Perpendicular Allyl and Cyclopropylcarbinyl Cations[1]

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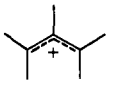
Abstract: The geometry dependence of allyl and cyclopropylcarbinyl resonance in carbonium ions is shown by determination of the solvolysis rates of 2-methylene-1-adamantyl (**5**) and of spiro[cyclopropane-1,2′-adamant-1′-yl] (**6**) derivatives. The double bond in **5** and the cyclopropyl ring in **6** are conformationally locked with respect to the leaving group, with their π systems perpendicularly oriented relative to the leaving groups and the developing cationic "empty" p orbitals. In contrast to the usually observed rate enhancements in allyl and cyclopropylcarbinyl systems, **5** and **6** solvolyze *slower* by factors of 10^4 and 10^3, respectively, than unsubstituted adamantyl model systems. Resonance between the developing cation and the adjacent double bond (in **5**) and the adjacent cyclopropane ring (in **6**) is inhibited, and the adverse inductive effects of the $\sim sp^2$-hybridized substituents produce the rate depressions observed. The magnitudes of these rate depressions are both about 10^6–10^7, when compared with tertiary allyl and cyclopropylcarbinyl models where resonance is not inhibited. While the rotational barriers in tertiary allyl and cyclopropylcarbinyl systems are comparably large, this does not appear to be the case for *primary* systems. Possible reasons for this difference are discussed.

The close analogies in the chemistry of the carbon–carbon double bond and the strained cyclopropane ring single bond become evident if one considers the bent-bond valence bond description of both systems.[4,5]

This analogy extends to molecules in which a positively charged sp^2-hybridized carbon is attached, as in the allyl and cyclopropylcarbinyl cations. Conjugation between the electron-deficient carbinyl carbon and the electron-rich substituents gives rise to a highly geometry-dependent stabilizing interaction, leading to a planar, completely delocalized, symmetrical allyl cation, **1a**,[6] and a cyclopropylcarbinyl cation, most stable in the bisected conformation **2a**, whose delocalization has been described in a variety of ways.[7] These conformations

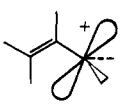


1a

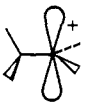
2a

differ from their 90° rotamers, the perpendicular[1] forms **1b** and **2b**, in that they allow maximum overlap between the formally empty p orbital of the carbinyl cation and the π system of the double bond in **1** and the pseudo-π system of the cyclopropyl ring in **2**.

That **1a** and **2a** are indeed the preferred structures of the cations is supported by experimental as well as theoretical evidence. Symmetrically substituted allyl cations exhibit ir spectra which can only be rationalized by assuming symmetrical, planar structures.[6] Also, nuclear magnetic resonance (nmr) spectra have been obtained for several of these species and show the equivalence of the terminal groups.[8] Furthermore, the ultraviolet absorption is in the range predicted by simple HMO calculations,[6] which also confirm the planar structure of the allyl cation.[9] The barrier to rotation of the parent allyl cation, **1a** → **1b**, has been calculated by *ab initio* methods to be 42[10a] and 35 (4–31 G)[10b] kcal/mol; a modified CNDO procedure gave an estimate of 11 kcal/mol[10c] which seems unrealistically low. Experimental values for the rotational barriers of a number of polymethyl-substituted allyl cations have been determined recently to be in the range $\Delta G^{\ddagger}$ 11.7–23.6 kcal/mol.[11] As is discussed in the last section of the present paper, the allyl cation barrier would be expected to be decreased significantly by alkyl substitution.



1b



2b

While the nonplanar structure of the cyclopropylcarbinyl cation makes this system inaccessible to π-electron calculations, the recent advent of semiempirical all-valence-electron calculations[12] and of *ab initio* methods with basis sets amenable for calculations of larger systems[13] has permitted a theoretical examination of this cation. By various methods, the bisected form **2a** is calculated to be more stable than **2b** by 9 (EHT),[14a]

(1) For a preliminary account of this work see P. von R. Schleyer and V. Buss, *J. Amer. Chem. Soc.*, **91**, 5880 (1969). Independently, Ree and Martin[2] carried out similar investigations.

(2) B. Ree and J. C. Martin, *ibid.*, **92**, 1660 (1970); preliminary communication, J. C. Martin and B. Ree, *ibid.*, **91**, 5882 (1969).

(3) Ph.D. Thesis, Princeton University, Princeton, N. J., 1970; Princeton University Fellow, 1968–1969; American Cyanamid Fellow, 1969–1970.

(4) See, *e.g.*, J. March, "Advanced Organic Chemistry: Reactions, Mechanisms and Structure," McGraw-Hill, New York, N. Y., 1968.

(5) (a) C. A. Coulson and E. T. Stewart in "The Chemistry of Alkenes," S. Patai, Ed., Wiley-Interscience, New York, N. Y., 1964; (b) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949); also W. A. Bernett, *J. Chem. Educ.*, **44**, 17 (1967).

(6) N. C. Deno in "Carbonium Ions," Vol. II, G. Olah and P. von R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, p 783.

(7) For recent reviews see (a) M. Hanack and H. J. Schneider, *Fortsch. Chem. Forsch.*, **8**, 554 (1967); *Angew. Chem.*, **79**, 709 (1967); *Angew. Chem., Int. Ed. Engl.*, **6**, 666 (1967); (b) S. Sarel, J. Yovell, and M. Sarel-Imber, *Angew. Chem.*, **80**, 592 (1968); *Angew. Chem., Int. Ed. Engl.*, 7, 577 (1968); (c) H. G. Richey in ref 6, Vol. III; (d) K. B. Wiberg, B. A. Andes, Jr., and A. J. Ashe, ref 6, Vol. III. Extensive bibliographies are given in ref 1 and in P. von R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, **88**, 2321 (1966).

(8) N. C. Deno, *Chem. Eng. News*, **42**, No. 40, 88 (1964).

(9) See, *e.g.*, L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, N. Y., 1966.

(10) (a) S. D. Peyerimhoff and R. J. Buenker, *J. Chem. Phys.*, **51**, 2528 (1969); (b) L. Radom and J. A. Pople, private communication; (c) H. Kollmar and H. O. Smith, *Theor. Chim. Acta*, **20**, 65 (1971).

(11) (a) P. v. R. Schleyer, T. M. Su, M. Saunders, and J. C. Rosenfeld, *J. Amer. Chem. Soc.*, **91**, 5174 (1969); (b) J. M. Bollinger, J. M. Brinich, and G. A. Olah, *ibid.*, **92**, 4025 (1970); (c) N. C. Deno, R. C. Haddon, and E. N. Nowak, *ibid.*, **92**, 6691 (1970).

(12) H. H. Jaffe, *Accounts Chem. Res.*, **2**, 136 (1969).

(13) J. A. Pople, *ibid.*, **3**, 217 (1970).

(14) (a) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964); *Tetrahedron Lett.*, 3819 (1965); (b) T. Yonezawa, H. Nakatsuji, and H. Kato, *Bull. Chem. Soc. Jap.*, **39**, 2788 (1966); (c) K. B. Wiberg, *Tetrahedron*, **24**,

19 (ASMO-SCF),[14b] 26 (CNDO),[14c] 22 (NDDO),[14d] 9 (modified CNDO),[10b] and 17.5 kcal/mol (*ab initio*, STO-3G).[14e]

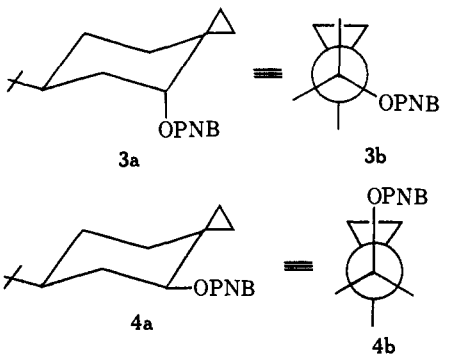
The nmr spectra of unsubstituted as well as substituted cyclopropylcarbinyl ions in strong acid[15,16] are in agreement with the bisected structure **2b** having the greatest stability. Recent nuclear magnetic double resonance studies[17] have suggested a barrier to rotation of 13.7 kcal/mol for the dimethylcyclopropylcarbinyl cation.

Molecules which have a keto group or a C–C double bond in conjugation with a three-membered ring, as in cyclopropyl methyl ketone[18] or vinylcyclopropane,[19] prefer the bisected conformation.[20] Also, the pronounced effect of a cyclopropane ring on the uv absorption of an α-carbonyl group is largest when the cyclopropyl group is bisected with respect to the C=O bond.[21]

The stabilization of an adjacent carbonium ion and the extensive rearrangements usually accompanying the solvolyses of cyclopropylcarbinyl derivatives have long been taken as indication for a significant charge delocalization from the carbinyl carbon to the cyclopropane ring.[7] The geometry dependence of these effects may be shown by either of two ways: the rate acceleration by a cyclopropyl group fixed in the favored bisected conformation in the transition state leading to the carbonium ion, or the rate deceleration to be expected from the inductive electron-withdrawing effect of the sp^2-hybridized cyclopropyl carbons in compounds in which the ring is conformationally locked in the perpendicular position.

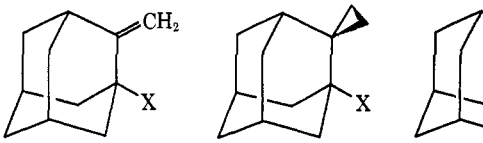
An example has been reported[22] which showed the enhanced solvolytic reactivity of a biscyclopropylcarbinyl system in which the cyclopropane rings were locked into the favorable bisected conformation with respect to the leaving group and developing empty p orbital. On the other hand, an actual *deceleration* by a perpendicular cyclopropyl group has not been observed before,[1,2] though the decreased reactivity in compounds where the bisected form is more difficult to obtain, is well documented.[23]

In our initial approach to this problem, compounds **3a** and **4a** were prepared[24] and their solvolytic behavior was examined. As can be seen from models and the Newman projections **3b** and **4b**, **3a** should most easily lead to the preferred bisected cyclopropylcarbinyl cation conformation, **2a**. On this basis, **3a** was expected to solvolyze much more rapidly than **4a**. In fact, however, the difference in rate constants between **3a** and **4a** was very small (see Table I). This made it probable that the *tert*-butyl-substituted cyclohexane ring in **3b** was insufficiently rigid to lock the solvolysis transition state into the unfavorable perpendicular conformation, **2b**. A more rigid system was needed.



3a **3b** **4a** **4b**

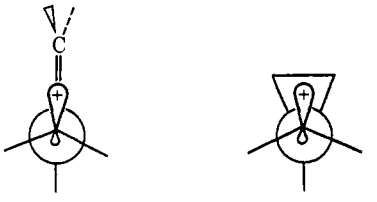
Using the adamantane skeleton as substrate, we have synthesized compounds **5** and **6**, together with the model compounds **7**. As can be seen from the Newman projections **10** and **11** for the cations from **5** and **6**, respectively, the methylene and cyclopropyl groups are held rigidly in the perpendicular forms (which differ from **1b** and **2b** only in the necessarily nonplanar conformation at the bridgehead carbinyl carbon). During the course of this work, compounds **8** and **9** also became available. These afforded an opportunity to assess the steric and inductive effects of remotely attached cyclopropyl and dimethyl groups.



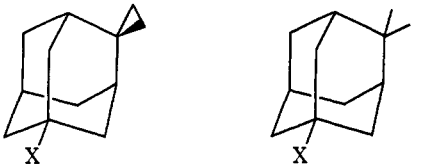
5a, X = OH
5b, X = OTs

6a, X = OH
6b, X = Cl
6c, X = Br

7a, X = OH
7b, X = Cl
7c, X = Br



10 **11**



8a, X = OH
8b, X = Cl

9a, X = OH
9b, X = Cl
9c, X = Br

Syntheses

The synthesis of the parent methylene- (**12**),[25] cyclopropano- (**13**), and *gem*-dimethyladamantane (**14**)[26] has

1083 (1968); (d) V. Buss, unpublished results; (e) L. Radom, J. A. Pople, V. Buss, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 6380 (1970).

(15) G. A. Olah, D. P. Kelly, C. L. Jewell, and R. D. Porter, *ibid.*, **92**, 2544 (1970).

(16) C. U. Pittman and G. A. Olah, *ibid.*, **87**, 2998 (1965); N. C. Deno, J. S. Liu, J. O. Turner, D. N. Lincoln, and R. E. Fruit, *ibid.*, **87**, 3000 (1965); *cf.* C. D. Poulter and S. Winstein, *ibid.*, **91**, 3650 (1969).

(17) D. S. Kabakoff and E. Namanworth, *ibid.*, **92**, 3234 (1970).

(18) L. S. Bartell, J. P. Guillory, and A. P. Parks, *J. Phys. Chem.*, **69**, 3043 (1965).

(19) A. de Meijere and W. Lüttke, *Tetrahedron*, **25**, 2047 (1969).

(20) See, *e.g.*, N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 129 (1964).

(21) E. M. Kosower, *Proc. Chem. Soc. London*, 25 (1962).

(22) L. Birladeanu, T. Hanafusa, B. Johnson, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 2316 (1966).

(23) H. C. Brown and J. D. Cleveland, *ibid.*, **88**, 2015 (1966); T. Sharpe and J. C. Martin, *ibid.*, **88**, 1815 (1966); A. P. Krapcho, R. C. H. Peters, and J. M. Conia, *Tetrahedron Lett.*, 4827 (1968); see, however, G. H. Schmid and A. Brown, *ibid.*, 4695 (1968).

(24) L. Joris, P. v. R. Schleyer, and R. Gleiter, *J. Amer. Chem. Soc.*, **90**, 327 (1968).

(25) P. von R. Schleyer and R. D. Nicholas, *ibid.*, **83**, 182 (1961).

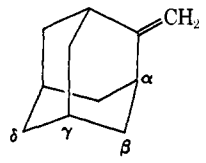
(26) C. W. Woodworth, V. Buss, and P. von R. Schleyer, *Chem. Commun.*, 569 (1968); J. Vais, H. Burkhard, and S. Landa, *Z. Chem.*, **8**, 303 (1968).

Table I. Solvolysis Rate Constants and Derived Data

Compd	Solvent	Temp, °C	k_1, sec^{-1} [a]	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Rel rates, 25°: Chlorides	Tosylates	Bromides
1-Adamantyl chloride	50% ethanol	100.6	$(2.44 \pm 0.06) \times 10^{-3}$	22.2	−11.6			
		75.3	$(2.60 \pm 0.02) \times 10^{-4}$					
		25.0[b]	1.00×10^{-6}			1.0		
6b	50% ethanol	100.2	$(1.53 \pm 0.05) \times 10^{-5}$	26.2	−10.7			
		76.4	$(1.29 \pm 0.03) \times 10^{-6}$					
		25.0[b]	1.64×10^{-9}			1.6×10^{-3}		
8b	50% ethanol	100.6	$(1.79 \pm 0.02) \times 10^{-3}$	23.7	−8.0			
		76.0	$(1.75 \pm 0.03) \times 10^{-4}$					
		25.0[b]	4.27×10^{-7}			0.4		
9b	50% ethanol	100.4	$(1.98 \pm 0.04) \times 10^{-3}$	23.1	−9.4			
		76.0	$(2.10 \pm 0.05) \times 10^{-4}$					
		25.0[b]	5.99×10^{-7}			0.6		
1-Adamantyl tosylate	Acetic acid	25.0[c]	5.15×10^{-4}	20.3	−4.5			
		25.0[d]	4.35×10^{-4}	20.6	−5.0		1.0	
		25.0[e]	5.86×10^{-4}					
5b	Acetic acid	100.4	$(6.26 \pm 0.07) \times 10^{-4}$	28.3	2.0			
		75.3	$(3.75 \pm 0.08) \times 10^{-5}$					
		25.0[b]	3.24×10^{-8}				7.5×10^{-5}	
1-Adamantyl bromide	80% ethanol	25.0[f]	5.1×10^{-7}	22.4	−12.0			1.0
7c	80% ethanol	100.1	$(1.58 \pm 0.01) \times 10^{-3}$	22.7	−11.0			
		75.4	$(1.69 \pm 0.01) \times 10^{-4}$					
		25.0[b]	5.70×10^{-7}					1.1
3a	60% acetone	100.1	$(2.08 \pm 0.24) \times 10^{-4}$	29.2	+2.5			
		75.0	$(1.23 \pm 0.05) \times 10^{-5}$					
		65.0[b]	3.48×10^{-6} [g]					
4a	60% acetone	125.2	$(8.02 \pm 0.56) \times 10^{-4}$	19.6	−24.3			
		100.1	$(1.18 \pm 0.18) \times 10^{-4}$					

[a] Rates determined conductometrically. [b] Calculated. [c] Reference 2. [d] M. L. Sinnott, H. J. Storesund, and M. C. Whiting, *Chem. Commun.*, 1000 (1969). [e] P. v. R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, **81**, 2700 (1961). [f] D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry, and P. v. R. Schleyer, *ibid.*, **92**, 5977 (1970). [g] This value is in reasonable agreement with the rate constant 2.56×10^{-6} sec^{-1}, reported for the parent compound, 4-spiro[2.5]octyl *p*-nitrobenzoate, by M. Hanack and H.-J. Schneider, *Justus Liebigs Ann. Chem.*, **686**, 8 (1965).

been described before, but the preparation of α-substituted derivatives from these hydrocarbons presented major difficulties.



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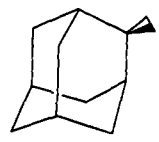

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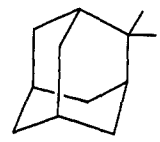

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Except for **14**, direct substitution reactions led either to difficultly separable mixtures of different isomers or to predominant substitution at the γ bridgehead position. That reaction at the γ bridgehead is preferred over the α position is understandable; steric factors favor the less crowded γ position, which is at the same time less sensitive to inductive electron withdrawal than the α position. Conjugative effects—in the form of resonance-stabilized enolic (from adamantanone), allylic, or cyclopropylcarbinyl intermediates, which usually account for attack at the α position of ketones, olefins, and cyclopropyl-substituted paraffins—are limited in their influence because of the unfavorable orbital arrangement in the adamantane systems. This interpretation is supported by solvolysis results (*vide infra*) and by recent experience in the ionic[27] and free-radical[28] bromination of adamantanone, both of which give preferential attack at the γ rather than the α position.

(27) M. A. McKervey, D. Faulkner, and H. Hamill, *Tetrahedron Lett.*, 1911 (1970).

(28) I. Tabushi, Y. Aoyama, and Z. Yoshida, private communication.

Of the three compounds **12**–**14**, the dimethyl group exerts the smallest inductive effect on the adamantane skeleton. The fact that chromic acid oxidation of **14** gives 98% of the γ isomer conforms with the reported sensitivity of the chromic acid oxidation reaction toward steric hindrance.[29]

Oxidation of **13** similarly led to attack at the remote γ bridgehead position exclusively. That not a trace of α product could be detected (glpc), as compared to 2% in the oxidation of **14**, shows that the difference in transition-state energies leading to the two isomers is at least 2–3 kcal/mol larger for **13** than for **14**. Because of the similar requirements of a cyclopropyl and *gem*-dimethyl group, this difference must be largely due to the different inductive effects of these groups.

The structure of the chromic acid oxidation product of **13**, which is obtained crystalline from the crude reaction mixture, could be unambiguously identified only after independent synthesis of the other isomer. In both **6a** and **8a**, the cyclopropyl protons should appear as two pairs of diastereotopic hydrogens giving rise to an A_2B_2 spectrum. The key difference is that **8a** has equivalent geminal hydrogens, whereas in **6a** the vicinal hydrogens are the equivalent ones. In the oxidation product of **13**, however, the four cyclopropyl protons absorb as one sharp singlet. This makes structure **8a**, in which the OH group is further removed from the ring system, more probable, an assignment which later proved to be correct. With **12**, chromic acid oxidation results in attack at the double bond and formation of

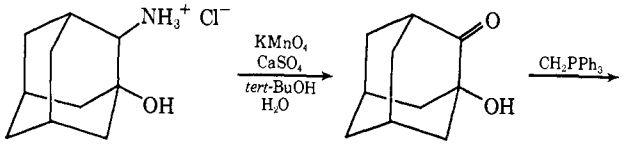
(29) F. Mares and J. Roček, *Collect. Czech. Chem. Commun.*, **26**, 2370 (1961).

adamantanone, a reaction well precedented under these conditions.[30]

Treatment of adamantane with refluxing bromine gives the bridgehead-substituted bromide by an ionic mechanism.[31] Not unexpectedly, bromination of **13** even under mild conditions gave only products in which the cyclopropane ring was attacked.[32] Bromination of **14** gave, in about 70% yield, the two isomers **7c** and **9c**, in a ratio depending on the reaction conditions; **9c** was favored at low temperatures (85°) 2:1, and at higher temperatures (105°) 5:4. The isomers could be separated on an alumina column and are easily distinguished by their nmr spectra; in **9a**, the two methyl groups are diastereotopic and absorb as two singlets 1.0 and 1.12 ppm downfield from TMS. In **7c**, the methyl groups are equivalent and give a single nmr peak at δ 1.22.

Finally, photochlorination[33] of **13** gave the desired chloride **6b**, together with **8b** and the three secondary isomers. No attack occurred at the cyclopropane ring during the primary chlorination reaction; the products, however, quickly became polyhalogenated, and no attempt was made to separate them. The identity of the two tertiary chlorides **6b** and **8b** was established by glpc comparison with independently synthesized compounds.

The initial attempts having failed to give **5** and **6** satisfactorily, it was decided to start with adamantane derivatives already substituted in the 1 and 2 positions. The most promising starting material seemed to be the amino alcohol **15**, prepared by Curran and Angier[34] in a sequence which included as key step a photochemically induced intramolecular nitrene insertion into the 2 position of adamantane. **15** could be oxidized in low yield with $KMnO_4$ in $CaSO_4$ buffered solution[35] to the corresponding keto alcohol **16**, which, in a modified Wittig reaction,[36] gave a 2-methylenadamantan-1-ol (**5a**). Simmons–Smith reaction[37] converted this olefin into **6a**, from which hydrogenation[26] led to **7a**.



15 16

Various interconversions proved the structures of the new compounds unequivocally. The chloride **6b**, obtained from **6a** by treatment with thionyl chloride, was found to be among the photochlorination products of **13**, and the bromide **7c**, obtained from **7a**, proved to be identical with one of the bromination products of **14**. The other isomer, upon aqueous hydrolysis, had the same spectral and analytical properties as the major chromic acid oxidation product of **14** and the hydrogenolysis product of **8a**.

(30) K. B. Wiberg in "Oxidation in Organic Chemistry," K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, p 131.
(31) R. C. Fort and P. von R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).
(32) See, *e.g.*, ref 4, p 117.
(33) G. W. Smith and H. D. Williams, *J. Org. Chem.*, **26**, 2207 (1961).
(34) W. V. Curran and R. B. Angier, *Chem. Commun.*, 563 (1967).
(35) S. S. Rawalay and H. Shechter, *J. Org. Chem.*, **32**, 2139 (1967).
(36) R. Greenwald, M. Cheykowsky, and E. J. Corey, *ibid.*, **28**, 1128 (1963).
(37) H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **81**, 4256 (1959); E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

In order to determine their solvolytic behavior, the alcohols **6**, **8**, and **9** were converted by treatment with thionyl chloride into the corresponding chlorides. Tosylate **5b** was obtained from the alcohol by conversion into its lithium salt and treatment with tosyl chloride. The bromide **7c**, after recrystallization, was used directly for solvolysis.

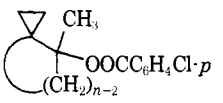
The solvolysis rates were determined conductometrically with a Wayne Kerr Autobalance Universal Bridge B 641. The reactions were run to at least three half-lives. The infinity conductance was determined experimentally as well as by fit of the data to a least-squares computer program. All compounds listed gave satisfactorily first-order behavior (Table I). Product studies were performed by glpc analysis and nmr spectroscopic comparison with authentic materials. In all cases, no rearrangements were observed.[38]

Results and Discussion

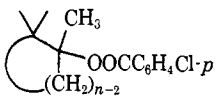
The remotely substituted model compounds **8b** and **9b** solvolyze only slightly more slowly than 1-adamantyl chloride (Table I), indicating no significant substituent effect to be present. Even 2,2-dimethyl-1-adamantyl bromide (**7c**), with the methyl groups adjacent to the reaction site, gives virtually identical rate constants with those from adamantyl bromide. The product is not rearranged.[38] These results indicate that steric factors (steric acceleration through relief of ground-state steric strain, or steric retardation due to greater encumbrance in the transition state or to steric inhibition of solvation) play a minor role with **7c**, and lead to similar expectations with **5b** and **6b**, the substrates upon which the major attention of our work is focused.

Both the exocyclic methylene group in **5b** and the spirocyclopropane ring in **6b** produce major rate *depressions*, $10^{-4.13}$ and $10^{-2.8}$, respectively. (These values agree well with those of Ree and Martin, $10^{-4.06}$ for **5b** and $10^{-3.19}$ for acetolysis of the tosylate of **6a**.[2]) These results are startling since **5b** is formally an allylic system, and **6b** a cyclopropylcarbinyl derivative, where large rate *enhancements* normally are expected. Of course, the unfavorable conformations (**1b** or **10** and **2b** or **11**), coupled with adverse inductive effects,[39] are responsible for these negative effects.

The cyclopropane rings in **17** (n = 5 and 6)[40] accelerate solvolysis over the corresponding tertiary model compounds **18** (n = 5 and 6)[40] by about $10^{4.3}$. In **6b**,



17



18

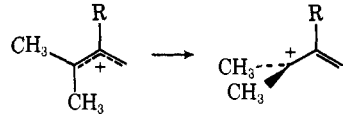
the deceleration is about 10^3. Thus, as we pointed out in the preliminary communication,[1] a rough estimate of the energy difference between conformations **1a** (model **17**) and **1b** (model **6b**), as transition states in tertiary systems, is 10 kcal/mol (corresponding to the 10^7 differ-

(38) In the preliminary communication,[1] we suggested that the solvolysis of 7 was abnormal, but we have found upon closer examination that this was due to an artifact. We are in agreement with Ree and Martin[2] that 7 solvolyzes in an apparently uncomplicated manner.
(39) Ree and Martin[2] present a detailed analysis, with which we concur and will not repeat here.
(40) T. Tsuji, I. Moritani, S. Nishida, and G. Tadokoro, *Tetrahedron Lett.*, 1207 (1967); *Bull. Chem. Soc. Jap.*, **40**, 2344 (1967); T. Tsuji, I. Moritani, and S. Nishida, *ibid.*, **40**, 2338 (1967).

ence in rate). This crude estimate is in quite good agreement with the value of 13.7 kcal/mol determined recently to be the barrier to rotation in the tertiary cyclopropyldimethylcarbinyl cation.[17]

In a similar manner, the barrier to rotation in the vinyldimethylcarbinyl cation can be estimated. The rate constant of vinyldimethylcarbinyl chloride exceeds that of *tert*-amyl chloride by about 10^2.[41] This value, coupled with the relative rate of **5b** ($10^{-4.1}$), corresponds to an estimated expected rate difference of 10^6 (or 9 kcal/mol) for transition states leading to **1a** *vs.* **1b**. On this basis, the barrier to rotation in the vinyldimethyl cation would be expected to be about the same,[10b] or slightly less than, the barrier in the cyclopropyldimethylcarbinyl cation,[17] or about 12–13 kcal/mol.

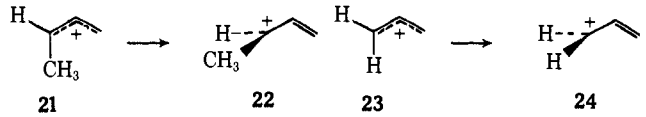
Recently, the rotational barriers of a number of allyl cations have been determined experimentally.[11] While the vinyldimethyl cation (**19**, R = H) was not included in these studies, the available data allow the estimation of the rotational barrier of this ion. The closely related 1,1,2-trimethylallyl cation (**19**, R = CH_3) has a barrier $\Delta G^{\ddagger} = 11.7 \pm 1$ kcal/mol, while the barrier in the 2-chloro-1,1-dimethylallyl cation (**19**, R = Cl) is $\Delta G^{\ddagger} = 12.5 \pm 1$ kcal/mol.[11b] Except for a minor steric effect, the 2 substituents would not be expected to have a significant influence on the rotational barrier. In fact, the barriers of the corresponding 1,3-dimethyl-, 1,2,3-trimethyl-, and 2-halo-1,3-dimethylallyl cations are the same within experimental error.[11,42] A minor $CH_3\cdots CH_3$ steric strain—estimated to be 1 kcal/mol



19 **20**

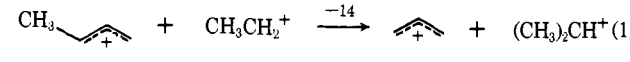
or less[42]—should be present in **19** when R = CH_3 but not when R = H. This strain should be relieved in going from **19**, R = CH_3 to **20**, R = CH_3, thus decreasing the barrier slightly. On this basis, the barrier of the vinyldimethyl cation (**19**, R = H) should be in the range 12.5–13.5 kcal/mol, in excellent agreement with the value already estimated above from our solvolysis data.

It is of interest to predict the barriers of the *cis*-1-methylallyl cation (**21** → **22**) and of the parent allyl cation (**23** → **24**) for which no experimental data yet exist. In making these estimates both steric and elec-

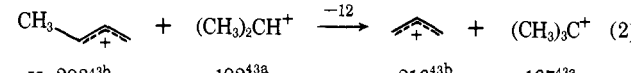


21 **22** **23** **24**

tronic effects have to be taken into account.[11b] The electronic effects arise because a methyl group has a smaller stabilizing effect on a delocalized allyl cation (*e.g.*, **19** or **21**) than on a more localized rotational transition state (*e.g.*, **20** or **21**). This difference can be estimated to be about 12–14 kcal/mol from eq 1 and 2 and available thermodynamic data.[43,44]



ΔH_1, kcal/mol: 203[43b] 219[43a] 216[43b] 192[43a]



ΔH_1, kcal/mol: 203[43b] 192[43a] 216[43b] 167[43a]

Since the steric effects in **19** (R = H) and **21** should be about the same, the rotational barrier of **21** should be about 25–27 kcal/mol, or about 12–14 kcal/mol higher than that of **19** (R = H). The *cis*-1-methyl group in **21** introduces a small (1–2 kcal/mol) steric strain, which should be relieved in the rotation transition state **22**. This should serve to reduce the barrier. Such steric effects are absent in the allyl cation **23**. Hence, its barrier can be calculated to be 38–43 kcal/mol (25–27 + 12–14 + 1–2 kcal/mol). This estimate is in excellent agreement with the results of recent *ab initio* molecular orbital calculations of the allyl cation rotational barrier: 42[10a] and 35 kcal/mol.[10b] While these *ab initio* calculations apply strictly to the gas state, one might expect them also to hold reasonably well in solution.[45]

Similar *ab initio* calculations (however, without complete geometry search) indicate a rotational barrier of only 17.5 kcal/mol for the cyclopropylcarbinyl cation,[14e] a value of only half of the allyl cation. This difference is not present in the barriers of corresponding tertiary cations, cyclopropyldimethylcarbinyl (13.7 kcal/mol)[17] and vinyldimethylcarbinyl (12.5–13.5 kcal/mol; see above). Why do the barriers of the allyl cations vary greatly with substitution, while the barriers in the cyclopropylcarbinyl system seem to be relatively insensitive to the primary or tertiary character of the cationic center? The answer to this question, being investigated by molecular orbital calculations,[10b] may lie in the different modes of electronic stabilization in the allyl and cyclopropylcarbinyl cations. As revealed by eq 1 and 2, a resonance-stabilized allyl cation is influenced less by alkyl substitution than is a hyperconjugation-stabilized alkyl cation. Alkyl groups stabilize cations chiefly through hyperconjugation,[10b,c,46] which appears to be roughly a cumulative effect.[43] This means that a hyperconjugatively stabilized system, like cyclopropylcarbinyl,[14e] will be stabilized additionally by other hyperconjugation-prone substituents, *e.g.*, alkyl groups, with only a slight diminishing of the magnitude of the effect. Thus, both bisected, **2a**, and perpendicular, **2b**, conformations of the cyclopropylcarbinyl cation should be stabilized to roughly comparable amounts by methyl substitution, and little change in the rotational barrier should result. By contrast, the hyperconjugating effect of alkyl groups is much more effective in the per-

(41) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 79.

(42) Based on the 1 kcal/mol nonbonded strain present in *cis*-2-butene: S. W. Benson, F. R. Cruickshank, D. M. Colden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

(43) (a) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970); (b) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 26, 43 (1969).

(44) Based on different data, Olah, *et al.*,[11b] also arrived at the same 12-kcal/mol estimate.

(45) See footnote 9 in J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2540 (1970).

(46) *Cf.* J. E. Williams, V. Buss, L. C. Allen, and P. v. R. Schleyer, *ibid.*, in press.

pendicular conformation **1b** than in the resonance-stabilized planar conformation **1a** of the allyl cation. For this reason, alkyl substituents reduce the rotational barriers in allyl cations markedly.

Conclusions

Steric inhibition of allylic and cyclopropylcarbinyl resonance can be achieved in the cations derived from the adamantyl derivatives **5b** and **6b**. Instead of the large rate enhancements normally observed due to the presence of adjacent vinyl groups and cyclopropane rings, **5b** and **6b** solvolyze, respectively, 10^4 and 10^3 more slowly than 1-adamantyl model compounds. This rate depression, attributed to the adverse, electron-withdrawing effect of sp^2 centers adjacent to the bridgehead where ionization is taking place,[2,39] contributes to the rotational barriers of the allyl and cyclopropylcarbinyl cations. These barriers result from a resonance or hyperconjugative *stabilization* of the bisected conformations **1a** and **2a**, as well as from an inductive *destabilization* of the perpendicular conformations **1b** and **2b**.

Experimental Section

Spiro[cyclopropane-1,2′-adamantane] (13). To 4 g of zinc–copper couple in 15 ml of absolute ether was added under stirring 1 g of methylene iodide, After the exothermic reaction had started, 8.6 g of methylene iodide and 4.0 g of methyleneadamantane (**12**) in 40 ml of ether were added over 1 hr. After heating for 24 hr at 50°, the solution was poured into 100 ml of 1 *N* HCl and ice. The ether layer was separated, combined with two more other extracts of the aqueous phase, and washed with more 1 *N* HCl, and then with $NaHCO_3$ solution and water. After drying with $MgSO_4$ and evaporation of the solvent, the oily crystalline residue was dissolved in pentane and chromatographed over alumina. Recrystallization from petroleum ether (bp 30–60°) at −60° yielded 3.2 g (80%) of **13**: mp 117–118° (lit.[26] mp 114–117°); ir (CCl_4) 3050, 2975, 1445, 1000, 860 cm^{-1}; nmr (CCl_4) δ 0.2 (sharp s, 4.0, C_2H_4), 0.9 (broad s, 2.0, bridgehead H), and 1.8 (m, 12); mass spectrum *m/e* 162. *Anal.* Calcd for $C_{12}H_{18}$: C, 88.94; H, 11.12. Found: C, 88.77; H, 11.25.

2,2-Dimethyladamantane (14). Hydrogenolysis of 2 g (12.2 mmol) of **13** in 40 ml of acetic acid at 60° and 50 psi pressure for 16 hr using 200 mg of PtO_2 catalyst gave, after the usual work-up, 1.8 g (11 mmol, 90%) of **14**, which after chromatography over alumina and crystallization from petroleum ether at −60°, had a melting point of 141–142° (lit.[26] mp 136–140°); ir (CCl_4) 2990, 1450, 1380, 1360, 1080, 900 cm^{-1}; nmr (CCl_4) δ 1.04 (s, 6, *gem*-dimethyl), 1.4–2.2 (m, 14); 220-MHz nmr (CCl_4)[47] δ 1.00 (s, 6), 1.32 (s, 2, α-C*H*), 1.5 (d, 4, J = 12 Hz, β-CH_2), 1.62 (s, 2, δ-CH_2), 1.76 (s, 2, δ-C*H*), 2.05 (d, 4, J = 12 Hz, β-CH_2); mass spectrum *m/e* 164. *Anal.* Calcd for $C_{12}H_{20}$: C, 87.78; H, 12.22. Found: C, 87.68; H, 12.39.

Photochlorination of 13. A solution of 0.3 g of **13** in 10 ml of CS_2 was irradiated with a 150-W Hanovia mercury lamp while chlorine gas was bubbled through the solution. The progress of the reaction was followed by taking samples, washing them with $NaHCO_3$ solution, and analyzing them (glc) on a Carbowax column, 150 ft × 0.02 in., oven temperature, 130°. The highest concentration of monochloride products was reached after about 1 hr. Two of these products had glc retention times identical with **6b** and **8b**, the three remaining peaks being tentatively assigned to the secondary chlorides. The ratio of products was: **6b**, 25%; **8b**, 45%; secondary chlorides ~10% each.

Spiro[cyclopropane-1,4′-adamantan-1′-ol] (8a). Oxidation of 1.5 g (9.3 mmol) of **13** in a mixture of 20 ml of acetic acid and 20 ml of acetic anhydride with 3 g of CrO_3 at 5° for 24 hr under stirring and extraction of the H_2O-diluted mixture with pentane yielded a crystalline residue, which was subjected, for removal of acetates, to reduction with $LiAlH_4$. Crystallization from heptane gave 1.1 g (6.2 mmol, 67%) of **8a**: mp 139–140°; ir (CCl_4) 3600, 3300, 3060, 2990, 1450, 1350, 1300, 1110, 1095, 900 cm^{-1}; nmr ($CDCl_3$) δ 0.3 (s, 4, C_2H_4 ring), 1.15 (broad s, 2); mass spectrum *m/e* 178. *Anal.* Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.68; H, 10.29.

4,4-Dimethyladamantan-1-ol (9a). (a) From 8a. Hydrogenolysis of 1 g (6.2 mmol) of **8a**, under the conditions described above, yielded 0.9 g (5.0 mmol, 81%) of **9a**, after recrystallization from heptane: mp 98–99°; ir (CCl_4) 3600, 2990, 1450, 1105, 1080, 955, 930 cm^{-1}; nmr (CCl_4) δ 1.0 (s, 6, *gem*-dimethyl); mass spectrum *m/e* 180. *Anal.* Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.84; H, 11.20.

(b) From 14. Oxidation of 0.8 g (1.2 mmol) of **14**, under the conditions described for the preparation of **8a**, gave 0.17 g of a mixture consisting of 98% of **9a** and 2% of its isomer, **7a** (glc analysis of the corresponding chlorides and comparison with authentic material, **7b** and **9b**, synthesized independently).

2,2-Dimethyladamant-1-yl Bromide (7c) and 4,4-Dimethyladamant-1-yl Bromide (9c). Under reflux, 0.5 g (3 mmol) of **14** was heated with 3 ml of Br_2 for 4 hr to 110°. After cooling, the mixture was taken up in 25 ml of CCl_4 and poured over 100 g of crushed ice. Sufficient Na_2SO_3 was added to destroy excess Br_2. The organic layer was separated, washed several times with water, dried ($CaCl_2$), and treated with activated charcoal. The solution was concentrated, and two components separated on a SE-30 column, 8 ft × 0.25 in., at 175°.

The first component, **9c**, showed: retention time, 20 min; oil solidifying at room temperature; ir (CCl_4) 2995, 1465, 1450, 1015 cm^{-1}; nmr (CCl_4) δ 1.0, 1.12 (s, 6, *gem*-dimethyl); mass spectrum *m/e* 242/244. *Anal.* Calcd for $C_{12}H_{19}Br$: C, 59.25; H, 7.82. Found: C, 59.34; H, 7.78.

The second component, **7c**, showed: retention time, 22 min; solid; mp 124–125°; ir (CCl_4) 2995, 1465, 1450, 1380, 1360, 1340, 1015, 855, 700 cm^{-1}; nmr (CCl_4) δ 1.22 (s, 6, *gem*-dimethyl); mass spectrum *m/e* 242/244. *Anal.* Calcd for $C_{12}H_{19}Br$: C, 59.25; H, 7.82. Found: C, 59.18; H, 7.79.

Separation on an alumina column was accomplished using pentane as eluent. Chromatography of **7c** and **9c**—here the former having the shorter retention time—had to be repeated in order to effect complete separation. With this procedure, a third component with longer retention time could be isolated in 20% yield: mp 108–109°; ir (CCl_4) 3000, 1465, 1375, 1260, 1245, 1115, 1020 cm^{-1}; nmr (CCl_4) δ 1.3 (s, 3), 1.65 (broad s, 3), 1.8–2.3 (m, 7), 2.6 (s, 2), 2.8 (s, 1), 3.75 (d, a, J = 10 Hz), 4.17 (d, 1, J = 10 Hz). This component was not identified.

2-Ketoadamantan-1-ol (16). In a mixture of 1.5 g of $CaSO_4$, 5 ml of 2 *N* NaOH, 15 ml of *tert*-butyl alcohol, and 10 ml of water was dissolved 1 g (5 mmol) of 2-aminoadamantan-1-ol hydrochloride (15).[34] Under stirring, a solution of 2 g of $KMnO_4$ in 20 ml of water was added. After 1 hr MnO_2 was dissolved with Na_2SO_3, and the reaction mixture was extracted several times with $CHCl_3$. The combined extracts were washed with 2 *N* HCl, $NaHCO_3$ solution, and water, and dried over $MgSO_4$. The solvent was evaporated, and the residue purified by chromatography over an alumina column: yield, 0.22 g (1.25 mmol, 25%) of **16**; mp 277–279° (lit.[2] mp 278–281°); ir (CCl_4) 3500, 1715, 1450, 1145, 1060, 965, 940, 885 cm^{-1}; nmr ($CDCl_3$) δ 3.8 (s, 1, O*H*), 2.75 (broad s, 1), 2.25 (broad s, 2), 2.1–1.75 (m, 10); mass spectrum *m/e* 166. *Anal.* Calcd for $C_{10}H_{14}O_2$: C, 72.23; H, 8.44. Found: C, 72.24; H, 8.52.

2-Methyleneadamantane-1-ol (5a). In a 25-ml three-necked round-bottomed flask with magnetic stirrer and reflux condenser and connection to a source of dry N_2 was placed 2.03 g of NaH, 47% (40 mmol), which was washed several times with pentane to remove the paraffin. Then 25 ml of dimethyl sulfoxide (DMSO), freshly distilled over calcium hydride, was added and the mixture heated to 70° for 1 hr to generate the methylsulfinyl carbanion. After cooling to room temperature, a solution of 14.3 g (40 mmol) of methyltriphenylphosphonium bromide in 20 ml of DMSO was added and stirring was continued for 2 hr. Then 2 g (13 mmol) of **16** in 20 ml of DMSO was added, and the reaction was kept at 70° for 20 hr. The reaction mixture was poured into 150 ml of ice–water and extracted several times with pentane. The combined pentane extracts were washed with a 1:1 mixture of DMSO and water with saturated NaCl solution and dried over $MgSO_4$. The solution was concentrated and chromatographed on alumina. Recrystallization from petroleum ether gave 1.4 g (8.5 mmol, 65%) of **5a**: mp 180–182° (lit.[2] 181–183°); ir (CCl_4) 3600, 3450, 3085, 1650, 1445, 1120, 1085, 975, 935, 895 cm^{-1}; nmr ($CDCl_3$) δ 4.85 and 4.75 (2 d, 2, J = 1.5 Hz, =CH_2), 2.75 (broad s, 1), 2.3 (broad s, 2), 2.0–1.7 (m, 11); mass spectrum *m/e* 164. *Anal.* Calcd for $C_{11}H_{16}O$: C, 80.45; H, 9.75. Found: C, 80.24; H, 9.68.

(44) We thank Professor A. Allerhand for the 220-MHz spectrum.

Spiro[cyclopropane-1,2′-adamantane-1′-ol] (6a). The synthesis of this compound follows essentially the procedure for the preparation of **13**. Purification of the crude reaction product by chromatography on alumina and recrystallization from petroleum ether yields 70–80% of **6a**: mp 192–194° (lit.[2] mp 192–194°); ir (CCl_4) 3550, 3400, 3050, 1110, 1085, 1010, 975, 935 cm^{-1}; nmr (CCl_4) δ 0.1 and 0.85 (2 g, 2.3 and 2, C_3H_4 ring), 1.15 (broad s, 1), 1.75 (m, 6), 2.1 (m, 7); mass spectrum *m/e* 178. *Anal.* Calcd for $C_{12}H_{18}O$: C, 80.86; H, 10.17. Found: C, 80.81; H, 10.28.

2,2-Dimethyladamantan-1-ol (7a). (a) From 6a. Hydrogenolysis of **6a**, under the conditions described above for the preparation of **14**, yielded 80% of **7a**, which after recrystallization from petroleum ether had a melting point of 220–222° (lit.[2] mp 220–22°); ir (CCl_4) 3650, 3500, 1450, 1110, 1075, 955, 925 cm^{-1}; nmr (CCl_4) δ 1.0 (s, 6, *gem*-dimethyl); mass spectrum *m/e* 180. *Anal.* Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.86; H, 11.23.

(b) From 7c. Hydrolysis of **7c** in water–THF with $AgNO_3$–K_2CO_3 yielded 70–80% of one product, which was identical with **7a** obtained from **6a**, with respect to all analytical and spectral properties.

2-Methyleneadamantane 1-Tosylate (5b). In a 25-ml round-bottomed flask connected to a source of dry N_2, 82 mg (0.5 mmol) of **5a** was dissolved in 10 ml of dry ether and 0.31 ml of 1.6 *M* *n*-butyllithium (0.5 mmol) in hexane was added. After 10 min 95.3 mg (0.5 mmol) of *p*-toluenesulfonyl chloride in 2 ml of ether was added to the stirred reaction mixture. After 24 hr the mixture was washed with 1 *N* HCl, $NaHCO_3$ solution, and water, and dried over $MgSO_4$. Removal of solvent gave an oily residue which was chromatographed over alumina and eluted with ether. Recrystallization from pentane at −60° gave 102 mg (0.32 mmol, 64%) of **5b**: mp 63–64° (lit.[2] mp 58–61°); nmr ($CDCl_3$) δ 7.8 and 7.3 (2 d, 4, J = 8 Hz), 4.86 and 4.68 (2 d, 2, $=CH_2$, J = 1.5 Hz), 2.9–1.3 (m, 17.8 *p*-CH_3 at 2.4).

Spiro[cyclopropane-1,2′-adamantyl 1′-chloride] (6b), Spiro[cyclopropan-1,4′-adamantyl 1′-chloride] (8b), and 4,4-Dimethyladamantyl 1-Chloride (9b). For conversion of the alcohols into the corresponding chlorides, 2 mmol of the alcohol was treated with 2.1 mmol of freshly distilled thionyl chloride at room temperature for 3 hr and then at 80° for 5 more hr. The reaction mixture was evaporated to dryness under vacuum; the residue was dissolved in pentane several times and the solvent was removed. After recrystallization from pentane in a Dry Ice–acetone bath the chlorides were obtained in varying (30–60%) yields and were identified by mass and nmr–ir spectral analysis: **6b**, mp 97–99°; ir (CCl_4) 3000, 1450, 1055, 1015, 875 cm^{-1}; nmr (CCl_4) δ 0.1 and 0.82 (2 q, 4, C_3H_4 ring), 1.1 (broad s, 1), 1.73 (s, 6), 2.1 (s, 6); mass spectrum *m/e* 196/198; **8b**, mp 38–39°; ir (CCl_4) 3000, 1460, 1055, 1015, 885 cm^{-1}; nmr (CCl_4) δ 0.28 (s, 4, C_3H_4) ring), 1.15 (broad s, 2), 1.75 (broad s, 5), 2.15 (broad s, 6); mass spectrum *m/e* 196/198; **9b**, mp 61–62°; ir (CCl_4) 1450, 1395, 1370, 1345, 1295, 1025, 800 cm^{-1}; mass spectrum *m/e* 198/200.

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The Thermal Reorganizations of C_6H_8 Hydrocarbons

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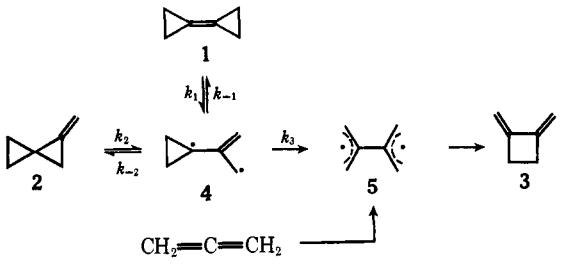
Abstract: Thermal isomerizations of *cis*- and *trans*-2,2,2′,2′-tetramethylbiscyclopropylidene and the further equilibration of their methylenespiropentane products have been quantitatively investigated. The results are discussed in view of the thermal isomerizations of homologous cyclopropylidenecycloalkanes, and *nonplanar* trimethylenemethane diradicals are hypothesized as the key intermediates. An improved synthesis of methylenespiropentane is presented along with its high-activation-energy isomerization to 1,2- and 1,3-dimethylenecyclobutane, and the relationship of this rearrangement to other thermal isomerizations thought to proceed *via* diallyl diradicals is described.

A number of molecules having the empirical formula C_6H_8 (*i.e.*, biscyclopropylidene, methylenespiropentane, and 1,2-dimethylenecyclobutane), and which are related through thermal reorganizations, have been of considerable interest since the degenerate reorganization of 1,2-dimethylenecyclobutane was first investigated by Gajewski and Shih[2a] and by Doering and Dolbier[2b] in 1967. These molecules are ostensibly interconverted *via* the pair of diradicals **4** and **5** (Scheme I), which are themselves of no small interest. The thermodynamic driving force is apparently strongly

Scheme I



from **1** → **2**[3] and from **2** → **3**,[3a] with there being a signif-

(1) (a) Alfred P. Sloan Fellow, 1970–1972; (b) NSF–RPCT Participant, Summer 1969; (c) NSF–URP Participant, Summer 1969.

(2) (a) J. J. Gajewski and C. N. Shih, *J. Amer. Chem. Soc.*, **89**, 4532 (1967); (b) W. von E. Doering and W. R. Dolbier, Jr., *ibid.*, **89**, 4534 (1967).

(3) (a) W. R. Dolbier, Jr., *Tetrahedron Lett.*, 393 (1968); (b) J. K. Crandall, D. R. Paulson, and C. A. Bunnel, *ibid.*, 4217 (1969), and personal communication; (c) W. R Dolbier, Jr., K. Akiba, M. Bertrand, A. Bezaguet, and M. Santelli, *Chem. Commun.*, 717 (1970); (d)