Free-radical Reactions of Halogenated Bridged Polycyclic Compounds. Part XVI.† Addition of Methanethiol and 1,1-Dimethylethanethiol to 5-substituted 1,2,3,4,7,7-Hexachloronorbornadienes

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The attack of alkylthio-radicals on a 5-substituted 1,2,3,4,7,7-hexachloronorbornadiene affords the 5-substituted 6-*endo*-alkylthio-1,2,3,4,7,7-hexachloronorborn-2-en-5-yl radical, which may undergo chain transfer from either the *exo*- or the *endo*-direction to afford a 5-*endo* (or 5-*exo*)-substituted 6-*endo*-alkylthio-1,2,3,4,7,7-hexachloronorborn-2-ene. Alternatively the radical can rearrange to the 4-substituted 7-*syn*-alkylthio-1,2,3,5,6,6-hexachloronorborn-2-en-5-yl radical, which on chain transfer affords the 4-substituted 7-*syn*-alkylthio-1,2,3,5-*endo*,-6,6-hexachloronorborn-2-ene. Product proportions depend on the nature of the 5-substituent in the diene, and may be rationalised in terms of the possible structure of the first-formed radical, and of interactions between the 5-substituent and the alkylthio-group in this radical. The major product from reaction of an alkanethiol with 5-chloromethyl-1,2,3,4,7,7-hexachloronorbornadiene is a 1,4,5,6,7,7-hexachloro-3-methylenenorborn-5-en-2-*endo*-yl alkyl sulphide.

THE major products formed in the addition of alkanethiols to hexachloronorbornadiene (Ia) are alkyl 1,4,5,6,7,7-hexachloronorborn-5-en-2-*endo*-yl sulphides (3a) and alkyl 1,2,3,5-*endo*,6,6-hexachloronorborn-2-en-7-*syn*-yl sulphides (7a) in the approximate ratio of 1 : 2 (R = Me or Et).[1] Both these products are derived by attack of thiyl radicals from the *endo*-direction to give the intermediate radical (2). This radical (2) either undergoes chain transfer to give (3) or, *via* the nortricyclyl-type radical (5), rearranges to radical (6), which

affords (7) on chain transfer. The driving force for the rearrangement was considered[2] to be the formation of a chlorine-stabilised radical.[3] It was of interest to study the addition of thiols to some 5-substituted hexachloronorbornadienes (1b—e) to discover the effect of the substituent on (i) the direction of chain transfer of intermediate (2), and (ii) the ease of rearrangement of intermediate (2) to intermediate (6). The proportions

† Part XV, R. Alexander and D. I. Davies, *J.C.S. Perkin I*, 1973, 83.

[1] Part II, C. K. Alden, J. A. Claisse, and D. I. Davies, *J. Chem. Soc. (C)*, 1966, 1540.
[2] D. I. Davies, *Chem. Soc. Special Publ. No. 24*, 1970, p. 201.
[3] A. N. Nesmeyanov, R. Kh. Friedlina, V. N. Kost, and M. Ya. Khorlina, *Tetrahedron*, 1961, 16, 94.

of the products (3), (4), and (7) formed in the addition of methanethiol and of 1,1-dimethylethanethiol to the dienes (1b—e) are recorded in the Table, which also includes, for comparison purposes, the proportions of (3a) or (4a) and (7a) formed in the respective additions of methanethiol and ethanethiol to hexachloronorbornadiene (Ia).

Studies on homolytic aromatic substitution[4] suggest that all types of substituent, in the absence of steric

to stabilise the radical centre in (2c), resulting in ready rearrangement of (2c) to (6c), *or* the structure of the radical centre is such that chain transfer is precluded so that rearrangement to (6c) is the only possible course of reaction.

The available evidence[5] suggests that substituted radicals (2) will be pyramidal, and the two possible quasitetrahedral structures are (8) and (9). In the absence of electrostatic interactions between groups X


a; X = H
b; X = Ph
c; X = Me
d; X = Cl
e; X = CO₂Me
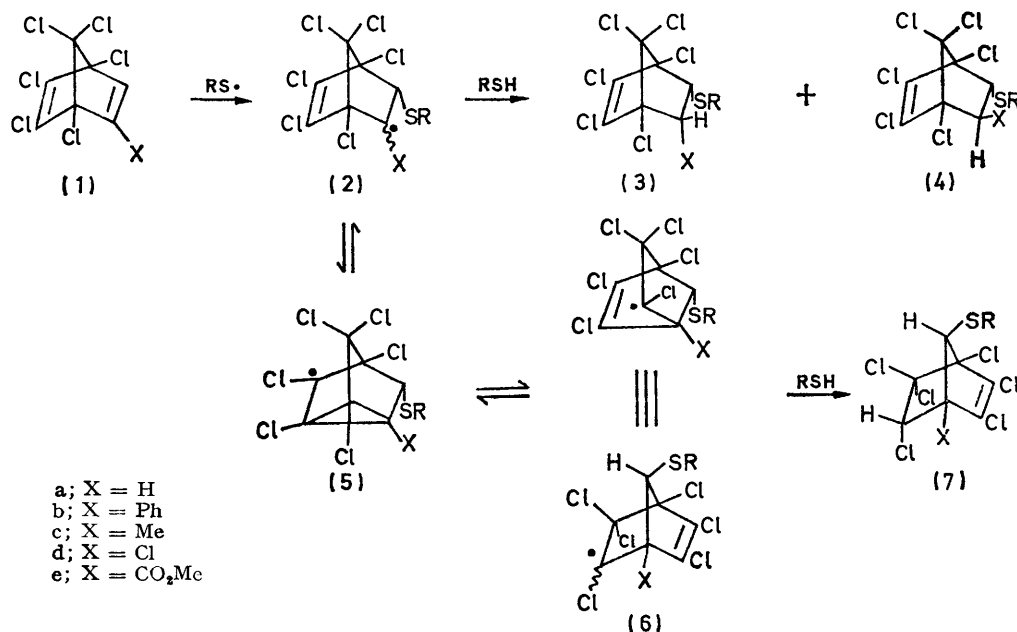
Products and conditions for thiol addition to 5-substituted hexachloronorbornadienes

| Diene | X | Thiol | Reaction time (h) | % Reaction | Product proportions (%) | | | Method of analysis † |
					(3)	(4)	(7)	
(1a)[1]	H	MeSH	48	75		31	69	N.m.r.
(1a)[1]	H	EtSH	48	65		31	69	N.m.r.
(1b)	Ph	MeSH	120	100	88	0	12	N.m.r.
(1b)	Ph	Bu^{t}SH	48	72 †	100	0	0	N.m.r.
(1c)	Me	MeSH	48	57 †	0	0	100	N.m.r.–G.l.c. (a)
(1c)	Me	Bu^{t}SH	72	50	0	0	100	N.m.r.–G.l.c. (a)
(1d)	Cl	MeSH	48	98	61	25	14	N.m.r.–G.l.c. (a)
(1d)	Cl	Bu^{t}SH	48	50	47	6	47	N.m.r.–G.l.c. (a)
(1e)	CO₂Me	MeSH	48	100	100	0	0	N.m.r.–G.l.c. (b)
(1e)	CO₂Me	Bu^{t}SH	48	100	100	0	0	N.m.r.–G.l.c. (b)

† G.l.c. analysis was carried out at 100—180° on a Perkin-Elmer F 11 gas chromatograph fitted with a 2 m × ⅛ in stainless steel column packed with (a) 5% Apiezon L on AW–DMCS Chromosorb W (80—100 mesh) or (b) 2·5% Silicone gum rubber E 301 on AW–DMCS Chromosorb W (80—100 mesh). ‡ Product contains *ca.* 20% of an unidentified compound.

effects, stabilise free radicals. This leads to the expectation that a radical (2b—e) with a 5-substituent should be more stable than the radical (2a) (X = H), and hence less prone to rearrange to radical (6) leading to the formation of product (7). This expectation is realised when X = Ph, Cl, or CO₂Me, but not when X = Me (Table), since the addition of thiols to (Ic) affords solely the rearranged product (7c). This anomalous result when X = Me implies that *either* the methyl group fails

and SR, structure (9) should be the most favoured because the unfavourable eclipsing of these groups in
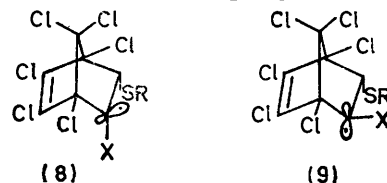
(8) is absent. Since both Me and SR are electron-donating groups, they would exert a repulsive interaction on each other when eclipsed as in (8c); this

[4] D. H. Hey, *Adv. Free Radical Chem.*, 1967, **2**, 47; D. I. Davies, D. H. Hey, and B. Summers, *J. Chem. Soc. (C)*, 1971, 2681.
[5] D. I. Davies and P. Mason, *J. Chem. Soc. (C)*, 1971, 288.

further favours (9c) over (8c). In the favoured intermediate (9c), overlap of the orbital at the radical centre with the π-electron orbitals of the chlorine-substituted double bond occurs, which allows the ready rearrangement of (2c) to (6c) to be rationalised. Studies on homolytic aromatic substitution [4] predict similar stabilisation of radical centres by Cl and Me; therefore the difference between (2c) and (2d) will be the relative importance of (8) and (9) when X is Cl and Me, respectively. The formation of appreciable quantities of (3d), derived from (2d), shows that in spite of the eclipsing of Cl and SR, appreciable amounts of product are derived from (8d). A possible explanation is that the attraction between groups of opposite inductive effect reduces the steric disadvantage occasioned by the eclipsing of Cl and SR. The importance of (8d) relative to (9d) decreases as the size of SR increases from SMe to SBu^t. Intermediate (9d) leads to products (4d) and (7d). Chain transfer of (9d) with thiol becomes sterically more difficult as the size of the thiol is increased and hence rearrangement to (6d) and formation of (7d) is favoured with Bu^{t}SH.

With X = Ph very little rearrangement of (2b) to (6b), and hence formation of (7b), occurs. With X = CO$_2$Me, no rearrangement of (2e) occurs at all and (3e), derived by chain transfer of (2e) with thiol, is the sole product. On the assumption of pyramidal intermediates this indicates that for these groups (8) should be favoured entirely over (9), which seems improbable on account of the size of the CO$_2$Me and Ph groups and their consequent unfavourable steric interaction with an SR group. Since the groups CO$_2$Me and Ph are

(10)   (11)
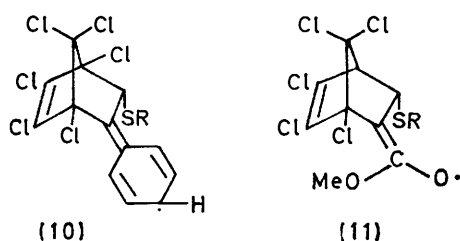
unsaturated, radical structures (2b) and (2e) are unlikely to be pyramidal as in (8) and (9), and probably have contributions from structures like (10) and (11). Such stabilisation effectively prevents interaction with the chlorine-substituted double bond, and consequent rearrangement. Examination of models, bearing in mind the well-known preference for *exo* chain transfer [2,6] in two-stage additions to norbornene-type double bonds, rationalises exclusive *exo* chain transfer from the planar radicals (2b) and (2e).

The reaction of the chloromethyl diene (12) with the

two alkanethiols did not lead to the 1 : 1 adducts (3), (4), and (7) (X = CH$_2$Cl). The only identifiable product from the reaction with methanethiol was the methyl
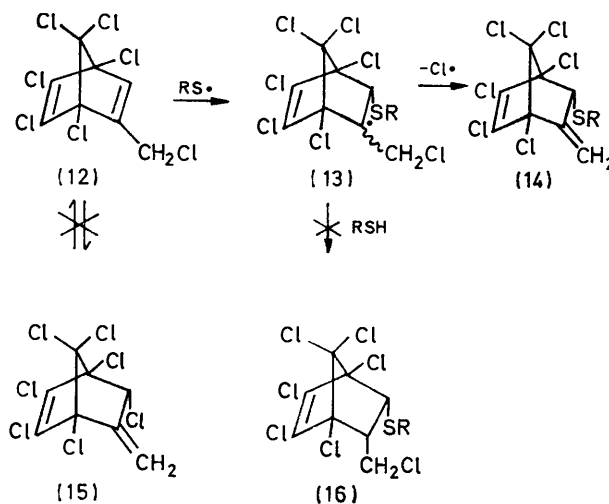
hexachloromethylenenorbornen-2-*endo*-yl sulphide (14; R = Me), which was characterised by oxidation to a sulphone. The reaction with 1,1-dimethylethanethiol gave, in low yield, the corresponding t-butyl sulphide (14; R = Bu^t), which was identified on the basis of its n.m.r. spectrum.

The formation of (14) is unlikely to involve addition of an alkylthio-radical to (12) to give the intermediate (13), which then loses a chlorine atom. Alternative routes such as (i) allylic rearrangement of (12) to (15) (control experiments show that this occurs less readily than with the corresponding bromides [7]) followed by nucleophilic substitution or (ii) chain transfer of (13) to afford (16) followed by loss of hydrogen chloride, are unlikely since neither (15) nor (16) could be detected as a reaction intermediate.

All new products reported in this paper were identified on the basis of their n.m.r. spectra, which were consistent with those reported for norbornenes [8] and chlorine-substituted norbornenes.[9]

EXPERIMENTAL

The following compounds were prepared by literature methods: 1,2,3,4,7,7-hexachloro-5-phenylnorborna-2,5-diene (1b),[10] 1,2,3,4,5,7,7-heptachloronorborna-2,5-diene (1d),[11] methyl 1,4,5,6,7,7-hexachloronorborna-2,5-diene-2-carboxylate (1e).[12]

1,2,3,4,7,7-*Hexachloro-5-methylnorborna-2,5-diene* (1c).— Hexachlorocyclopentadiene (10·0 g, 0·04 mol) and prop-1-yne (4·0 g, 0·1 mol) were heated at 180° for 7 h in a Carius tube sealed under nitrogen. The tube was cooled, opened, and the excess of prop-1-yne allowed to evaporate. Distillation of the residue afforded the diene (1c) (11·1 g),

[6] H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, 1970, **92**, 201, 1990; H. C. Brown and Kwang-Ting Liu, *ibid.*, p. 3502; H. C. Brown, J. H. Kawakami, and S. Ikegami, *ibid.*, p. 6914.

[7] R. Alexander and D. I. Davies, *J. Chem. Soc.* (C), 1971, 5.

[8] 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.

[9] 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.*, p. 5712.

[10] A. J. Fry, *J. Org. Chem.*, 1966, **31**, 1863.

[11] M. J. Parrott, Ph.D. Thesis, London, 1971; C. H. M. Adams, K. Mackenzie, and P. R. Young, *J.C.S. Perkin II*, 1972, 1856.

[12] D. I. Davies, P. Mason, and M. J. Parrott, *J. Chem. Soc.* (C), 1971, 3428.

b.p. 50° at 0·01 mmHg, n_D^{25} 1·5460 (lit.,[13] 1·5440) (Found: C, 30·9; H, 1·4. Calc. for $C_8H_4Cl_6$: C, 30·7; H, 1·3%), τ (60 MHz) 3·70 (q, H-6) and 8·03 (d, CH_3), J(6,CH_3) 2·2 Hz, $v_{max.}$ 1600s (cis-ClC=CCl) and 1635m cm⁻¹ (cis-MeC=CH).

5-Chloromethyl-1,2,3,4,7,7-hexachloronorborna-2,5-diene (12).—Hexachlorocyclopentadiene (22·0 g, 0·08 mol) and prop-2-ynyl chloride (18·0 g, 0·24 mol) were heated at 135° for 24 h in a Carius tube sealed under nitrogen. The tube was opened and the product mixture distilled to afford successively: prop-2-ynyl chloride (3·5 g), b.p. 45° at 20 mmHg; a mixture (15·3 g), b.p. 90—96° at 0·3 mmHg of hexachlorocyclopentadiene and the diene (12); and the diene (12) (11·7 g), n_D^{25} 1·5640, b.p. 74° at 0·01 mmHg (Found: C, 27·9; H, 1·0. $C_8H_3Cl_7$ requires C, 27·7; H, 0·9%), τ (60 MHz) 3·35 (t, H-6) and 5·73 (d, CH_2Cl), J(6,CH_2Cl) 1·5 Hz, $v_{max.}$ 1603s (cis-ClC=CCl) and 1630m cm⁻¹ (cis-ClCH₂·C=CH).

Addition of Methanethiol and 1,1-Dimethylethanethiol to 5-Substituted Hexachloronorborna-2,5-dienes (1b—e).—The diene (0·003 mol) and excess of thiol (0·015 mol) were mixed, azobisisobutyronitrile (0·1 g) was added, and the mixture was heated at 60° in a sealed tube. Where necessary further amounts (0·1 g) of initiator were added every 2 days. When the reaction was largely complete, the tube was opened and the excess of thiol allowed to evaporate. The crude product was analysed for product proportions by g.l.c. (Table) and product structures were deduced from the n.m.r. spectrum of the mixture, which also allowed a check on product portions. Single products were purified by recrystallisation from methanol; where possible mixtures were separated by column chromatography. N.m.r. and i.r. data and analyses and properties of products are available as Supplementary Publication No. SUP 20895 (3 pp.)* Control experiments showed that product proportions did not vary during the course of the reaction.

Reaction of Methanethiol with 5-Chloromethylhexachloronorbornadiene (12).—The diene (12) (1·0 g, 0·0029 mol), an excess of methanethiol (1·0 g, 0·02 mol), and azobisisobutyronitrile (0·1 g) were mixed and the mixture was heated at 60° in a sealed tube for 84 h. The tube was then cooled and opened, and the excess of thiol allowed to evaporate. G.l.c. of the residue on column (a) (see Table) showed that it consisted of unchanged diene (12) and one

major product believed to be 1,4,5,6,7,7-hexachloro-3-methylenenorborn-5-en-2-endo-yl methyl sulphide (14; R = Me), τ 4·21 (m) and 4·43 (m) (=CH_2) and 7·71 (s, SCH_3). The reaction mixture (0·5 g) in methanol (5 ml) was stirred for 24 h with a solution of hydrogen peroxide (30 w/v; 2 ml) containing ammonium molybdate (0·1 g). The mixture was then poured into water (20 ml) and extracted with ether (3 × 20 ml); the extract was washed with ferrous sulphate solution (2 × 20 ml) and water (2 × 20 ml), dried ($MgSO_4$), and evaporated. The residue was chromatographed on silica gel (B.D.H. 60—120 mesh) with light petroleum (b.p. 40—60°) and mixtures of light petroleum and ether as eluants to afford, successively, unchanged diene (12) (0·2 g) and 1,4,5,6,7,7-hexachloro-3-methylene-norborn-5-en-2-endo-yl methyl sulphone (0·1 g), b.p. 97—98° (Found: C, 27·2; H, 1·6. $C_9H_6Cl_6SO_2$ requires C, 27·7; H, 1·5%), τ (60 MHz) 3·89 (t, H-8 transoid), 4·09 (q, H-8 cisoid), 5·47 (t, H-6-exo), and 7·00 (s, $SO_2·CH_3$), J(8-transoid,8-cisoid) 1·3, J(8-transoid,6-exo) 1·7, J(8-cisoid,6-exo) 1·5 Hz, $v_{max.}$ 1603 (cis-ClC=CCl), 1145, and 1330 cm⁻¹ (SO_2).

Reaction of 1,1-Dimethylethanethiol with 5-Chloromethyl-hexachloronorbornadiene (12).—The diene (12) (1 g, 0·0029 mol), an excess of thiol (1·8 g, 0·02 mol), and azobisiso-butyronitrile (0·1 g) were mixed and heated at 60° in a sealed tube for 77 h. The tube was then cooled and opened, and excess of thiol allowed to evaporate. G.l.c. analysis of the residue on column (a) (see Table) showed it to consist of unchanged diene (12) and one major component. Chromatography on silica gel (Fisons 100—200 mesh) with light petroleum (b.p. 40—60°) as eluant afforded unchanged diene (12) (0·05 g), a mixture (0·3 g) of unchanged diene (12) and product (14; R = Buᵗ), and crude 1,4,5,6,7,7-hexachloro-3-methylenenorborn-5-en-2-endo-yl t-butyl sulphide (14; R = Buᵗ) (0·2 g), b.p. 90° at 0·05 mmHg, τ (60 MHz) 4·30 (H-8 transoid), 4·47 (H-8 cisoid), 5·92 (t, H-6-exo), and 8·58 (s, Buᵗ), J(8-cisoid,8-transoid) 1, J(8-transoid,6-exo) 1·8, J(8-cisoid,6-exo) 2·1 Hz, $v_{max.}$ 1598 cm⁻¹ (cis-ClC=CCl). Attempts to characterise the sulphide via oxidation to a sulphone led to decomposition.

* For details of Supplementary Publications, see Notice to Authors No. 7 in J. Chem. Soc. (A), 1970, Index Issue.

[13] D. Seyferth and A. B. Envin, J. Amer. Chem. Soc., 1967, 89, 1458.