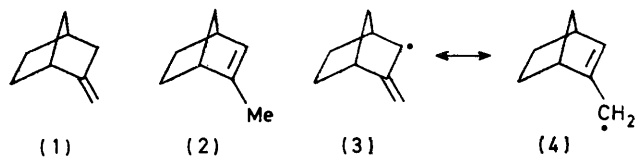


Free-radical Reactions of Halogenated Bridged Polycyclic Compounds. Part XVII.¹ Reaction of 5-Alkyl-1,2,3,4,7,7-hexachloronorborna-2,5-dienes and 5-Alkenyl-1,2,3,4,7,7-hexachloronorborn-2-enes with *N*-Bromosuccinimide

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5-Alkyl-1,2,3,4,7,7-hexachloronorborna-2,5-dienes react with *N*-bromosuccinimide in refluxing carbon tetrachloride to form allylic bromides in a process in which the 5,6-double bond migrates to become exocyclic to the ring system. Products from the corresponding 5-alk-1-enylhexachloronorbornenes are identical. 5-(1-Methylalk-1-enyl)hexachloronorbornenes react to form allylic bromides in which the position of the double bond is unchanged, but in which C-3 of the side chain prefers to be *trans* rather than *cis* to the norbornene ring system.

THE reaction of 2-methylenenorbornane (1) or 2-methylnorborn-2-ene (2) with *N*-bromosuccinimide in refluxing carbon tetrachloride solution has been reported as involving the allylic radical system (3) \longleftrightarrow (4),²

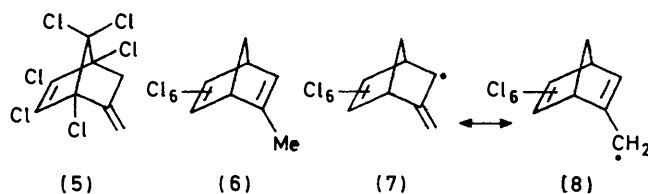


although product formation by way of ionic intermediates is also very important.³ In comparison

¹ Part XVI, D. R. Adams and D. I. Davies, *J.C.S. Perkin I*, 1974, 246.

² C. K. Alden and D. I. Davies, *J. Chem. Soc. (C)*, 1968, 709.

with (1) and (2), hexachloromethylenenorbornene (5) is relatively unreactive, and the bromide (9) is produced in about 5% yield after several weeks.⁴ [The properties

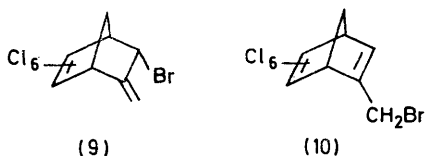


The symbol Cl₆ indicates a 1,2,3,4,7,7-hexachloro-derivative.

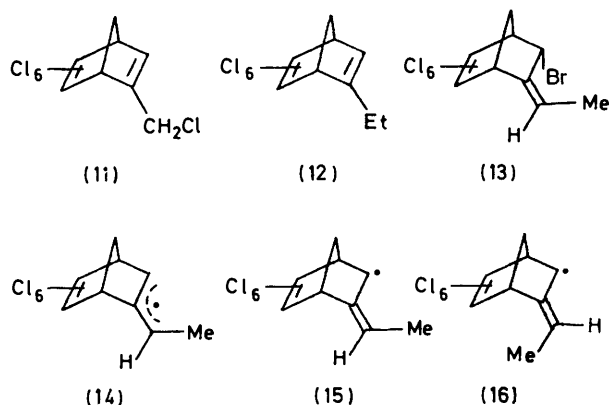
³ C. W. Jefford and W. Wojnarowski, *Helv. Chim. Acta*, 1972, 55, 2244.

⁴ Part III, C. K. Alden and D. I. Davies, *J. Chem. Soc. (C)*, 1967, 1017.

of (9) were consistent with those subsequently reported⁵ for material prepared by unambiguous routes.] The ability¹ to prepare the methyl-diene (6) in satisfactory



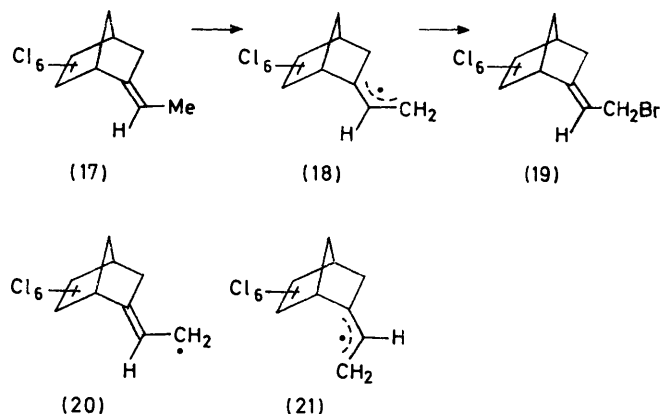
quantities has permitted a study of its reaction with *N*-bromosuccinimide to afford the bromide (9) as sole product (50% yield after 21 h). The reactions of the dienes (5) and (6) with *N*-bromosuccinimide can best be interpreted as involving the allylic radical system (7) \longleftrightarrow (8), from which (9) is derived on chain transfer with a bromine atom donor. This allylic radical system must tend towards the canonical species (7) since it has a less strained ring system than that in (8) owing to the presence of three as opposed to four sp^2 -hybridised carbon atoms. Additional stability is conferred on (7) relative to (8) since it is a secondary rather than a primary radical. No trace of the allylic bromide (10) was detected in the reaction product, and clearly the bromide (9) cannot have its origin in the allylic rearrangement of (10), since the reaction conditions are appreciably less vigorous than those needed⁵ to bring about this rearrangement. Since (10) is not formed, the canonical species (8) must be of little importance in the allylic radical system; otherwise its steric accessibility in a chain-transfer step would have favoured formation of (10). Further confirmation of the importance of (7) was provided by the observation that reduction of the allylic chloride (11), with triphenyltin hydride, gave a 14:1 mixture of hydrocarbons (5) and (6).



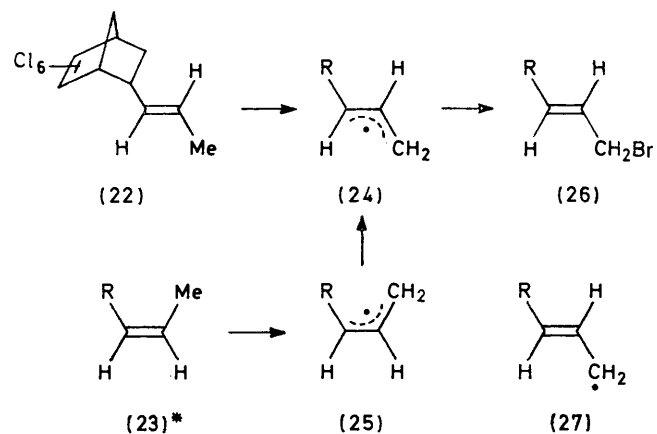
The reaction of *N*-bromosuccinimide with 5-ethylhexachloronorbornadiene (12) is comparable to that with (6) and the allylic bromide (13) is obtained as the sole product. This reaction is readily explained by the intermediacy of the allylic radical system (14), in which (15), having only three sp^2 -hybridised carbons in the ring system, is the major canonical species. Once again it is the relative stability of the ring system,

rather than steric factors affecting the approach of the bromine atom donor, that results in the formation of product (13). The canonical species (16) does not appear to be involved in spite of having a ring system of comparable stability to (15) and exhibiting less steric hindrance than does (15) to the approach of a bromine atom donor. This may possibly be due to some instability of (16) occasioned by the proximity of the vinyl methyl to the bridgehead chlorine.

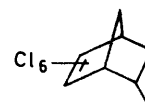
5-Ethylidenehexachloronorborene (17) reacts with *N*-bromosuccinimide to afford, as the sole identified product, the allylic bromide (19) *via* chain transfer with



the allylic radical system (18), in which the canonical species (20) must predominate. Isomerisation about the double bond system to afford the alternative allylic radical system (21) apparently does not occur, analogously to the non-participation of (16) in reactions of (12).



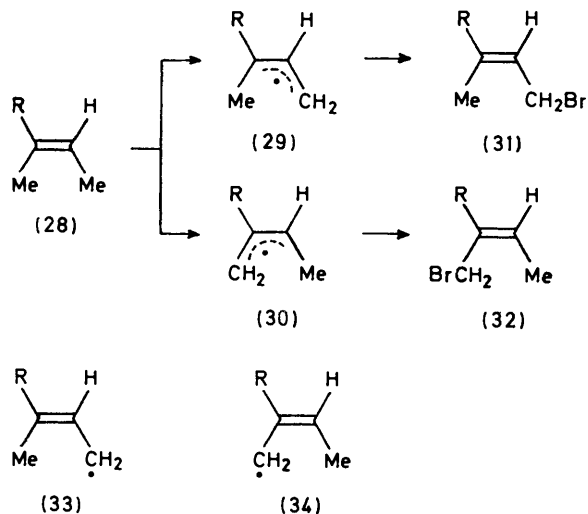
* In formulae (23)—(46), R represents the group



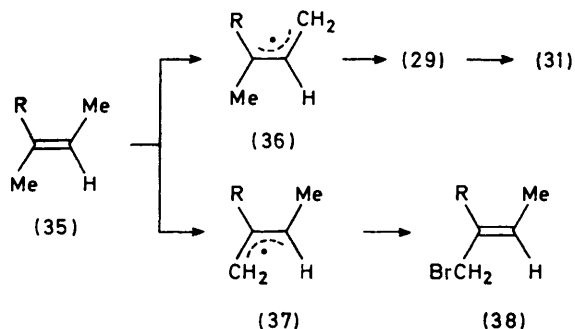
Both the *trans* (22) and the *cis*-diene (23) give rise to the *trans*-allylic bromide (26), which is derived from the allylic radical system (24), for which (27) is the major canonical species. The diene (23) will form

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

initially the allylic radical system (25), which must rapidly isomerise to (24). This kind of *cis-trans* isomerisation is well known in allylic radical chemistry⁶ and presumably there is a low energy barrier.⁷



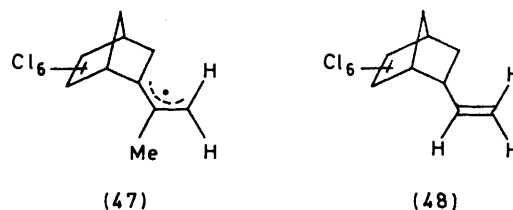
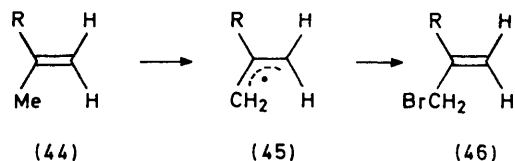
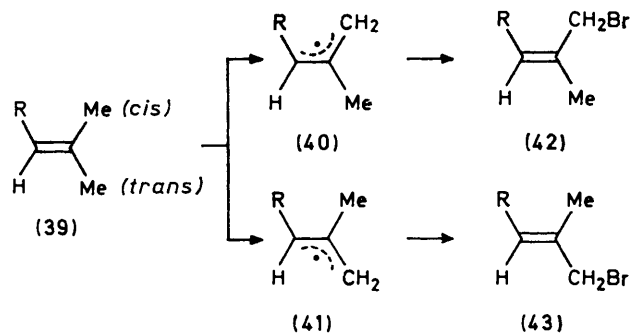
The diene (28) afforded a 3 : 2 mixture of the allylic bromides (31) and (32) as a result of reaction with *N*-bromosuccinimide. This may well represent a steric preference of 3 : 2 for the formation of the allylic radical system (29) relative to (30). These systems clearly tend towards canonical species (33) and (34), having the more highly substituted double bond systems. The double bond system in (29) and (30) is configurationally stable under the reaction conditions, indicating that C-3 in the side chain, which is *trans* to the ring system, has no tendency to become *cis*.



The diene (35) is an isomer of (28) in which the methyl groups are *trans* to each other, and it affords a 1 : 1 mixture of bromides (31) and (38). This reflects a slight decrease in the reactivity of the terminal methyl group in the side chain of (35) compared with that in (28), owing to its *cis*- as opposed to *trans*-relationship with the ring system. The formation of (38) will occur *via* the allylic radical system (37). Reaction is sufficiently ready to prevent isomerisation of (37) to (30). The bromide (31) will be derived from (35) *via cis*-

trans isomerisation of (36) to (29), which again suggests the importance of the side chain C-3 being *trans* rather than *cis* to the ring system. The failure to observe isomerisation of (37) to (30) will be because the side chain C-3 is not part of the allylic radical system.

The importance of the side chain C-3 being *trans* to the ring system explains the formation of the diene (39) of the allylic bromides (42) and (43) in the approximate ratio 1 : 2. The allylic radical system (41) is clearly more important than (40).



The diene (44) reacted with *N*-bromosuccinimide to give the allylic bromide (46), which is derived from chain transfer with the allylic radical system (45). The alternative allylic radical system (47) does not appear to be formed because (a) of the steric inaccessibility of the 5-*exo*-proton in (44) towards abstraction and (b) of the high energy of (47) occasioned by C-5 in the ring system becoming *sp*² hybridised. Consistent with this is the failure of (48) to react, although the steric inaccessibility of the C-5 proton may also contribute to the lack of reactivity of (48).

The results described here suggest that the factors controlling allylic radical formation in the systems described are (i) production of the ring system with the smallest number of *sp*²-hybridised carbon atoms; (ii) the tendency of allylic radical systems towards the more stable canonical species; (iii) the preference of radical centres at the side-chain 3-position of allylic systems derived from 5-(1-methylalk-1-enyl)hexachloro-

⁶ See for example C. Walling in 'Molecular Rearrangements,' ed. P. de Mayo, vol. I, ch. 7, Interscience, New York, 1963.

⁷ R. Sustmann and H. Trill, *J. Amer. Chem. Soc.*, 1974, **96**, 4343.

norbornenes to be *trans* rather than *cis* to the ring system.

Test experiments showed that products in the reactions described are formed as a result of kinetic control and they are not interconverted under the conditions of reaction. Where the products were known compounds they were identified by comparison with authentic specimens. New compounds were identified by their definitive spectral properties, which were compared with published data on norbornenyl⁸ and allylic systems.^{5,9}

EXPERIMENTAL

G.l.c. analyses were carried out with a Perkin-Elmer F11 gas chromatograph and the following 2 m × $\frac{1}{8}$ in columns: (A) 5% Apiezon L on AW DMCS Chromosorb W (80–100 mesh); (B) 2.5% silicone gum rubber E 301 on AW DMCS Chromosorb G (80–100 mesh).

Preparation of Dienes.—The following dienes, prepared by literature methods, had properties as reported: hexachloromethylenenorbornene (1),² 5-methylhexachloronorbornadiene (6),¹ 1,2,3,4,7,7-hexachloro-5-ethylidenenorborn-2-ene (17),¹⁰ 1,2,3,4,7,7-hexachloro-5-endo-(*trans*-prop-1-enyl)norborn-2-ene (22),¹¹ 1,2,3,4,7,7-hexachloro-5-endo-(*cis*-prop-1-enyl)norborn-2-ene (23),¹¹ 1,2,3,4,7,7-hexachloro-5-endo-(*cis*-1-methylprop-1-enyl)norborn-2-ene (28),¹¹ 1,2,3,4,7,7-hexachloro-5-endo-(*trans*-1-methylprop-1-enyl)norborn-2-ene (35),¹¹ 1,2,3,4,7,7-hexachloro-5-endo-(2-methylprop-1-enyl)norborn-2-ene (39),¹¹ and 1,2,3,4,7,7-hexachloro-5-endo-(1-methylvinyl)norborn-2-ene (44).¹¹

evaporation and distillation of the product afforded (i) a mixture (0.4 g), b.p. 55–65° at 0.01 mmHg of hexachlorocyclopentadiene and the diene (48), and (ii) the diene (48) (9.7 g, 69%), b.p. 65–66° at 0.1 mmHg, n_D^{25} 1.5506 (Found: C, 33.4; H, 2.1. C₉H₆Cl₆ requires C, 33.1; H, 1.9%); τ (60 MHz) 4.62 (m, RCH=), 4.70 (s, CH₂=), 6.64 (m, H-5-*exo*), 7.30 (q, H-6-*exo*), and 8.07 (q, H-6-*endo*) [J (CH=,H-5-*exo*) 5.2, J (5-*exo*,6-*exo*) 8.7, J (5-*exo*,6-*endo*) 4.0, J (6-*exo*,6-*endo*) 12.3 Hz]; ν_{\max} 1605 (*cis*-C=C) and 1642 cm⁻¹ (CH=CH₂).

Reaction of Dienes with N-Bromosuccinimide.—The reaction procedure is typified for the diene (6). A solution of the diene (1.0 g, 0.003 mol) and *N*-bromosuccinimide (0.57 g, 0.0035 mol) in carbon tetrachloride (20 ml) was boiled under reflux for 21 h in the presence of dibenzoyl peroxide (0.1 g). The cooled mixture was filtered and the filtrate concentrated. G.l.c. of the residue [column (A) at 165°] showed the presence of a 1 : 1 mixture (0.6 g) of unchanged diene and a single product, which was purified by distillation (b.p. 45–60° at 0.01 mmHg). Extraction of the distillation residue with chloroform (20 ml) followed by sublimation (90–100° at 0.05 mmHg) afforded 6-*endo*-bromo-1,2,3,4,7,7-hexachloro-5-methylenenorborn-2-ene (9) (0.2 g), with properties identical with those reported.⁵ The following compounds resulted from reactions of compounds (12) and (17), respectively: 6-*endo*-Bromo-1,2,3,4,7,7-hexachloro-5-ethylidenenorborn-2-ene (13), b.p. 74–76° at 0.02 mmHg, m.p. 90–92° (Found: C, 26.1; H, 1.5. C₉H₅BrCl₆ requires C, 26.6; H, 1.2%); τ (100 MHz) 3.80 (octet, CH=), 4.91 (m, H-6-*exo*), and 8.11 (q, Me) [J (CH=, CH₃) 7.1, J (CH=,H-6-*exo*) 2.0, J (H-6-*exo*,CH₃) 1.0 Hz]; ν_{\max} 1607

TABLE I
Reactant * and product quantities †

Diene			CCl ₄ ml	N-Bromosuccinimide		Reaction time h	Products			
No.	g	mmol		g	mmol		No.	g	No.	g
(6)	1.0	3	20	0.57	3.3	21	(9)	0.3		
(12)	1.9	3	20	0.52	3.0	5	(13)	0.8		
(17)	0.5	1.5	5	0.3	1.7	7	(19)	0.6		
(22)	1.0	3	10	0.6	3.4	27	(26)	0.74		
(23)						24	(26)	0.49		
(28)						7	(31)	0.36	(32)	0.24
(35)						7	(31)	0.31	(38)	0.31
(39)						7	(42)	0.21	(43)	0.42
(44)						24	(46)	0.74		
(48)					30					

* Benzoyl peroxide (0.1 g) added in each case. † Product quantities represent material isolated and purified.

1,2,3,4,7,7-Hexachloro-5-ethylnorborna-2,5-diene (12).—Hexachlorocyclopentadiene (15.0 g, 0.055 mol) and but-1-yne (9 g, 0.17 mol) were heated at 180° under nitrogen in a sealed tube for 7 h. Distillation afforded the diene (12) (11.6 g, 65%), b.p. 74° at 0.1 mmHg, n_D^{25} 1.5439 (Found: C, 33.2; H, 2.2. C₉H₆Cl₆ requires C, 33.0; H, 1.9%), τ (100 MHz) 3.84 (t, H-6), 7.69 (m, CH₂), and 8.88 (t, CH₃) [J (6,CH₂) 2.2, J (CH₂,CH₃) 7.25 Hz]; ν_{\max} 1598 (*cis*-C=C) and 1625 cm⁻¹ (>C=CH).

1,2,3,4,7,7-Hexachloro-5-endo-vinylnorborn-2-ene (48).—*trans*-Buta-1,3-diene (4.0 g, 0.07 mol) and hexachlorocyclopentadiene (11.0 g, 0.04 mol) were heated in a sealed tube at 100° for 14 h. Removal of the excess of diene by

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 G. P. Newsoroff and S. Sternhell, *Tetrahedron Letters*, 1968, 6117.

cm⁻¹ (*cis*-C=C); 5-(2-bromoethylidene)-1,2,3,4,7,7-hexachloronorborn-2-ene (19), b.p. 115° at 0.2 mmHg, n_D^{25} 1.5891 (Found: C, 27.1; H, 1.4. C₉H₅BrCl₆ requires C, 26.6; H, 1.2%); τ (60 MHz) 3.80 (sextet, CH=), 6.12 (d, CH₂Br), 6.86 (q, H-6-*exo*), and 7.23 (q, H-6-*endo*) [J (CH=, CH₂Br) 8.2, J (CH=,H-6-*exo*) 1.6, J (CH=,H-6-*endo*) 2.0, J (6-*exo*,6-*endo*) 16 Hz]; ν_{\max} 1603 cm⁻¹ (*cis*-C=C).

For the dienes (22), (23), (28), (35), (39), (44), and (48), after filtration and evaporation of the reaction mixture the residue was analysed by g.l.c. [column (B) at 180°]. Products were isolated by chromatography (sometimes repeated) on silica gel (Fisons 100–200 mesh) with light petroleum (b.p. 40–60°) as eluant.

Table 1 records reactant proportions and product yields

¹⁰ D. R. Adams and D. I. Davies, *J.C.S. Perkin I*, 1974, 2012.

¹¹ D. S. Weinberg, C. Stafford, and C. G. Cardenaz, *J. Org. Chem.*, 1971, **36**, 1631.

and Table 2 physical properties. Spectral data of the products from reaction of alkenylhexachloronorbornenes with *N*-bromosuccinimide are available as Supplementary Publication No. SUP 21270 (2 pp.).†

TABLE 2

Properties of products from the reaction of *N*-bromosuccinimide with alk-1-enylhexachloronorbornenes

No.	Found (%)		Required (%)		B.p. (M.p.) (°C)
	C	H	C	H	
(26) ^a	29.1	2.0	28.6	1.7	(67—68; from MeOH)
(31) ^b	[M ⁺ 431 (C ₁₁ H ₉ Br ³⁵ Cl ₆)]				100 at 0.02 mmHg
(32) ^b	31.0	2.2	30.5	2.1	105 at 0.05 mmHg
(38) ^b	30.7	2.1	30.5	2.1	100 at 0.02 mmHg
(42) ^b	31.0	2.2	30.5	2.1	100 at 0.1 mmHg
(43) ^b	31.1	2.2	30.5	2.1	(56—57; from MeOH)
(46) ^a	29.1	1.9	28.6	1.7	100 at 0.02 mmHg

Reduction of 1,2,3,4,7,7-Hexachloro-5-chloromethylnorborna-2,5-diene (11) with Triphenyltin Hydride.—The diene (11)¹ (1 g, 0.0029 mol) and triphenyltin hydride (1.03 g, 0.0029 mol)¹² were dissolved in ether (10 ml) and irradiated under nitrogen with a Hanovia U.V.S. 450 W medium-pressure lamp for 24 h. The solvent was evaporated off, carbon tetrachloride was added, and the mixture was filtered to remove triphenyltin chloride (0.4 g), m.p. 106—107° (lit.,¹³

† For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1974, Index issue.

106°). The filtrate was evaporated and the residue distilled to afford a mixture (0.9 g; b.p. 50—62° at 0.01 mmHg) of unchanged diene (11), hexachloromethylene-norbornene (5), 5-methylhexachloronorbornadiene (6), and an unidentified component, shown by n.m.r. and g.l.c. analysis [column at 140°] to be in the proportions 20:67:5:8. The residue from the distillation was extracted with ether (20 ml) and the extract was evaporated; crystallisation of the product from carbon tetrachloride (10 ml) afforded triphenyltin chloride (0.8 g).

In an alternative procedure a solution of the diene (11) (1 g, 0.0029 mol) and triphenyltin hydride (1.03 g, 0.0029 mol) in benzene (10 ml) was boiled at reflux with added azobisisobutyronitrile (0.1 g) for 48 h. The cooled mixture was evaporated and the residue mixed with carbon tetrachloride (10 ml) and filtered to remove triphenyltin chloride. The filtrate was concentrated by evaporation; g.l.c. and n.m.r. analysis showed compounds (11), (5), and (6) and the unknown in the same proportions as above.

D. R. A. thanks the S.R.C. for a Research Studentship.

[4/1848 Received, 9th September, 1974]

¹² H. G. Kuivila and O. F. Beumel, jun., *J. Amer. Chem. Soc.*, 1961, **83**, 1246.

¹³ 'Handbook of Chemistry and Physics,' 46th edn., ed. R. C. Weast, The Chemical Rubber Co., Cleveland, Ohio.