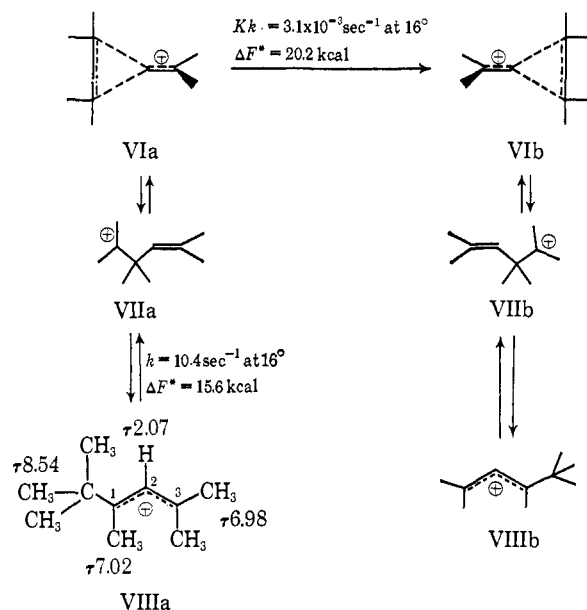


of 300. It is obvious that the cyclopropane ring is heavily involved in electron delocalization during the ionization of V-OBz. All the solvolysis products could be formulated as arising from the "symmetrical homoallyl" ("bisected") cation¹⁰ VI. In solvolysis, the cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement is not competitive, and neither is the rearrangement to the allylic ion VIII.



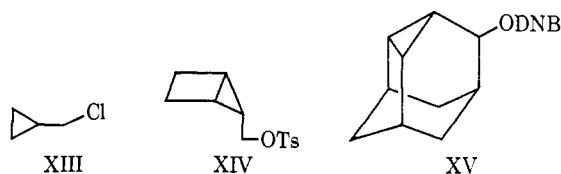
Under conditions of long carbonium ion life in $\text{FSO}_3\text{H-SO}_2\text{ClF}$ or related solvents, the first and only ion visible, even at -125° , is the rearranged allylic ion VIII. For simplicity, this rearrangement may be formulated *via* the classical open ion VII; however, other alternatives are conceivable, for example, *via* a nonclassical transition state between a nonclassical homoallyl ion and VIII. The allylic ion VIII is obviously more stable than VI or any other ion through which the rearrangement from VI to VIII occurs. At higher temperatures, *e.g.*, 16° , the four-methyl scrambling of the *t*-butyl and C_1 -methyl groups occurs with a rate constant of *ca.* 5 sec^{-1} . Since four-methyl scrambling represents the exchange of the methyl group at C_1 with a methyl in the *t*-butyl group, the rate of $\text{VIII} \rightarrow \text{VII}$ is $2k_{1-\text{CH}_3}$. For example, at 16° $k = 10.4 \text{ sec}^{-1}$, ΔF^* being 15.6 kcal/mole. This process is obviously related to the cyclopropylcarbinyl \rightarrow allyl rearrangement and it may proceed through the same rate-determining transition state, but not necessarily.¹¹ If classical homoallylic ion VII is an intermediate in the cyclopropylcarbinyl \rightarrow allyl rearrangement, we cannot determine from the available data whether $\text{VII} \rightarrow \text{VIII}$ or $\text{VII} \rightarrow \text{VI}$ has a higher transition state. We do know,² however, that the rate-determining transition state from $\text{VI} \rightarrow \text{VIII}$ is less than 9.6 kcal/mole above VI and the rate-determining transition state for $\text{VIII} \rightarrow \text{VI}$ must be at least 15.6 kcal/mole above VIII. Thus, VI must be at least 6.0 kcal/mole less stable than VIII

(10) Actually, no evidence is available that the products do not arise at least partially from another species, such as an unsymmetrical homoallylic ion.

(11) Alternatively, if $\text{VII} \rightarrow \text{VI}$ is faster than $\text{VII} \rightarrow \text{VIII}$ or if four-methyl scrambling proceeds directly between VI and VIII, k could be as low as $\frac{1}{2}k_{1-\text{CH}_3}$ ($k = 6.9 \text{ sec}^{-1}$) and ΔF^* could be as high as 15.8 kcal/mole. The variation in k results from statistical factors for each mechanism.

and would obviously not be observed by nmr. Considerably slower than four-methyl scrambling is the observed six-methyl scrambling process. This is best accounted for by way of the cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement ($\text{VIa} \rightleftharpoons \text{VIb}$; rate constant k_r) superimposed on the four-methyl scrambling. The apparent rate constant for six-methyl scrambling ($k = 3.1 \times 10^{-3} \text{ sec}^{-1}$ at 16° ; $\Delta F^* = 20.2 \text{ kcal/mole}$) is $k_r K$, where K , the equilibrium constant for $\text{VIII} \rightleftharpoons \text{VI}$, corresponds to a free-energy difference equal to or greater than 6.0 kcal/mole. Thus, the actual value of k_r is still not available.

It is quite clear that with the hexamethylcyclopropylcarbinyl ion VI, the cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement is much slower than with previously studied symmetrically substituted primary and secondary cyclopropylcarbinyl systems^{4,12} such as XIII, XIV, and XV, which rearrange during solvolysis. With ion VI, the present work shows that in the solvolysing solvents solvent capture is faster than rearrangement to the allylic ion by at least a factor of 50. Similarly, in the $\text{FSO}_3\text{H-SO}_2\text{ClF}$ type of solvent, rearrangement to allylic ion is at least 50 times as rapid as the cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement. With ions from XIII, XIV, and XV, the cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement and solvent collapse occur at comparable rates.¹³ Since we would judge solvent capture of the ions from XIII, XIV, and XV to be at least as rapid as that of VI, we arrive at the conclusion that the cyclopropylcarbinyl-cyclopropylcarbinyl rearrangements of the ions from XIII, XIV, and XV are faster than that of VI by at least a factor of 10^3 . Additional work is needed to reconcile the remarkable retardation of the cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement for VI with current mechanistic proposals.⁴



(12) (a) R. H. Mazur, W. H. White, D. A. Semenov, C. C. Lee, M. S. Silver, and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 4390 (1959); (b) K. B. Wiberg and A. J. Ashe, III, *ibid.*, **90**, 63 (1968); (c) J. E. Baldwin and W. D. Foglesong, *ibid.*, **90**, 4311 (1968).

(13) In some solvents, the rate of reaction with solvent may be two to three times as fast as that of the cyclopropylcarbinyl rearrangement for the ion in the simple XIII system.^{4,12a}

(14) National Institutes of Health Postdoctoral Fellow, 1967-1969.

C. Dale Poulter,¹⁴ S. Winstein

Contribution No. 2398, Department of Chemistry
University of California, Los Angeles, California 90024

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The Stereochemistry of the Reactions of Secondary Cyclopropyl Bromides with Lithium¹

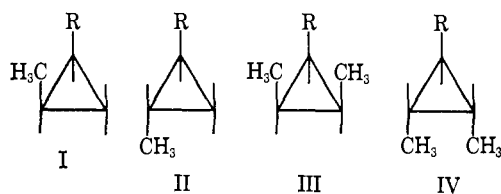
Sir:

The mechanism of the reactions of alkyl halides with metals to form metal alkyls, and the geometry of the cyclopropyl radical, are problems of current in-

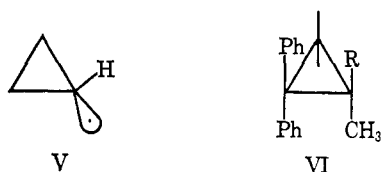
(1) This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

terest; we wish to report some observations that seem to have a bearing on both of them.

In the course of another investigation² we had occasion to convert the two stereoisomeric bromides Ia and IIa and the two stereoisomeric bromides IIIa and IVa to the corresponding 2-cyclopropylethanol (Ib-IVb) *via* the lithio derivatives Ic-IVc. When the latter



a, R = Br; b, R = CH₂CH₂OH; c, R = Li



a, R = $\frac{1}{2}(\text{COO})_2$
b, R = Cl, Br, or I

were formed from the bromides by exchange with *n*-butyllithium and allowed to react with ethylene oxide, the resulting alcohols were formed with complete overall retention of configuration, confirming that cyclopropyllithium derivatives are conformationally stable.³ When, however, the bromides were converted to the lithio derivatives with metallic lithium, racemization took place with partial retention of configuration; detailed product analyses are listed in Table I.

Table I. Isomer Ratios from Direct Metalation of I-IV

Starting compd	% <i>cis</i> alcohol ^a	% <i>trans</i> alcohol ^b
Ia	58	42
IIa	35	65
IIIa	54	46
IVa	31	69

^a *I.e.*, Ic or IIIc. ^b *I.e.*, IIc or IVc.

Fessenden and Schuler⁴ have studied the very complex esr spectrum of irradiated liquid cyclopropane. In addition to lines corresponding to the allyl radical they observed ten weak lines which they attributed to cyclopropyl. If this identification is correct, the low coupling constant (6.5 G) of the α proton would indicate a pyramidal structure (V) for the radical center, since in normal planar radicals the coupling constants are much greater (~ 20 G) (*cf.* ref 5). Unfortunately this identification is not supported by any independent evidence.

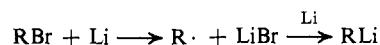
(2) M. J. S. Dewar and J. M. Harris, *J. Am. Chem. Soc.*, **90**, 4468 (1968).

(3) See D. E. Applequist and A. H. Peterson, *ibid.*, **83**, 862 (1961); H. M. Walborsky, F. J. Impastato, and A. E. Young, *ibid.*, **86**, 328 (1964).

(4) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(5) G. A. Peterssoon and A. D. McLachlan, *ibid.*, **45**, 628 (1966).

The loss of configuration observed in the reactions of I-IV (R = Br) with lithium must have taken place prior to the formation of lithio derivatives since these were configurationally stable under the conditions used. A natural explanation would be that the reactions take place by two successive one-electron transfers *via* intermediate cyclopropyl radicals; *i.e.*



Such a mechanism has of course often been suggested for the reaction of alkyl halides with alkali metals, and it is supported by recent work on the reactions of alkyl halides with sodium naphthalenide.⁶

Walborsky and his collaborators⁷ have observed partial retention of configuration in certain reactions involving tertiary cyclopropyl radicals as intermediates, *i.e.*, decomposition^{7a} of the peroxide VIa or reduction of the halides VIb by sodium in liquid ammonia^{7b} or lithium.^{7c} They attributed this to the radical having a rapidly inverting pyramidal structure, the rate of inversion being, however, too low for complete loss of configuration.

The evidence of Walborsky, *et al.*,⁷ refers to a tertiary radical; secondary radicals such as V itself would be expected to invert more readily since they can do so by proton tunneling. Indeed, Applequist and Peterson⁸ found no evidence for retention of configuration in the 2-methylcyclopropyl radicals presumably formed as intermediates in the brominative decarboxylation of silver 2-methylcyclopropanecarboxylate. Our results show that a similar partial retention of configuration can also be observed in reactions which apparently involve secondary cyclopropyl radicals as intermediates.

The partial retention of configuration in our case might be attributed to a cage effect, the intermediate cyclopropyl radical being effectively coplanar but reacting with lithium before it has time to turn over. This, however, seems to us unlikely, because such cage effects seem to be significant only in cases where the reacting species are in contact. In the present case, the bromide must either react with lithium on bromine, in which case the radical is formed not in contact with the metal but separated from it by Br⁻ and solvent molecules, or it must react *trans* to bromine, in which case the cage effect would lead to inversion, not retention. It seems to us more likely that the radical is in fact pyramidal and that its inversion is sufficiently slow for configuration to be partly retained; in this case the barrier to inversion must be quite large since otherwise proton tunneling would be extremely rapid. This argument of course provides further support for the arguments of Fessenden and Schuler⁴ concerning V.

(6) See J. F. Garst and F. E. Barton, II, *Tetrahedron Letters*, 587 (1969).

(7) (a) H. M. Walborsky and Ch. Chen, *J. Am. Chem. Soc.*, **89**, 5499 (1967); (b) H. M. Walborsky, F. P. Johnson, and J. B. Pierce, *ibid.*, **90**, 5222 (1968); (c) H. M. Walborsky and M. S. Aronoff, *J. Organometal. Chem.*, **4**, 418 (1965).

(8) D. E. Applequist and A. H. Peterson, *J. Am. Chem. Soc.*, **82**, 2372 (1960).

Michael J. S. Dewar, J. Milton Harris

Department of Chemistry, The University of Texas
Austin, Texas 78712

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