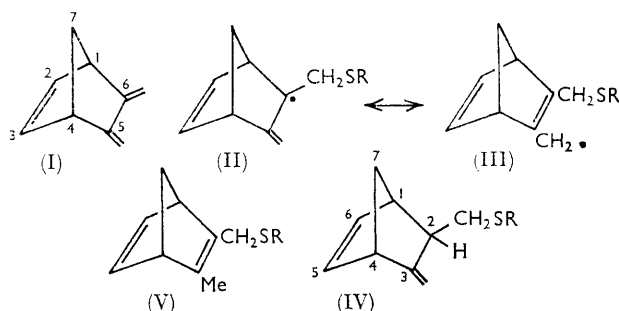


Free-radical Reactions of Halogenated Bridged Polycyclic Compounds. Part VIII.† The Addition of Thiols to 1,2,3,4,7,7-Hexachloro-5,6-dimethylenenorborn-2-ene

By C. K. Alden, J. A. Claisse, and D. I. Davies,* Department of Chemistry, King's College, Strand, London W.C.2

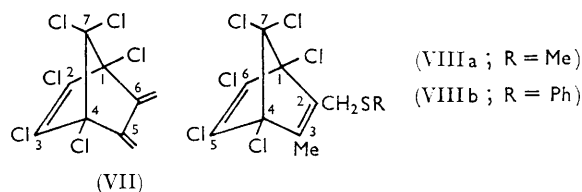
The addition of methanethiol and thiophenol to 1,2,3,4,7,7-hexachloro-5,6-dimethylenenorborn-2-ene affords 1,4,5,6,7,7-hexachloro-3-methylnorborna-2,5-dien-2-ylmethyl methyl and phenyl sulphide respectively. These products are derived from 1,4-addition to the diene system, and this preference for 1,4- rather than 1,2-addition is discussed. Attempts to add bromotrichloromethane resulted in polymer formation. A new method for the synthesis of 1,2,3,4,7,7-hexachloro-5,6-dimethylenenorborn-2-ene by the catalytic hydrogenolysis of 1,2,3,4,7,7-hexachloro-5,6-bis(chloromethyl)norborna-2,5-diene is reported.

THE addition of thiols to 5,6-dimethylenenorborn-2-ene (I) gives 3-methylenenorborn-5-ene-2-ylmethyl aryl (or alkyl) sulphides (IV) as the major isolated 1 : 1 adducts of thiol and triene.¹ This preference for the product of



1,2- rather than 1,4-addition to the diene system may be due to the intermediate allylic radical being best represented as the canonical species (II) as a result of localisation of the radical centre due to the presence of the endocyclic double bond, and to a large energy barrier to the formation of the product (V) of 1,4-addition to the diene system, since this has the highly strained norbornadiene system.

In our study of the corresponding hexachloro-analogue 1,2,3,4,7,7-hexachloro-5,6-dimethylenenorborn-2-ene (VII) we find that the addition of thiophenol and of methanethiol both result in the formation of the products (VIIIa and b) of 1,4-addition to the diene system, together with polymer. Elemental analysis demonstrated that the products were 1 : 1 adducts of thiol and



triene (VII); the absence of olefinic protons in the n.m.r. spectrum of the products indicated that 1,2-addition to the diene system had not occurred. The

† Part VII, C. K. Alden, D. I. Davies, and (in part) P. J. Rowley, *J. Chem. Soc. (C)*, 1968, 705.

¹ J. A. Claisse and D. I. Davies, *J. Chem. Soc. (C)*, 1966, 1045.

² S. B. Soloway, A. M. Damiana, J. W. Sims, H. Bluestone, and R. E. Lidov, *J. Amer. Chem. Soc.*, 1960, **82**, 5377.

³ G. Herzberg, 'Infrared and Raman Spectra of Polyatomic Molecules,' Van Nostrand, New York, 1945, p. 330.

i.r. spectra showed the chlorine-substituted double-bond absorption at 1610 cm.⁻¹,^{2,3} and an additional weak absorption at 1650 cm.⁻¹, which we suggest is due to the fully substituted 2,3-double bond of (VIII). The methanethiol adduct (VIIIa) showed in its n.m.r. spectrum two singlets (each 3H) at τ 8.01 and 8.14 due to the methyl groups adjacent to sulphur and to the double bond. The non-equivalent protons of the methylene group adjacent to both sulphur and the double bond exhibit a four line pattern centred at τ 6.58, which we consider to be made up of two doublets, J 14 c./sec. at τ 6.43 and 6.73. The thiophenol adduct (VIIIb) showed the aromatic protons as a singlet at τ 2.7, the vinylic methyl as a singlet at 8.81, and the methylene group as a triplet, J 13 c./sec., centred at 6.37, which is probably made up of two overlapping doublets. The rather high τ value for the vinylic methyl group suggests that it is shielded by the aromatic ring.

The reasons for 1,4-addition to the diene system of the chlorine-substituted triene (VII) compared with 1,2-addition to the unsubstituted triene (I) appear to be threefold.

(i) On account of the electron withdrawal by the chlorines, the chlorine-substituted double bond is relatively electron-deficient. It therefore has less tendency to interact with the tertiary radical centre in the canonical species (IX), and thus localisation of the radical centre giving increased importance to the canonical species (IX) is reduced. This is supported by our work on the free-radical addition of thiols to 2,3-dichloronorborna-2,5-diene in which we demonstrated a reduced tendency for the radical centre in the intermediate (XI) to attack the chlorine-substituted double bond⁴ compared with attack of the radical centre with an unsubstituted double bond as in (XII).⁵

(ii) We find that hexachloronorbornadiene reacts much less readily with free-radical reagents than does norbornadiene,⁶ which may indicate a greater stability of the former diene. Thus the energy barrier to the formation of the hexachloronorbornadiene system in (VIII) may be less than to the formation of the norbornadiene system in (V).

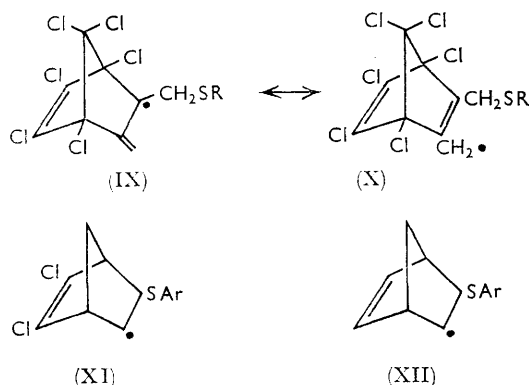
⁴ C. K. Alden and D. I. Davies, *J. Chem. Soc. (C)*, 1967, 2007.

⁵ S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Amer. Chem. Soc.*, 1958, **80**, 635.

⁶ J. A. Claisse, D. I. Davies, and C. K. Alden, *J. Chem. Soc. (C)*, 1966, 1498; C. K. Alden, J. A. Claisse, and D. I. Davies, *ibid.*, p. 1540.

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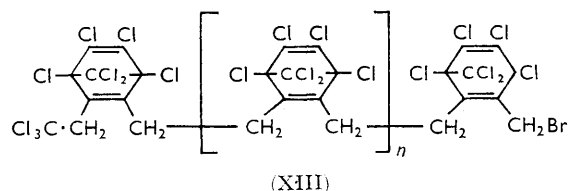
(iii) Our studies on the free-radical addition reactions of a variety of polychlorinated norbornadienes and related compounds^{6,7} have demonstrated that the



presence of substituent chlorines, particularly at the bridge and bridgehead positions, causes considerable steric hindrance toward free-radical attack. The presence of six chlorines will thus hinder chain transfer with the allylic radical centre leading to the product of 1,2-addition to the diene system, and thus chain transfer leading to the products (VIII) of 1,4-addition is relatively favoured.

The free-radical addition of thiols to 1,2,3,4,7,7-hexachloro-5,6-dimethylenenorborn-2-ene (VII) thus parallels the addition of halogens, which was demonstrated by Hoch and Clegg⁸ to give the products of 1,4-addition to the diene system. No explanation was provided, but reasons similar to (i)–(iii) probably apply.

The azobisisobutyronitrile-catalysed reaction of 1,2,3,4,7,7-hexachloro-5,6-dimethylenenorborn-2-ene (VII) with bromotrichloromethane produced no 1:1 addition product, but only a polymeric material together with hexachloroethane. The polymer had m.p. $>200^\circ$ compared with the softening point of 180° reported by Hoch and Clegg⁸ for the polymer of (VII) produced under a variety of different conditions. Elemental analysis of our polymer suggested, however, that it probably incorporated some bromotrichloromethane. The n.m.r. spectrum of the polymer showed the absence of olefinic proton resonances and a broad hump at τ 8.0–8.2 corresponding to allylic methylene group. We therefore suggest that the polymer is composed largely of units linked together by 1,4-addition to the diene system, and may be represented by the formula (XIII).

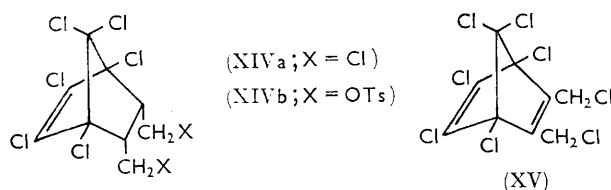


⁷ C. K. Alden and D. I. Davies, *J. Chem. Soc. (C)*, 1967, 1017; D. I. Davies and P. J. Rowley, *ibid.*, pp. 2245, 2249.

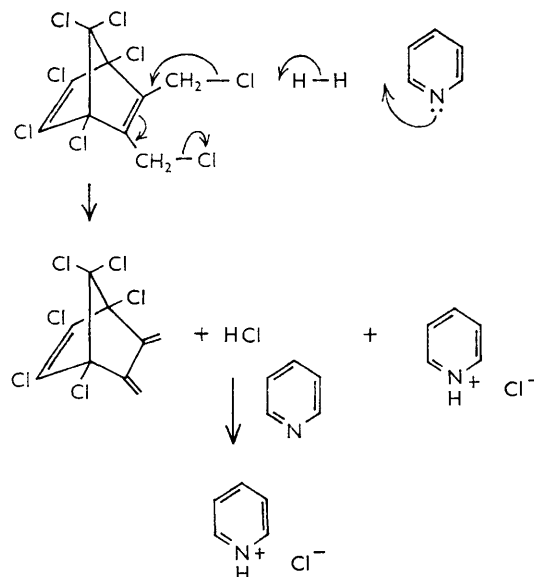
⁸ P. E. Hoch and J. M. Clegg, *J. Amer. Chem. Soc.*, 1959, **81**, 5413.

⁹ M. A. P. Bowe, R. G. J. Miller, J. B. Rose, and D. G. M. Wood, *J. Chem. Soc.*, 1960, 1541.

This structure is supported by the presence of the chlorine-substituted double-bond absorption^{2,3} and fully substituted double-bond absorption at 1615 and 1650 cm^{-1} respectively in the i.r. spectrum of the polymer. Bowe, Miller, Rose, and Wood⁹ have found that polymers formed from related (non-chlorine-substituted) bicyclic dienes are derived from 1,4-addition to the diene systems.



The triene (VII) has been prepared by the elimination of two molecules of hydrogen chloride from the Diels-Alder adduct (XIVa) of hexachlorocyclopentadiene and *cis*-1,4-dichlorobut-2-ene^{8,10} or the elimination of toluene-*p*-sulphonic acid from the corresponding ditosylate (XIVb).¹¹ The Diels-Alder adduct (XV) of hexachlorocyclopentadiene and 1,4-dichlorobut-2-yne is readily prepared and although initial attempts by Hoch and Clegg⁸ to convert it into the triene by treatment with zinc were unsuccessful, this method of synthesis was later accomplished by Fust and Worms using specialised conditions.¹² We now find that the compound (XV) may be readily converted into the triene (VII) by catalytic hydrogenolysis using benzene as solvent, 10% palladium on charcoal as catalyst, and slightly in excess



of two molar proportions of pyridine. Uptake of one mol. of hydrogen is complete in approximately 5 min., when reaction is stopped to prevent any appreciable reduction of the product triene (VII). By analogy with

¹⁰ V. Mark, U.S.P. 3,221,067 (*Chem. Abs.*, 1966, **65**, 5382).

¹¹ J. G. Kuderna and G. R. Haynes, U.S.P. 3,265,721 (*Chem. Abs.*, 1966, **65**, 20,033).

¹² K. J. Fust and H. F. Worms, Ger.P. 1,089,377 (*Chem. Abs.*, 1961, **55**, 25,805).

our study of the catalytic hydrogenolysis of some polychloronorbornenes¹³ we assume that the compound (XV), hydrogen, and pyridine are adsorbed on the catalyst. This results in a partial bonding of the reactants to the catalyst, thus weakening some of the covalent bonds. We would suggest that hydrogenolysis is then possible in accord with the mechanistic pathway represented here. It is likely that the zinc dechlorination method of Fust and Worms¹² proceeds in a similar manner.

EXPERIMENTAL

Synthesis of 1,2,3,4,7,7-Hexachloro-5,6-dimethylenenorborn-2-ene (VII).—1,2,3,4,7,7-Hexachloro-5,6-bis(chloromethyl)norborna-2,5-diene (XV) (19.5 g.), formed by the Diels-Alder addition⁸ of 1,4-dichlorobut-2-yne to hexachlorocyclopentadiene, was dissolved in benzene (250 ml.) to which pyridine (10 ml.) and 10% palladium on charcoal (2 g.) was added. The mixture took up 1 mol. of hydrogen at 1 atmos. during 5 min. The reaction was then stopped, the reaction mixture filtered, and the solvent removed from the filtrate to leave a residue. This residue was chromatographed on alumina (Spence type H), using light petroleum (b.p. 40–60°) as eluent, to afford 1,2,3,4,7,7-hexachloro-5,6-dimethylenenorborn-2-ene (VII) as a white solid (14.5 g.), m.p. 84–85°, having identical properties with material prepared by the base elimination of two mol. of hydrogen chloride from 1,2,3,4,7,7-hexachloro-5,6-bis(chloromethyl)norborn-2-ene (XIVa) according to the method of Hoch and Clegg.⁸

Free-radical Addition Reactions of 1,2,3,4,7,7-Hexachloro-5,6-dimethylenenorborn-2-ene (VII).—(a) *Methanethiol*. Methanethiol (4 g.) and triene (VII) (9 g.) were mixed and azobisisobutyronitrile (0.1 g.) was added. The mixture was heated at 60° in a sealed tube for 24 hr. Distillation of the

reaction mixture afforded 1,4,5,6,7,7-hexachloro-3-methylnorborna-2,5-dien-2-ylmethyl methyl sulphide (VIIIa) as a pale yellow liquid (2 g.), b.p. 140°/0.3 mm., n_D^{25} 1.5664 (Found: C, 32.2; H, 2.05. $C_{10}H_8Cl_6S$ requires C, 32.2; H, 2.15%). An involatile polymeric residue remained behind in the flask.

(b) *Thiophenol*. 1,2,3,4,7,7-Hexachloro-5,6-dimethylenenorborn-2-ene (VII) (2.0 g.) was dissolved in thiophenol (0.7 g.) at room temperature. The reaction was initiated with a few drops of a 10% solution of peroxydiethyldicarbonate in cyclohexane, when an exothermic reaction took place. After 3 hr. the reaction mixture was worked up by alumina chromatography (Spence type H), using light petroleum (b.p. 40–60°) as eluent, to afford 1,4,5,6,7,7-hexachloro-3-methylnorborna-2,5-dien-2-ylmethyl phenyl sulphide (VIIIb) as white crystals, m.p. 69° (Found: C, 41.2; H, 2.2. $C_{15}H_{10}Cl_6S$ requires C, 41.7; H, 2.3%).

(c) *Bromotrichloromethane*. 1,2,3,4,7,7-Hexachloro-5,6-dimethylenenorborn-2-ene (VII) (5 g.) was dissolved in bromotrichloromethane (50 ml.) and the solution heated at 80° for 24 hr. with azobisisobutyronitrile (0.1 g.) as catalyst. Removal of solvent gave a brownish solid material which when chromatographed on an alumina column (Spence type H) using light petroleum (b.p. 40–60°) as eluent afforded unchanged triene (VII) (1.2 g.), hexachloroethane (2 g.), and a yellow polymeric material (1.3 g.), m.p. >200° (Found: C, 29.65; H, 1.5. Calc. for $(C_6H_4Cl_6)_n$: C, 32.75; H, 1.2. $CBrCl_3(C_6H_4Cl_6)_4$ requires C, 29.65; H, 1.1%).

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¹³ C. K. Alden and D. I. Davies, *J. Chem. Soc. (C)*, 1968, 700.