Free-radical Reactions of Halogenated Bridged Polycyclic Compounds. Part XV.[1] The Reaction of Methyl-lithium with Some Chlorine-substituted Norbornenes and Norbornadienes

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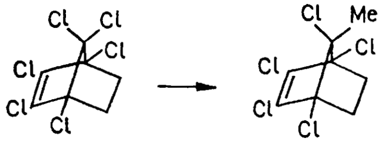
The reaction of methyl-lithium with chlorine-substituted norbornenes and norbornadienes not containing C-5 or C-6 substituents results in the replacement of a bridge chlorine atom by a methyl group. The methyl group prefers to enter a position *anti* to a double bond, and product formation can be accommodated in terms of the formation of C-7 radical pairs. If a C-5 *endo*-halogen atom is also present, reaction products are different as typified by the formation, in the proportions 20 : 1, of 3,4,5,6-tetrachloro-7-methyltricyclo[4,1,0,0^{3,7}]hept-4-ene and 1,2,3,5-tetrachloro-4,6-dimethylnorborna-2,5-diene as products from 5-*endo*-bromo-1,2,3,4,7,7-hexachloronorborn-2-ene. The formation of the tricyclic product is explicable in terms of C-5 and C-7 radical pairs, but diene formation is more complex, and is best accounted for by initial formation and combination of a C-7 radical pair, followed by the formation ands ubsequent rearrangement of a methyl-substituted C-5 radical. Tricyclic and diene products result from other compounds having halogen substituents at both C-5 and C-7. A choice between reaction paths is finely balanced, and depends on both the position and the reactivity of the various halogen substituents.

AMONG the products of the reactions of alkyl-lithium reagents with alkyl halides are those formally derived by replacement of the halogen of the alkyl halide by the alkyl group from the alkyl-lithium.[2-4] In an attempt to prepare norbornenes and norbornadienes with both chlorine and methyl substituents, the reaction of methyl-lithium with some chlorine-substituted norbornenes and norbornadienes was examined. Gassman had already shown that reaction of methyl-lithium with 2-chloronorborn-2-ene afforded 2-methylnorborn-2-ene.[5]



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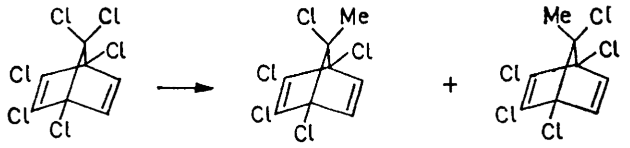
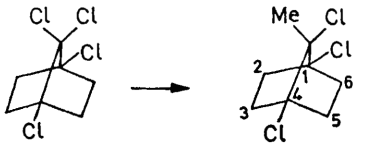
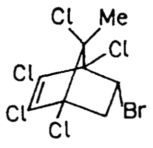


(3) (4) (5)



(6) (7)

The reaction of methyl-lithium with 1,2,3,4,7,7-hexachloronorborn-2-ene (1) was found to give 1,2,3,4,7-*syn*-pentachloro-7-*anti*-methylnorborn-2-ene (2) as sole product. Structure (2) was established by comparison with the product of reductive debromination, with zinc and acetic acid, of the 5-*endo*-bromide (8). The C-7 isomers (8) and (9) are among the products of the Diels-Alder addition of 1,2,3,4,5-pentachloro-5-methylcyclopenta-1,3-diene (10) to vinyl bromide. Reductive debromination of the isomer (9) affords 1,2,3,4,7-*anti*-pentachloro-7-*syn*-methylnorborn-2-ene (11) the C-7 isomer of (2). Compounds (11) and (2) are readily distinguishable: the former, which has a C-7 halogen atom near to the C-5 and C-6 protons, shows an n.m.r. pattern for the 5- and 6-protons very similar to that for the corresponding protons in hexachloronorborn-2-ene (1). In the spectrum of compound (2) the pattern for these protons is significantly different (see Table 1).



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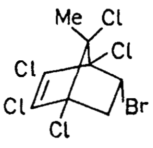

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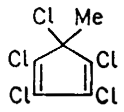

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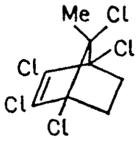

(11)

The reaction of hexachloronorbornadiene (3) with methyl-lithium similarly results in the replacement of a bridge chlorine atom by a methyl group, and the 7-*anti*-methylnorbornadiene (4) and its 7-*syn*-epimer (5) † are formed in the approximate ratio of 1 : 5. Product structures were established by comparison with products of the elimination of hydrogen bromide from the bromides (8) and (9), respectively. 1,4,7,7-Tetrachloronorbornane (6) reacted with methyl-lithium to give

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† In this paper the terms *syn* and *anti* are used with reference to the chlorine-substituted double bond.

[1] Part XIV, R. Alexander, D. I. Davies, D. H. Hey, and J. N. Done, *J. Chem. Soc.* (*C*), 1971, 2367.

[2] D. Bryce-Smith, *J. Chem. Soc.*, 1956, 1603; C. S. Marvel, F. D. Hager, and D. D. Coffman, *J. Amer. Chem. Soc.*, 1927, **49**, 2323.

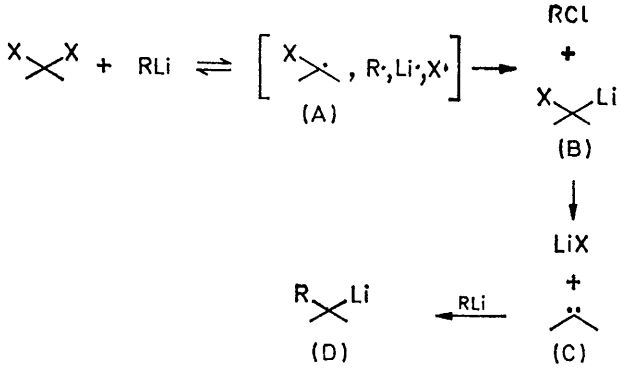
[3] H. R. Ward, R. G. Lawler, and R. A. Cooper, *J. Amer. Chem. Soc.*, 1969, **91**, 746.

[4] G. A. Russell and D. W. Lamson, *J. Amer. Chem. Soc.*, 1969, **91**, 3967.

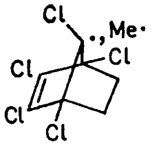
[5] P. G. Gassman, J. P. Andrews, jun., and D. S. Patton, *Chem. Comm.*, 1969, 437.

1,4,7-trichloro-7-methylnorbornane (7), identical with the product of hydrogenolysis[6] of the 5-*endo*-bromide (9). In the replacement of a chlorine atom by a methyl group in compounds (1), (3), and (6) any involvement of a methyl anion as a nucleophile seems unlikely, since in compounds related to (1) and (3) reaction with other nucleophiles results in replacement of a vinylic chlorine atom or addition across the unsubstituted double bond.[7] The reaction of 2-chloronorborn-2-ene with methyl-lithium, studied by Gassman,[5] is much slower than those of compounds (1) and (3), and results in replacement of a vinylic chlorine atom by a methyl group.

Initially the reaction of *gem*-dihalides with alkyl-lithium reagents was believed to involve a four-centred transition state resulting in nucleophilic substitution,[8] but recent evidence, based on CIDNP experiments, clearly implicates the participation of free radicals, which may be converted into carbenes[9,10] in the route to product formation. Scheme 1 summarises some of the possible intermediates. Initial reaction of methyl-lithium with the *gem*-dihalides (1), (3) and (6) should thus lead to the tight radical pairs (12), [(13) + (14)], and (15) respectively, which could combine to give products (2), (4), (5), and (7). The reactions of compounds (1), (3), and (6) with methyl-lithium require 2, 1, and 24 h, respectively, for completion, indicating that the presence of a double bond has an accelerating effect on product formation in addition to its directive effect. On the basis of suggestions made by Russell[11] a non-planar C-7 radical, produced by reaction of compound (1) with methyl-lithium, may be expected to have the C-7 chlorine atom *syn* to the double bond as in (12) rather than *anti* as in (16), owing to the reduced non-bonded interactions in (12) as compared with (16). Additionally the double bond in structure (1) appears to be strategically placed to aid loss of a C-7 *anti*-chlorine atom, leading to structure (12). In the reaction of hexachloronorbornadiene (3) with methyl-lithium there are two possible intermediate radicals, (13) and (14). Since (5) is the predominant product, intermediate (14) is favoured over (13). This may be because non-bonded interactions of a C-7 bridge chlorine atom are less with an unsubstituted than with a chlorine-substituted double bond, and also because an unsubstituted double bond is more efficient than a chlorine-substituted double bond in aiding the loss of chlorine *anti* to itself.



SCHEME 1



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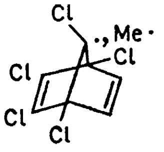

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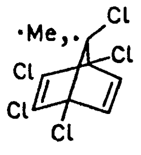

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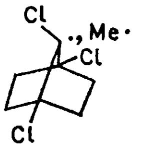

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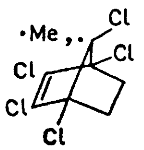

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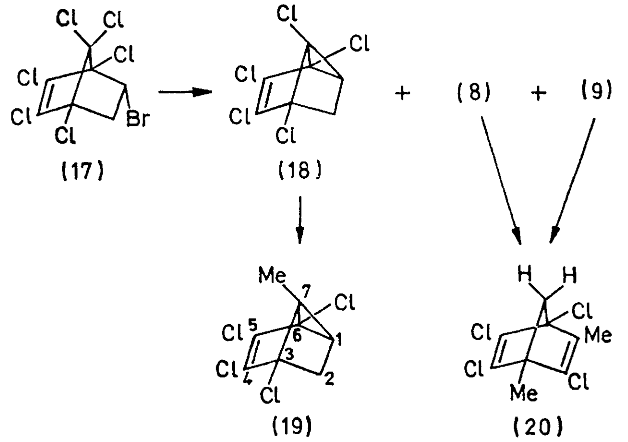

TABLE 1

Spectroscopic data for norbornene derivatives

Compd.	N.m.r. (100 MHz; τ values) 7-Me	 7-H	 5-*exo*-H 6-*exo*-H	 5-*endo*-H 6-*endo*-H	$\nu_{max.}$/cm^{-1} *cis*-ClC=CCl
(1)			7·50(m)	7·98(m)	1609
(2)	8·39(s)		7·78(m)	8·00(m)	1605
(11)	8·44(s)		7·47(m)	8·09(m)	1605
(51)		5·82(s)	7·73(m)	7·92(m)	1598
(52) †	8 90(d)		7·7—8·2(m)		1603
(54) *		6·06(t)	7·55(t)	8·06(m)	1598

* J[7-*syn*,5-*endo* (or 6-*endo*)] 1·3 Hz. † J(7-Me, 7-*anti*) 6·8 Hz. The 7-H signal is in the τ 7·7—8·2 multiplet.

The reaction of methyl-lithium with the 5-*endo*-bromide (17) did not result simply in replacement of a bridge chlorine atom by a methyl group; the more

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[6] K. L. Williamson, Y. Fang Li Hsu, and E. I. Young, *Tetrahedron*, 1968, **24**, 6007.

[7] K. Mackenzie, *J. Chem. Soc.*, 1962, 457; D. R. Adams and D. I. Davies, *J.C.S. Perkin I*, 1972, 1237; D. I. Davies and P. J. Rowley, *J. Chem. Soc.* (*C*) 1969, 288.

[8] *E.g.* E. T. Marquis and P. D. Gardner, *Tetrahedron Letters*, 1966, 2793.

[9] H. R. Ward, R. G. Lawler, and H. Y. Loken, *J. Amer. Chem. Soc.*, 1968, **90**, 7359.

[10] L. Skattebøl, *Tetrahedron*, 1967, **23**, 1107; M. S. Baird and C. B. Reese, *Chem. Comm.*, 1972, 523.

[11] G. A. Russell and G. W. Holland, *J. Amer. Chem. Soc.*, 1969, **91**, 3968.

complex tricyclo[4,1,0,0^{3,7}]hept-4-ene (19) and the diene (20) were formed in the ratio 20 : 1. The tricyclic product (19) was recognised from its n.m.r. spectral data (Table 2).[12,13] Models indicate that the bridgehead H-1 and H-2-*endo* are orthogonal, which accounts for the absence of coupling between them (*cf.* norborn-2-ene derivatives in which bridgehead H-1 and H-4 are respectively orthogonal to H-6-*endo* and H-5-*endo*, leading to zero coupling[14]). Based on comparison with related systems, the position of the methyl proton resonance is more appropriate for a methyl group on a cyclopropane ring[15,16] than on a double bond.[1,15]

TABLE 2

Spectroscopic data for tricyclo[4,1,0,0^{3,7}]hept-4-ene derivatives

	τ Values *				*J*/Hz *			
Compound	1-H	2-*exo*-H	2-*endo*-H	7-Me	1,2-*exo*	2-*exo*, 2-*endo*	2-*exo*, 2-*endo*-Me	$\nu_{max.}$/cm^{-1} *cis*-ClC=CCl
(19)	7·69(d)	7·24(q)	8·19(d)	8·55(s)	3·0	9·8		1590
(37) †	7·73(d)	7·02 (octet)		8·57(s)	3·0		7·0	1590
(39) ‡	7·50(s)		6·93(s)	8·41(s)				1590
(42) §		7·42(d)	8·04(d)	8·54(s)		10·0		1590

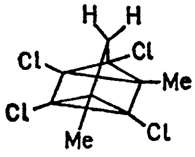
* At 100 MHz. † 2-*endo*-Me at τ 9·32(d). ‡ 2-*endo*-Ph at τ 2·65 (narrow m). § 1-Me at τ 8·66(s).

Further spectroscopic evidence in support of the tricyclic [4,1,0,0^{3,7}] ring structure (19) was obtained from near-i.r. and u.v. spectra. The former contains a maximum at 1·668 μm characteristic of a strained cyclopropane C–H stretching overtone,[17] and in the u.v. spectrum the main band due to the $n \rightarrow v$ transition (electronic ground state to the lowest excited singlet state) of the olefinic chromophore,[18] at 224 nm is red-shifted relative to chlorine-substituted norbornenes (210 nm), possibly as a result of the olefinic bond becoming slightly non-planar and/or quasi-conjugated with the cyclopropane ring.

Chemical evidence for the presence of the tricyclo[4,1,0,0^{3,7}]hept-4-ene ring system was provided by the ease of bromine addition and catalytic addition of hydrogen without the chlorine-substituted double bond being affected. This type of reactivity is identical with that recorded for known tricyclo[4,1,0,0^{3,7}]-heptanes.[12,19,20]

The structural assignment for the diene (20) is based on its n.m.r. data [τ 7·31 (s, 7-H), 8·12 (s, 6-Me), and 8·58 (s, 4-Me)]. The methyl resonance assignments are appropriate for vinylic[1,15] and bridgehead[15] substituents, respectively. The adventitious equivalence of the C-7 protons in (20) has been observed[1] in other similar norbornadiene derivatives. The i.r. spectrum contains absorptions characteristic of two olefinic bonds, one doubly substituted by chlorine (1598 cm^{-1})[21] and the other singly substituted by chlorine (1640 cm^{-1}).[7] U.v. irradiation converted the diene (20) into the quadricyclene (21).

Alkyl monohalides, like *gem*-dihalides, have been shown to react with alkyl-lithium reagents to form radical pairs[3,4] [*e.g.* (E) in Scheme 2]. The electron-withdrawing halogen atom makes the α-proton acidic, so that an alternative reaction path involving metal–hydrogen exchange to give (F) can occur. Elimination of LiX affords the carbene (G), which gives (H) on reaction with an alkyl-lithium[22] (see Scheme 2).



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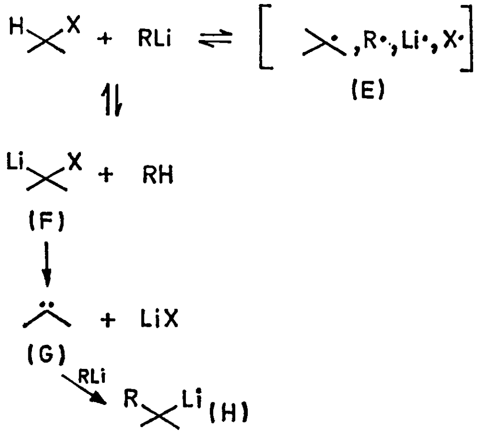

SCHEME 2

Product formation should be possible by way of any of the intermediates (E)—(H). Excess of methyl-lithium

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[12] J. J. Tufariello, T. F. Mich, and R. J. Lorence, *Chem. Comm.*, 1967, 1202; H. Tanida, T. Tsuji, and T. Irie, *J. Amer. Chem. Soc.*, 1966, **88**, 864.

[13] A. A. Bothner-By, 'Advances in Magnetic Resonance,' ed. J. S. Waugh, Academic Press, London, 1965, vol. 1, p. 195.

[14] J. C. Davis, jun., and T. V. Van Auken, *J. Amer. Chem. Soc.*, 1965, **87**, 3900.

[15] D. Seyferth and A. B. Evnin, *J. Amer. Chem. Soc.*, 1967, **89**, 1468.

[16] C. W. Jefford and W. Wojnarowski, *Helv. Chim. Acta*, 1970, **53**, 1194; S. J. Cristol, T. W. Russell, and D. I. Davies, *J. Org. Chem.*, 1965, **30**, 207.

[17] P. G. Gassman and W. M. Hooker, *J. Amer. Chem. Soc.*, 1965, **87**, 1079.

[18] A. J. Merer and R. S. Mulliken, *Chem. Rev.*, 1969, **69**, 639.

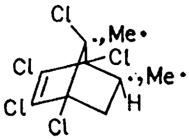
[19] W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Amer. Chem. Soc.*, 1961, **83**, 2019.

[20] P. G. Gassman and G. D. Richmond, *J. Amer. Chem. Soc.*, 1970, **92**, 2090.

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

[22] G. Köbrich, *Angew. Chem. Internat. Edn.*, 1967, **6**, 41; W. Kirmse, *ibid.*, 1965, **4**, 1.

is used in the reaction of compound (17), and the species (22), containing four radicals within the solvent cage, may well be formed. The known tetrameric nature of methyl-lithium [23] makes such a species by no means impossible. It is assumed that the radical centre at C-5 will take up the more stable [24] *exo*-position; bond formation could then take place between the radical centres at C-5 and C-7 to afford (18), which then reacts further with methyl-lithium to give the radical pair (23), which can combine to give product (19). An alternative route to (18) would involve metal–halogen exchange between methyl-lithium and the hexachloro-bromide (17), leading to the carbanion (24), which might undergo an internal nucleophilic substitution as indicated. Unfortunately such a mechanism is inconsistent with other reactions, in related systems, in which generation of a C-5 carbanion does not lead to this type of substitution,[7] although it has been suggested as a possibility in certain much less substituted norbornenes and norbornadienes.[25,26] The mechanism for the formation of (19) involving radical pairs is in contrast to that involved in the preparation of other known derivatives of tricyclo-[4,1,0,0^{3,7}]hept-4-ene, usually from norbornadien-7-yl chloride (25a) and tosylate (25b), by processes involving the non-classical carbonium ion (26).[12,27]



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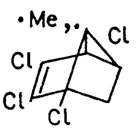

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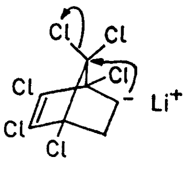

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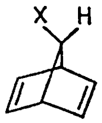
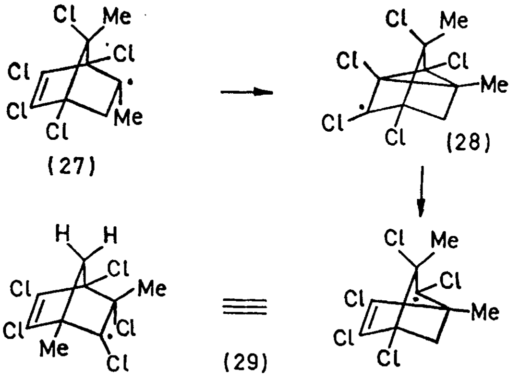


(25) a; X = Cl
b; X = OTs

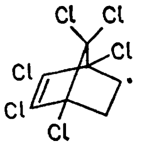
(26)

The formation of the diene (20) is best explained in terms of the intermediacy of the radical (27), which undergoes rearrangement to (29), from which diene (20) could be derived by loss of a chlorine atom. The comparable rearrangement (30) ⟶ (31) has been previously established.[1,28]

Small quantities of the 5-*endo*-bromides (8) and (9) were isolated, in addition to (19) and (20), from the reaction of the bromide (17) with a reduced amount of methyl-lithium. Since the bromides (8) and (9) give solely the diene (20) on reaction with methyl-lithium, they seem likely to be precursors of the diene (20) in the reaction of the bromide (17). Although equal quantities of (8) and (9) were isolated in the reaction of (17) with methyl-lithium, bromide (8) is likely to be the major precursor of (20), since (8) is very much more reactive than (9) (see Table 3) and therefore an artificially high proportion of (9) relative to (8) would be built up in the reaction mixture. Preferential formation of (8) is consistent with earlier ideas that a chlorine atom *anti* to the double bond is preferentially replaced by a methyl group in comparison with a chlorine atom *syn* to the double bond. The formation of compounds (8) and (9) requires a small proportion of (17) to react preferentially with methyl-lithium to form a C-7 radical pair [(32) or its C-7 epimer], which combines to form (8) and (9) before reaction occurs with the C-5 bromine atom. The inertness of a C-7 chlorine atom when a C-7 methyl group is also present in compounds (2), (4), (5), and (7) indicates that once (8) and (9) are formed, subsequent reaction will occur only at C-5. Such reaction (Scheme 2) *via* intermediates of type (F) and (G) could provide the type (H) intermediate (33), which can lead to the required radical (27) on reaction with any alkyl halide present. It would appear that unless a C-5 radical of type (E) (Scheme 2) can combine with a C-7 radical, the alternative reaction path *via* (F), (G),



(27) (28) (29)



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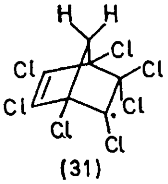

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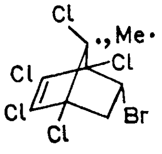

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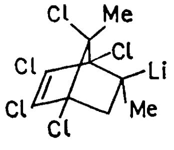

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[24] Part XI, D. I. Davies and P. Mason, *J. Chem. Soc.* (*C*), 1971, 288.

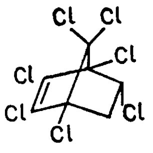
[25] H. Tanida, T. Tsuji, and T. Irie, *J. Amer. Chem. Soc.*, 1966, **88**, 864.

[26] J. T. Lumb and G. H. Whitham, *Chem. Comm.*, 1966, 400.

[27] P. R. Story, *J. Amer. Chem. Soc.*, 1961, **83**, 3347; B. Franzus, and E. I. Snyder, *ibid.*, 1963, **85**, 3902; H. C. Brown and H. M. Bell, *ibid.*, p. 2324; H. Tanida and Y. Hata, *J. Org. Chem.*, 1965, **30**, 977.

[28] Part XII, D. I. Davies and P. Mason, *J. Chem. Soc.* (*C*), 1971, 295.

and (H) (Scheme 2) is favoured at C-5 leading finally to the more stable and highly-substituted radical (27), prior to product formation.



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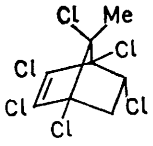
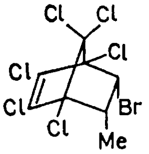


(35)

The heptachloronorbornene (34) affords the tricyclic product (19) and the diene (20) in the ratio 9 : 11 [*cf.* 20 : 1 from (17)]. The increase in yield of diene (20) from (34) may be explained (*a*) by the increased inductive effect of chlorine compared to bromine, which makes metal–hydrogen exchange at C-5 more favourable than radical pair formation as the initial reaction at C-5 (Scheme 2), and (*b*) by reduced reactivity of the C-5 chlorine atom in (34) compared with the C-5 bromine atom in (17), which results in an increased tendency for reaction at C-7 to give (35), a precursor of (20) but not (19), before any reaction has taken place at C-5.



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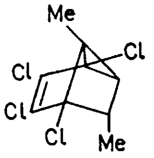

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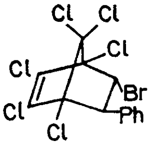

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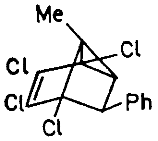

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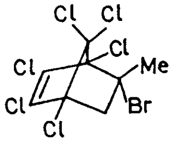

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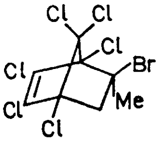

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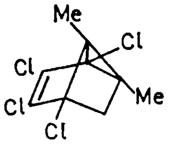


(42)

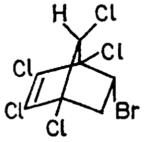
TABLE 3

Reactants and products in reactions of methyl-lithium with chlorine-substituted norbornenes and norbornadienes

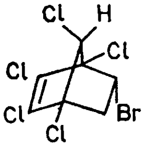
Compound No.	g	mol	Hexane (ml)	MeLi soln. (ml) †	MeLi (mol)	Time (min) for MeLi Addn.	Reaction time (h)	Product (g)	Products and % yields
(1)	0·75	0·0025	100	3·6	0·0063	10	2	0·60	(2) (86%)
(3)	2·3	0·0075	125	10·8	0·019	15	1	1·6	(4) (13%) (5) (63%)
(6)	0·30	0·0013	50	3·9	0·0069	5	24	0·22	(7) (79%)
(8)	0·09	0·00025	40	0·6	0·001	1	4	0·041	(20) (64%)
(9)	0·18	0·0005	50	2·9	0·005	5	72	0·064	(20) (50%)
(17)	1·9	0·005	100	7·2	0·013	10	2	1·0	(19) (78%) (20) (4%)
(34)	1·7	0·005	100	7·2	0·013	10	2	1·2	(19) (44%) (20) (51%)
(36)	2·0	0·005	100	7·2	0·013	10	2	0·93	(37) (72%)
(38)	0·31	0·00068	50	1·9	0·0034	3	2	0·12	(39) (55%)
(40) + (41) *	0·30	0·00075	75	1·3	0·0023	3	2	0·09	(42) (50%)
(43)	0·35	0·0010	75	2·9	0·005	3	4·5	0·13	(19) (54%)
(44)	0·086	0·00025	50	0·36	0·00063	0·5	2	0·042	(19) (9%) + unknowns
(46)	0·23	0·0005	50	0·75	0·0015	1	2	0·094	(47) (67%)
(51)	0·085	0·00032	50	0·91	0·0016	2	5	0·060	(52) (72%) + unknown
(54)	0·27	0·001	75	2·9	0·005	2	144	0·18	(52) (10%), (2) (41)%, + unknown

* A 32 : 68 mixture. † 1·75M-solution in diethyl ether (Alpha Inorganics).

The formation of tricyclic products seems to be general provided that the halogen atoms at C-7 and C-5 have comparable reactivity with methyl-lithium. Thus the bromides (36) and (38) are readily converted into the tricyclic products (37) and (39), respectively. The tertiary bromides (40) and (41) both afford the same tricyclic product (42). The intermediates derived from (40) and (41) must initially have radical centres at C-5 which are respectively *endo* and *exo*, but prior to product formation radical centres of the same stereochemistry, presumably *exo*,[24] must be produced at C-5. The pentachloro-bromides (43) and (44) both lead to the same tricyclic product (19) as is derived from the hexachloro-bromide (17). We assume that combination of radical centres in a species like (45) will be involved in the production of (19). For the formation from the pentachloro-bromides (43) and (44) of the methyl-substituted C-7 radical centre in (45), a reaction scheme (*via* intermediates of Scheme 2) must be invoked similar to that required to produce a methyl-substituted C-5 radical centre in the route to the diene (20) from (17) and (34). Clearly in compounds (43) and (44) the chlorine atom at C-7 is more reactive than the bromine atom at C-5, since the formation of (45) requires more extensive reaction (*via* Scheme 2) at C-7 than at C-5. The yield of tricyclic product from the C-7 *syn*-chloride (44) (9%) much less than that (54%) from the C-7 *anti*-chloride (43) which is consistent with the earlier observation that there is preferential reaction of a C-7 chlorine atom when *anti* to a double bond. The C-5 *gem*-dibromide (46)



(43)



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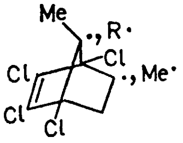
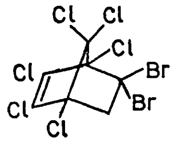


(45)

reacts with methyl-lithium to afford the diene (47). It appears that the two bromo-substituents at C-5 are much more reactive than the C-7 chlorine atoms, and reaction occurs at C-5 [*via* Scheme 1 intermediates (A)—(D)] to give compound (48), which then reacts with any alkyl halide to give the radical (49) without any reaction taking place at C-7. Radical (49) then rearranges in the conventional way [1,28] to give the radical (50), from which the diene (47) is derived by loss of a chlorine atom.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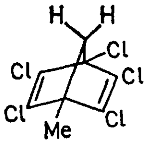
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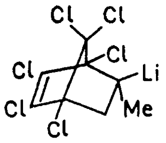
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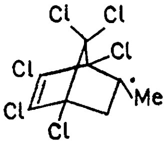
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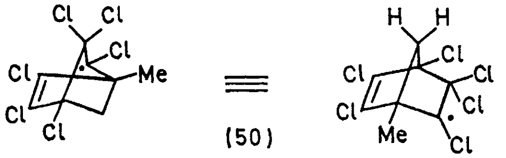
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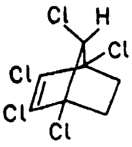
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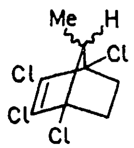
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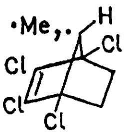
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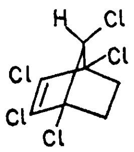
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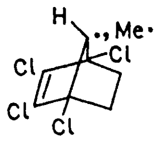
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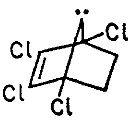
(56)

The reaction of 1,2,3,4,7-*syn*-pentachloronorborn-2-ene (51) with methyl-lithium affords as sole identified product 1,2,3,4-tetrachloro-7-methylnorborn-2-ene (52) (72%). The stereochemistry at C-7 cannot be determined, as the C-7 proton multiplet overlaps that of the C-5 and C-6 protons, so that the presence or absence of coupling between a C-7 *syn*-proton and 5-*endo*- and 6-*endo*-protons cannot be ascertained. The formation of compound (52) is readily explicable in terms of combination of the radical pair (53).

1,2,3,4,7-*anti*-Pentachloronorborn-2-ene (54) afforded as identifiable products the same 1,2,3,4-tetrachloro-7-methylnorborn-2-ene (52) (10%) and 1,2,3,4,7-*syn*-pentachloro-7-*anti*-methylnorborn-2-ene (2) (41%), identical with the product of the reaction of hexachloronorborn-2-ene (1) with methyl-lithium. Since both compounds (51) and (54) give the same tetrachloromethylnorborn-2-ene (52), one of the radical pairs (53) and (55) must invert stereochemistry at C-7 prior to product formation. The formation of compound (2) may be rationalised in terms of the intermediate carbene (56) [Scheme 2 (G)], which reacts with methyl chloride present in the reaction mixture.

It is clear that a number of intermediates are possible (Schemes 1 and 2) for reactions of methyl-lithium with alkyl halides and *gem*-dihalides. The choice of reaction path is finely balanced, and varies with the type and location of halogen in the molecule.

EXPERIMENTAL

N.m.r. measurements (100 MHz) were carried out by the PCMU service at Harwell for 20% solutions in deuteriochloroform (tetramethylsilane as internal standard); 60 MHz n.m.r. spectra were obtained with a Perkin-Elmer R12 instrument; for i.r. spectra (Nujol mulls) a Perkin-Elmer 257 grating spectrometer was used; u.v. spectra (solutions in iso-octane) and near-i.r. spectra (in carbon tetrachloride) of the tricyclic product (19) were measured with a Cary model 17 spectrometer. Analytical g.l.c. was carried out with a Perkin-Elmer F11 gas chromatograph (nitrogen as carrier gas) fitted with a 4 m × $\frac{1}{8}$ in column packed with a mixture of 15% SE 30, 15% PPE, and 5% potassium hydroxide on Chromosorb W (80—100 mesh), at 180°. Column chromatography was carried out on Woelm acid alumina (activity I) with light petroleum (b.p. 40—60°) as eluant.

The following compounds were obtained by literature methods: 1,2,3,4,7,7-hexachloronorborn-2-ene (1),[29] purified hexachloronorbornadiene (3),[30] 5-*endo*-bromo-1,2,3,4,7,7-hexachloronorborn-2-ene (17),[31,32] 1,2,3,4,5-*endo*-7,7-heptachloronorborn-2-ene (34),[31] 5-*endo*-bromo-1,2,3,4,7,7-hexachloro-6-*exo*-phenylnorborn-2-ene (38),* a 68 : 32 mixture of 5-*exo*-bromo-1,2,3,4,7,7-hexachloro-5-*endo*-methylnorborn-2-ene (41) and its 5-*endo*-bromo-5-*exo*-methyl epimer (40),[33] 5-*endo*-bromo-1,2,3,4,7-*anti*-pentachloronorborn-2-ene (43),[1,34] 5-*endo*-bromo-1,2,3,4,7-*syn*-pentachloronorborn-2-ene (44),[1,34] and 5,5-dibromo-1,2,3,4,7,7-hexachloronorborn-2-ene (46).[24]

1,2,3,4,7-*Pentachloro*-7-*methylnorborna*-2,5-*dienes* (4) *and* (5).—The 5-*endo*-bromide (9) (0·5 g, 0·0014 mol) was dissolved in t-butyl alcohol (20 ml) and sodium t-butoxide

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* Specimen provided by Dr. M. J. Parrott, King's College; prepared by the addition (free radical) of hydrogen bromide to 1,2,3,4,7,7-hexachloro-5-phenylnorborna-2,5-diene.

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

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

[31] B. A. Arbuzov and A. N. Vereshchagin, *Bull. Acad. Sci., U.S.S.R.*, 1965, 586.

[32] L. Schmerling, U.S.P. 2,912,356/1960 (*Chem. Abs.*, 1960, **54**, 3271).

[33] Part XIII, R. Alexander and D. I. Davies, *J. Chem. Soc.* (*C*), 1971, 896.

[34] K. L. Williamson, Yuan-Fang Li Hsu, R. Lacko, and Chung He Youn, *J. Amer. Chem. Soc.*, 1969, **91**, 6129.

(0·4 g, 0·0042 mol) was added. The mixture was stirred under reflux for 4 days, cooled, and evaporated. Water (60 ml) was added to the residue, and the mixture was extracted with methylene chloride (4 × 25 ml). The combined extracts were dried ($MgSO_4$), filtered, and evaporated. Distillation of the residue afforded the 7-syn-*methyl-diene* (5) (0·11 g), b.p. 76° at 0·4 mmHg, n_D^{23} 1·5330 (Found: C, 34·3; H, 1·8. $C_8H_5Cl_5$ requires C, 34·5; H, 1·8%), τ (60 MHz) 3·43 (s, olefinic H) and 8·33 (s, 7-*syn*-Me). A similar reaction with the bromide (8) gave the 7-anti-*methyl-diene* (4), b.p. 73° at 0·3 mmHg, n_D^{23} 1·5307 (Found: C, 34·3; H, 1·6%), τ (60 MHz) 3·45 (s, olefinic H) and 8·22 (s, 7-*anti*-Me).

1,4,7,7-*Tetrachloronorbornane* (6).—Hexachloronorbornadiene (3) (15 g) in 95% ethanol (125 ml) was hydrogenated over 10% palladium–charcoal (3·0 g) at atmospheric pressure (uptake 4 mol. equiv. in 3 days). Filtration, evaporation, and recrystallisation of the residue from ethanol afforded 1,4,7,7-tetrachloronorbornane (6) (9·8 g), sublimes 160—165°, m.p. 216° (lit.,[35] 216—216·5°) (Found: C, 36·05; H, 3·4. Calc. for $C_7H_8Cl_4$: C, 35·9; H, 3·45%). The m.p. (96—97°) previously reported [29] is in error; the compound merely softens at this temperature.

1,4,7-*Trichloro-7-methylnorbornane* (7).—The 5-*endo*-bromide (9) (0·36 g, 0·001 mol) and triethylamine (0·20 g, 0·002 mol) were dissolved in 95% ethanol (10 ml) and the mixture was hydrogenated over palladium–charcoal (10%; 0·036 g) at atmospheric pressure. The reaction was stopped after uptake of 90 ml of hydrogen (0·004 mol). Filtration, evaporation, and recrystallisation of the residue from ethanol afforded 1,4,7-*trichloro-7-methylnorbornane* (7) (0·87 mg), sublimes 145—147° (Found: C, 45·3; H, 5·1. $C_8H_{11}Cl_3$ requires C, 45·0; H, 5·2%), τ (100 MHz) 7·58 (m, 5-*exo*-H and 6-*exo*-H), 8·00 (m, 2-*exo*-H, 2-*endo*-H, 3-*exo*-H, 3-*endo*-H, 5-*endo*-H, and 6-*endo*-H), and 8·39 (s, 7-Me).

5-endo-*Bromo*-1,2,3,4,7-syn-*pentachloro*-7-anti-*methylnorborn*-2-*ene* (8) *and* 5-endo-*Bromo*-1,2,3,4,7-anti-*pentachloro*-7-syn-*methylnorborn*-2-*ene* (9).—Vinyl bromide (5·6 g, 0·052 mol) and pentachloromethylcyclopentadiene (10) [36,37] (6·5 g, 0·026 mol) were heated in a sealed tube at 220° for 2·5 h. The crude product was distilled (b.p. 120° at 0·3 mmHg) and analysed (Found: C, 26·8; H, 1·5. $C_8H_6BrCl_5$ requires C, 26·7; H, 1·7%). G.l.c. indicated four products, of which the following were isolated by column chromatography: the 7-syn-*methylnorbornene* (9) (0·97 g), m.p. 119—120° (from methanol) (Found: C, 26·5; H, 2·0. $C_8H_6BrCl_5$ requires C, 26·7; H, 1·7%), τ 5·22 (q, 5-*exo*-H), 6·84 (q, 6-*exo*-H), 7·71 (q, 6-*endo*-H), and 8·34 (s, 7-*syn*-Me), *J*(5-*exo*,6-*exo*) 8·3, *J*(5-*exo*,6-*endo*) 3·3, *J*(6-*exo*,6-*endo*) 13·0 Hz, $\nu_{max.}$ (*cis*-ClC=CCl) 1604 cm^{-1}; 5-endo-*bromo*-2,3,4,7,7-*pentachloro*-1-*methylnorborn*-2 *ene* (0·05 g), m.p. 120—122° (from methanol) (Found: C, 27·0; H, 2·0%), τ 5·38 (q, 5-*exo*-H), 7·29 (q, 6-*exo*-H), 8·05 (q, 6-*endo*-H), and 8·59 (s, 1-Me), *J*(5-*exo*,6-*exo*) 8·0, *J*(5-*exo*,6-*endo*) 3·5, *J*(6-*exo*,6-*endo*) 13·5 Hz, $\nu_{max.}$ (cis-ClC=CCl) 1609 cm^{-1}; the 7-anti-*methylnorbornene* (8) (0·12 g), m.p. 110—114° (from methanol) (Found: C, 26·9; H, 1·8%), τ 5·57 (q, 5-*exo*-H), 7·17 (q, 6-*exo*-H), 7·62 (q, 6-*endo*-H), and 8·37 (s, 7-*anti*-Me), *J*(5-*exo*,6-*exo*) 8·3, *J*(5-*exo*,6-*endo*) 3·8, *J*(6-*exo*,6-*endo*) 13·5 Hz, $\nu_{max.}$ (*cis*-ClC=CCl) 1609 cm^{-1}.

5-*endo*-Bromo-2,3,4,7,7-pentachloro-1-methylnorborn-2-ene originates *via* Diels–Alder addition of vinyl bromide to 1,2,3,5,5-pentachloro-4-methylcyclopenta-2,5-diene, which is produced [36] from 1,2,3,4,5-pentachloro-5-methylcyclopenta-2,5-diene *via* a unique 1,5-sigmatropic shift of chlorine under the reaction conditions.

1,2,3,4,7-anti-*Pentachloro*-7-syn-*methylnorborn*-2-*ene* (11) *and* 1,2,3,4,7-syn-*Pentachloro*-7-anti-*methylnorborn*-2-*ene* (2).—*Method A*. The *endo*-bromide (9) (0·5 g, 0·0014 mol) dissolved in glacial acetic acid (35 ml) was brought to reflux and zinc powder (0·29 g, 0·0042 mol) was added with vigorous stirring. The mixture was then heated under reflux for 15 min, cooled, and filtered. Water (100 ml) was added to the filtrate and the mixture was extracted with carbon tetrachloride (4 × 30 ml). The combined extracts were washed with a saturated aqueous sodium hydrogen carbonate solution (2 × 50 ml), dried ($MgSO_4$), filtered, and evaporated. G.l.c. of the residue showed it to consist of a single compound. Recrystallisation from methanol afforded the 7-syn-*methylnorbornene* (11) (0·30 g), m.p. 43—43·5° (Found: C, 34·4; H, 2·6. $C_8H_7Cl_5$ requires C, 34·3; H, 2·5%); for n.m.r. and i.r. data see Table 1.

A similar reduction with zinc and acetic acid of the bromide (8) (0·075 g) afforded the 7-anti-*methylnorbornene* (2) (0·047 g), m.p. 44—45° (from methanol) (Found: C, 34·6; H, 2·7%); for n.m.r. and i.r. data see Table 1.

Method B. 1,2,3,4,7-*anti*-Pentachloro-7-*syn*-methylnorborna-2,5-diene (5) (0·10 g, 0·00036 mol) in 95% ethanol (25 ml) was hydrogenated over 10% palladium–charcoal (0·010 g) at atmospheric pressure. After uptake of 1 mol. equiv. (8 ml), filtration, evaporation, and recrystallisation of the residue from methanol afforded the 7-*syn*-methylnorbornene (11) (0·87 g), m.p. 43—43·5° (Found: C, 34·3; H, 2·2%).

In a similar procedure 1,2,3,4,7-*syn*-pentachloro-7-*anti*-methylnorborna-2,5-diene (4) (0·070 g, 0·00025 mol) was hydrogenated to afford 1,2,3,4,7-*syn*-pentachloro-7-*anti*-methylnorborn-2-ene (2) (0·053 g), m.p. 44—44·5° (Found: C, 34·8; H, 2·7%).

5-endo-*Bromo*-1,2,3,4,7,7-*hexachloro*-6-endo-*methylnorborn*-2-*ene* (36).—Hexachlorocyclopentadiene (11·0 g, 0·04 mol) and 1-bromopropene (6·1 g, 0·05 mol) were heated in a sealed tube at 170° for 19 h. The crude product was decolourised with activated charcoal in methanol, and recrystallised from methanol to afford the *bromonorbornene* (36) (14·2 g), m.p. 193—195° (Found: C, 24·7; H, 1·4; Br, 20·5. $C_8H_5BrCl_6$ requires C, 24·4; H, 1·3; Br, 20·5%), τ (60 MHz) 5·11 (d, 5-*exo*-H), 6·92 (m, 6-*exo*-H), and 8·78 (d, 6-*endo*-Me), *J*(5-*exo*,6-*exo*) 8·0, *J*(6-*exo*,6-*endo*-Me) 7·0 Hz.

1,2,3,4,7-*Pentachloronorborn*-2-*enes* (51) *and* (54).—A 28 : 14 : 54 mixture [1] (6·9 g, 0·02 mol) of 5-*endo*-bromo-1,2,3,4,7-*syn*-pentachloronorborn-2-ene (44), 5-*exo*-bromo-1,2,3,4,7-*syn*-pentachloronorborn-2-ene, and 5-*endo*-bromo-1,2,3,4,7-*anti*-pentachloronorborn-2-ene (43) dissolved in glacial acetic acid (12 g) was brought to reflux, and zinc powder (7·9 g, 0·12 mol) was added with vigorous stirring. The mixture was then heated under reflux for 5 min, cooled, and filtered. Water was added to the filtrate and the mixture was extracted with carbon tetrachloride (4 × 30 ml). The combined extracts were washed with a saturated aqueous sodium hydrogen carbonate solution (2 × 50 ml), dried ($MgSO_4$), filtered, and evaporated. Column chromatography of the residue afforded successively 1,2,3,4,7-*syn*-pentachloronorborn-2-ene (51) (1·8 g), m.p. 58—58·5°

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(from ethanol) (lit.,[38] 59·2—59·8°) (Found: C, 31·5; H, 2·0. Calc. for $C_7H_5Cl_5$: C, 31·6; H, 1·9%), and 1,2,3,4,7-anti-*pentachloronorborn-2-ene* (54) (1·6 g), b.p. 64° at 0·05 mmHg, n_D^{25} 1·5470 (Found: C, 31·9; H, 2·0. $C_7H_5Cl_5$ requires C, 31·6; H, 1·9%). N.m.r. and i.r. data for (51) and (54) are recorded in Table 1.

Reaction of Chlorine-substituted Norbornenes and Norbornadienes with Methyl-lithium.—Full details of a typical experimental procedure are given for the reaction of methyl-lithium with hexachloronorborn-2-ene (1). For other compounds details of isolated products are recorded. Quantities of reactants and product yields are summarised in Table 3. The n.m.r. data for norbornene products are given in Table 1 and for the tricyclic products in Table 2. The crude product was always examined by g.l.c., and unless otherwise stated was always a single compound (>98%).

Hexachloronorborn-2-ene (1). The olefin (1) (0·75 g, 0·0025 mol) was dissolved in hexane (100 ml) under nitrogen, and a 1·75M-solution of methyl-lithium in diethyl ether (3·6 ml, 0·0063 mol) was added dropwise during 10 min. After 2 h stirring, water (50 ml) was added, and the hexane layer was separated. The aqueous layer was extracted with hexane (2 × 25 ml) and the combined extracts were dried ($MgSO_4$) and evaporated. The residue, shown by g.l.c. to be a single product, crystallised from methanol to afford 1,2,3,4,7-*syn*-pentachloro-7-*anti*-methylnorborn-2-ene (2) (0·60 g), m.p. 44—44·5° (Found: C, 34·4; H, 2·6. Calc. for $C_8H_7Cl_5$: C, 34·3; H, 2·5%). Decomposition of the reaction mixture with solid carbon dioxide (5 g) instead of water did not give any acidic material; compound (2) was again the only product isolated.

Hexachloronorbornadiene (3). The crude product was shown by g.l.c. to consist of two compounds in the approximate ratio of 5 : 1, which were separated by column chromatography into 1,2,3,4,7-*anti*-pentachloro-7-*syn*-methylnorborna-2,5-diene (5), n_D^{23} 1·5330, b.p. 73° at 0·3 mmHg (Found: C, 34·5; H, 2·0. Calc. for $C_8H_5Cl_5$: C, 34·5; H, 1·8%), and 1,2,3,4,7-*syn*-pentachloro-7-*anti*-methylnorborna-2,5-diene (4), n_D^{23} 1·5307, b.p. 73° at 0·3 mmHg (Found: C, 34·3; H, 1·6%).

1,4,7,7-*Tetrachloronorbornane* (6). The crude product crystallised from methanol to afford 1,4,7-trichloro-7-methylnorbornane (7), sublimes 145—147° (Found: C, 45·0; H, 5·1. Calc. for $C_8H_{11}Cl_3$: C, 45·0; H, 5·2%).

5-endo-*Bromo*-1,2,3,4,7-syn-*pentachloro*-7-anti-*methylnorborn-2-ene* (8). The crude product crystallised from methanol to give 1,2,3,5-*tetrachloro*-4,6-*dimethylnorborna-2,5-diene* (20), m.p. 93—94° (Found: C, 42·3; H, 3·5. $C_9H_8Cl_4$ requires C, 41·9; H, 3·1%); n.m.r. details in text.

5-endo-*Bromo*-1,2,3,4,7-anti-*pentachloro*-7-syn-*methylnorborn-2-ene* (9). The crude product crystallised from methanol to give 1,2,3,5-tetrachloro-4,6-dimethylnorborna-2,5-diene (20), m.p. 93—94° (Found: C, 41·9; H, 3·0. Calc. for $C_9H_8Cl_4$: C, 41·9; H, 3·1%); n.m.r. details in text.

5-endo-*Bromo*-1,2,3,4,7,7-*hexachloronorborn-2-ene* (17). The crude product was shown by g.l.c. to consist of two compounds, in the ratio *ca.* 20 : 1, which were separated by column chromatography into 3,4,5,6-*tetrachloro*-7-*methyltricyclo*[4,1,0,$0^{3,7}$]*hept-4-ene* (19), n_D^{21} 1·5308, b.p. 52° at 0·03 mmHg (Found: C, 39·0; H, 2·6. $C_8H_6Cl_4$ requires C, 39·4; H, 2·5%), *m/e* 242, 244, and 246 (M^+); and 1,2,3,5-tetrachloro-4,6-dimethylnorborna-2,5-diene (20), m.p. 93—94° (from methanol) (Found: C, 41·9; H, 3·2. Calc. for $C_9H_8Cl_4$: C, 41·9; H, 3·1%). When the reaction was repeated with a 1 : 1·75 molar ratio of halide (17) to methyl-lithium instead of 1 : 2·5, it was possible to isolate by column chromatography a 1 : 1 mixture (0·025 g) of 5-*endo*-bromo-1,2,3,4,7-*syn*-pentachloro-7-*anti*-methylnorborn-2-ene (8) and its 7-*syn*-methyl epimer (9), identical with an authentic 1 : 1 mixture separated from the products of Diels–Alder addition of vinyl bromide to pentachloromethylcyclopentadiene.

1,2,3,4,5-endo,7,7-*Heptachloronorborn-2-ene* (34). The crude product was shown by g.l.c. to contain 3,4,5,6-tetrachloro-7-methyltricyclo[4,1,0,$0^{3,7}$]hept-4-ene (19) and 1,2,3,5-tetrachloro-4,6-dimethylnorborna-2,5-diene (20). The diene (20), m.p. 93—94°, was obtained by crystallisation of the mixture from methanol (Found: C, 42·1; H, 3·1. Calc. for $C_9H_8Cl_4$: C, 41·9; H, 3·1%). The tricyclic compound (19), n_D^{22} 1·5301, was isolated as a liquid by column chromatography (Found: C, 39·7; H, 2·7. Calc. for $C_8H_6Cl_4$: C, 39·4; H, 2·5%).

5-endo-*Bromo*-1,2,3,4,7,7-*hexachloro*-6-endo-*methylnorborn-2-ene* (36). Distillation of the crude product afforded 3,4,5,6-*tetrachloro*-2-endo-7-*dimethyltricyclo*[4,1,0,$0^{3,7}$]*hept-4-ene* (37), n_D^{25} 1·5264, b.p. 62° at 0·3 mmHg (Found: C, 42·2; H, 3·3. $C_9H_8Cl_4$ requires C, 41·9; H, 3·1%).

5-endo-*Bromo*-1,2,3,4,7,7-*hexachloro*-6-exo-*phenylnorborn-2-ene* (38). Distillation of the crude product gave 3,4,5,6-*tetrachloro-7-methyl*-2-exo-*phenyltricyclo*[4,1,0,$0^{3,7}$]*hept-4-ene* (39), n_D^{26} 1·5402, b.p. 97—98° at 0·4 mmHg (Found: C, 52·3; H, 3·2. $C_{14}H_{10}Cl_4$ requires C, 52·5; H, 3·15%).

A 68 : 32 *mixture*[35] *of* 5-exo-*bromo*-1,2,3,4,7,7-*hexachloro*-5-endo-*methylnorborn-2-ene* (41) *and its* 5-endo-*bromo*-5-exo-*methyl epimer* (40). Distillation of the crude product gave 3,4,5,6-*tetrachloro*-1,7-*dimethyltricyclo*[4,1,0,$0^{3,7}$]*hept-4-ene* (42), n_D^{25} 1·5209, b.p. 59° at 0·3 mmHg (Found: C, 42·2; H, 3·5. $C_9H_8Cl_4$ requires C, 41·9; H, 3·1%)..

5-endo-*Bromo*-1,2,3,4,7-anti-*pentachloronorborn-2-ene* (43). Distillation of the crude product gave 3,4,5,6-tetrachloro-7-methyltricyclo[4,1,0,$0^{3,7}$]hept-4-ene (19), n_D^{22} 1·5304, b.p. 52° at 0·3 mmHg (Found: C, 39·7; H, 2·8. Calc. for $C_8H_6Cl_4$: C, 39·4; H, 2·5%).

5-endo-*Bromo*-1,2,3,4,7-syn-*pentachloronorborn-2-ene* (44). G.l.c. showed the product mixture to contain 3,4,5,6-tetrachloro-7-methyltricyclo[4,1,0,$0^{3,7}$]hept-4-ene (19) and other compounds. The mixture could not be separated but the n.m.r. spectrum contained the appropriate proton resonances for compound (19).

5,5-*Dibromo*-1,2,3,4,7,7-*hexachloronorborn-2-ene* (46). Recrystallisation of the crude product from methanol gave 1,2,3,5,6-*pentachloro*-4-*methylnorborna-2,5-diene* (47), m.p. 120—121° (Found: C, 34·6; H, 1·95. $C_8H_5Cl_5$ requires C, 34·5; H, 1·8%), τ (60 MHz) 7·17 (s, 7-H_2) and 8·54 (s, 4-Me).

1,2,3,4,7-syn-*Pentachloronorborn-2-ene* (51). The crude product was shown by g.l.c. to consist of two components in the ratio *ca.* 1 : 20. Column chromatography afforded the major component, 1,2,3,4-*tetrachloro*-7-*methylnorborn-2-ene* (52) as a liquid (Found: C, 39·3; H, 3·4. $C_8H_8Cl_4$ requires C, 39·1; H, 3·3%). The minor component could not be separated or identified.

1,2,3,4,7-anti-*Pentachloronorborn-2-ene* (54). The crude product was shown by g.l.c. to consist of three components in the ratio of 3 : 2 : 9. Column chromatography gave the major product, 1,2,3,4,7-syn-*pentachloro*-7-anti-*methylnorborn-2-ene* (2), m.p. 44—45° (from methanol) (Found: C,

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[38] C. F. Wilcox, jun., and J. G. Zajacek, *J. Org. Chem.*, 1964, **29**, 2209.

34·6; H, 2·5. Calc. for $C_8H_7Cl_5$: C, 34·3; H, 2·5%). The minor product was identified by g.l.c. retention time, and by appropriate proton resonances in the n.m.r. spectrum of the crude product mixture, as 1,2,3,4-tetrachloro-7-methylnorborn-2-ene (52). The other component was not identified, but had the same g.l.c. retention time as the unidentified product from the reaction of compound (51) with methyl-lithium.

1,2,3,4,5-*Tetrachloro*-4,6-*dimethylquadricyclene* (21).—A solution of 1,2,3,5-tetrachloro-4,6-dimethylnorborna-2,5-diene (20) (0·4 g) in diethyl ether (10 ml), in a quartz tube fitted with a reflux condenser, was irradiated for 20 h at a distance of 7 in from a 450 W medium-pressure mercury arc. Evaporation, and recrystallisation of the residue from ethanol, afforded the *quadricyclene* (21) (0·26 g), m.p. 93—94° (Found: C, 42·1; H, 3·2. $C_9H_8Cl_4$ requires C, 41·9; H, 3·1%), τ (60 MHz) 7·51 (s, 7-H_2) and 8·64 (s) and 8·73(s) (4- and 6-Me). The g.l.c. retention time and m.p. are identical with those of the starting diene, suggesting that the quadricyclene is not thermally stable.

Addition of Bromine to 3,4,5,6-*Tetrachloro*-7-*methyltricyclo*[4,1,0,$0^{3,7}$]*hept*-4-*ene* (19).—Compound (19) (0·55 g, 0·0023 mol) was dissolved in carbon tetrachloride (10 ml) and bromine (0·38 g, 0·0024 mol) was added dropwise. The bromine was instantly decolourised and the mixture was then diluted with carbon tetrachloride (30 ml), washed with saturated aqueous sodium hydrogen carbonate solution (2 × 15 ml) and with water, dried ($MgSO_4$), and evaporated. The residue, n_D^{24} 1·5950, slowly solidified (Found: C, 24·2; H, 1·8; Cl, 34·4. $C_8H_6Br_2Cl_4$ requires C, 23·8; H, 1·5; Cl, 35·1%). The product is a mixture of compounds, which tends to lose bromine and/or hydrogen bromide when purification is attempted.

Hydrogenation of 3,4,5,6-*Tetrachloro*-7-*methyltricyclo*-[4,1,0,$0^{3,7}$]*hept*-4-*ene* (19).—Compound (19) (0·17 g, 0·0007 mol) in 95% ethanol (25 ml) was hydrogenated over palladium–charcoal (10% : 0·012 g) at atmospheric pressure (uptake 1 mol. equiv. during 10 min followed by a steady uptake of a further 3·5 mol. equiv. over the next 4 h). A mixture of products was formed, which were not separated or identified. Under the same hydrogenation conditions 1,2,3,4,7,7-hexachloronorborn-2-ene (1) took up only a trace of hydrogen.

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