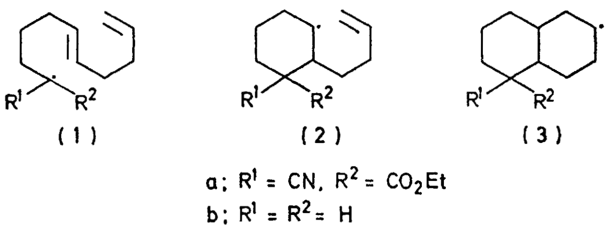
Cyclization of 3-Allylhex-5-enyl Radical: Mechanism, and Implications concerning the Structures of Cyclopolymers

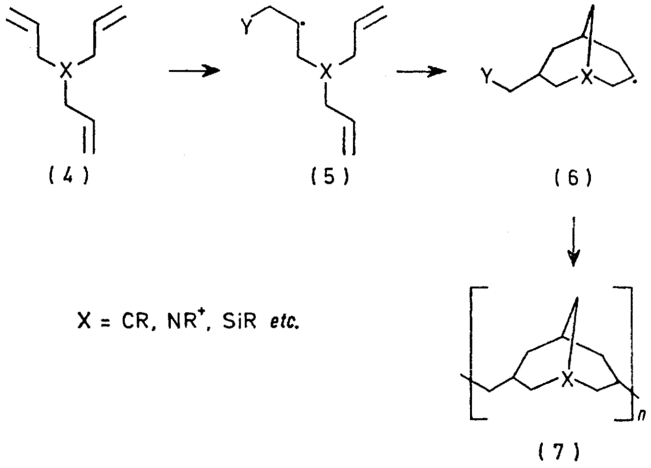
By **Athelstan L. J. Beckwith** * and **Graeme Moad**, Organic Chemistry Department, University of Adelaide, Adelaide, South Australia, Australia

Radical-initiated reduction of 3-allylhex-5-enyl bromide (15) with tributylstannane affords 4-ethylhepta-1,6-diene (17), *cis*- and *trans*-1-allyl-3-methylcyclopentane (23) and (19), bicyclo[4.2.1]nonane (33), *exo*-3-methylbicyclo[3.2.1]octane (35), and other hydrocarbons. The formation of bicyclic systems from the 3-allylhex-5-enyl radical (16) involves two discrete steps, the kinetic parameters of which have been determined. The results suggest that homoconjugative interaction between the double bonds in the dienyl radical (16) affects the rate and stereoselectivity but not the regioselectivity of the first cyclization step. The failure of the reaction to afford bicyclo[3.3.1]nonane indicates that structures previously assigned to the cyclopolymers derived from triallyl monomers may be incorrect.

INTRAMOLECULAR homolytic addition in radicals containing two suitably disposed olefinic bonds provides a route to bicyclic products from acyclic precursors. However, although a number of such reactions leading to radicals containing the decalin system [*e.g.* (1a) → (3a)] [1] have been reported,[2] some of the mechanistic features require clarification. Questions which arise are whether these processes are concerted, or occur in stepwise fashion involving two discrete cyclizations [*e.g.* (1a) → (2a) → (3a)], and, in either case, whether homoconjugative interaction between the two double bonds enhances their reactivity towards homolytic attack. It may be significant that the unsubstituted radical (1b) affords no bicyclic radical (3b) on intramolecular addition; the only cyclic product contains one five-membered ring.[3] The radical (2b) also undergoes cyclization exclusively in the 1,5-direction.[3] The rate constant for cyclization of the radical (1b) is of the same order of magnitude as those observed for intramolecular addition in related species containing only one double bond.[4] We conclude that in this example of homolytic attack on a 1,5-diene, interaction between the double bonds is negligible. However, in the case of 1,6-dienes the existence of a homoconjugative interaction has been adduced from spectral data, and has been advanced as an explanation for the facility with which such compounds undergo cyclopolymerization.[5-11]



The ability of branched radicals of the general type (5) to form bridged bicyclic structures is also of importance in polymerization, for the radical-initiated conversion of triallyl compounds (4) to soluble linear polymers (7) is believed to involve the intermediacy of radicals (5) and (6).[8,11-13] There is little chemical evidence to support the proposed structure (7) for triallyl cyclopolymers; indeed, the structures advanced for cyclopolymers generally appear to rest mainly on the preconception that radicals containing the hex-5-enyl system will undergo cyclization preferentially by 1,6-intramolecular addition. In view of the recent substantial evidence that hex-5-enyl radical [14-16] and many of its simple derivatives [3,4,17] and related species [18-22] predominately form five-membered cyclic products, it appears probable that the structures involving recurring six-membered cyclic units proposed for many polymers derived from 1,6-dienes are incorrect.



The present study of the cyclization of the 3-allylhex-5-enyl radical (16), which is closely related to the species (5) believed to be involved in cyclopolymerization of triallyl compounds was designed to provide similar evidence for the validity or otherwise of the structure (7) for the cyclopolymer, and to detect any enhancement of reactivity of the double bonds arising from their homoconjugative interaction.

RESULTS AND DISCUSSION

The 3-allylhex-5-enyl radical (16) was generated by reaction of tributylstannane with the bromide (15), the preparation of which was accomplished *via* the routes outlined in Scheme 1. Initially, some difficulty was

---

[1] M. Julia, F. Le Goffic, and L. Katz, *Bull. Soc. chim. France*, 1964, 1122.

[2] For recent reviews of radical cyclization see (*a*) M. Julia, *Pure Appl. Chem.*, 1967, **15**, 167; *Accounts Chem. Res.*, 1971, **4**, 386; (*b*) J. W. Wilt in 'Free Radicals,' ed. J. K. Kochi, Wiley–Interscience, New York, 1973, vol. 1. ch. 8; (*c*) A. L. J. Beckwith, 'Essays in Free-Radical Chemistry,' Chemical Society Special Publication No. 24, London, 1970, p. 239.

[3] A. L. J. Beckwith and G. Phillipou, *J.C.S. Chem. Comm.*, 1973, 280.

[4] A. L. J. Beckwith, I. A. Blair, and G. Phillipou, *Tetrahedron Letters*, 1974, 2251.

[5] G. B. Butler, *J. Polymer Sci.*, 1960, **48**, 279.

[6] G. B. Butler and M. A. Raymond, *J. Org. Chem.*, 1965, **30**, 2410.

[7] G. B. Butler and S. Kimura, *J. Macromol. Sci.*, 1971, **5**, 181.

[8] G. B. Butler and B. Iachia, *J. Macromol. Sci.*, 1969, **3**, 803.

[9] G. B. Butler and W. L. Miller, *J. Macromol. Sci.*, 1969, **3**, 1493.

[10] G. B. Butler and T. W. Brooks, *J. Org. Chem.*, 1963, **25**, 2699.

[11] For recent reviews of cyclopolymerization see G. C. Cornfield, *Chem. Soc. Rev.*, 1972, **1**, 523; W. E. Gibbs and J. M. Barton in 'Kinetics and Mechanism of Polymerization,' ed. G. E. Ham, Dekker, New York, 1967, vol. 2, part 1, ch. 2; G. B. Butler in 'Encyclopedia of Polymer Science and Technology,' eds. H. F. Mark, N. G. Gaylord, and N. M. Bikales, Wiley–Interscience, New York, 1956, vol. 4, p. 568; C. L. McCormich and G. B. Butler, *J. Macromol. Sci.*, *Rev. Macromol. Chem.*, 1972, **8**, 201; D. Solomon, *J. Macromol. Sci.*, 1975, 97.

[12] D. S. Trifan and J. J. Hogben, *J. Amer. Chem. Soc.*, 1961, **83**, 2021.

[13] G. S. Matsoyan, G. M. Pogosyan, and M. A. Eliazyan, *Vysokomol. Soedineniya*, 1963, **5**, 777.

[14] C. Walling, J. H. Colley, A. A. Ponaras, and E. J. Racah, *J. Amer. Chem. Soc.*, 1966, **88**, 5363.

[15] A. L. J. Beckwith and G. Moad, *J.C.S. Chem. Comm.*, 1974, 472.

[16] C. L. Jenkins and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 843; and references cited therein.

[17] A. L. J. Beckwith, I. Blair, and G. Phillipou, *J. Amer. Chem. Soc.*, 1974, **96**, 1613.

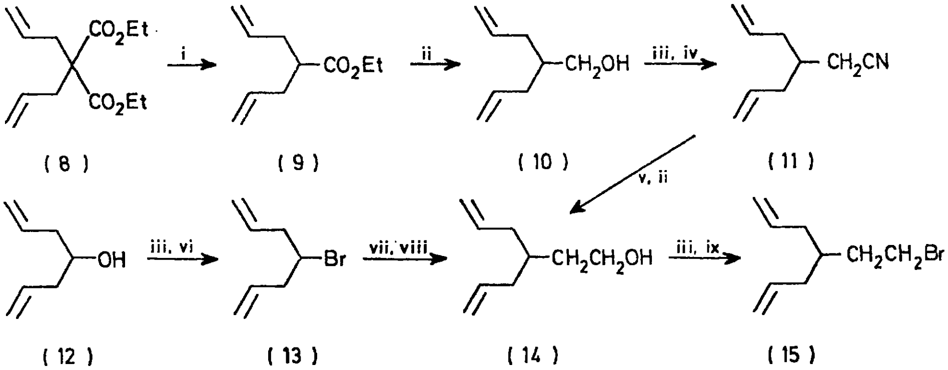
[18] A. L. J. Beckwith and W. B. Gara, *J.C.S. Perkin II*, 1975, 795, 593.

[19] A. L. J. Beckwith, A. K. Ong, and D. H. Solomon, *J. Macromol. Sci.*, 1975, 115.

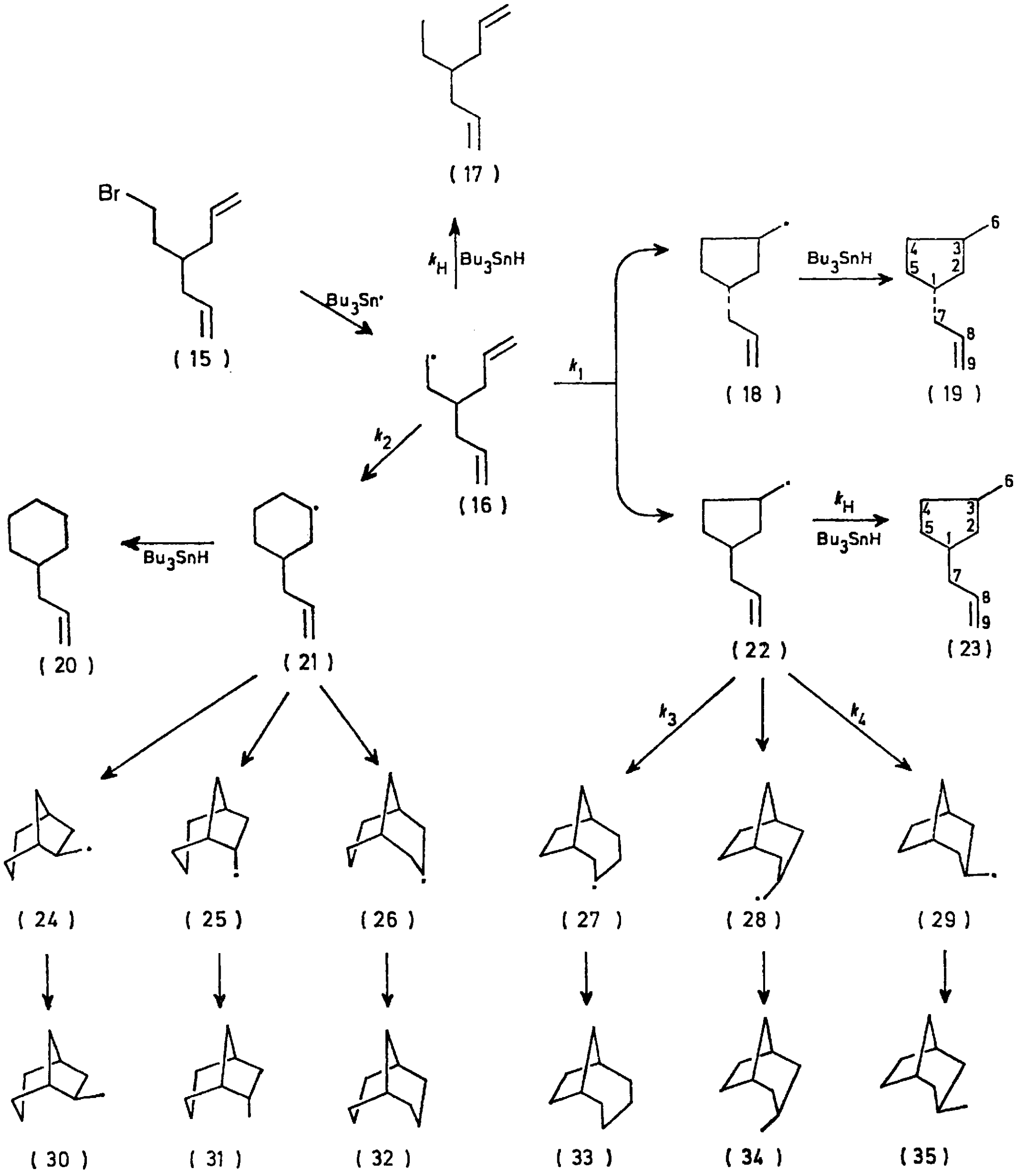
[20] A. L. J. Beckwith, A. K. Ong, and D. H. Solomon, *J. Macromol. Sci.*, 1975, 125.

[21] N. O. Brace, *J. Org. Chem.*, 1971, **36**, 3187.

[22] N. O. Brace, *J. Org. Chem.*, 1973, **38**, 3167.



SCHEME 1 Reagents: i, NaCN–dimethyl sulphoxide; ii, $LiAlH_4$; iii, TsCl–pyridine; iv, NaCN–*N*-methylpyrrolidone; v, Bu^i_2AlH; vi, LiBr–hexamethylphosphoramide; vii, Mg–ether; viii, ethylene oxide; ix, pyridinium bromide–dimethylformamide



SCHEME 2

experienced in the preparation of the intermediate halide (13), since the reaction of the tosylate of the alcohol (12) with lithium bromide in dimethylformamide or dimethyl sulphoxide gave poor yields, and sometimes afforded elimination products. These problems were overcome by the use of lithium bromide in hexamethylphosphoramide, but unfortunately we were unable to find conditions under which the reaction between the Grignard reagent derived from the halide (13) and ethylene oxide proceeds cleanly. Consequently, samples of the alcohol (14) were later prepared *via* the route from diallylmalonic ester (8) which, although longer, gives good overall yields.

The only difficulty experienced in the preparation of the bromide (15) from the alcohol (14) was the concomitant formation of small amounts (*ca.* 1%) of the analogous chloride, which was identified by comparison with a sample prepared by treatment of the toluene-*p*-sulphonate of (14) with pyridinium chloride in dimethylformamide. In view of the instability of the bromide (15) towards g.l.c. no attempt was made to remove from it the small amount of chloride impurity.

Products which might reasonably be expected to be formed by interaction of the bromide (15) with tributylstannane, and the probable mechanisms of their formation, are set out in Scheme 2. To facilitate analysis of the reaction mixtures a number of the expected products were synthesized by unequivocal routes. 4-Ethylhepta-1,6-diene (17) was prepared by reduction of the toluene-*p*-sulphonate of the alcohol (14), and also, by a coupling reaction between allyl bromide and the Grignard reagent derived from 4-bromohex-1-ene. A similar coupling reaction of allyl bromide with 3-methylcyclopentylmagnesium bromide gave a mixture of *cis*- and *trans*-1-allyl-3-methylcyclopentane (23) and (19). Unfortunately, all attempts to separate the two isomers by g.l.c. were unsuccessful, but an estimate of the composition of the mixture was obtained by ^{13}C n.m.r. spectroscopy.

The broad-band decoupled ^{13}C n.m.r. spectrum of the mixture contained sixteen lines, two of which, at δ 41.0 and 138.5, clearly comprised overlapping signals. The tentative assignments given in Table 1 are based on the correlation of the observed chemical shifts with values obtained by the application of additivity factors [23] to the data available [24] for the two isomers of 1,3-dimethylcyclopentane. In general the agreement between observed and calculated chemical shifts is very satisfactory. Each of the peaks assigned to the *cis*-isomer was found to be more intense by a factor of *ca.* 1.2 than that for the corresponding position in the *trans*-isomer. We conclude that the coupling reaction between allyl bromide and 3-methylcyclopentylmagnesium bromide shows a slight preference for formation of the *cis*-compound (23).

Preparation of the two isomers (34) and (35) of 3-methylbicyclo[3.2.1]octane was accomplished by catalytic hydrogenation of the 3-methylene compound (37) obtained by a Wittig reaction on the ketone (36).[25] The *endo*-isomer (34), was the major component of the product mixture. Treatment of 2-norbornanone with diazomethane afforded a mixture of starting material and the ring-expanded products (36) and (38)—(40). The last two could be isolated by preparative gas chromatography, but it proved to be more convenient to subject the mixture of ketones to Clemmensen reduction, and to separate the required bicyclo[4.2.1]nonane (33) from the crude product. Consecutive treatment of borabicyclononane with 2,3-dimethylbut-2-ene and sodium cyanide [26] afforded bicyclo[3.3.1]nonan-9-one (41) from which the hydrocarbon (32) was formed by Clemmensen reduction. However, the overall yield of the hydrocarbon (32) was very poor and later a larger sample was prepared by Wolff–Kishner reduction of the dione (42).[27] The two isomers (30) and (31) of 6-methylbicyclo[3.2.1]octane were not prepared because it was expected that they would be, at best, very minor products of the free-radical reaction, and, if formed, could be identified on the basis of g.l.c. data already available.[28]

TABLE 1

Chemical shifts [a] for ^{13}C nuclei in 1,3-disubstituted cyclopentane

	cis-Dimethyl	*cis*-Allylmethyl (23)		*trans*-Dimethyl	*trans*-Allylmethyl (19)	
	Obs [b]	Calc [c]	Obs	Obs [b]	Calc [c]	Obs
C-1	35.5	39.2	39.9	33.6	37.3	38.3
C-2	45.1	42.9	42.1	43.2	41.0	40.2
C-3	35.5	35.9	34.8	33.6	34.0	33.2
C-4	34.4	34.8	33.8	35.3	35.7	34.7
C-5	34.4	32.2	31.5	35.3	33.1	32.6
C-6	21.2	21.2	20.9	21.5	21.5	21.3
C-7	21.2	41.6	41.0	21.5	41.9	41.0
C-8			138.5			138.5
C-9			114.6			114.7

[a] δ_C (p.p.m.) from Me_4Si. [b] Converted from the original data (ref. 24) using $\delta_C^{CS_2}$ 192.8 p.p.m. [c] Calculated by the use of additivity factors (ref. 23).

The relative yields of products formed when the bromide (15) was treated in pentane with tributylstannane and a trace of a free-radical initiator (azobisisobutyronitrile) are given in Table 2. Perhaps the most significant feature of these results is the clear demonstration they provide that the formation of bicyclic species from the radical (16) proceeds in two discrete steps, the first of which is highly regiospecific and affords predominantly the two stereoisomers (18) and (22) of the five-membered monocyclic radical product. Thus, the

---

[23] J. B. Stothers, 'Carbon-13 N.M.R. Spectroscopy,' Academic Press, New York, 1972, pp. 58 and 75.

[24] M. Christl, H. J. Reich, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1971, **93**, 3463.

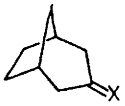
[25] C. W. Jefford, *Proc. Chem. Soc.*, 1963, 64.

[26] A. Pelter, M. G. Hutchings, and K. Smith, *Chem. Comm.*, 1971, 1048.

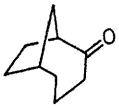
[27] I. A. MacDonald, A. S. Dreiding, H. Hutmacher, and H. Musso, *Helv. Chim. Acta*, 1973, **56**, 1385; H. Stetter and P. Tacke, *Chem. Ber.*, 1963, **96**, 694.

[28] Ye I. Bagri, P. I. Sanin, N. S. Vorob'eva, and Al. A. Petrov, *Petroleum Chem. U.S.S.R.*, 1967, **7**, 159; A. F. Platé, N. A. Belikova, A. A. Bobyleva, N. I. Gusar, and S. V. Vitt, *Doklady Chem.*, 1965, **163**, 737.

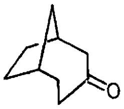
cyclization of the radical (16) provides yet another example of a phenomenon exhibited by many radicals containing the hex-5-enyl system, namely the formation, by 1,5-addition, of the thermodynamically less stable primary radical in preference to the more stable secondary cyclohexyl radical resulting from 1,6-addition.



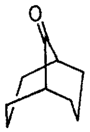
(36) X = O
(37) X = CH$_2$



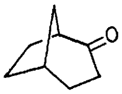
(39)



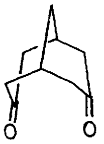
(40)



(41)



(38)



(42)

TABLE 2

Relative yields (%)[a] of products from reduction of 3-allylhex-5-enyl bromide (15) with tributylstannane in pentane

T/°C	[Bu$_3$SnH]/M	(17)	(19) + (23)	(20)	(34)	(35)	(33)	(30)[b]	(31)[b]
30	0.467	14	84	2	0	<1	<1	0	0
60	0.467	9	88	2	0	<1	<1	0	0
60	0.098	2	97	<1	0	<1	<1	0	0
65	0.014	<1	89	<1	<1	6	5	0	0
65	0.005	0	78	<1	<1	12	10	<1	<1
65	0.0027	0	69	0	<1	17	14	<1	<1
84	0.110	2	98	<1	0	<1	<1	0	0
84	0.0096	0	79	<1	<1	11	10	0	0
100	0.0027	0	59	0	<1	22	18	<1	<1

[a] Absolute yields were 80—100% when [Bu$_3$SnH] $\geqslant$ 0.098M, *ca.* 80% when [Bu$_3$SnH] = 0.0096 or 0.014M, *ca.* 50% when [Bu$_3$SnH] = 0.0049M, and *ca.* 40% when [Bu$_3$SnH] = 0.0027M. [b] Tentatively identified on the basis of g.l.c. data.

As before,[1c,17,18,29] we ascribe the preferential 1,5-cyclization of the radical (16) to the fact that the stereoelectronic requirements of the transition state can most readily be satisfied in structures lying on the reaction co-ordinate which leads to the product containing the new radical centre exocyclic to the new ring.

The relative proportions of the two stereoisomers (18) and (22) of the radical formed by 1,5-cyclization of the radical (16), cannot be accurately determined because of our inability to separate the *cis*- and *trans*-forms (23) and (19) of 1-allyl-3-methylcyclopentane. However, the ^{13}C n.m.r. spectrum of a sample of 1-allyl-3-methylcyclopentane isolated directly from the reaction mixture of an experiment conducted with an initial stannane concentration of 0.098M showed that it consisted mainly (*ca.* 80%) of the *cis*-isomer, and we conclude, therefore, that the ratio of the rate constants for formation of the radicals (22) and (18) from radical (16) is *ca.* 4 : 1.

Since each cyclization step in the reaction mechanism is in competition with a bimolecular, hydrogen-atom transfer reaction from tributylstannane to the appropriate open-chain radical, the yields of hydrocarbon products are related to stannane concentration. At relatively high stannane concentrations ($\geqslant$ 0.098M), monocyclic radicals are trapped efficiently and the yields of bicyclic compounds are very small. Consequently, the relative yields of 1-allyl-3-methylcyclopentane and allylcyclohexane formed under these conditions reflect the ratio of the rate constants (k_1/k_2) for 1,5- and 1,6-cyclization. It is noteworthy that this ratio (*ca.* 40 and 60°) is the same, within the limits of experimental error, as that exhibited by hex-5-enyl radical under similar conditions.[4] We conclude that the presence of each double bond in the radical (16) is without effect on the regioselectivity of intramolecular homolytic addition to the other. This accords with the observation that intermolecular radical addition to hexa-1,6-diene and related dienes affords five-membered cyclic products,[19-22] and suggests that the hypothesis that the size of the rings formed in cyclopolymerization of 1,6-dienes is influenced by homoconjugation[5] is invalid.

The values of k_1/k_H and k_2/k_H, where k_1 and k_2 are the rate constants for 1,5- and 1,6-cyclization respectively, and k_H is that for reaction of tributylstannane with a primary alkyl radical[30] were computed by application of the appropriate integrated rate expression[15] to the results of experiments conducted with [Bu$_3$SnH] $\geqslant$ 0.11M. The values obtained (see Table 3) are considerably greater than those determined for cyclization of the hex-5-enyl radical and related monoenyl species, the reactivity at 60° of each double bond in the radical (16) being *ca.* 5 times greater than that of the double bond in the hex-5-enyl radical under similar conditions.[4,14,15] This observation together with other relevant experimental evidence, namely, the enhanced reactivity of

TABLE 3

Relative rate constants for cyclization of radicals (16) and (22)

Reaction	[Bu$_3$SnH]$_0$/M	T/°C	$k_c k_H^{-1}$/ l mol^{-1}
(16) $\xrightarrow{k_1}$ (18) + (22)	0.467	30	1.37
	0.467	60	2.19
	0.098	60	2.2
	0.110	84	3.02
(16) $\xrightarrow{k_2}$ (21)	0.467	60	*ca.* 0.05
(16) $\xrightarrow{k_3}$ (27)	0.014	65	0.0006
	0.0049	65	0.0006
	0.0027	65	0.0006
	0.0096	84	0.0010
	0.0027	100	0.0010
(22) $\xrightarrow{k_4}$ (29)	0.014	65	0.0007
	0.0049	65	0.0008
	0.0027	65	0.0008
	0.0096	84	0.0011
	0.0027	100	0.0012

---

[29] A. L. J. Beckwith, G. E. Gream, and D. L. Struble, *Austral. J. Chem.*, 1972, **25**, 1081.

[30] D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, 1968, **90**, 7047.

1,6-dienes in polymerization[7,31] and other free-radical addition reactions,[22] the small bathochromic shift exhibited in their u.v. spectra,[6,8,10] and unusual features of their in-plane deformation vibrations,[9] persuade us that there is indeed a homoconjugative interaction between the double bonds of 1,6-dienes.*

Homoconjugative interaction in the radical (16) could enhance its rate of cyclization relative to other radicals containing the hex-5-enyl system both by stabilizing conformations favourably disposed for intramolecular attack, and by lowering the energy of the orbital which is involved in the formation of the new bond.[17] The preference shown by the radical (16) for cyclization to the *cis*-radical (22) is attributed to the former effect.

Treatment in the usual way of the kinetic data for cyclization of the radical (16) allowed the calculation of $\Delta\Delta H^\ddagger$ ($\Delta H^\ddagger_{\text{cyclization}} - \Delta H^\ddagger_{\text{H transfer}}$) and $\Delta\Delta S^\ddagger$. The values obtained were 13 kJ mol^{-1} and 46 J mol^{-1} K^{-1} respectively. The fact that the latter value is exceptionally high, even after allowance is made for the statistical factor due to the presence of two double bonds, provides further evidence for the stabilization by homoconjugative interaction of favourable conformations.

Since only the *cis*-form (22) of the 3-allylcyclopentylcarbinyl radical is capable of undergoing further cyclization the integrated rate equation[15] cannot be used for the calculation of the relative rate constants k_3/k_H and k_4/k_H. The values presented in Table 3 were therefore obtained by use of the approximate expression (1) where

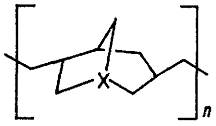
$$k_c/k_\text{H} = \frac{[\text{yield of cyclized products}]}{[\text{yield of (23)}]} \cdot [\text{R}_3\text{SnH}]_m \quad (1)$$

$[\text{R}_3\text{SnH}]_m$ is the mean stannane concentration during the experiment. Because of our inability to determine precisely either the absolute overall yields, or the proportion of the *cis*-isomer (23) in the monocyclic product, the results obtained are insufficiently accurate for the calculation of Arrhenius parameters. However, it is clear that the value of k_4/k_H is a good deal less than that (0.0052M) for the 1,6-cyclization of hept-6-enyl radical.[15] Presumably the reaction is disfavoured by the ring strain engendered in the formation of the bicyclic system (29). The relative rate constant k_3/k_H for formation of the less strained bicyclic radical (27) is of the same order of magnitude as that (0.0009 at 65°) for 1,7-cyclization of hept-6-enyl radical.[15]

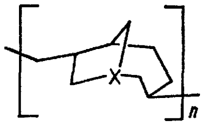
The data do not allow us to obtain a relative rate constant for the formation of the *endo*-radical (28) from the monocyclic species (22), but it is clearly very small. Presumably, the reaction is hindered by non-bonded interactions between the protons at the 4- and 5-positions of the radical (22) and those on the remote terminus of the double bond. Nor is it possible to obtain relative rate constants for the formation of bicyclic species from the radical (21). However, it is significant that no trace could be detected of the expected product (32) of 1,6-cyclization.

Our results indicate that the general structure (7) usually assigned to the linear cyclopolymers prepared from triallyl monomers is probably incorrect. We expect that such polymers will comprise a variety of recurring units of which the most numerous will be those, (43) and (44), resulting from consecutive 1,5;1,6 and 1,5;1,7 cyclizations respectively. The product (7) of repeated 1,6-cyclizations is the least likely.

Finally, our observation that there is a very great difference in magnitude between the rate constants for the first and second cyclization reactions of the radical (16) indicates that the structures of cyclopolymers generated from triallyl compounds are likely to be highly dependent on monomer concentration. The formation of linear polymers containing a high proportion of saturated bicyclic units will be favoured by conditions of very low monomer concentration. At high concentration intermolecular chain propagation may compete effectively with the second cyclization step, and the resulting polymer will then contain a high proportion of monocyclic units and will show considerable unsaturation and/or cross-linking.



(43)



(44)

X = CR, SiR, NR$^+$, *etc.*

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded for solutions in carbon tetrachloride on either a Varian T60 or DP 60 spectrometer. ^{13}C N.m.r. spectra were recorded for solutions in deuteriochloroform on a Bruker HX90-E spectrometer fitted with a Nicolet B-NC12 Fourier system and a Bruker B-SV3PM pulse unit. Mass spectra were determined with a Perkin-Elmer–Hitachi RMU-6D instrument operating at 70 eV. G.l.c. was conducted on either a Perkin-Elmer 990 or 881 instrument using the following columns: (*a*) 3 m × 3.2 mm 2.5 FFAP on Chromasorb W metal column; (*b*) 6.1 m × 3.2 mm 3—4% FFAP on Varaport 30 metal column; (*c*) 6.1 m × 3.2 mm 30% Carbowax 20 M on Varaport 30 metal column. Preparative g.l.c. was carried out on an Aerograph Autoprep 705 chromatograph using either a 3 m × 6.3 mm 15% Carbowax 20 M TPA on Chromasorb A glass column, or a 1.4 m × 6 mm 14% FFAP on Varaport 30 glass column.

Products were identified by comparison of their retention times with those of authentic samples, and confirmed by peak enhancement. The areas of peaks were determined with either a Perkin-Elmer 194B printing integrator or with a disc integrator, and were checked by triangulation. The relationship between peak areas of products and internal standard was determined from synthetic mixtures. Microanalyses were performed by the Australian Microanalytical Service, Melbourne.

---

* *Note added in proof.* Recent work in these laboratories has shown that 3-propylhex-5-enyl radical also cyclizes more rapidly than the parent hex-5-enyl radical. We conclude that the enhanced reactivity of (16) cannot be attributed solely to homoconjugation.

[31] D. Mikulasova and A. Hvirik, *Chem. Zvesti*, 1957, **11**, 641.

4-*Bromohepta*-1,6-*diene* (13).—Treatment of 4-hydroxyhepta-1,6-diene [32] with toluene-*p*-sulphonyl chloride in pyridine at 10° in the usual way afforded the toluene-*p*-sulphonate (97%) as a yellow oil, a sample (54 g) of which was stirred with lithium bromide (25 g) in hexamethylphosphoramide (250 ml) at room temperature for 24 h. After dilution with water, the mixture was shaken with light petroleum, and the organic layer was washed with water, dried, and evaporated *in vacuo*. Distillation of the residue gave the required bromo-compound (29.1 g, 76%), b.p. 43—45° at 8.5 mmHg (lit.,[33] 66.5—67.5° at 25 mmHg); δ2.6 (4 H, t, *J* 7 Hz, CH_2), 3.9 (1 H, quin, *J* 7 Hz, CHBr), 4.8—5.2 (4 H, m, $=CH_2$), and 5.4—6.2 (2 H, m, CH=).

Ethyl 2-*Allylpent*-4-*enoate* (9).—A solution of diethyl diallylmalonate (30 g) and sodium cyanide (12 g) in dimethyl sulphoxide (100 ml) was heated at 160° under nitrogen for 6 h, then allowed to stand at room temperature overnight.[34] After dilution with water, the mixture was extracted with light petroleum, and the organic layer was washed with water, dried, and evaporated. Distillation of the residue afforded ethyl 2-allylpent-4-enoate (15.2 g, 72%), b.p. 62—63° at 6 mmHg (lit.,[35] 69—71° at 9 mmHg); δ 1.3 (3 H, t, *J* 7 Hz, CH_3), 2.2—2.7 (5 H, m, CH_2CHCH_2), 4.2 (2 H, q, *J* 7 Hz, OCH_2), 4.9—5.3 (4 H, m, $=CH_2$), and 5.4—6.2 (2 H, m, CH=); $\nu_{max.}$ 1 725, 1 640, 995, and 920 cm^{-1}.

3-*Allylhex*-5-*enenitrile* (11).—Reduction of the foregoing ester with lithium aluminium hydride afforded 2-allylpent-4-en-1-ol (84%) which was converted into its toluene-*p*-sulphonate (99%) in the usual way. A solution of the tosylate (20 g) and sodium cyanide (7 g) in *N*-methylpyrrolidone (80 ml) was stirred at room temperature for 48 h, then diluted with water, and extracted with light petroleum. Distillation of the dried extract gave the required nitrile (6.5 g, 64%), b.p. 75—76° at 7 mmHg (lit.,[36] 90—91° at 14 mmHg); δ 1.8—2.6 (7 H, complex m, CH_2CH), 4.9—5.4 (4 H, m, $=CH_2$), and 5.4—6.3 (2 H, m, CH=); $\nu_{max.}$ 2 250, 1 635, 995, and 920 cm^{-1}.

3-*Allylhex*-5-*en*-1-*ol* (14).—(a) Di-isobutylaluminium hydride (9.5 g) in dry hexane (90 ml) was added dropwise during 30 min to a stirred solution of the foregoing nitrile (6.0 g) in hexane (150 ml) under nitrogen at −60°. After the addition the mixture was stirred for a further 30 min at −60° then allowed to warm to room temperature. The excess of reagent was destroyed by dropwise addition of ethyl acetate (10 ml) followed by saturated aqueous ammonium chloride (50 ml). After stirring of the mixture for 30 min, 5% aqueous sulphuric acid was added, and the organic layer was separated. The aqueous solution was extracted with ether, and the combined organic extracts were washed with sodium hydrogen carbonate solution and water. Evaporation of the dried ether solution afforded crude 3-allylhex-5-enal (4.6 g, 77%); δ 1.9—2.6 (7 H, complex m, CH_2CH), 4.9—5.4 (4 H, m, $=CH_2$), 5.4—6.3 (2 H, m, CH=), and 9.8 (1 H, s, CHO); $\nu_{max.}$ 1 710, 1 635, 995, and 920 cm^{-1}. Reduction of a sample (4.0 g) of the crude aldehyde with lithium aluminium hydride (0.75 g) in ether (20 ml) in the usual manner afforded 3-*allylhex*-5-*en*-1-*ol* (2.5 g, 62%), b.p. 81—82° at 4.5 mmHg, n_D^{18} 1.4639 (Found: C, 77.1; H, 11.5. $C_9H_{16}O$ requires C, 77.2; H, 11.3%); δ 1.3—2.3 (7 H, complex m, CH_2CH), 3.3 (2 H, t, *J* 6 Hz, CH_2O), 4.8—5.3 (4 H, m, $=CH_2$), and 5.4—6.2 (2 H, m, CH=); $\nu_{max.}$ 3 300, 1 635, 995, and 910 cm^{-1}.

(b) A solution of the Grignard reagent prepared from 4-bromohepta-1,6-diene (10 g) and magnesium (1.38 g) in dry ether (100 ml) was cooled to −10° and stirred whilst a stream of ethylene oxide vapour (5 g) was slowly run from a tube *ca.* 1 cm above the surface. When the addition was complete (45 min) the mixture was set aside overnight. Benzene (60 ml) was then added, and the mixture was distilled until its temperature reached 60°, after which it was refluxed for 6 h. The cooled mixture was then poured onto ice, ammonium chloride was added, and the organic layer was separated and washed with water. Distillation of the product afforded a mixture (1.9 g), b.p. 70—75° at 4.5 mmHg, which was shown by g.l.c. (column *a*, 150°) to contain *ca.* 55% of the required alcohol and *ca.* 45% of 4,5-diallylocta-1,7-diene. A sample of the alcohol separated by preparative gas chromatography was identical with that prepared by method (a).

4-*Allyl*-7-*bromohept*-1-*ene* (15).—3-Allylhex-5-en-1-ol (2.4 g) was converted in the usual way into its toluene-*p*-sulphonate, which was stirred with pyridine hydrobromide (4.5 g) in dimethylformamide (30 ml) at ambient temperature for 48 h. The mixture was then poured into water and extracted with low-boiling light petroleum. The organic layer was washed, dried, and distilled to afford the required *bromo-compound*, b.p. 80—81° at 2 mmHg (Found: C, 53.3; H, 7.4. $C_9H_{16}Br$ requires C, 53.2; H, 7.4%); δ 1.6—2.3 (7 H, m, CH_2CH), 3.5 (2 H, t, *J* 7 Hz, CH_2Br), 4.8—5.3 (4 H, m, $=CH_2$), and 5.4—6.2 (2 H, m, CH=); $\nu_{max.}$ 1 635, 995, and 910 cm^{-1}. The product was shown by g.l.c. [column (*b*), 130°] to contain *ca.* 0.5% of the corresponding chloro-compound. The same chloro-compound, δ 1.4—2.2 (7 H, m, CH_2CH), 3.4 (2 H, t, *J* 7 Hz, CH_2Cl), and 4.8—6.3 (6 H, m, $CH=CH_2$), was obtained in 98% yield when the toluene-*p*-sulphonate of 3-allylhex-5-en-1-ol was treated as above with pyridine hydrochloride in dimethylformamide.

1-*Allyl*-3-*methylcyclopentane*.— 1-Bromo-3-methylcyclopentane [37] (0.60 g), prepared by treatment of the tosylate of 3-methylcyclopentanol [38] with lithium bromide in hexamethylphosphoramide, was converted into its Grignard reagent by stirring with magnesium turnings in tetrahydrofuran (25 ml) at the reflux temperature for 2 h. The Grignard reagent was then added slowly with stirring under nitrogen to allyl bromide (0.50 g) in tetrahydrofuran (10 ml), and the mixture was set aside overnight. Work-up of the mixture in the usual way afforded a liquid (0.30 g) shown by g.l.c. to contain the required hydrocarbon (60%), hexa-1,5-diene (20%), and 3-methylcyclopentane. Preparative g.l.c. of this mixture gave a pure sample of 1-*allyl*-3-*methylcyclopentane*, n_D^{25} 1.4360 (Found: C, 87.4, H. 13.1. C_9H_{16} requires C, 87.0; H, 13.0%), *m/e* 124 (M^+), δ 1.0 (3 H, d, *J* 6 Hz, CH_3), 4.7—5.2 (2 H, m, $=CH_2$), and 5.3—6.2 (1 H, m, CH=), $\nu_{max.}$ 1 635, 990, and 910 cm^{-1}, The ^{13}C n.m.r. spectrum (see Table 1) showed the *cis*/*trans* isomer ratio to be *ca.* 1.2.

Allylcyclohexane (20).—Coupling of cyclohexylmagnesium bromide with allyl bromide as in the preceding experiment,

---

[32] M. P. Dreyfuss, *J. Org. Chem.*, 1963, **28**, 3269.

[33] J. L. Everett and G. A. R. Kosi, *J. Chem. Soc.*, 1950, 3131.

[34] A. P. Krapcho, G. A. Glynn, and B. J. Grenn, *Tetrahedron Letters*, 1967, 215.

[35] S. G. Matsoyan, G. M. Progosyan, R. K. Skripnikova, and L. G. Nikogosyan, *Izvest. Akad. Nauk Arm. S.S.R., Khim. Nauk*, 1962, **15**, 463 (*Chem. Abs.*, 1963, **59**, 7655).

[36] R. Paul and H. Cottin, *Bull. Soc. chim. France*, 1937, **4**, 933.

[37] G. L. Jenkins and J. C. Kellert, *J. Org. Chem.*, 1962, **27**, 624.

[38] J.-P. Battioni and W. Chodkiewicz, *Bull. Soc. chim. France*, 1971, 1824.

and purification of the product by preparative g.l.c. afforded allylcyclohexane, b.p. 75—76° at 52 mmHg, n_D^{25} 1.4487 (lit.,[39] b.p. 68.2—68.5° at 50 mmHg, n_D^{25} 1.4482), δ 0.8—2.1 (13 H, m, CH_2CH), 4.7—5.1 (2 H, m, $=CH_2$), and 5.4—6.1 (1 H, m, $CH=$).

4-*Ethylhepta*-1,6-*diene* (17).—(a) Interaction of allyl bromide with the Grignard reagent prepared from 4-bromohex-1-ene following the general procedure described above afforded a mixture of hydrocarbons shown by g.l.c. [column (*c*), 160°] to contain 40% 4-*ethylhepta*-1,6-*diene*, a sample of which was separated by preparative g.l.c. (Found: C, 87.2; H, 12.7. C_9H_{16} requires C, 87.0; H, 13.0%), *m/e* 124 (*M*$^+$), δ 0.8—1.8 (6 H, m, CH_3CH_2CH), 2.1 (4 H, t, *J* 6 Hz, allylic CH_2), and 4.7—6.3 (6 H, m, $CH=CH_2$). A second product (20%) was tentatively identified as 4,5-diethylocta-1,7-diene, *m/e* 166 (*M*$^+$), δ 0.8—1.8 (12 H, m, CH_3CH_2CH), 2.1 (4 H, t, *J* 3 Hz, allylic CH_2), and 4.7—6.3 (6 H, m, $CH=CH_2$).

(b) A solution of the toluene-*p*-sulphonate of 3-allylhex-5-en-1-ol (400 mg) in ether (5 ml) was added to a suspension of lithium aluminium hydride (250 mg) in ether (5 ml), and the mixture was heated under reflux for 24 h. Work-up in the usual way afforded a colourless oil (50 mg) which was shown by g.l.c. to contain the required hydrocarbon (60%) and 3-allylhex-5-en-1-ol (35%).

3-*Methylenebicyclo*[3.2.1]*octane* (37).—A suspension of methyltriphenylphosphonium iodide (163 mg) and potassium t-butoxide (46 mg) in ether (20 ml) was stirred at room temperature, then cooled to 0°, and stirred whilst a solution of bicyclo[3.2.1]octan-3-one [25] (500 mg) in ether (10 ml) was added dropwise. After being stirred at room temperature for 24 h, the mixture was diluted with water, and the ether layer was washed, dried, and evaporated. The residue was dissolved in light petroleum and chromatographed on silica gel. Distillation of the non-polar fraction afforded the required olefin [40] (300 mg, 61%), b.p. 78—79° at 20 mmHg, δ 1.4—2.3 (12 H, m, ring H) and 4.6 (2 H, s, $=CH_2$), $\nu_{max.}$ 3 040, 1 640, and 890 cm^{-1}.

3-*Methylbicyclo*[3.2.1]*octane*.—The foregoing olefin (275 mg) in ether (25 ml) was hydrogenated at 4 atmospheres pressure over Adam's catalyst. After filtration, the mixture was evaporated, and the residue was distilled to afford 3-methylbicyclo[3.2.1]octane [41] (240 mg, 76%), b.p. 80—85° at 20 mmHg, *m/e* 124 (*M*$^+$). The isomer ratio was shown by g.l.c. [column (*c*)] to be *endo* : *exo* = 3 : 1. Heating of the mixture of isomers with platinum on charcoal catalyst at 180° for 72 h caused a change in the isomer ratio to *endo* : *exo* = 1 : 8.

Bicyclo[4.2.1]*nonane* (33).—An ethereal solution of diazomethane [prepared from toluene-*p*-sulphonylnitrosamide (21 g)] was slowly distilled into a stirred solution of 2-norbornanone (2.0 g) in chloroform (100 ml) and methanol (50 ml) at 0°. The mixture was then stirred at 20° for 54 h, after which time the excess of diazomethane was destroyed by addition of dilute sulphuric acid. The organic layer was then separated, washed, dried, and evaporated. The residual oil (2.0 g) was shown by g.l.c. [column (*b*)] to comprise 2-norbornanone (20%), bicyclo[3.2.1]octan-2-one (13%), bicyclo[3.2.1]octan-3-one (15%), bicyclo[4.2.1]nonan-2-one(32%), and bicyclo[4.2.1]nonan-3-one (20%). Preparative g.l.c. enabled the separation of samples of bicyclo[4.2.1]nonan-2-one, m.p. 90—91° (lit.,[42,43] 91—92, 95—96°) and bicyclo[4.2.1]nonan-3-one, m.p. 115—116° (lit.,[42] 122—123°).

The mixture of bicyclic ketones (2.0 g) was heated with zinc amalgam (1.8 g) and concentrated hydrochloric acid under reflux for 2 h. After being cooled the mixture was extracted with pentane, and the organic layer was washed successively with concentrated sulphuric acid, aqueous sodium carbonate, and water. Evaporation of the dried pentane solution gave an oil (1.6 g) which was shown by g.l.c. [column (*c*)] to contain norbornane (20%), bicyclo-[3.2.1]octane (28%), and bicyclo[4.2.1]nonane (52%). Preparative g.l.c. of the oil gave a sample of bicyclo[4.2.1]-nonane, m.p. 93—95° (lit.,[42] 95—96°), *m/e* 124 (*M*$^+$), ^{1}H n.m.r. identical with that previously described.[44]

Bicyclo[3.3.1]*nonane* (32).—(a) A solution of 9-(1,1,2-trimethylpropyl)-9-borabicyclononane [45] in tetrahydrofuran (11.6 ml; 1.6M) was added to a stirred suspension of powdered sodium cyanide (2.7 g) in tetrahydrofuran. After being stirred at room temperature for 1 h the mixture was cooled to −78° and trifluoroacetic anhydride (11.6 g) was added. The mixture was then allowed to warm up to ambient temperature, and after 1 h a further quantity (19.5 g) of trifluoroacetic anhydride was added. After heating of the mixture at 45° for 18 h, the excess of anhydride was destroyed by addition of sodium hydroxide solution. A mixture of aqueous sodium hydroxide (50 ml, 3M) and hydrogen peroxide (60 ml, 30%) was then added to the mixture which was stirred at 25° for 3 h and at 50° for 30 min. The product was extracted with ether, washed with dilute hydrochloric acid and with aqueous sodium bicarbonate, dried, and chromatographed on silica-gel to afford bicyclo[3.3.1]-nonan-9-one [46] (200 mg, 8%). Reduction of this ketone by the Clemmensen method as previously described [46] afforded a product which was shown by g.l.c. [column (*c*)] to be identical with that prepared by the following method.

(b) Wolff–Kishner reduction of bicyclo[3.3.1]nonane-3,7-dione as previously described [46] afforded the required hydrocarbon (65%) which, after purification by sublimation and crystallisation from methanol, had m.p. 142—144° (lit.,[46] 143—144.5°).

Reduction of 4-*Allyl*-7-*bromohept*-1-*ene with Tributylstannane*.—Accurately weighed samples of tributylstannane, the bromo-compound (1.2 equiv.), and the internal standard (bicyclopentyl), in a volumetric flask, were made up to the mark with n-pentane. Aliquot portions of the solution were pipetted into ampoules (1 ml) containing very small quantities of azobisisobutyronitrile, and the samples were cooled to −78°, deaerated with a stream of nitrogen, sealed, and immersed in a constant temperature bath at the required temperature for 24 h. The ampoules were then opened and the contents analysed by g.l.c. [column (*c*)]. Details of conditions and yields are given in Table 2.

We thank the Australian Research Grants Committee for support.

[5/768 *Received*, 23*rd April*, 1975]

---

[39] C. Azo, T. Kunitake, and K. Watanabe, *Kogyo Kagaku Zasshi*, 1967, **70**, 1001 (*Chem. Abs.*, 1968, **69**, 10,788).

[40] W. Kraus and R. Dewald, *Annalen*, 1965, **689**, 21.

[41] N. A. Belikova, A. A. Bobyleva, A. F. Plate, and Kh. E. Sterin, *Zhur. Org. Khim.*, 1966, **2**, 53.

[42] M. Hartmann, *Annalen*, 1969, **724**, 102.

[43] K. H. Baggaley, J. R. Dixon, J. M. Evans, and S. H. Graham, *Tetrahedron*, 1967, **23**, 299.

[44] D. I. Schuster and F.-T. Lee, *Tetrahedron Letters*, 1965, 4119.

[45] E. F. Knights and H. C. Brown, *J. Amer. Chem. Soc.*, 1968, **90**, 5280, 5283.

[46] C. S. Foote and R. B. Woodward, *Tetrahedron*, 1964, **20**, 687.