J. Chem. Soc. (C), 1971

896

## Free-Radical Reactions of Halogenated Bridged Polycyclic Compounds. Part XIII.<sup>†</sup> The Addition of Hydrogen Bromide to Hexachloromethylenenorbornene

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The free-radical addition of hydrogen bromide to hexachloromethylenenorbornene affords a 60:40 mixture of 1-bromomethyl-2,3,4,5,5,6-*endo*-hexachloronorborn-2-ene and 5-*endo*-bromomethyl-1,2,3,4,7,7-hexachloronorborn-2-ene. The aluminium bromide-catalysed ionic addition gives a 68:32 mixture of 5-*exo*-bromo-1,2,3,4,7,7-hexachloro-5-*endo*-methylnorborn-2-ene and its 5-*endo*-bromo-epimer.

DETAILED studies by Kharasch and his co-workers in the 1930's established that in the addition of hydrogen bromide to asymmetric olefins, the structure of products formed was dependent on the mechanism of addition.<sup>1</sup> Ionic addition afforded products consistent with the empirical rules of Markoffnikov, whereas free-radical addition afforded anti-Markoffnikov products. In many reactions, unless stringent conditions for purification of reagents are employed, a mixture of products is formed as a result of competing ionic and free-radical reactions. We have now devised conditions for the addition of hydrogen bromide to hexachloromethylenenorbornene (I) in which the products formed are consistent with ionic and free-radical mechanisms, respectively.

† Part XII, D. I. Davies and P. Mason, J. Chem. Soc. (C), 1971, 295.

The reaction of (I) with dissolved hydrogen bromide gas, during 2 months at room temperature affords a 60:40 mixture of 1-bromomethyl-2,3,4,5,5,6-endo-hexachloronorborn-2-ene (VI) identified from its n.m.r. data (see Experimental section), and 5-endo-bromomethyl-1,2,3,4,7,7-hexachloronorborn-2-ene (V) identified by comparison with an authentic specimen,<sup>2</sup> as sole detectable products. The presence of catalytic quantities of diethyl peroxydicarbonate accelerated the reaction. Bromine atom attack on (I) gives the initial radical (II) from which (V) is derived by chain transfer with hydrogen bromide. Alternatively (II) can rearrange to

<sup>1</sup> See for example M. S. Kharasch, H. Engelmann, and F. R. Mayo, J. Org. Chem., 1937, 2, 288; M. S. Kharasch, S. C. Kleiger, and F. R. Mayo, J. Org. Chem., 1939, 4, 428.
<sup>2</sup> E. K. Fields, J. Amer. Chem. Soc., 1954, 76, 2709.



that involved in the addition of thiols to (I),<sup>3</sup> which affords products comparable to (VI) but not to (V). This suggests that when the intermediate radicals (II) and (VII) are concerned, rearrangement of the latter is more favoured than of the former. This suggests that the chain-transfer step of (II) is more favourable than of (VII) on either or both energetic and steric grounds. Since work in the gas phase,<sup>4,5</sup> if it can be extended to solution, points to little difference in the bond strengths of H-Br and RS-H, and in the heats of formation of bromine atoms and RS radicals, it appears that the respective ease of chain transfer of (II) with hydrogen bromide, and of (VII) with thiols, may be controlled largely by steric factors.

The aluminium bromide-catalysed reaction of hydrogen bromide with (I) afforded a 68:32 mixture of 5-exo-bromo-1,2,3,4,7,7-hexachloro-5-endo-methylnorborn-2-ene (IX) and its 5-endo-bromo-epimer (X),

identical with authentic specimens obtained in the reaction of 1,4,5,6,7,7-hexachloro-2-exo-methylnorborn-5-en-2-endo-carboxylic acid with mercury(II) oxide and bromine.<sup>6</sup> The formation of these products may be



rationalised as involving the attack of bromide ion on either side of the intermediate carbonium ion (VIII). The carbonium ion should be planar and steric interactions to the approach of a bromide ion might have been expected to favour formation of the endo-bromide (X). However, the formation of this bromide occasions disadvantageous torsional strain,<sup>7</sup> since in (VIII) the methyl group is below the plane of the adjacent bridgehead chlorine, and therefore must eclipse this chlorine in the transition state leading to the formation of (X). A similar strain is not involved in the experimentally favoured attack of bromide ion on (VIII) from the exodirection. These results may be compared with those involved in the reaction of the corresponding radical (XI) with bromine, where an even greater tendency for



attack from the exo-direction is observed.<sup>6</sup> This, however, may be a reflection of a more tetrahedral than planar structure for free radical (XI) in which the odd electron is in an unfilled  $sp^3$  orbital in the *exo*-direction. The failure to observe any rearrangement products in the

<sup>5</sup> V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, 'Bond Energies, Ionization Potentials, and Electron Affinities,' Arnold, London, 1966, pp. 116 and 38.

<sup>6</sup> D. I. Davies and P. Mason, J. Chem. Soc. (C), 1971, 288. <sup>7</sup> P. von R. Schleyer, J. Amer. Chem. Soc., 1967, **89**, 699, 701.

<sup>&</sup>lt;sup>2</sup> C. K. Alden and D. I. Davies, *J. Chem. Soc.* (C), 1967, 1017. <sup>4</sup> C. T. Mortimer, 'Reaction Heats and Bond Strengths,' Pergamon, Oxford, 1962, pp. 137-139.

ionic addition is expected since the tertiary and therefore stabilised carbonium ion would have to undergo the unfavourable step of rearrangement to a chlorine-substituted and therefore destabilised carbonium ion. Earlier work on the addition of bromine and chlorine to hexachloronorbornadiene has demonstrated that the formation of chlorine-substituted carbonium ion centres is less favourable than the formation of the corresponding free radicals.<sup>8</sup>

## EXPERIMENTAL

The 60 MHz n.m.r. spectrum was recorded with a Perkin-Elmer R10 instrument. Analytical g.l.c. was carried out with a Griffin D6 density balance chromatograph employing nitrogen as carrier gas, and fitted with a 6 ft  $\times$  0.25 in column of 20% Silicon Oil on Chromsorb W (80—100 mesh). Column chromatography was carried out on Woelm acid alumina with light petroleum, b.p. 40—60°, as eluant.

The Addition of Hydrogen Bromide to Hexachloromethylenenorbornene (I).—(a) Free radical. The olefin (I), (10 g) was saturated with gaseous hydrogen bromide and kept in a stoppered flask at room temperature for 2 months. Periodically more hydrogen bromide was added to compensate for material consumed. After 2 months the product was dissolved in benzene and acidic material was removed by washing with water ( $2 \times 25$  ml), saturated sodium hydrogen carbonate solution ( $2 \times 25$  ml), and water ( $2 \times 25$  ml). The solution was dried (MgSO<sub>4</sub>) and solvent was removed; g.l.c. analysis of the residue showed that it contained 60:40 mixture of two products together with 20% of unchanged olefin (I). Column chromatography afforded successively 5-endo-bromomethyl-1,2,3,4,7,7-hexachloronor-

## J. Chem. Soc. (C), 1971

born-2-ene (V) (3.6 g), m.p. 79—80°, identical with an authentic specimen,<sup>2</sup> and 1-bromomethyl-2,3,4,5,5,6-endohexachloronorborn-2-ene (VI) (5.2 g),  $n_{\rm p}^{25}$  1.5804, as a pale yellow viscous liquid (Found: C, 24.8; H, 1.45. C<sub>8</sub>H<sub>5</sub>-BrCl<sub>6</sub> requires C, 24.4; H, 1.3%);  $\tau$  7.55 (d, J 10 Hz, syn-7-H), 7.25 (d, J 10 Hz, anti-7-H), 4.99 (s, exo-6-H), and 6.33 (s, CH<sub>2</sub>Br). The i.r. spectrum showed strong absorption at 1610 cm.<sup>-1</sup> indicative of the presence of a chlorine-substituted double bond. In the presence of diethyl peroxydicarbonate (5 mg added every two days) at room temperature, the reaction mixture being saturated with hydrogen bromide gas every 2 days, 25% reaction was accomplished after 8 days.

(b) Ionic. Hexachloromethylenenorbornene (I) (10 g) was dissolved in sodium-dried AnalaR benzene (20 ml), and aluminium bromide (0.4 g) was added. After nitrogen had been passed through the mixture (15 min) to remove oxygen, hydrogen bromide gas was passed in for 3 h. The mixture was freed from acidic material as in (a), and after removal of solvent afforded a residue (11.3 g) shown by g.l.c. to contain two products in the ratio 68:32. Chromatography afforded 5-exo-bromo-1,2,3,4,7,7-hexachloro-5-endosuccessively methylnorborn-2-ene (IX) (6.7 g), m.p. 188-189° (Found: C, 24.7; H, 1.3. Calc. for C<sub>8</sub>H<sub>5</sub>BrCl<sub>6</sub>: C, 24.4; H, 1.3%), and 5-endo-bromo-1,2,3,4,7,7-hexachloro-5-exo-methylnorborn-2-ene (X) (2.5 g), m.p. 179-180° (Found: C, 24.85; H, 1.4). The two products were identical with authentic specimens.6 The ratio of products formed in 6% yield after reaction for 5 min was also 68:32.

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<sup>8</sup> D. I. Davies and M. J. Parrott, J. Chem. Soc. (C), 1970, 659.