The Reaction of Some Chlorine-substituted Norbornadienes and Norbornenes with Sodium Thiomethoxide

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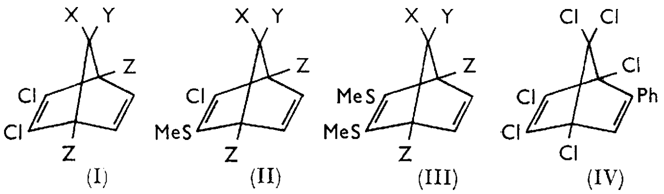
The reaction of 1,2,3,4,7,7-hexachloronorborna-2,5-diene and related norbornadienes containing a dichloro-substituted 2,3-double bond, with sodium thiomethoxide in dimethylformamide as solvent, results in successive replacement of the vinylic double-bond chlorines. The corresponding 1,2,3,4,7,7-hexachloronoroborn-2-ene and related norbornenes are less reactive, and only with norbornenes containing at least one bridge chlorine is it possible to isolate even a monosubstitution product. Aldrin does not react, and isodrin gives a low yield of monosubstitution product. Competitive studies suggest that replacement of vinylic chlorines is aided to a comparable degree by both an unsubstituted double bond, and by bridge chlorines. Bridgehead chlorines have less effect on reactivity. The rate-determining step of reaction is likely to be attack by thiomethoxide ions on the chlorine-substituted double bond. The disubstitution product 1,4,7,7-tetrachloro-2,3-dithiomethoxynorborna-2,5-diene derived from hexachloronorbornadiene deteriorates on keeping, for more than 2 weeks, to afford 1,4,7,7-tetrachloro-2,3,5-*endo*-trithiomethoxynorborn-2-ene. This compound is also formed in the hydrogen chloride catalysed addition of methanethiol to 1,4,7,7-tetrachloro-2,3-dithiomethoxynorborna-2,5-diene, whereas in the free-radical catalysed addition it is only a minor product formed together with the major product 1,5-*endo*-6,6-tetrachloro-2,3,7-*syn*-trithiomethoxynorborn-2-ene.

The reaction of nucleophilic reagents with vinyl halides can lead to products in which the halogen has been formally replaced by the attacking nucleophile. In such reactions, mechanisms of either elimination–addition or addition–elimination are operative.[1,2]



	X	Y	Z
a:	Cl	Cl	Cl
b:	H	Cl	Cl
c:	Cl	H	Cl
d:	H	H	Cl
e:	H	H	H

In the reaction of nucleophilic reagents with the vinylic chlorines of hexachloronorbornadiene (Ia), a mechanism of addition–elimination is alone possible if reaction is to occur without rupture of the ring system. The reaction of this diene (Ia) with potassium ethoxide was studied by Mackenzie,[3] who obtained the product of replacement of one of the vinylic chlorines by an ethoxy-group. This invalidated the earlier studies of Molotsky [4] in which replacement of one of the bridge C-7 chlorines was reported. The work of Mackenzie [3] should be contrasted with that of McBee [5] who showed that reaction of 1,2,3,4,7,7-hexachloro-5-phenylnorborna-2,5-diene (IV) with sodium methoxide afforded 2,3,4,5-tetrachlorobiphenyl as sole product. This product was considered to be formed by decomposition of the product of replacement of the two bridge chlorines in 1,2,3,4,7,7-hexachloro-5-phenylnorborna-2,5-diene (IV) by methoxy-groups.

Our studies have been concerned with the reaction of the chlorine-substituted norbornadienes (Ia—e) with thiomethoxide ions in the dipolar aprotic solvent dimethylformamide. With hexachloronorbornadiene (Ia) and sodium thiomethoxide in equimolar amounts, it is possible to isolate, from the reaction mixture after 48 hours, unchanged hexachloronorbornadiene (Ia), the monosubstitution product 1,3,4,7,7-pentachloro-2-thiomethoxynorborna-2,5-diene (IIa), and the disubstitution product 1,4,7,7-tetrachloro-2,3-dithiomethoxynorborna-2,5-diene (IIIa) in the approximate ratio of 1·5 : 1 : 1. A good yield of the disubstitution product (IIIa), alone, may be obtained when the reactant mixture contains hexachloronorbornadiene (Ia) and sodium thiomethoxide in the mole ratio of 1 : 5. The reactions of sodium thiomethoxide with 1,2,3,4,7-*anti*-pentachloronorborna-2,5-diene (Ib) and 1,2,3,4,7-*syn*-pentachloronorborna-2,5-diene (Ic) were similar. With 1,2,3,4-tetrachloronorborna-2,5-diene (Id) and 2,3-dichloronorborna-2,5-diene (Ie) appreciable reaction takes place only in the presence of an excess of sodium thiomethoxide, and requires an elevated temperature of 80°. Under these conditions it is only the disubstitution products (IIId) and (IIIe) that are isolated.

The establishment of the structure of the disubstitution product from hexachloronorbornadiene (Ia) as 1,4,7,7-tetrachloro-2,3-dithiomethoxynorborna-2,5-diene (IIIa) was provided by reaction of (IIIa) with Raney nickel (freshly prepared active material containing adsorbed hydrogen) in refluxing ethanol to give the known 1,4,7,7-tetrachloronorbornane.[6] This proves that in the reaction of hexachloronorbornadiene (Ia) with thiomethoxide ions, substitution occurs exclusively for the vinylic chlorines. By analogy the disubstitution pro-

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[1] W. E. Truce, M. M. Boudakian, R. F. Heine, and R. J. McManimie, *J. Amer. Chem. Soc.*, 1956, **78**, 2743; W. E. Truce and M. M. Boudakian, *ibid.*, p. 2748; W. E. Truce and R. Kassinger, *ibid.*, 1958, **80**, 1916, 6450; W. E. Truce, ' Organic Sulfur Compounds,' ed. N. Kharasch, vol. 1, Pergamon, Oxford, 1961, p. 112—120.

[2] L. K. Montgomery, F. Scardiglia, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1965, **87**, 1917.

[3] K. Mackenzie, *J. Chem. Soc.*, 1962, 457.

[4] H. M. Molotsky, U.S.P. 2,897,240/1959 (*Chem. Abs.*, 1960, **54**, 1364).

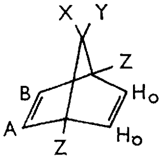
[5] E. T. McBee, J. Idol, jun., and C. W. Roberts, *J. Amer. Chem. Soc.*, 1955, **77**, 6674.

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

ducts derived from reaction of thiomethoxide ions with the chlorine substituted norbornadienes (Ib—e) have the structures (IIIb—e) as a consequence of the replacement of their vinylic chlorines. Table 1 records spectroscopic data which supports the structures (IIa—c) and (IIIa—e) for the mono- and di-substitution products. A *cis*-dichloroethylene olefinic system shows strong infrared absorption at 1610 cm.$^{-1}$.[7] Successive substitution of the vinylic chlorines results in a progressive reduction in the intensity of absorption coupled with a shift to lower wavenumber. In all monosubstitution and disubstitution products the methyl protons of the methylthio-group appear as a singlet in the n.m.r. spectrum in the region τ 7·6—7·7. In the disubstitution products (IIIa—e) the observation of only one singlet suggests that both methylthio-groups, in each of these compounds, have an identical environment. An independent synthesis of 1,2,3,4-tetrachloro-7,7-dithiomethoxynorborna-2,5-diene (V) and 1,2,3,4,7-pentachloro-7-thiomethoxynorborna-2,5-diene (VI), which have bridge thiomethoxy-groups, was carried out. As shown in Table 1 the spectral properties of these compounds are different from those of the monosubstitution and disubstitution products formed from reaction of thiomethoxide ions with hexachloronorbornadiene (Ia).

TABLE 1

Accumulated spectral data for the products of the reaction of thiomethoxide ions with chlorine-substituted norbornadienes and also for certain synthetic norbornadienes

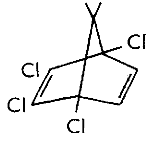


	N.m.r. data τ-Values and multiplicities					I.r. data Position (cm.$^{-1}$) and relative intensities for $A\!>\!C{=}C\!<\!B$
Compound	H_o	X	Y	CH_3S	*J*-Values (c./sec.)	
(IIa) A = SCH_3 X = Y = Z = B = Cl	3·47 s			7·65 s		**1580, 1555** m
(IIIa) A = B = SCH_3 X = Y = Z = Cl	3·55 s			7·70 s		**1565, 1525** w
(IIb) A = SCH_3, X = H Y = Z = B = Cl	3·61 d	5·61 t		7·60 s	*J*(X,H_o) 1·1	**1580, 1557** m
(IIIb) A = B = SCH_3 Y = Z = Cl, X = H	3·66 d	5·63 t		7·64 s	*J*(X,H_o) 1·0	**1566, 1530** w
(IIc) A = SCH_3, Y = H X = Z = B = Cl	3·26 s		5·40 s	7·68 s		**1575** m
(IIIc) A = B = SCH_3 X = Z = Cl, Y = H	3·38 s		5·61 s	7·66 s		**1535, 1562** w
(IIId) A = B = SCH_3 X = Y = H, Z = Cl	3·44 br	7·31 br	7·17 d	7·67 s	*J*(X,Y) 5·7	**1565** w
(IIIe) * A = B = SCH_3 X = Y = Z = H	3·15 t	7·81 t		7·71 s	*J*(X,H_o) = *J*(Z,H_o) = 1·9	**1565** w
(V) A = B = Z = Cl X = Y = SCH_3	3·61 s			6·61 s		**1609** s
(VI) A = B = Z = Cl X or Y = SCH_3, X or Y = Cl	3·37 s			6·74 s		**1611** s

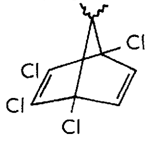
* Protons Z as a quartet τ 6·62 (*J* 1·9 c./sec.).

The diene 1,2,3,4-tetrachloro-7,7-dimethoxynorborna-2,5-diene (VII) certainly underwent transformation in the presence of thiomethoxide ions in dimethylformamide at room temperature. However the reaction mixture was very tarry indicating breakdown of starting diene and/or products, and we were unable to isolate any identifiable substitution product. The instability of reactant and/or products is in line with the presumed instability of 1,2,3,4-tetrachloro-7,7-dimethoxy-5-phenylnorborna-2,5-diene.[5]

The disubstitution products (IIIa—e) were white crystalline solids, which were stable on keeping with the exception of 1,4,7,7-tetrachloro-2,3-dithiomethoxynorborna-2,5-diene (IIIa). This compound was apparently transformed, after keeping for periods in excess of 2



(V)



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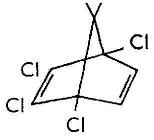

(VII)

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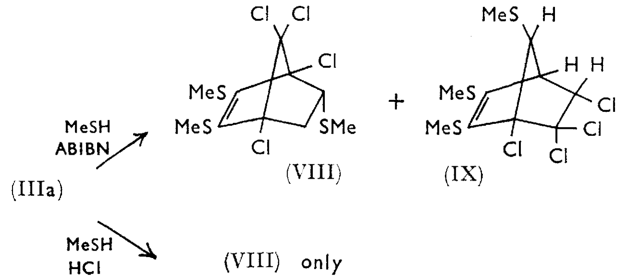
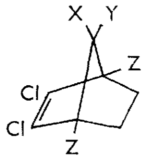
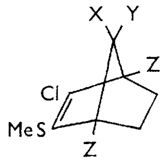
[7] S. B. Soloway, A. M. Damiana, J. W. Sims, H. Bluestone, and R. E. Lidov, *J. Amer. Chem. Soc.*, 1960, **82**, 5377; G. Herzberg, 'Infra Red and Raman Spectra of Polyatomic Molecules,' Van Nostrand, New York, 1945, p. 330.

weeks, into 1,4,7,7-tetrachloro-2,3,5-*endo*-trithiomethoxynorborn-2-ene (VIII). This transformation product (VIII) was readily recognised from its n.m.r. spectrum which showed H(5-*exo*) as a quartet at τ 6·37 (*J* 4·1, 9·1); H(6-*exo*), quartet, 7·13 (*J* 9·1, 12·8); H(6-*endo*), quartet, 8·38 (*J* 4·1, 12·8); CH_3S, singlets, 7·47, 7·56, 7·73. By analogy with the established correlations for norbornenes [8] and chlorine-substituted norbornenes [9,10] these data characterise the structure (VIII). We assume that decomposition of the disubstitution product (IIIa), possibly aided by the presence of some adventitious moisture, produces some methanethiol and hydrogen chloride. The product (VIII) is then derived by acid-catalysed addition of methanethiol to the unsubstituted double bond (*cf.*, acid-catalysed addition of thiols to hexachloronorbornadiene (Ia) [10b] and tetrachloronorbornadiene (Id).[11] The formation of (VIII) during the decomposition of (IIIa) by the free-radical catalysed addition of methanethiol to (IIIa) can be ruled out since using freshly prepared (IIIa) the azobisisobutyronitrile catalysed addition of methanethiol afforded (VIII) plus the product of skeletal rearrangement 1,5-*endo*,6,6-tetrachloro-2,3,7-*syn*-trithiomethoxynorborn-2-ene (IX) in the ratio of 1 : 11. The formation of a rearrangement product, in addition to the product of 1,2-addition to the unsubstituted double bond, is characteristic of the free-radical catalysed addition of thiols to hexachloronorbornadiene (Ia)[10a,b] and related compounds.[10c,11,12] The addition of methanethiol in the presence of hydrogen chloride affords exclusively the product (VIII) of 1,2-addition to the unsubstituted double bond.





(X)



(XI)

	X	Y	Z
a:	Cl	Cl	Cl
b:	H	Cl	Cl
c:	Cl	H	Cl
d:	H	H	Cl
e:	H	H	H

Product of type (XI) is not formed from (Xd) and (Xe)

TABLE 2

Relative reactivities [hexachloronorbornadiene (Ia) = 1] of various chlorine-substituted norbornadienes and norbornenes toward reaction with thiomethoxide ions

Chlorine-substituted norbornadienes		Chlorine-substituted norbornenes	
1,2,3,4,7,7-Hexachloronorborna-2,5-diene (Ia)	1·00	1,2,3,4,7,7-Hexachloronorborn-2-ene (Xa)	0·32
1,2,3,4,7-*anti*-Pentachloronorborna-2,5-diene (Ib)	0·61	1,2,3,4,7-*anti*-Pentachloronorborn-2-ene (Xb)	0·20
1,2,3,4,7-*syn*-Pentachloronorborna-2,5-diene (Ic)	0·32	1,2,3,4,7-*syn*-Pentachloronorborn-2-ene (Xc)	0·17
1,2,3,4-Tetrachloronorborna-2,5-diene (Id)	0·21	1,2,3,4-Tetrachloronorborn-2-ene (Xd)	0·03
2,3-Dichloronorborna-2,5-diene (Ie)	0·15	2,3-Dichloronorborn-2-ene (Xe)	<0·10
1,2,3,4-Tetrachloro-7,7-dimethoxynorborna-2,5-diene (VII)	*	1,2,3,4-Tetrachloro-7,7-dimethoxynorborn-2-ene (XVI)	0·39
1,2,3,4,7,7-Hexachloro-5-phenylnorborna-2,5-diene (IV)	1·18	1,2,3,4,7,7-Hexachloro-5,6-dimethylenenorborn-2-ene (XV)	1·51

Aldrin (XVII) and isodrin (XVIII) were virtually unreactive under the conditions of the competitive reactions.

* No measurement possible since diene decomposes as well as reacts.

When the unsubstituted double bond of the norbornadienes (Ia—e) is reduced the resultant norbornenes (Xa—e) are much less reactive toward thiomethoxide ions. Even in the presence of a large excess of sodium thiomethoxide it was only with hexachloronorbornene (Xa) and the two pentachloronorbornenes (Xb,c) that any products could be isolated, and these were solely those (XIa—c) of monosubstitution. No products in isolatable quantities could be obtained from attempted reaction of 1,2,3,4-tetrachloronorborn-2-ene (Xd) and 2,3-dichloronorborn-2-ene (Xe).

In order to discover further the factors controlling reaction of chlorine-substituted norbornadienes and norbornenes with thiomethoxide ions, a series of competitive experiments was carried out in which approximately equimolar amounts of hexachloronorbornadiene (Ia) and another norbornadiene or norbornene were allowed to compete for thiomethoxide ions sufficient for about one-third reaction. The amounts of hexachloronorbornadiene (Ia) and other norbornadiene or norbornene were accurately measured (relative to an inert standard) by gas-chromatographic analysis at the beginning of reaction, and after 48 hours. This allowed the reactivity of the norbornadienes and norbornenes relative to hexachloronorbornadiene (Ia) to be com-

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[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.

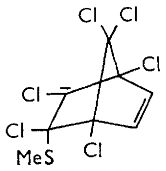
[10] (*a*) J. A. Claisse, D. I. Davies, and C. K. Alden, *J. Chem. Soc.* (*C*), 1966, 1498; (*b*) C. K. Alden, J. A. Claisse, and D. I. Davies, *ibid.*, p. 1540; (*c*) C. K. Alden and D. I. Davies, *ibid.*, 1967, 1017; (*d*) C. K. Alden and D. I. Davies, *ibid.*, p. 2007.

[11] D. I. Davies and P. J. Rowley, *J. Chem. Soc.* (*C*), 1967, 2249.

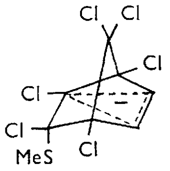
[12] D. I. Davies and P. J. Rowley, *J. Chem. Soc.* (*C*), 1967, 2245.

puted, and the results are given in Table 2. The theory and method are comparable to those used in the determination of the relative reactivity of olefins toward free radical attack.[13]

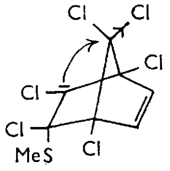
The most noticeable fact from Table 2 is that, when a norbornadiene is compared with the corresponding norbornene, a substantial reduction in reactivity is occasioned as a result of removal of the 5,6-double bond in the diene. This suggests that the intermediate (XII) formed on thiomethoxide ion attack on hexachloronorbornadiene (Ia), for example, is stabilised by delocalisation of the carbanion centre as a result of interaction with the 5,6-double bond as in (XIII). Such stabilisation was proposed by Mackenzie[3] in the intermediate formed on reaction of ethoxide ions with hexachloronorbornadiene (Ia). The high reactivity of 1,2,3,4,7,7-hexachloro-5-phenylnorborna-2,5-diene (IV) and 1,2,3,4,7,7-hexachloro-5,6-dimethylenenorborna-2,5-diene (XV) is a measure of the increased stabilisation of the carbanion centre, in the intermediates formed on thiomethoxide ion attack, by the extended unsaturated system across the ring.



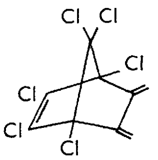
(XII)



(XIII)



(XIV)



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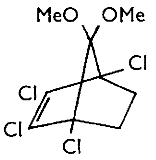
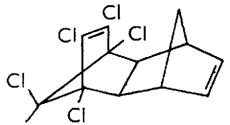


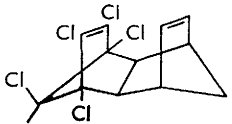
(XVI)

When the separate series of norbornadienes and norbornenes are compared it is clear that chlorines at the bridgehead, and more particularly at the bridge positions, enhance reactivity. Therefore the delocalised carbanion (XIII) does not adequately describe the intermediate formed on thiomethoxide attack of hexachloronorbornadiene (Ia), since stabilisation by chlorine is also important. The results suggest that a 7-*anti*-chlorine is better able to contribute to stabilisation than a 7-*syn*-chlorine. This is because a 7-*anti*-chlorine has a geometry more conveniently set up to stabilise a carbanion as is depicted in the example (XIV). The greater reactivity of 1,2,3,4,7-*anti*-pentachloronorborna-2,5-diene (Ib) and of 1,2,3,4,7-*anti*-pentachloronorborn-2-ene (Xb) relative to their corresponding 7-*syn*-isomers (Ic) and (Xc) respectively may also be due in part to a preference of thiomethoxide ions to attack the chlorine-substituted double bond from the *exo*-side of the molecule. Such a preference is favoured in the 7-*anti*-isomers (Ib) and (Xb) on both steric and electronic factors. The comparable reactivity of 1,2,3,4,7,7-hexachloronorborn-2-ene (Xa) and 1,2,3,4-tetrachloro-7,7-dimethoxynorborn-2-ene (XVI) suggests that chloro- and methoxy-substituents, in the intermediates formed on thiomethoxide ion attack, induce a comparable degree of stabilisation at the carbanion centre.

Aldrin (XVII) are isodrin (XVIII) are virtually unreactive when compared with hexachloronorbornadiene (Ia) by the competitive method. The lack of reactivity of aldrin (XVII) is explained by the absence of a conveniently placed double bond to stabilise the intermediate formed on thiomethoxide ion attack. In addition the methylene bridge will hinder attack from the *endo*-side of the chlorine-substituted double bond, and the chlorines of the dichloromethylene bridge from the *exo*-side. Isodrin (XVIII) was also unreactive under the conditions of the competitive method, but reaction at 80°, with a five-fold excess of thiomethoxide ions, gave 10% of the monosubstitution product as a result of replacement of one of the vinylic chlorines. Isodrin (XVIII) has the 6,7-double bond suitably placed to assist reaction, but as with aldrin (XVII) steric factors will hinder attack on the chlorine-substituted double bond.



(XVII)



(XVIII)

By analogy with our results, the disubstitution product reported by Fry[14] to be formed by reaction with thiomethoxide ions on 1,2,3,4,7,7-hexachloro-5-phenylnorborna-2,5-diene (IV) must be 1,4,7,7-tetrachloro-2,3-dithiomethoxy-5-phenylnorborna-2,5-diene, which is produced by replacement of the two vinylic chlorines in (IV). The n.m.r. spectrum of this product is reported[14] to show the methyl protons of the thiomethoxy-groups as a singlet at τ 7·53 consistent with this analogy (*cf.* Table 1).

Our results with thiomethoxide ions on hexachloronorbornadiene (Ia) and related compounds shows that it is possible to replace both vinylic chlorines, whereas with ethoxide ion only one chlorine is replaced;[3] this probably represents the superior nucleophilicity of the thiolate anion.[14,15] The reaction of 1,2,3,4,7,7-hexachloro-5-phenylnorborna-2,5-diene (IV) with alkoxide ions seems to be anomalous, and the results of McBee,[5] in which the diene (IV) reacts with methoxide ions to afford 2,3,4,5-tetrachlorobiphenyl, may be explicable by simple decomposition of diene (IV) in the reaction medium

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[13] C. Walling and W. Helmreich, *J. Amer. Chem. Soc.*, 1956, **81**, 1144; J. I. G. Cadogan and I. Sadler, *J. Chem. Soc.* (*B*), 1966, 1191; J. A. Claisse and D. I. Davies, *J. Chem. Soc.*, 1965, 4894; J. A. Claisse and D. I. Davies, *J. Chem. Soc.* (*C*), 1966, 1045.

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

[15] J. Hine and R. D. Weimar, jun., *J. Amer. Chem. Soc.*, 1965, **87**, 3387; J. Hine and W. H. Brader, jun., *ibid.*, 1953, **75**, 3964.

without an initial replacement of the bridge chlorines by methoxyl.

EXPERIMENTAL

The n.m.r. spectra were obtained using a Perkin-Elmer R.10 permanent-magnet spectrometer operating at 60 Mc./sec., and the i.r. spectra with a Perkin-Elmer 237 grating infrared spectrometer. Alumina (Laporte, H) was used for column chromatography. The light petroleum used had b.p. 40—60°.

Chlorine-substituted Norbornadienes and Norbornenes.—1,2,3,4,7,7-Hexachloronorborna-2,5-diene (Ia) (Aldrich) was dried in an ethereal solution (1 : 5) over magnesium sulphate. After removal of solvent it was obtained on distillation as a pale yellow liquid, b.p. 140—142°/19 mm. (lit.,[16] 149°/30 mm.). 1,2,3,4,7-*anti*-Pentachloronorborna-2,5-diene [11] (Ib), b.p. 140—141°/12 mm.; 1,2,3,4,7-*syn*-pentachloronorborna-2,5-diene [11] (Ic), b.p. 133—135°/10 mm.; 1,2,3,4-tetrachloronorborna-2,5-diene [11] (Id), b.p. 110—115°/5 mm.; 2,3-dichloronorborna-2,5-diene [17] (Ie), b.p. 173—174°/760 mm.; 1,2,3,4-tetrachloro-7,7-dimethoxynorborna-2,5-diene [18] (VII), m.p. 54—55°; 1,2,3,4,7,7-hexachloro-5-phenylnorborna-2,5-diene [14] (IV), m.p. 63—64°; 1,2,3,4,7,7-hexachloro-5,6-dimethylenenorborn-2-ene [19] (XV), m.p. 84—85°. The norbornadienes (Ia—e) and (VII) were catalytically reduced in ethanol solution with hydrogen at atmospheric pressure using 10% palladium–charcoal as catalyst to afford the corresponding norbornenes: 1,2,3,4,7,7-hexachloronorborn-2-ene [20] (Xa), m.p. 36—38°; 1,2,3,4,7-anti-*pentachloronorborn-2-ene* (Xb), m.p. 45—46° (Found: C, 31·5; H, 2·0. $C_7H_5Cl_5$ requires C, 31·6; H, 1·9%); 1,2,3,4,7-*syn*-pentachloronorborn-2-ene [21] (Xc), m.p. 57—59°; 1,2,3,4-tetrachloronorborn-2-ene [21] (Xd), m.p. 38—40°; 2,3-*dichloronorborn-2-ene* (Xe), b.p. 73—80°/0·1 mm. (Found: C, 51·2; H 4·75. $C_7H_8Cl_2$ requires C, 51·5; H, 4·9%), 1,2,3,4-tetrachloro-7,7-dimethoxynorborn-2-ene [22] (XVI), b.p. 136—142°/12 mm.

1,2,3,4-*Tetrachloro*-7,7-*dithiomethoxynorborna*-2,5-*diene* (V).—Hexachlorocyclopentadiene (5 g.) was added to a solution of sodium thiomethoxide (5 g.) in methanol (250 ml.), and the mixture stirred at room temperature for 48 hr. The product was then poured into water (500 ml.) and extracted with ether (2 × 250 ml.). The ether solution was dried (magnesium sulphate) and the solvent removed by evaporation to give a mixture, b.p. 90—100°/0·1 mm., of unchanged hexachlorocyclopentadiene and 1,2,3,4-tetrachloro-5,5-dithiomethoxycyclopenta-1,3-diene.[23] The latter diene exhibited CH_3S as a singlet in the n.m.r. at τ 6·68. The mixture (4·5 g.) and *cis*-1,2-dibromethylene (10 g.) were heated in a sealed Carius tube at 160° for 16 hr. The tube was opened, and unreacted *cis*-1,2-dibromoethylene removed by distillation to afford a black residual oil containing 5-*endo*,6-*endo*-dibromo-1,2,3,4,7,7-hexachloronorborn-2-ene [H(5-*exo*) and H(6-*exo*) as a singlet at τ 5·0] and 5-*endo*,6-*endo*-dibromo-1,2,3,4-tetrachloro-7,7-dithiomethoxynorborn-2-ene [H(5-*exo*) and H(6-*exo*) as a singlet at τ 5·18; CH_3S as singlets at 6·38, 6·44] in the ratio of 1·25 : 1 respectively. The residual oil was not purified but dissolved in glacial acetic acid (100 ml.) and zinc dust (5 g.) added. The mixture was stirred (2 hr.), filtered, poured into water (250 ml.), and extracted with ether (2 × 250 ml.). The ether was washed successively with water, saturated sodium hydrogen carbonate, and water, and dried (magnesium sulphate). Evaporation of solvent ether afforded a residual dark oil, which was purified by alumina chromatography using light petroleum as eluant to give 1,2,3,4,7,7-hexachloronorborna-2,5-diene (Ia) (1·0 g.) followed by 1,2,3,4-*tetrachloro*-7,7-*dithiomethoxynorborna*-2,5-*diene* (V) (0·7 g.), b.p. 155—160°/0·1 mm., n_D^{25} 1·5554 (Found: C, 33·7; H, 2·6. $C_9H_8Cl_4S_2$ requires C, 33·5; H, 2·5%).

1,2,3,4,7-*Pentachloro*-7-*thiomethoxynorborna*-2,5-*diene* (VI).— 1,2,3,4,5-Pentachloro-5-thiomethoxycyclopenta-1,3-diene [24] (2 g.) and *cis*-1,2-dibromoethylene (5 g.) were heated in a sealed Carius tube at 160° for 16 hr. Zinc debromination of the crude product followed by alumina chromatography using light petroleum as eluant, as in the preparation of (V), allowed isolation of 1,2,3,4,7-*pentachloro*-7-*thiomethoxynorborna*-2,5-*diene* (VI) (0·2 g.), b.p. 120—125°/0·1 mm., n_D^{25} 1·5676 (Found: C, 30·3; H, 1·16. $C_8H_5Cl_5S$ requires C, 30·9; H, 1·6%). The relatively poor analysis may be accounted for by the observation of some decomposition on distillation.

Reaction of Chlorine-substituted Norbornadienes with Sodium Thiomethoxide.—*Hexachloronorbornadiene* (Ia). (*Method A*). Hexachloronorbornadiene (Ia) (6 g.; 0·02 mole) was dissolved in dimethylformamide (100 ml.) and a solution of sodium thiomethoxide (1·4 g.; 0·02 mole) in dimethylformamide (100 ml.) was added, with stirring, during 10 min. Stirring was continued for 48 hr., and the solution then poured into water (500 ml.), and extracted with ether (2 × 250 ml.). The ether solution was washed twice with water, dried (magnesium sulphate), and the ether removed by evaporation to leave a brown oil. Chromatography on alumina using light petroleum as eluant afforded unreacted hexachloronorbornadiene (Ia) (2·4 g.); 1,3,4,7,7-*pentachloro*-2-*thiomethoxynorborna*-2,5-*diene* (IIa) (1·6 g.), b.p. 135—138°/0·1 mm., n_D^{25} 1·5724 (Found: C, 31·3; H, 1·5. $C_8H_5Cl_5S$ requires C, 30·9; H, 1·6%); 1,4,7,7-*tetrachloro*-2,3-*dithiomethoxynorborna*-2,5-*diene* (IIIa) (1·8 g.), m.p. 60—61° on recrystallisation from light petroleum containing benzene (10%) (Found: C, 33·6; H, 2·6. $C_9H_8Cl_4S_2$ requires C, 33·5; H, 2·5%).

(*Method B*). Hexachloronorbornadiene (Ia)(6 g.; 0·02 mole) was dissolved in dimethylformamide (100 ml.), and a solution of sodium thiomethoxide (7 g.; 0·1 mole) in dimethylformamide (500 ml.) was added, with stirring, during 15 min., during which period the temperature rose to 50°. The temperature then fell to room temperature during 2 hr., but stirring was continued for 48 hr. The mixture was worked up as for Method A and afforded 1,4,7,7-tetrachloro-2,3-dithiomethoxynorborna-2,5-diene (IIIa) (4·3 g.).

1,2,3,4,7-anti-*Pentachloronorborna*-2,5-*diene* (Ib). Using Method A the diene (Ib) (6 g.) afforded unreacted diene (Ib) (3·0 g.); 1,3,4,7-anti-*tetrachloro*-2-*thiomethoxynorborna*-2,5-*diene* (IIb) (1·1 g.), b.p. 125—128°/0·1 mm., n_D^{25} 1·5743 (Found: C, 34·6; H, 2·3. $C_8H_6Cl_4S$ requires C,

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34·8; H, 2·15%); 1,4,7-anti-*trichloro*-2,3-*dithiomethoxynorborna*-2,5-*diene* (IIIb) (0·9 g.), m.p. 71—72° on recrystallisation from light petroleum containing benzene (10%) (Found: C, 37·7; H, 3·05. $C_9H_9Cl_3S_2$ requires C, 37·6; H, 3·15%). With Method B the diene (Ib) (2 g.) gave the disbustitution product (IIIb) (1·1 g.) as sole isolatable product. 1,2,3,4,7-syn-*Pentachloronorborna*-2,5-*diene* (Ic). Using method A the diene (Ic) (3 g.) afforded unreacted diene (Ic) (2·4 g.); 1,3,4,7-syn-*tetrachloro*-2-*thiomethoxynorborna*-2,5-*diene* (IIc) (0·1 g.), b.p. 130—135°/0·1 mm., n_D^{25} 1·5762 (Found: C, 34·4; H, 2·4. $C_8H_6Cl_4S$ requires C, 34·8; H, 2·15%); 1,4,7-syn-*trichloro*-2,3-*dithiomethoxynorborna*-2,5-*diene* (IIIc) (0·2 g.), m.p. 63—64° (Found: C, 37·4; H, 3·2. $C_9H_9Cl_3S_2$ requires C, 37·6; H, 3·15%). With Method B the diene (Ic) (2·0 g.) afforded the disubstitution product (IIIc) (1·0 g.) as sole isolatable product.

1,2,3,4-*Tetrachloronorborna*-2,5-*diene* (Id). Using Method A little reaction took place and no products were isolated. With Method B for 48 hr., at 80°, the diene (Id) (2 g.) afforded 1,4-*dichloro*-2,3-*dithiomethoxynorborna*-2,5-*diene* (IIId) (0·9 g.), m.p. 62—63° on recrystallisation from pentane, as sole isolatable product (Found: C, 42·5; H, 3·9. $C_9H_{10}Cl_2S_2$ requires C, 42·7; H, 3·95%).

2,3,-*Dichloronorborna*-2,5-*diene* (Ie). Using Method A little reaction took place and no products were isolated. With Method B for 48 hr. at 80° the diene (Ie) (1 g.) afforded 2,3-*dithiomethoxynorborna*-2,5-*diene* (IIIe) (0·34 g.), m.p. 43—44° on crystallisation from light petroleum (Found: C, 58·5; H, 6·6. $C_9H_{12}S_2$ requires C, 58·7; H, 6·5%).

1,2,3,4-*Tetrachloro*-7,7-*dimethoxynorborna*-2,5-*diene* (VII). This diene (VII) decomposed under the conditions of both Method A and Method B.

Stability of Disubstitution Products.—The disubstitution product 1,4,7,7-tetrachloro-2,3-dithiomethoxynorborna-2,5-diene (IIIa) derived from hexachloronorbornadiene (Ia) deteriorated on keeping, for 2 weeks or longer, to afford 1,4,7,7-*tetrachloro*-2,3,5-endo-*trithiomethoxynorborn*-2-*ene* (VIII), m.p. 46—47° on recrystallisation from light petroleum containing benzene (10%) (Found: C, 32·1; H, 3·1. $C_{10}H_{12}Cl_4S_3$ requires C, 32·4; H, 3·25%). The disubstitution products (IIIb—e) derived from the dienes (Ib—e) were stable on keeping for several months.

Reaction of Chlorine-substituted Norbornenes with Sodium Thiomethoxide.—1,2,3,4,7,7-*Hexachloronorborn*-2-*ene* (Xa) (*Method C*). 1,2,3,4,7,7-Hexachloronorborn-2-ene (Xa) (2 g.) was dissolved in dimethylformamide (50 ml.), and a solution of sodium thiomethoxide (2 g.) in dimethylformamide (150 ml.) added, with stirring, during 10 min. Stirring was continued for 48 hr., and the reaction worked up as in Method A to afford 1,3,4,7,7-*pentachloro*-2-*thiomethoxynorborn*-2-*ene* (XIa) (1·7 g.), m.p. 58—59° (Found: C, 31·0; H, 2·3. $C_8H_7Cl_5S$ requires C, 30·7; H, 2·25%). The n.m.r. spectrum showed C-5 plus C-6 hydrogens as a multiplet at τ 7·6—8·2, and CH_3S, singlet, 7·60. The i.r. spectrum showed double bond absorption at 1520 and 1562 cm.$^{-1}$ of medium intensity.

1,2,3,4,7-*anti*-*Pentachloronorborn*-2-*ene* (Xb). Using Method C, but at 80°, the olefin (Xb) (1·0 g.) afforded 1,3,4,7-anti-*tetrachloro*-2-*thiomethoxynorborn*-2-*ene* (XIb) (0·5 g.), m.p. 67—69° (Found: C, 34·4; H, 2·75. $C_8H_8Cl_4S$ requires C, 34·5; H, 2·9%). The n.m.r. spectrum showed C-5 plus C-6 hydrogens as a multiplet τ 7·5—8·3; H(7-*syn*), triplet, 6·04 (J 2·1 c./sec.); CH_3S, singlet, 7·67. The i.r. spectrum showed double bond absorption at 1565 cm.$^{-1}$ of medium intensity.

1,2,3,4,7-syn-*Pentachloronorborn*-2-*ene* (Xc). Using Method C, but at 80°, the olefin (Xc) (1·0 g.) afforded 1,3,4,7-syn-*tetrachloro*-2-*thiomethoxynorborn*-2-*ene* (XIc) (0·4 g.), m.p. 75—77° (Found: C, 34·2; H, 2·65. $C_8H_8Cl_4S$ requires C, 34·5; H, 2·9%). The n.m.r. spectrum showed C-5 plus C-6 protons as a multiplet at τ 7·4—8·2; H(7-*anti*), singlet, 5·97; CH_3S, singlet, 7·65. The i.r. spectrum showed double bond absorption at 1525 and 1563 cm.$^{-1}$ of medium intensity.

1,2,3,4-*Tetrachloro*-7,7-*dimethoxynorborn*-2-*ene* (XVI). Using Method C the olefin (XVI) (2·0 g.) gave 1,3,4-*trichloro*-7,7-*dimethoxy*-2-*thiomethoxynorborn*-2-*ene* (1·1 g.), m.p. 102—103° (Found: C, 39·6; H, 4·1. $C_{10}H_{13}Cl_3O_2S$ requires C, 39·5; H, 4·3%). The n.m.r. spectrum showed CH_3O as singlets at τ 6·42, 6·51; CH_3S, singlet, 7·61; C-5 plus C-6 hydrogens as a multiplet 7·6—8·4.

The olefins 1,2,3,4-tetrachloronorborn-2-ene (Xd), 2,3-dichloronorborn-2-ene (Xe), and aldrin (XVII) failed to give any isolatable products under the conditions of Method C even at 80° for 72 hr.

Isodrin (XVIII). Using Method C, but at 80°, isodrin (XVIII) (1·0 g.) afforded 1,3,4,10,10-*pentachloro*-2-*thiomethoxy*-1,4,4a,5,8,8a-*hexahydro*-exo,exo-1,4:5,8-*dimethanonaphthalene* (0·1 g.), m.p. 212—214° (Found: C, 41·4; H. 2·9. $C_{13}H_{11}Cl_5S$ requires C, 41·1; H, 2·6%). The n.m.r. spectrum showed H(6) plus H(7), triplet, τ 4·01 (J 1·9 c./sec.), H(4a) plus H(8a), quartet, 6·75 (J 1·8, 1·9 c./sec.); H(5) plus H(8), multiplet, 7·11; CH_3S, singlet, 7·62; H(9) hydrogens, multiplet, 8·40. The i.r. spectrum showed double bond absorption of medium to weak intensity at 1585 cm.$^{-1}$.

Measurement of Relative Rates.—(a) *Derivation of kinetics*. The reaction of two vinylic halides AX and BX with thiomethoxide ions may be written:

$$AX + MeS^- \underset{k_{-1A}}{\overset{k_{1A}}{\rightleftharpoons}} (AXSMe)^- \xrightarrow{k_{2A}} ASMe + X^-$$

$$BX + MeS^- \underset{k_{-1B}}{\overset{k_{1B}}{\rightleftharpoons}} (BXSMe)^- \xrightarrow{k_{2B}} BSMe + X^-$$

If the reverse rates k_{-1A} and k_{-1B} are very slow compared with k_{1A} and k_{1B} respectively, and the second step rates k_{2A} and k_{2B} are very fast compared with k_{1A} and k_{1B} respectively, then the rate of disappearance of AX and BX is given by

$$-d[AX]/dt = k_{1A}[AX][MeS^-]$$

$$-d[BX]/dt = k_{1B}[BX][MeS^-]$$

In these equations $[MeS^-]$ is common to both olefins. Therefore

$$k_{1B}\frac{d[AX]}{dt}\cdot\frac{1}{[AX]} = k_{1A}\frac{d[BX]}{dt}\cdot\frac{1}{[BX]}$$

Integrating from initial concentrations $[AX]_0$ and $[BX]_0$ to the final concentrations [AX] and [BX], the equation becomes:

$$k_{1B}\ln\frac{[A]_0}{[A]} = k_{1A}\ln\frac{[B]_0}{[B]}$$

and the rate ratio is given by

$$\frac{k_{1A}}{k_{1B}} = \frac{\ln [A]_0/[A]}{\ln [B]_0/[B]}$$

(b) *Determination of relative rates*. Hexachloronorbornadiene (Ia) was used as standard. In each case, approximately 0·003 mole of the standard olefin (Ia) was mixed with 0·003 mole of olefin under test, and toluene (~0·3 g.) added as an inert marker. A sample of this mixture was set aside for the accurate determination of reactant proportions. To the remainder a solution of sodium thiomethoxide (~0·002 mole) in dimethylformamide (15 ml.) was added, and the mixture stirred at 25° for 48 hr. The concentrations of vinyl halides at the beginning and end of reaction were determined, relative to the internal standard toluene, using a Griffin D6 Density Balance Chromatograph employing nitrogen as carrier gas, and fitted with a 6 ft. column of 12% Apiezon L grease on Chromsorb W (60—80 mesh) at 150—210°. [The temperature employed for analysis was dependent on the relative retention times of hexachloronorbornadiene (Ia) and the olefin under test.] Peak areas were estimated using a Fisons 1E.165A on-line integrator. Relative rates were then computed according to the final equation in (a), and the results are in Table 2.

Addition of Methanethiol to 1,4,7,7-*Tetrachloro*-2,3-*dithiomethoxynorborna*-2,5-*diene* (IIIa).—(a) *Ionic addition.* The diene (IIIa) (1 g.) and methanethiol (5 ml.) saturated with hydrogen chloride were heated in a sealed Carius tube at 80° for 48 hr. After cooling, the tube was opened and the excess of methanethiol allowed to evaporate and the residue chromatographed on alumina using light petroleum as eluant to afford 1,4,7,7-tetrachloro-2,3,5-*endo*-trithiomethoxynorborn-2-ene (VIII) (0·85 g.), m.p. 45—46°.

(b) *Free radical addition.* The above reaction was repeated using azobisisobutyronitrile (50 mg.) in place of hydrogen chloride. Separation of the products by chromatography on alumina using light petroleum as eluant gave 1,4,7,7-tetrachloro-2,3,5-*endo*-trithiomethoxynorborn-2-ene (VIII) (0·07 g.), m.p. 46—47°, followed by 1,5-endo-6,6-*tetrachloro*-2,3,7-syn-*trithiomethoxynorborn*-2-*ene* (IX) (0·8 g.), m.p. 114—115° (Found: C, 32·3; H, 3·3. $C_{10}H_{12}Cl_4S_3$ requires C, 32·4; H, 3·25%).

Reductive Desulphurisation of 1,4,7,7-*Tetrachloro*-2,3-*dithiomethoxynorborna*-2,5-*diene* (IIIa).—The diene (IIIa) (1 g.) was dissolved in ethanol (25 ml.), and freshly prepared [25] Raney nickel (2 g.), containing adsorbed hydrogen, added. The mixture was boiled at reflux for 2 hr., filtered, and the ethanol evaporated to give 1,4,7,7-tetrachloronorbornane (0·7 g.), m.p. 97—98° (lit.,[6] 96—97°).

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