IIIb)	2.8		2.8	1.7	400	3.3	l day
(IIIc)	5	2.3		$2 \cdot 3$	150	5.2	18 5 hr.
(IIIc)	5		3.55	$2 \cdot 3$	150	5	2 hr.
(XIII)	$2 \cdot 8$	1.7		1.7	400	2.95	18.5 hr.
(XIII)	$2 \cdot 8$		2.8	1.7	400	3.3	l day
$XVIIa) + (XVIIIa) \dagger$	5	$2 \cdot 2$		$2 \cdot 2$	160	5.6	18.5 hr.
XVIIb) + (XVIIIb) *	5	2		2	125	5.3	18·5 hr.
	* 4:	1. $\pm 2:1. \pm V_{0}$	olume of CCl.	overned by solub	ility of acid.		

TABLE 3

obtained on evaporation of solvent showed a decrease in the absorptions at τ 6.58d and 7.04d of (XVIIb) compared with those at τ 6.30d and 7.34d due to (XVIIIb).

Cristol-Firth ² Reactions of Carboxylic Acids.—The experimental procedures used are exemplified by the reactions of 1,4,5,6,7,7-hexachloronorborn-5-en-2-endo-ylacetic acid (I) with mercuric oxide and bromine and iodine respectively. For the other acids only brief details of products. isolated are given. Reaction times and weights of reproduct. Some reactions were repeated in the presence of some added product halides to establish that no interconversion of products took place under the reaction conditions.

1,4,5,6,7,7-Hexachloronorborn-5-en-2-endo-ylacetic Acid

(I).-Reaction with mercuric oxide and bromine. The acid (I), (5 g., 0.014 mole) and mercuric oxide (2.3 g., 0.011 mole) were added to carbon tetrachloride (50 ml.) and the mixture was stirred and boiled under reflux. Bromine

(2.3 g., 0.014 mole) was added dropwise during 0.5 hr., and the reaction mixture was then stirred under reflux in the dark for 18 hr. The reaction mixture was cooled, filtered to remove mercury salts, and the filtrate washed with saturated aqueous sodium thiosulphate $(2 \times 25 \text{ ml.})$ to remove unchanged bromine, and with saturated aqueous sodium hydrogen carbonate (4×50 ml.) to remove unchanged acid (I). The resultant carbon tetrachloride solution was dried (MgSO4), filtered, and the solvent evaporated to leave a residue (4 g.). Purification by column chromatography on basic alumina (Laporte type 'H') with light petroleum as eluant afforded 1,4,5,6,7,7hexachloronorborn-5-en-2-endo-ylmethyl bromide (IIa), m.p. 76-77° identical with an authentic specimen prepared by the Diels-Alder addition of allyl bromide to hexachlorocyclopentadiene.5

Reaction with mercuric oxide and iodine. The acid (I), (5 g., 0.014 mole) and mercuric oxide (2.3 g., 0.011 mole) were added to carbon tetrachloride (50 ml.) and the mixture was stirred and boiled at reflux in the dark. Iodine (3 g., 0.012 mole) was added by way of a Soxhlet extraction thimble during 12 hr. After 1 day further iodine (1 g.) was added and the stirring and refluxing was continued for a further 3 days. The cooled reaction mixture was filtered to remove the mercury salts and the filtrate was washed with sodium this solution $(3 \times 25 \text{ ml.})$ to remove the excess of iodine, and with saturated aqueous sodium hydrogen carbonate (4 \times 50 ml.) to remove unchanged acid (I). The residual carbon tetrachloride solution was dried (MgSO₄) and filtered. Evaporation of the solvent afforded a residue which was recrystallised from methanol to give 1,4,5,6,7,7-hexachloronorborn-5-en-2-endo-ylmethyl iodide (IIb) (6.2 g.), m.p. 105–106° (Found: C, 21.95; H, 1.1. Calc. for $C_8H_5Cl_6I$: C, 21.75; H, 1.15%). The product was identical with material, m.p. 105-106°, prepared by the Diels-Alder addition of allyl iodide to hexachlorocyclopentadiene (lit., 6 m.p. 109-110°).

1,4,5,6,7,7-Hexachloronorborn-5-en-2-endo-ylcarboxylic Acid (IIIa).—Reaction with mercuric oxide and bromine. The crude product discoved in acetone (10 ml) and set

The crude product dissolved in acetone (10 ml.) and set aside deposited 5-exo-bromo-1,2,3,5-endo-6,6-hexachloronorborn-2-ene (XIIa) (0.5 g.), m.p. 127—128° (Found: C, 22·1; H, 0.8. $C_7H_3BrCl_6$ requires C, 22·1; H, 0.8%). Successive column chromatography of the remaining product with light petroleum as eluant gave 5-endo-bromo-1,2,3,4,7,7-hexachloronorborn-2-ene (VIIIa) (1 g.), m.p. 142—144° identical with an authentic specimen m.p. 146— 148°,^{11a} and 5-exo-bromo-1,2,3,4,7,7-hexachloronorborn-2-ene (VIIa) (0.25 g.), n_p^{20} 1.5852 (Found: C, 22·2; H, 0.75. $C_7H_3BrCl_6$ requires C, 22·1; H, 0.8%). N.m.r. integral measurements and g.l.c. analysis at 180° of the crude product showed product ratio of (VIIa): (VIIIa): (XIIa) was 4:3:1. The i.r. spectrum of the crude product showed possible γ -lactone absorption at 1830 cm.⁻¹.

Reaction with mercuric oxide and iodine. Successive column chromatography with light petroleum as eluant allowed isolation of 1,2,3,4,7,7-hexachloro-5-endo-iodonorborn-2-ene (Xa), (1·I g.), m.p. $61\cdot5-62\cdot5^{\circ}$ identical with a specimen prepared by the Diels-Alder addition of vinyl iodide to hexachlorocyclopentadiene * (Found: C, 19·75; H, 0·7. $C_7H_3Cl_6I$ requires C, 19·65; H, 0·7%), and 1,2,3,4,7,7-hexachloro-5-exo-iodonorborn-2-ene (IXa) (0.05 g.), m.p. 25—30° (Found: C, 19.75; H, 0.7. C₇H₃Cl₆I requires C, 19.65; H, 0.7%). N.m.r. integral measurements on the crude products showed that (IXa) and (Xa) were present in the ratio 4:3. The i.r. spectrum of the crude product showed possible γ -lactone absorption at 1830 cm⁻¹.

1,4,5,6-Tetrachloronorborn-5-en-2-endo-ylcarboxylic Acid (IIIb).—Reaction with mercuric oxide and bromine. A specimen of the crude reaction product (0·1 g.) dissolved in benzene was examined by g.l.c. at 165° and shown to contain a 5·76:1 mixture of 5-exo-bromo-1,2,3,4-tetrachloronorborn-2-ene (VIIb) and 5-endo-bromo-1,2,3,4-tetrachloronorborn-2-ene (VIIb). The products could not be separated by chromatography, but were recognised by comparative g.l.c. retention times and n.m.r. spectra with those of a 1:1 mixture of (VIIb) and (VIIIb), b.p. 100— $103^{\circ}/0.05$ mm., $n_{\rm D}^{25}$ 1·5522 (Found: C, 27·1; H, 1·8. Calc. for C₇H₅BrCl₄: C, 27·0; H, 1·6%) prepared by the Diels-Alder addition of vinyl bromide to tetrachlorocyclopentadiene.²⁵ The i.r. spectrum of the crude product showed possible γ -lactone absorption at 1830 cm.⁻¹.

Reaction with mercuric oxide and iodine. Repeated chromatography of the reaction product with light petroleum as eluant gave 1,2,3,4-tetrachloro-5-endo-iodonorborn-2-ene (Xb) (1.5 g.), m.p. 25-30° (Found: C, 23.85; H, 1.65. C₇H₅Cl₄I requires C, 23.5; H, 1.4%), and 1,2,3,4tetrachloro-5-exo-iodonorborn-2-ene (IXb) (1 g.), n_p²³ 1.5725 (Found: C, 23.8; H, 1.45. C₇H₅Cl₄I requires C, 23.5; H, 1.4%). The iodides were further identified by the preparation of a 1:1 mixture of (IXb) and (Xb) (9.6 g.), $n_{\rm D}^{23}$ 1.5943 (Found: C, 23.5; H, 1.25. Calc. for $C_7H_5Cl_4I$: C, 23.5; H, 1.4%) by heating vinyl iodide (5 g.) with tetrachlorocyclopentadiene (7 g.) in a sealed tube at 175° for 18 hr. N.m.r. integral measurements and g.l.c. analysis at 150° of the crude product showed that (IXb) and (Xb) were present in the ratio $2 \cdot 2 : 1$. The i.r. spectrum of the crude product showed possible y-lactone absorption at 1830 cm⁻¹.

1,4,5,6-Tetrachloronorborn-5-en-2-exo-ylcarboxylic Acid (XIII).—Reaction with mercuric oxide and bromine. N.m.r. integral values and g.l.c. analysis of the crude product at 165° showed that the bromides (VIIb) and (VIIIb) were present in the ratio 5.4:1.

Reaction with mercuric oxide and iodine. N.m.r. integral values and g.l.c. analysis of the crude product at 150° showed that the iodides (IXb) and (Xb) were present in the ratio $2 \cdot 1 : 1$.

1,4,5,6,7,7-Hexachloro-2-exo-methylnorborn-5-en-2-endoylcarboxylic Acid (IIIc).—Reaction with mercuric oxide and bromine. Successive chromatography of the crude product with light petroleum as eluant afforded 5-exo-bromo-1,2,3,4,7,7-hexachloro-5-endo-methylnorborn-2-ene (VIIc) (1 g.), m.p. 188·5—189·5° (Found: C, 24·6; H, 1·25. C₈H₅-BrCl₆ requires C, 24·4; H, 1·3%), 5-endo-bromo-1,2,3, 4,7,7-hexachloro-5-exo-methylnorborn-2-ene (VIIIc) (0·05 g.), m.p. 179—180° (Found: C, 24·3; H, 1·25. C₈H₅BrCl₆ requires C, 24·4; H, 1·3%), 5-exo-bromo-1,2,3,5endo,6,6-hexachloro-4-methylnorborn-2-ene (XIIc) (0·15 g.), m.p. 184—185° (Found: C, 24·5; H, 1·4. C₈H₅BrCl₆ requires C, 24·4; H, 1·3%), and 3-exo-bromo-1,2,3endo,4,7,7-hexachloro-6-methyltricyclo[2,2,1,0^{2,6}]heptane

(XIc) (0.06 g.), m.p. 185–186° (Found: C, 24.8; H, 1.3. $C_8H_5BrCl_6$ requires C, 24.4; H, 1.3%). Compounds (VIIc), (VIIIc), and (XIIc) showed absorption at 1610 cm.⁻¹ in their i.r. spectra characteristic of a chlorine-

^{*} Specimen provided by Mr. R. Alexander of Kings College.

²⁵ Work of Dr. P. J. Rowley.

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substituted double bond.²⁶ There was no similar absorption in the spectrum of (XIc). N.m.r. integral measurements and g.l.c. analysis at 180° on the crude product showed that (VIIc), (VIIIc), (XIc), and (XIIc) were present in the ratio 8:3:2:1.

Reaction with mercuric oxide and iodine. Repeated chromatography of the crude product with light petroleum as eluant gave hexachloromethylenenorbornene (1 g.), 1,2,3,4,7,7-hexachloro-5-endo-iodo-5-exo-methylnorborn-2-

ene (Xc) (1.6 g.), $n_{\rm p}^{22.5}$ 1.5578 (Found: C, 21.6; H, 1.2. $C_8H_5Cl_6I$ requires C, 21.75; H, 1.15%), and 1,2,3,4,7,7hexachloro-5-exo-iodo-5-endo-methylnorborn-2-ene (IXc), (2.0 g.), $n_{\rm p}^{22.5}$ 1.5090 (Found: C, 21.6; H, 1.2. $C_8H_5Cl_6I$ requires C, 21.75; H, 1.15%). N.m.r. integral values on the crude product showed that (IXc) and (Xc) were present in the ratio 3:2. This reaction of acid (IIIc) was very much more rapid (2 hr.) than comparable reactions of the other acids (see Table 3). The products (IXc) and (Xc) readily lose hydrogen iodide under the reaction conditions, and if reaction time is increased to 18.5 hr., hexachloromethylenenorbornene is the sole product.

1,2,4,5,6,7,7-Heptachloronorborn-5-en-2-ylcarboxylic Acids (XVIIa) and (XVIIIa). Reaction with mercuric oxide and bromine. The crude product could not be separated into individual components by either preparative g.l.c. or column chromatography. Crystallisation from methylene chloride-light petroleum afforded a 4:8:1 mixture (based on n.m.r. integrals), m.p. 175° of 5-endo-bromo-1,2,3,4,5exo-7,7-heptachloronorborn-2-ene (XXIIa), 5-exo-bromo-1,2,3,4,5-endo-7,7-heptachloronorborn-2-ene (XXIa), and

²⁶ G. Herzberg, 'Infra-Red and Raman Spectra of Polyatomic Molecules,' D. Van Nostrand Co. Inc., New York, 1945, p. 330; S. B. Soloway, A. M. Damiana, J. W. Sims, H. Bluestone, and R. E. Lidov, J. Amer. Chem. Soc., 1960, **82**, 5377.

5-exo-bromo-1,2,3,4,5-endo,6,6-heptachloronorborn-2-ene

(XXIIIa). To distinguish the bromides (XXIa) and (XXIIa) a mixture of the three bromides (0.35 g.) was heated under reflux with a 0.33% solution (7.5 ml.) of potassium hydroxide in ethanol for 2 hr. The mixture was cooled, acidified, and poured into water (30 ml.) and the precipitated product was extracted with methylene chloride (4 × 30 ml.). The n.m.r. spectrum of the product showed a decrease in absorptions at τ 6.52d and 6.87d due to (XXIa) compared with those at τ 6.6d and 7.1d due to (XXIIa).

2-Bromo-1,4,5,6,7,7-hexachloronorborn-5-en-2-ylcarboxylic Acids (XVIIb) and (XVIIIb).—Reaction with mercuric oxide and bromine. The crude product could not be separated into individual components by preparative g.l.c. or column chromatography. Crystallisation from methylene chloride– light petroleum afforded a 10:1 mixture (based on n.m.r. integrals), m.p. 160—161° (Found: C, 18.75; H, 0.5; Br, 34.7. C₇H₂Br₂Cl₆ requires C, 18.3; H, 0.45; Br, 34.9%) of 5,5-dibromo-1,2,3,4,7,7-hexachloronorborn-2-ene (XXIb) or (XXIIb) and 4,5-exo-dibromo-1,2,3,5-endo,6,6-hexachloronorborn-2-ene (XXIIIb).

When hexachlorocyclopentadiene (13.6 g.) and vinylidene bromide (9.3 g.) were heated in a sealed tube at 200° for 27 hr. a very tarry product was obtained, the n.m.r. spectrum of which contained the absorptions at 6.28d and 6.82d of (XXIb) or (XXIIb) and hence permitted distinction from (XXIIIb).

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