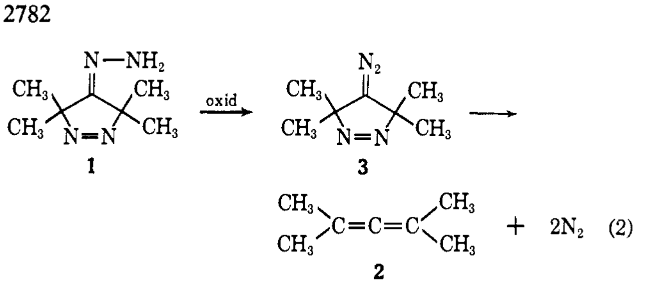
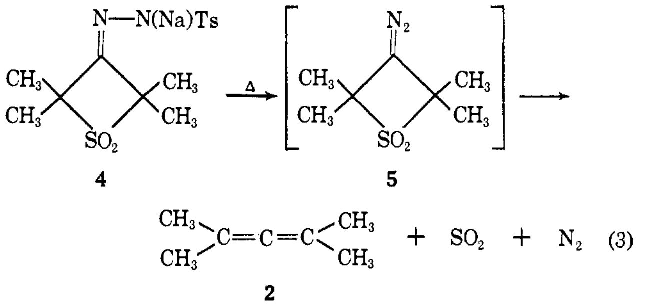


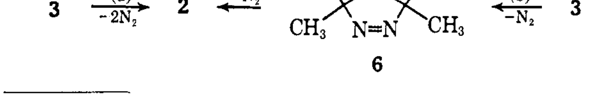
cm^{-1} in cyclohexene) which fades rapidly if the solution is allowed to warm. Although hydrazone **1** is less soluble in hydrocarbon solvents than it is in ether, the yields of allene **2** are but little affected, averaging *ca.* 82% in tetramethylethylene and cyclohexene and 77% in *n*-hexane and *n*-decane.

Cycloelimination leading to the formation of tetramethylallene can also be effected when one of the leaving groups is sulfur dioxide (eq 3). When the dry sodium salt, **4**, of the tosylhydrazone of 2,2,4,4-tetramethyl-3-thietanone dioxide,[1] prepared by treatment of a tetrahydrofuran solution of the tosylhydrazone with excess sodium hydride, was pyrolyzed *in vacuo* at *ca.* 110–160° according to the method of Shechter, *et al.*,[5] a 54–56% yield of tetramethylallene was obtained (presumably *via* diazo compound **5**) along with sulfur dioxide (identified by its glpc retention time on two different columns and by its infrared spectrum) and sodium *p*-toluenesulfinate (identified by its infrared spectrum).



Preliminary attempts to extend this cycloelimination reaction to the sodium salt of 2,2,4,4-tetramethylcyclobutanedione monotosylhydrazone (elimination of carbon monoxide) have not yielded sufficient tetramethylallene to be detectable by glpc.[6]

Since the two cycloelimination reactions would appear to be mechanistically similar, only the first will be discussed. It is clear that diazo compound **3** is a precursor of allene **2**. Whether the two nitrogen molecules are lost simultaneously (pathway a) or stepwise (pathway b) is yet unknown.[7,8] Preliminary attempts to trap carbene **6** with cyclohexene or with tetramethylethylene have been unsuccessful; high yields of tetramethylallene are obtained in these solvents and only trace amounts (<2%) of additional reaction products are detectable by glpc.[9] While failure to trap carbene **6** cannot be used as evidence against its existence,[10] the absence of intramolecular C–H insertion products, expected for a dialkylcarbene with available β-hydrogen atoms,[11,12] suggests that carbene **6**, if formed at all, is extremely short-lived, cycloelimination of nitrogen being faster than intramolecular C–H insertion or intermolecular addition to olefins. Possibly both pathways a and b may be operative.[13]



Experiments designed to test the generality and stereochemical course of this type of cycloelimination reaction are in progress.

Acknowledgment. This research was partially supported by a grant from the Research Corp.

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[4] P. Yates, B. L. Shapiro, N. Yoda, and J. Fugger, *J. Am. Chem. Soc.*, **79**, 5756 (1957).

[5] G. M. Kaufman, J. A. Smith, G. G. Vander Stouw, and H. Shechter, *ibid.*, **87**, 936 (1965).

[6] The products of this reaction are under investigation. See G. Maier and M. Strasser, *Tetrahedron Letters*, 6453 (1966), and references cited therein, for the pyrolysis of similar systems in which cycloelimination does not occur.

[7] For possibly related reactions involving the formation of olefins, see (a) E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Am. Chem. Soc.*, **87**, 934 (1965); (b) D. M. Lemal and E. H. Banitt, *Tetrahedron Letters*, 245 (1964).

[8] Allenes and other cumulenes have been synthesized by means of carbenic rearrangements. See (a) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, pp 61-64, and references cited therein; (b) L. Skattebøl, *Acta Chem. Scand.*, **17**, 1683 (1963); (c) L. Skattebøl, *J. Org. Chem.*, **31**, 2789 (1966); (d) K. G. Untch, D. J. Martin, and N. T. Castellucchi, *ibid.*, **30**, 3572 (1965). For the synthesis of optically active allenes, see (e) W. M. Jones, J. W. Wilson, Jr., and F. B. Tutwiler, *J. Am. Chem. Soc.*, **85**, 3309 (1963); (f) W. M. Jones and J. W. Wilson, Jr., *Tetrahedron Letters*, 1587 (1965). For the synthesis of strained cyclic allenes, see (g) E. T. Marquis and P. D. Gardner, *ibid.*, 2793 (1966). For the synthesis of higher cumulenes, see (h) F. T. Bond and D. E. Bradway, *J. Am. Chem. Soc.*, **87**, 4977 (1965); (i) G. Maier, *Tetrahedron Letters*, 3603 (1965); (j) L. Skattebol, *ibid.*, 2175 (1965).

[9] In some reactions small (*ca.* 4–5%) amounts of 4-keto-3,3,5,5-tetramethylpyrazoline were detected, presumably formed by hydrolysis of hydrazone 1 by the hydrated nickel peroxide.

[10] The 2,2-diphenylcyclopropylidene has been trapped by olefins; see W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *J. Am. Chem. Soc.*, **85**, 2754 (1963).

[11] See ref 8a, pp 52–57.

[12] Treatment of 1,1-dibromotetramethylcyclopropane with methyllithium gives no tetramethylallene, instead yielding 1-methyl-1-isopropenylcyclopropane (95%) whose formation is attributed to intramolecular C–H insertion by initially formed tetramethylcyclopropylidene.[8b] For another viewpoint, see M. J. Goldstein and W. R. Dolbier, Jr., *J. Am. Chem. Soc.*, **87**, 2293 (1965).

[13] W. M. Jones and M. H. Grasley, *Tetrahedron Letters*, 927 (1962).

[14] National Science Foundation Teaching Assistant, summer 1966; National Science Foundation Predoctoral Fellow, 1966–1968.

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The Rearrangement of Phosphorane Boranes

Sir:

The numerous examples of substituent rearrangement from negatively charged boron,[1] and the previously observed[2] reduction of triphenylphosphine oxide by organoboranes, suggested that phosphorane boranes might undergo similar reactions. Although these 1,3-dipolar adducts are in general sufficiently stable to allow isolation under normal conditions,[3,4] rearrangement does in fact occur at higher temperatures.

When triphenylphosphinemethyleneborane[3] (I) is refluxed in chlorobenzene (bp 131°) for 40 min, a clear

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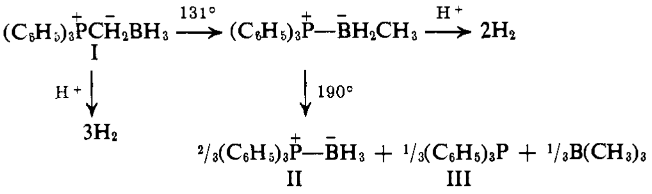
[1] For an analogous rearrangement involving a sulfur ylide and leading references, see J. J. Tufariello and L. T. C. Lee, *J. Am. Chem. Soc.*, **88**, 4757 (1966).

[2] R. Köster and Y. Morita, *Angew. Chem. Intern. Ed. Engl.*, **4**, 593 (1965).

[3] M. F. Hawthorne, *J. Am. Chem. Soc.*, **80**, 3480 (1958); **83**, 367 (1961).

[4] D. Seyferth and S. O. Grim, *ibid.*, **83**, 1613 (1961).

solution results which evolves 2 moles of hydrogen (per mole of I) on treatment with acid.



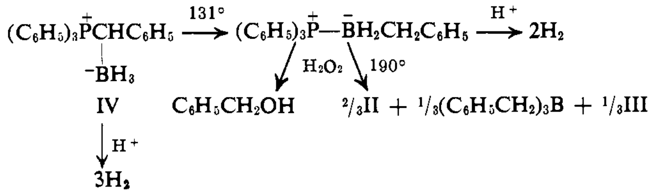
$$\underset{\text{I}}{(C_6H_5)_3\overset{+}{P}\overset{-}{C}H_2BH_3} \xrightarrow{131^\circ} (C_6H_5)_3\overset{+}{P}-\overset{-}{B}H_2CH_3 \xrightarrow{H^+} 2H_2$$

$$\text{I} \xrightarrow{H^+} 3H_2$$

$$(C_6H_5)_3\overset{+}{P}-\overset{-}{B}H_2CH_3 \xrightarrow{190^\circ} {}^2/_3\underset{\text{II}}{(C_6H_5)_3\overset{+}{P}-\overset{-}{B}H_3} + {}^1/_3\underset{\text{III}}{(C_6H_5)_3P} + {}^1/_3B(CH_3)_3$$

On refluxing in decalin (bp 185–190°) for 20 min, rearrangement of I is followed by alkyl redistribution of the boron component. Triphenylphosphineborane (II), which crystallizes from this solvent on cooling, was isolated in 85% yield. Trimethylborane, swept from the reaction vessel by a slow stream of argon, was trapped (in high yield) and identified as the pyridinate. Infrared analysis of the residual decalin solution indicated that it contained essentially only triphenylphosphine (III).

Triphenylphosphinebenzylideneborane[3] (IV) is similarly rearranged by heating for a short time in chlorobenzene or diglyme, as shown by the formation of benzyl alcohol on oxidation with basic peroxide.[5] When a slurry of IV in decalin is refluxed for 15 min, the resulting clear solution on cooling deposits crystals of II, which again could be isolated in good yield.



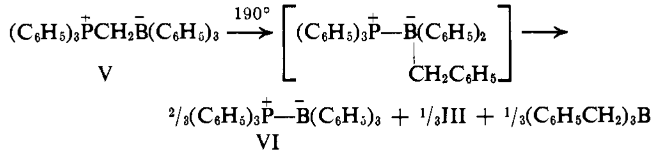
$$\underset{\text{IV}}{\underset{-BH_3}{(C_6H_5)_3\overset{+}{P}CHC_6H_5}} \xrightarrow{131^\circ} (C_6H_5)_3\overset{+}{P}-\overset{-}{B}H_2CH_2C_6H_5 \xrightarrow{H^+} 2H_2$$

$$(C_6H_5)_3\overset{+}{P}-\overset{-}{B}H_2CH_2C_6H_5 \xrightarrow{H_2O_2} C_6H_5CH_2OH$$

$$(C_6H_5)_3\overset{+}{P}-\overset{-}{B}H_2CH_2C_6H_5 \xrightarrow{190^\circ} {}^2/_3\text{II} + {}^1/_3(C_6H_5CH_2)_3B + {}^1/_3\text{III}$$

$$\text{IV} \xrightarrow{H^+} 3H_2$$

The generality of the rearrangement was extended by showing that both aryl and alkyl groups will migrate in analogous phosphorane boranes. Triphenylphosphinemethylenetriphenylborane[4] (V), heated without solvent to 205°, or in decalin for 15 min, gives crystalline triphenylphosphinetriphenylborane[6,7] (VI), indicating migration of the phenyl group followed by phenyl–benzyl redistribution. The formation of a benzylborane species was again demonstrated by alkaline peroxide formation of benzyl alcohol.[5]

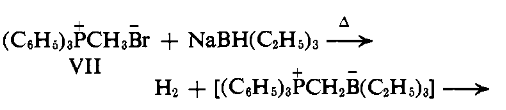


$$\underset{\text{V}}{(C_6H_5)_3\overset{+}{P}CH_2\overset{-}{B}(C_6H_5)_3} \xrightarrow{190^\circ} \left[(C_6H_5)_3\overset{+}{P}-\underset{CH_2C_6H_5}{\overset{-}{B}}(C_6H_5)_2\right] \longrightarrow$$

$${}^2/_3\underset{\text{VI}}{(C_6H_5)_3\overset{+}{P}-\overset{-}{B}(C_6H_5)_3} + {}^1/_3\text{III} + {}^1/_3(C_6H_5CH_2)_3B$$

Evidence has been presented[4] that, unlike borane and triphenylborane, trialkylboranes do not form stable complexes with triphenylmethylenephosphorane. Consequently, the question of possible rearrangement of a trialkylborane adduct (viewed as an especially unstable intermediate) was of particular interest.

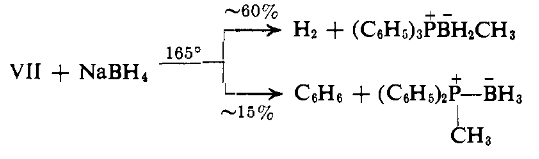
When methyltriphenylphosphonium bromide (VII) is heated in refluxing triethylborane (bp 94°) or diglyme (bp 165°) with sodium triethylborohydride,[8] hydrogen is evolved with concurrent development of a deep red color. The color disappears after a few minutes of refluxing in either solvent. The formation of *n*-propyldiethylborane was demonstrated by vpc.[9]



$$\underset{\text{VII}}{(C_6H_5)_3\overset{+}{P}CH_3\overset{-}{Br}} + NaBH(C_2H_5)_3 \xrightarrow{\Delta}$$

$$H_2 + [(C_6H_5)_3\overset{+}{P}CH_2\overset{-}{B}(C_2H_5)_3] \longrightarrow \text{III} + CH_3CH_2CH_2B(C_2H_5)_2$$

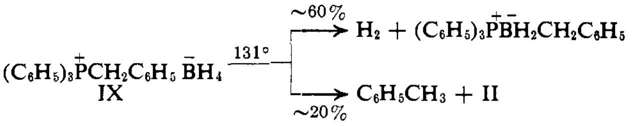
The reaction of phosphonium salts with sodium borohydride has also been investigated. A mixture of VII and sodium borohydride in diglyme on heating evolves hydrogen (60%), again with development and subsequent disappearance of a deep red color. Benzene is formed directly in a side reaction, along with methyldiphenylphosphine (VIII)[10] (presumably as the borane adduct).



$$\text{VII} + NaBH_4 \xrightarrow[\sim 60\%]{165^\circ} H_2 + (C_6H_5)_3\overset{+}{P}\overset{-}{B}H_2CH_3$$

$$\text{VII} + NaBH_4 \xrightarrow[\sim 15\%]{165^\circ} C_6H_6 + (C_6H_5)_2\underset{CH_3}{\overset{+}{P}}-\overset{-}{B}H_3$$

Benzyltriphenylphosphonium borohydride (IX) (mp 150–154° dec), which is obtained in nearly quantitative yield on mixing aqueous solutions of the phosphonium chloride and sodium borohydride, decomposes in boiling chlorobenzene in an analogous manner.



$$\underset{\text{IX}}{(C_6H_5)_3\overset{+}{P}CH_2C_6H_5\,\overset{-}{B}H_4} \xrightarrow[\sim 60\%]{131^\circ} H_2 + (C_6H_5)_3\overset{+}{P}\overset{-}{B}H_2CH_2C_6H_5$$

$$\text{IX} \xrightarrow[\sim 20\%]{131^\circ} C_6H_5CH_3 + \text{II}$$

The mechanism of thermal decomposition of IX is to be contrasted with that of the reaction between the corresponding phosphonium halide and lithium aluminum hydride. The latter proceeds rapidly at room temperature (in diglyme) with negligible gas evolution. Toluene is again formed directly, along with a high yield (>80%) of triphenylphosphine (isolated subsequent to hydrolysis).[11]

The toluene obtained from the triphenylbenzylphosphonium salt (in both the borohydride reaction and the lithium aluminum hydride reduction), as well as the benzene obtained in the reaction of VII, presumably arise *via* hydride attack on positive phosphorus to give intermediate (or transition state) pentavalent phosphorus compounds. Evidence for the formation of a related intermediate pentavalent phosphorus hydride (isolable at low temperature) has recently been presented.[12] Formation of toluene by nucleophilic displacement on carbon would seem to be ruled out by

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(5) The starting material is inert under these conditions; no benzyl alcohol is formed, and the phosphorane borane is recovered in high yield. Lack of reaction may be due to low solubility, as typical phosphonium salts would be expected to react rapidly under these conditions.

(6) G. Wittig and W. Haag, *Chem. Ber.*, **88**, 1654 (1955).

(7) In the absence of solvent, this material (impure) sublimes to the top of the reaction vessel. In a separate experiment, VI, prepared by the method of Wittig and Haag,[6] was partially sublimed to give material of depressed melting point. Presumably sublimation occurs *via* prior dissociation of this complex, and consequently the sublimed VI is contaminated with free triphenylboron and/or triphenylphosphine.

(8) H. C. Brown, H. I. Schlesinger, I. Sheft, and D. M. Ritter, *J. Am. Chem. Soc.*, **75**, 192 (1953).

(9) G. Schomburg, R. Köster, and D. Henneberg, *Z. Anal. Chem.*, 170, 285 (1959); as anticipated, in the higher boiling solvent (diglyme) some isomerization to isopropyldiethylborane occurred.

(10) The formation of III and VIII was demonstrated by mass spectral analysis; borane complexes, it was shown, display strong free phosphine parent peaks.

(11) (a) W. J. Bailey and S. A. Buckler, *J. Am. Chem. Soc.*, **79**, 3567 (1957); (b) W. J. Bailey, S. A. Buckler, and F. Marktscheffel, *J. Org. Chem.*, **25**, 1966 (1960); (c) S. T. D. Gough and S. Trippett, *J. Chem. Soc.*, 4263 (1961).

(12) D. Hellwinkel, *Angew. Chem. Intern. Ed. Engl.*, **5**, 968 (1966).

the fact that no methane is obtained in the reaction of VII.

It is also significant that only trace amounts (<1%) of benzene were formed in the thermal decomposition of IX. The ylide triphenylbenzylidenephosphorane, presumably an intermediate in the borohydride reaction, has been reported[11c] to give benzyldiphenylphosphine on reduction with lithium aluminum hydride. It appears that complex formation between the ylide and generated borane, with subsequent rearrangement, competes more successfully with an alternate cleavage process in the borohydride than in the lithium aluminum hydride reaction.

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(13) National Science Foundation Senior Postdoctoral Fellow, 1966–1967.

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Received March 3, 1967

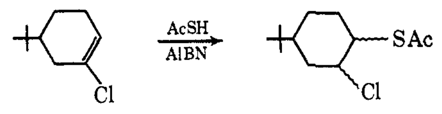
The Stereochemistry of the Free-Radical Addition of Thiolacetic Acid to 2-Chloro-4-*t*-butylcyclohexene

Sir:

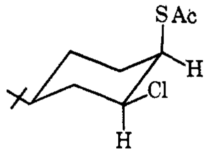
Contemporary studies of radical-chain additions to cyclohexenes[1] have been directed toward determination of both the *trans/cis* addition stereoselectivity and the conformational preference imparted to both the addition and the displacement steps by use of "conformationally fixed" cyclohexenes.[2–5] Although the additions of thiols are not stereospecific in contrast to those of hydrogen bromide,[2,6] *trans* stereoselectivity with a predominance of *trans*-diaxial addition has been observed.[2–4] In at least one case, the results have been attributed to the intervention of an unsymmetrically bridged thiyl radical which was said to account for ~88% of the reaction pathway.[3] The reported dependence of isomeric adduct (*trans/cis*) composition from 1-halocyclohexenes[7] on the ratio of thiol addenda to olefin was not verified with the 4-substituted cyclohexenes.[3–5]

We wish to report a study of the AIBN-initiated addition of thiolacetic acid to 2-chloro-4-*t*-butylcyclohexene (**1**). The *four* possible diastereomeric products were detected and characterized, and reproducible temperature and concentration effects were observed.[8] The results provide significant new data for a more detailed description of the stereochemical course of free-radical additions to cyclohexenes.

Typical runs afforded the following product distributions: 53.2% **2**, 5.7% **3**, 28.3% **4**, and 12.8% **5** in hexane at 63°; 78.7% **2**, 1.6% **3**, 12.8% **4**, and 6.9% **5** in hexane at −78°. A summary of pertinent stereochemical data is given in Table I. The products were separated by gas chromatography and characterized independently; in addition, **2** and **3** were compared with authentic samples. Proton nmr and infrared spectra completely supported the structural assignments.



1 **2-5**



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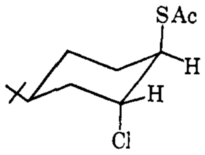

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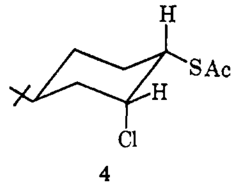

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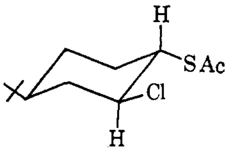

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Table I

Run	Molar ratio[a]	Solvent (temp, °C)[b]	(**2** + **3**)/(**4** + **5**)	**2**/**3**	**4**/**5**
1	1:10	Hexane (63)	1.2	6.3	1.9
2	1:1	Hexane (−78)[c]	4.1	49.2	1.8
3		Pentane (37)	2.2	12.4	2.4
4		Hexane (63)	1.4	9.3	2.2
5		Heptane (86)	1.2	7.5	2.5
6		Heptane (106)	1.2	6.6	2.6
7		Methanol (64)	1.3	6.9	1.8
8	10:1	None (67)	2.4	11.4	2.0
9		Pentane (40)	3.1	15.5	2.4
10		Hexane (63)	2.5	10.0	2.2
11		Heptane (86)	1.8	8.2	2.2
12		Methanol (63)	1.9	7.7	1.8
13	30:1	None (63)	3.0	10.5	2.1
14		Methanol (66)	2.2	8.2	2.0

[a] AcSH:olefin. Most solutions were made by adding AcSH to 3 ml of a 1 *M* solution of **1** in the solvent. [b] Reactions were generally run for 1 hr to 40–60% completion with 5 mole % AIBN. Analyses were by gc; deviations in normalized percentages were ±1.0% for **2** and **4**, and ±0.5% for **3** and **5**. [c] Ultraviolet initiated.

The results unequivocally demonstrate that the relative proportions of adducts vary significantly with changes in the molar ratio of starting materials and with temperature. These variations persisted in solvents of widely different polarity. The ratio of adducts resulting from axial relative to equatorial attachment of the thiyl group in the addition step [(**2** + **3**)/(**4** + **5**)] increases with lower reaction temperatures (runs 2–6, 8–11) and with higher molar ratios of thiol (runs 1, 4, 10; 5, 11; 7, 12, 14; 8, 13).

It is reasonable to attribute these *primary* concentration and temperature effects to reversibility of the addition step. Stereoelectronic control leads to preferential axial attack by the thiyl radical, affording intermediate **6**, whereas **7** would result from less-favored "equatorial attack."[9] This initial preference is at least 4:1 (run 2) and is probably much higher. Elevated temperatures and low thiol concentration favor reversal and

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(1) The stereochemistry of free-radical additions to olefins has been reviewed: B. A. Bohm and P. I. Abell, *Chem. Rev.*, **62**, 599 (1962).

(2) N. A. LeBel, R. F. Czaja, and A. DeBoer, to be published.

(3) P. D. Readio and P. S. Skell, *J. Org. Chem.*, **31**, 759 (1966).

(4) F. G. Bordwell and G. S. Whitney, Abstracts, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1962, p 64Q; F. G. Bordwell, P. S. Landis, and G. S Whitney, *J. Org. Chem.*, **30**, 3764 (1965).

(5) *Cf.* also E. S. Huyser and J. R. Jeffrey, *Tetrahedron*, **21**, 3083 (1965); E. S. Huyser, H. Benson, and H. J. Sinnige, *J. Org. Chem.*, **32**, 622 (1967).

(6) See P. D. Readio and P. S. Skell, *ibid.*, **31**, 753 (1966).

(7) H. L. Goering, D. I. Relyea, and D. W. Larsen, *J. Am. Chem. Soc.*, **78**, 348 (1956).

(8) The synthesis of **1** and the results of other additions to **1** will be reported in the full article. Satisfactory elemental analyses have been obtained for most new compounds reported herein.