(dioxane) 256 (60,000), 274 (sh), 296 (12,750), 306 (12,750), 326 (sh, 1150), 342 (1840), 364 nm (2000); ir (KBr) 3.1, 6.15, 6.23, 6.3 μ; nmr ($CDCl_3$) δ 5.95 (1 H, disappeared upon addition of D_2O), 6.90 (d, J = 9 Hz, 1 H), 7.17 (d, J = 9, 1 H), 7.35–7.85 (m, 6 H), 8.2–8.8 (m, 2 H).

Anal. Calcd for $C_{20}H_{13}O_2Cl$: C, 74.89; H, 4.08; mol wt, 320. Found: C, 75.16; H, 4.05; M^+, 320.

Elution with benzene gave 60 mg of amorphous material which was not characterized. Elution with ethyl acetate gave 200 mg of PQ (40%).

Spiropentylcarbinyl Cation Rearrangement. Stereochemistry of Nucleophilic Attack in a Cyclopropylcarbinyl to Cyclobutyl Cation Rearrangement and Stereochemistry of the Ring Opening of the 1-Cyclopropylcyclopropyl Cation[1]

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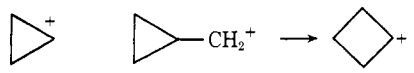
Abstract: Buffered acetolysis of spiropentylcarbinyl tosylate at room temperature gave 5-spirohexyl acetate (**11**), 1-cyclopropylcyclopropyl acetate (**12**), and 2-cyclopropylallyl acetate (**13**) as major identifiable products. Deuterium labeling of the carbinyl carbon verified the hypothesis that **11** was the result of a cyclopropylcarbinyl to cyclobutyl cation rearrangement with C_3 as the migrating carbon while **12** and **13** were the result of a cyclopropylcarbinyl to cyclopropylcarbinyl cation rearrangement with the latter material resulting from subsequent opening of the derived 1-cyclopropylcyclopropyl cation. Acetolysis of 4-methylspiropentylcarbinyl tosylates revealed that the cyclopropylcarbinyl to cyclobutyl rearrangement proceeded with predominant inversion at the migration origin upon nucleophilic attack and that the opening of the 1-cyclopropylcyclopropyl cation was highly stereospecific but did not depend on the orientation of the carbon leaving group, thus leading to the conclusion that the cyclopropyl cation was, in fact, planar. The magnitude and origin of the stabilization of the cyclopropyl cation by an adjacent cyclopropane ring is discussed.

Foremost among small ring cationic ion systems are cyclopropyl[3] and cyclopropylcarbinyl ones[4] (**1** and **2**) because of their surprising and unique reactivity among saturated systems and the relationship of their reactivity and reaction pathways to early[5] and recent theory.[6]



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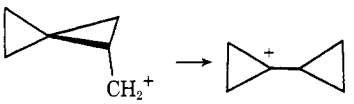
When this work was begun, little was known of the stereochemistry of nucleophilic attack at the migration origin in the cyclopropylcarbinyl to cyclobutyl cation (**3**) rearrangement. This was the case because Roberts very early[4] and Schleyer later on[7] had shown that methyl stereochemical labels placed on the system to answer this question so severely perturbed it that the product emerged with the stereochemical label on the carbinyl carbon. Since a nonclassical or delocalized cation had been invoked for this reaction,[3] and since the delocalized ion hypothesis predicts inversion,[5] the test appeared to be crucial. We attempted to resolve the problem by using the spiropentylcarbinyl system **4** where it was hoped that the additional cyclopropyl group would not lend itself to stabilization of the cation on the carbinyl carbon in **5**. Our concern, however, was deeper than simply testing the nonclassical ion hypothesis. We had already shown[8] that in a similar rearranging system, namely the cyclobutylcarbinyl to cyclopentyl cation, where nonclassical intermediates appeared likely on the basis of fast solvolytic rates, that *net retention* (67%) at the migration origin was observed; thus, the Ingold rule[5] was violated for some reason, and so our concern spread to the lower homolog. As our work proceeded others, Dauben[9] particularly, and Schleyer[4b] later, but most elegantly, showed that complete inversion at the migration origin occurred in the formation of the cyclobutyl product from the cyclopropylcarbinyl system.



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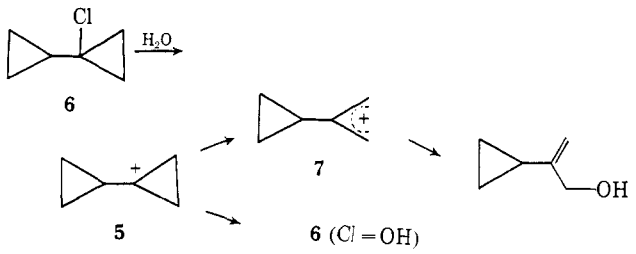
Our results reported below confirm this but also lead to a study of the opening of cyclopropyl cations when stabilized by adjacent cyclopropane rings since

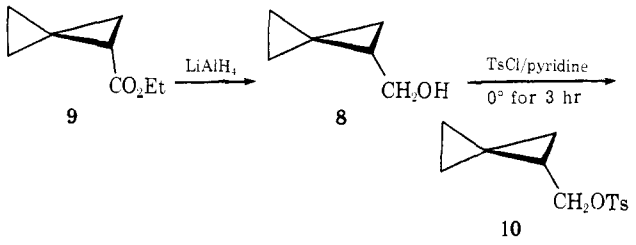
(1) Taken from the Thesis of J. P. O., submitted in partial fulfillment of the M.S. degree requirements of Indiana University, Sept 1971.
(2) Fellow of the Alfred P. Sloan Foundation, 1971–1973.
(3) For review see C. H. De Puy, *Accounts Chem. Res.*, **1**, 33 (1968).
(4) For reviews see (a) R. Breslow in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963. (b) References in F. Majerski and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 665 (1971).
(5) See C. K. Ingold in "Structure and Mechanisms in Organic Chemistry," 1st ed, Cornell University Press, Ithaca, N. Y., 1953, Chapter 14.
(6) For a summary of 5 years of development see R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).
(7) P. v. R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, **88**, 2321 (1966).
(8) J. J. Gajewski, R. E. Lyle, and R. P. Gajewski, *Tetrahedron Lett.*, 1189 (1970).
(9) W. G. Dauben and E. I. Aoyagi, *Tetrahedron*, **26**, 1249 (1970).

what we had hoped would not happen, in fact, happened because the 1-cyclopropylcyclopropyl cation (**5**) was formed from **4** (*vide infra*). The cation **5** was not unknown when our work began. Landgrebe[10] had shown that 1-cyclopropylcyclopropyl chloride (**6**) rearranged to 2-cyclopropyl allyl cation (**7**) upon solvolysis much slower than solvent capture of the unrearranged cation **5**. Because of our interest in spiropentyl systems and the availability of stereochemically labeled monomethyl derivatives,[11] we decided to examine the stereochemistry of the **5** → **7** rearrangement.



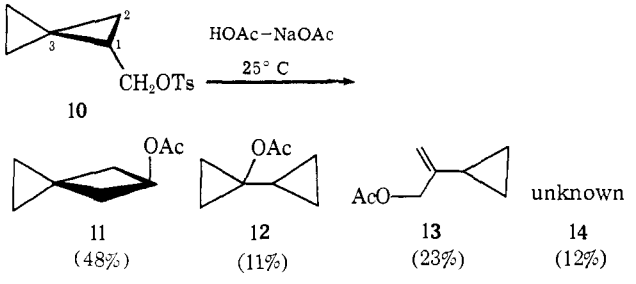
Results

Acetolysis of Spiropentylcarbinyl Tosylate. Spiropentylcarbinol (**8**) was prepared from ethyl spiropentanecarboxylate[11] (**9**) by lithium aluminum hydride reduction and was subsequently converted to the tosylate **10** by the Tipson procedure[12] with care being taken to



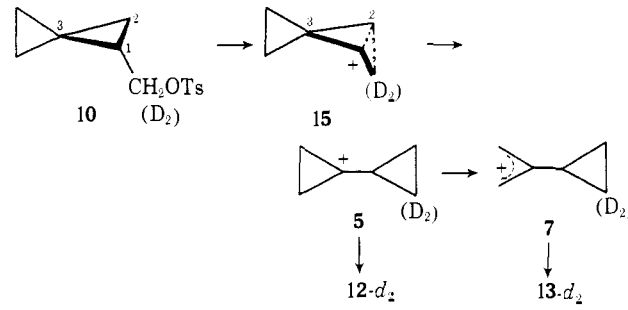
keep the material cold and away from acid.

Acetolysis of **10** in the presence of excess sodium acetate was complete in about 5 hr at room temperature. Work-up and vpc analysis revealed the presence of seven components with retention times similar to C_6 acetates. The four major components, 5-spirohexyl acetate (**11**), 1-cyclopropylcyclopropyl acetate (**12**), 2-cyclopropylallyl acetate (**13**), and an unknown (**14**)



present to the extent of 48, 11, 23, and 12%, respectively, were isolated by preparative vpc for characterization by spectroscopic methods.

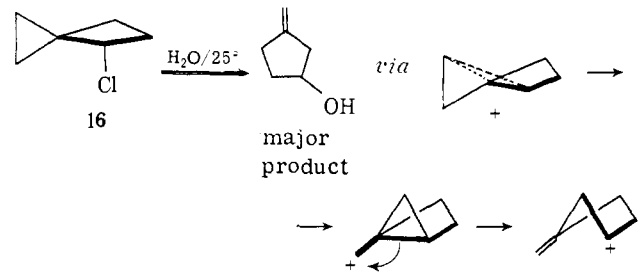
Compound **11** is clearly the result of a simple cyclopropylcarbinyl to cyclobutyl cation rearrangement involving migration of C_3 to the carbinyl cation. On the other hand, compounds **12** and **13** can easily be imagined to arise by migration of C_2 to the carbinyl carbon to give a species like **15** which could undergo a second



migration (of the C_2–C_3 bond) to give the 1-cyclopropylcyclopropyl cation (**5**) which could ring open to the 2-cyclopropylallyl cation (**7**).

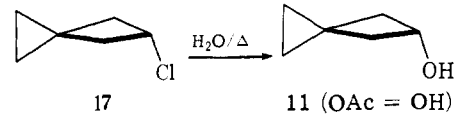
To confirm that the products derived from **10** followed these pathways, α,α-dideuterio-1-spiropentylcarbinyl tosylate (**10**-d_2) was prepared and subjected to acetolysis. Integration of the nmr spectra of the products coupled with reasonable assignments of the resonance lines revealed that, in fact, the gross pathways assumed were correct.

Interestingly, the **12**/**13** ratio (0.37) in the acetolysis of **10** was similar to that from acetolysis of 1-cyclopropylcyclopropyl tosylate (0.47) under comparable conditions.[13] Thus, the two solvolyses probably proceed in similar intermediates with **5** being trapped by solvent slightly faster when derived from **10** than from the structurally similar tosylates. Whether or not **5** is formed directly from **10** or *via* **15** is presently unknown, although if **15** is involved it must be structurally unrelated to whatever species is formed initially in the hydrolysis of 4-spirohexyl derivatives **16**. This latter system gives mostly 3-methylenecyclopentanol (60%) and smaller amounts of other materials.[14] The major product from **16** is not among the major products from **10**, and therefore intermediates from **16**, which presum-



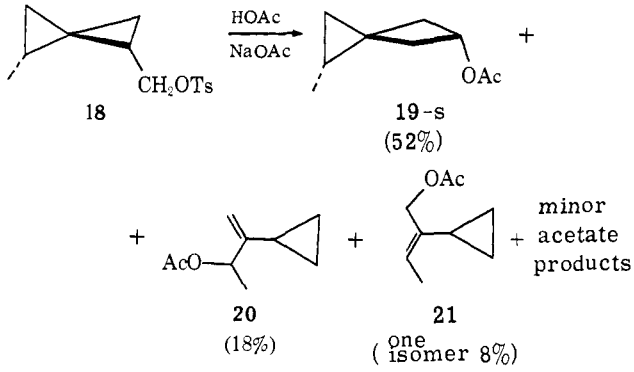
ably have extensive involvement of the cyclopropane electrons, are not involved in the solvolysis of **10**.

Finally, it is important to note that hydrolysis of 5-chlorospirohexane (**17**) gives only 5-spirohexanol[15] (**11**, OAc = OH) so once C_3 migrates to the carbinyl carbon in **10**, to give **11** (OAc = OH) ultimately, no subsequent rearrangements are expected.



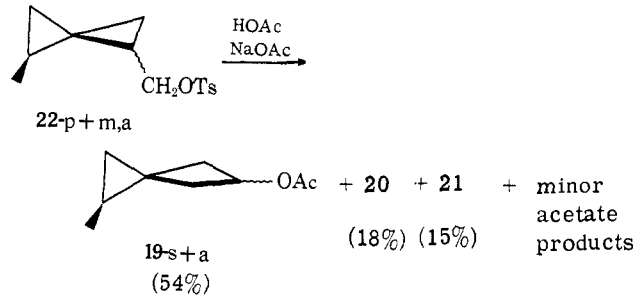
(10) J. A. Landgrebe and L. W. Becker, *J. Amer. Chem. Soc.*, **89**, 2505 (1967).
(11) J. J. Gajewski and L. T. Burka, *J. Org. Chem.*, **35**, 2190 (1970).
(12) R. S. Tipson, *ibid.*, **9**, 235 (1944).
(13) D. A. Howell and J. J. Jewett, *J. Amer. Chem. Soc.*, **93**, 798 (1971).
(14) K. B. Wiberg and J. E. Hiatt, *Tetrahedron Lett.*, 3009 (1968).
(15) D. E. Applequist and W. A. Bernett, *ibid.*, 3005 (1968).

Acetolysis of 4-Methylspiropentylcarbinyl Tosylates. In order to determine the stereochemistry of nucleophilic attack on the migration origin (C_1 of **10**) in the formation of **11**, acetolysis of the 4-methylspiropentylcarbinyl tosylates was in order. In addition to answering this question, the stereochemistry of the ring opening of the 1-cyclopropylcyclopropyl cation (**5**) to the 2-cyclopropylallylic cation (**7**) could also be determined. Thus, *medial,syn*-4-methylspiropentylcarbinyl tosylate (**18**) was prepared from the corresponding ester[11] as above and was subjected to buffered acetolysis at room temperature. Eight acetates were found, five of which were identified by their spectral data, and the three major products were found to be methylated derivatives of **11** and **13**, namely, *syn*-5-methylspiro[3.2]hex-2-yl acetate (**19**-s), 2-cyclopropyl-1-buten-3-yl acetate (**20**), and one isomer of 2-cyclopropyl-2-buten-1-yl acetate (**21**). However, no monomethylcyclopropylcyclopropyl acetate (**12**-Me) was found perhaps indicating that addition of a methyl group to the cyclopropyl cation enhanced the rate of rearrangement to the 2-cyclopropylmethylallyl cation relative to solvent capture. Schleyer[16] estimated that β-methyl groups on cyclopropyl derivatives increased their solvolytic rate by a factor of 70 in the absence of any steric effect so this suggestion has some support. It is important to note that only one isomer of **19** was produced, the syn one (*vide infra*), and that only one isomer of **21** was found.



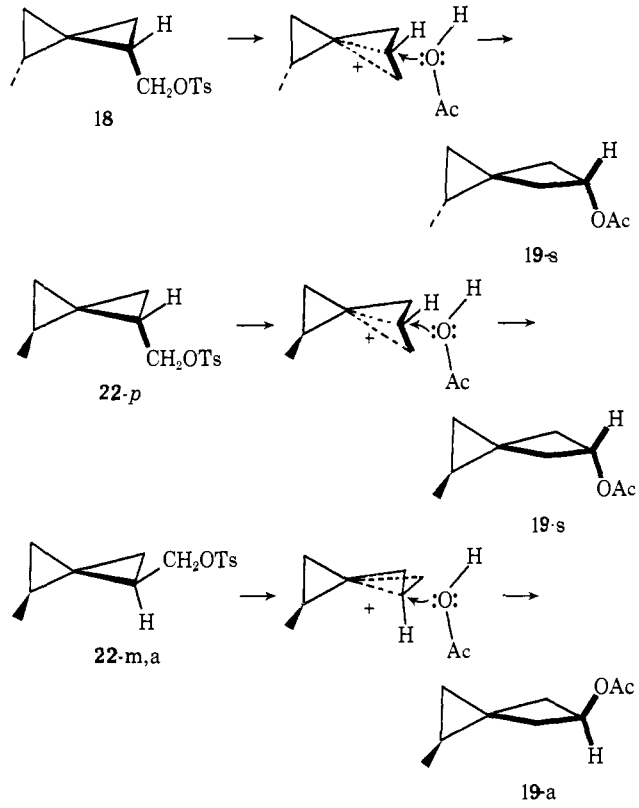
The unknowns did not contain the allyl acetate moiety corresponding to the other isomer of 21.

To assist in the assignment of structures, and, more importantly, to prove that the stereospecificity was not a result of thermodynamic or product development control but of intrinsic selectivity, a 0.8:1.0 mixture of *proximal*- and *medial,anti*-4-methylspiropentylcarbinyl tosylates, **22**-p and **22**-m,a, respectively, were subjected to acetolysis. This time two isomers of **19** were produced in the ratio of 3:2 (54%), **20** was again formed



(18%), and only one isomer of **21** was formed, the same one that was produced from **18**. In addition, 20% of other materials were formed which did not have allylic acetate functionalities like that in **21**.

The formation of two isomers of **19** is not unexpected if nucleophilic attack at the migration origin of **22**-p and **22**-m,a occurred with high stereospecificity. Thus, **22**-p should give the same epimer as **18** and this should be the syn isomer if inversion was the preferred pathway. Analogously, **22**-m,a should give **19**-a.



The demonstration of the stereochemistry of **19**-s and **19**-a rests on the nmr chemical shifts of the proton on C_5, the carbon bearing the acetoxy group. In **19**-a derived from the mixture of **22**-p and **22**-m,a, this proton was at 0.1 ppm higher field than that of **19**-s derived from **18** and at 0.1 ppm higher field than that of **11**, the parent structure, derived from **10**. Since methyl groups in rigid structures, particularly in cyclopropyl and cyclobutyl systems, invariably cause a 0.5 ppm upfield shift of cis hydrogens on adjacent carbons,[17] and since the methyl group on C_2 of **19**-a is situated not unreasonably far from the hydrogen at C_5, the shifts can be rationalized in terms of the assigned stereochemistry. The conclusion, therefore, is that net inversion at the migration origin does occur in nucleophilic attack in a cyclopropylcarbinyl to cyclobutyl cation rearrangement in accord with Dauben's and Schleyer's observations.

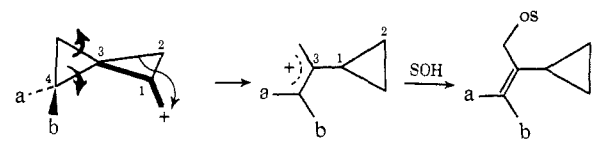
The formation of only one isomer[18a] of **21** from both **18** and the **22**-p and **22**-m,a mixture is remarkable in light of the high directional dependence of disrotatory

(16) P. v. R. Schleyer, G. W. Van Dine, U. Schöllkopf, and J. Paust, *J. Amer. Chem. Soc.*, **88**, 2868 (1966).

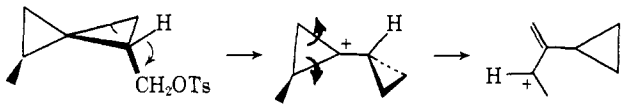
(17) For examples in cyclopropyl and cyclobutyl systems see J. J. Gajewski, *ibid.*, **93**, 4450 (1971); J. J. Gajewski and C. N. Shih, *ibid.*, **91**, 5900 (1969).

(18) (a) While no evidence conclusively excludes the presence of two isomers, it would be remarkable if both isomers of **21** had identical nmr spectra. (b) To a first approximation the position of the carbinyl carbon, up or down with respect to C_4, should be immaterial in these considerations; see Discussion section for further details.

cyclopropyl cation ring opening on the leaving group.[3] If, in the transformation of the spiropentylcarbinyl cation to the 2-cyclopropylallyl one, there is concertion, then the leaving group in the formal cyclopropyl to allyl cation rearrangement is C_2 and so the disrotatory motions[3,6,16] should be



This concerted process predicts that different 2-cyclopropylmethylallyl cations should be produced from **18** and **22**-p (or **22**-m,a) where the methyl group on C_4 is in the a and b position, respectively.[18b] The fact that the same isomer of **21** is produced strongly suggests a series of stepwise rearrangements in the formation of the cyclopropylallyl cations, each step of which is probably concerted, involving a planar cyclopropyl cation intermediate with an attached orthogonal cyclopropane **23** which opens disrotatory in a direction dictated by steric preferences to give, we suggest (see Discussion) the transoid 2-cyclopropylmethylallyl cation (**24**).



22-*p* **23** **24**

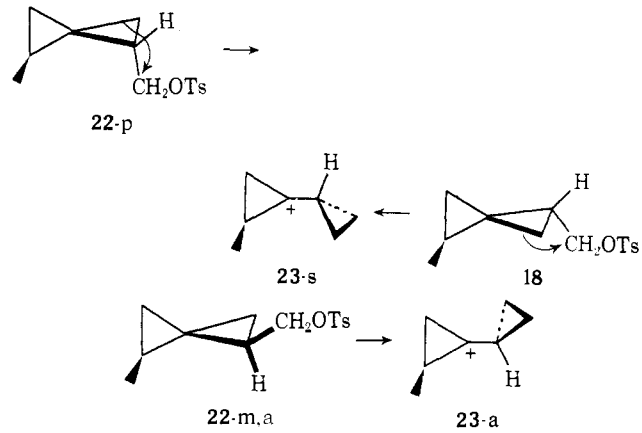
Discussion

There is little need to discuss the overall stereochemistry of the cyclopropylcarbinyl to cyclobutyl cation rearrangement since our results and interpretation are in accord with previous studies.[19] More important is the observation that the 4-methylspiropentylcarbinyl tosylates, **18**, **22**-p, and **22**-m,a gave the same 2-cyclopropyl-2-buten-1-yl acetate. As previously indicated, this is inconsistent with a completely concerted rearrangement unless the allylic acetates interconverted or their precursor cation was reversibly converted to the 1-cyclopropylcyclopropyl cation. While the first point was not checked specifically, it is unlikely that allylic acetates ionize or otherwise interconvert in buffered acetic acid at room temperature;[20] furthermore, a mixture of both cis and trans acetates might be expected since they appear, at least from molecular models, to be equally stable on steric grounds. This latter argument also applies to the question of reversible formation of the 1-cyclopropylcyclopropyl cation from a 2-cyclopropyl allylic one, assuming thermodynamic control in product formation. Thus, the formation of an identical allylic acetate in the acetolyses of **18** and of **22**-p and **22**-m,a is consistent with the intermediacy of a planar cyclopropyl cation like **23**.

(19) We feel, however, compelled to point out that Schleyer's dissection[4b] of k_Δ and k_s pathways in the formation of cyclopropylcarbinyl product from 2-protiohexadeuteriocyclopropylcarbinyl mesylate assumed that complete scrambling of the label in the cyclobutyl product which was, in fact, not the case. Careful reassessment of Schleyer's result assuming the accepted equilibrating bisected cyclopropylcarbinyl intermediates requires that these intermediates interconvert at a rate of about 1.5 times faster than solvent trapping and that only 24% (not 33%) of the cyclopropylcarbinyl product be derived by a so-called direct k_s pathway not involving rearrangement.

(20) R. H. De Wolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956).

The reason for the high stability of the cyclopropyl cation **23** over all others[13] is, no doubt, a result of interaction with the adjacent cyclopropane ring. This interaction is best accomplished in a bisected structure as has been demonstrated experimentally[21] and theoretically.[22] Since this interaction would slow the rate of rotation around the cyclopropane–carbinyl carbon bond, there are two possible structures for cation **23**, syn and anti with the former being easily derived from **18** and **22**-p and the latter from **22**-m,a. These two, of course, would be identical in the absence of the methyl substituent.



These two cations, no doubt, only slowly interconvert relative to ring opening so different product distributions might have been possible in the two acetolyses, even allowing the planar cyclopropyl cation. That this was not the case and that only our methylallyl acetate was formed may simply be the result of steric effect on the ring opening reaction. Molecular models suggest that the opening to produce a transoid methyl allylic cation is more favorable than that to produce a cisoid methyl allylic cation, although the prediction is by no means clear-cut since the position of the transition state along the reaction coordinate is unknown nor are the steric interactions at that point known. Recourse to Schleyer's estimate of relative rates of solvolysis of methyl-substituted cyclopropyl chlorides[16] for an insight into this problem is improper in this case since he assumed that the transition state for the solvolysis is the same as the allylic cation: a reasonable assumption since the rate-determining step was, in fact, the highly endothermic ionization, but in our case, the ionization to **23** is presumably complete and all that matters is the transition state for conversion of **23** to the methyl allylic cation, a process which is probably exothermic.

Interestingly, the cations **23**-s and **23**-a are homologs of the 1-cyclopropylvinyl cations studied by Bergman[23] which have also been shown to be planar or effectively so. That cyclopropyl groups are effective at stabilizing electron-deficient centers is not unexpected: however, it is remarkable that the cyclopropane ring can stabilize the cyclopropyl cation so effectively since there appears to be great resistance to placing a double bond exocyclic onto a cyclopropane ring. In fact, it is instructive to

(21) (a) G. A. Olah, D. P. Kelly, C. T. Jeuell, and R. D. Porter, *J. Amer. Chem. Soc.*, **92**, 2544 (1970); (b) C. U. Pittman and G. A. Olah, *ibid.*, **87**, 2998 (1965).

(22) K. B. Wiberg, *Tetrahedron Lett.*, **84**, 1083 (1968).

(23) (a) S. A. Sherrod and R. G. Bergman, *J. Amer. Chem. Soc.*, **93**, 1925 (1971); (b) D. R. Kelsey and R. G. Bergman, *ibid.*, **93**, 1941 (1971).

compare the Foote[24] and Schleyer[25] predictions for the rate of unassisted solvolysis of cyclopropyl derivations. Foote, using only carbonyl stretching frequencies, indicated that the nonconcerted acetolysis rate of cyclopropyl arenesulfonates should be $10^{-12.5}$ that of cyclohexyl derivatives, while Schleyer, who also included relief of torsional strain, predicted a rate factor of only $10^{-7.2}$. If introduction of a double bond exocyclic to a cyclopropane ring destabilizes the ring by 13.6 kcal/mol,[26] and if the double bond introduction is comparable to introduction of a planar cationic center, then the cyclopropyl derivatives should solvolyze $\epsilon[-(13.6 - 0.6)/RT/1000]$ or $10^{-9.4}$ times as fast as cyclohexyl derivatives in a nonconcerted process. This value, which is a more direct measure of ring strain and torsional strain in the two carbonium ion systems, is intermediate between the Foote and Schleyer estimates, which is reasonable since Schleyer's estimate of torsional strain in cyclopropane is probably too large since he assumed it was the same as in ethane where the C–H orbitals are much closer compared with those in cyclopropane. In general, steric effects are reduced in cyclopropyl systems; for instance, *cis*- and *trans*-1,2-dimethylcyclopropane differ in stability by only 1.07 kcal/mol.[27] Since cyclopropyl derivatives actually solvolyze $10^{-5.3}$ times as fast as cyclohexyl ones,[16] concertion in cyclopropyl solvolyses is worth a factor of $10^{4.1}$ in rate.[28] However, the solvolysis of 1-cyclopropylcyclopropyl tosylate does not give completely rearranged product; yet it solvolyzes $10^{4.2}$ times as fast as 1-isopropylcyclopropyl tosylate which does rearrange completely.[13] The latter reaction must be like the usual electrocyclic reaction but the former is not, so the former system must solvolyze $10^{4.2} \times 10^{4.1} = 10^{8.3}$ times faster than a nonconcerted cyclopropyl solvolysis indicating that stabilization of the cyclopropyl cation by an attached cyclopropane is about of the same stabilization imparted to primary cationic systems by a cyclopropane.

Thus, our finding that the 1-cyclopropylcyclopropyl cation is planar, or at least does not open in a direction dependent on the position of the leaving group (C_2 in this spiropentyl case), is consistent with the large degree of stabilization imparted to the cyclopropyl cation by the cyclopropyl group.

Experimental Section

General. Nuclear magnetic resonance spectra were recorded on Varian A-60, HA-100, and HR-220 spectrometers. Carbon tetrachloride was used as a solvent unless otherwise specified. Chemical shifts are reported as δ values in parts per million relative to TMS. Infrared spectra were obtained with Perkin-Elmer Models 621, 137, and 137 G spectrophotometers in the indicated solvent. Gas–liquid phase chromatography was performed on Varian Aerograph A90P-3 instruments using the indicated columns. Exact masses were obtained using an AEI MS-9 mass spectrometer.

Spiropentylcarbinol (8). To a suspension of 0.50 g (0.013 mol) of lithium aluminum hydride in 20 ml of anhydrous ether was added 1.46 g (0.010 mol) of ethyl carbethoxyspiropentane (**9**). After allowing to stir for 15 min, a freshly prepared, saturated solution of anhydrous sodium sulfate was added slowly until a white precipitate was obtained. The solid was filtered from the solution and washed three times with tetrahydrofuran. The washings were combined with the original filtrate and the solvent was removed. Pure **8** (0.70 g, 0.007 mol) was obtained by passing the residue through a 5 ft × 0.25 in. 20% SE-30 column (T_c = 120°, F 100 ml/min).

The following spectral data for **8** were recorded: ir (neat) 3300, 3040, 2980, 2900, 2860, 1400, 1240 (w), 1160, 1130 (w), 1080, 1040, 1020, 1000, 925 (w), 825 (w), 860, 850 (sh), 820 (w) cm^{-1}; nmr (60 MHz) broad singlet at δ 4.75 (1 H), doublet (J = 7 Hz) at δ 3.46 (2 H), a symmetrical multiplet from δ 1.6 to 1.1 centered at δ 1.35 (1 H), a non-first-order triplet (ratio of peaks 0.8:1:0.8) with equal spacings of 4 Hz between peaks centered at δ 0.94 (1 H), complex multiplet from δ 0.85 to 0.45 (5 H); exact mass 98.0705 (calcd 98.0732).

1-Spiropentylcarbinyl Tosylate (10). The alcohol **8** (0.63 g, 0.0064 mol) was dissolved in 0.2 ml of pyridine, cooled to 0°, and then added dropwise to a solution of 1.33 g (0.0070 mol) of *p*-toluenesulfonyl chloride dissolved in 4 ml of pyridine which was held at 0°. After 2.5 hr, the reaction was quenched with ice. The reaction mixture was taken up in 50 ml of ether, and the ethereal solution was washed twice with 50-ml portions of ice-cold 5% hydrochloric acid, once with 50 ml of cold water, and once with 50 ml of saturated sodium bicarbonate solution. After drying over anhydrous magnesium sulfate, the solvent was removed to give a clear oil which was used without further purification.

The following spectral data for **10** were recorded: ir (neat) 3020, 2950, 2920, 2890, 2860, 2820, 1600, 1490 (w), 1450, 1400, 1360, 1290 (w), 1210 (w), 1190, 1180, 1120 (w), 1100, 1040 (w), 1020 (w), 1005. 935 (br), 865. 835, 815, 790, 780 (sh) cm^{-1}; nmr (60 MHz) doublet, (J = 8 Hz) at δ 7.75 (2 H), doublet (J = 8 Hz) at δ 7.32 (2 H), apparent doublet of doublets (J = 7 Hz and J = 3 Hz) centered at δ 3.99 (2 H), singlet at 2.41 (3 H), complex multiplet from δ 1.6 to 0.8 (2 H), broad singlet with fine splitting at δ 0.7 (5 H); nmr (220 MHz, acetone-d_6) doublet (J = 8 Hz) at δ 7.75 (2 H), doublet (J = 8 Hz) at δ 7.32 (2 H); six-line symmetrical multiplet from δ 3.74 to 3.98 centered at δ 3.37 (2 H), singlet at δ 3.21 (3 H), symmetrical multiplet from δ 1.37 to 1.15 centered at δ 1.28 (1 H). complex multiplet from δ 0.96 to 0.80 (1 H), complex multiplet from δ 0.69 to 0.42 (5 H).

Acetolysis of 1-Spiropentylcarbinyl Tosylate (10). The tosylate **10** (100 μl) was added to a rapidly stirred solution of 0.10 g of sodium acetate in 100 ml of glacial acetic acid. The reaction mixture was allowed to stir for 5–6 hr at room temperature. After this time had elapsed 50 ml of saturated brine was added. Enough water was added to dissolve the precipitate. This mixture was then extracted three times with 50-ml portions of pentane. The pentane extracts were combined, washed with saturated sodium bicarbonate solution until no longer acidic, and dried over anhydrous sodium sulfate. Most of the solvent was removed by flash distillation. Injection of the residue on a 12 ft × 0.25 in. glpc column containing 20% TCEP on Chromosorb W (T_c = 120°, F_c = 100 ml/min) revealed that it was a mixture of at least seven components. The major components (ratio 1:4:1:2) were then separated and collected by preparative glpc. The following spectral data were recorded. The compounds are listed in order of elution from the glpc column.

1-Cyclopropylcyclopropyl acetate (12):[13] ir (CCl_4) 3090, 3015, 2915 (sh), 2877 (w), 1747, 1447, 1411, 1384 (sh), 1362, 1311 (w), 1233, 1178, 1162, 1121 (w), 1094, 1037, 1010, 975, 922, 912 (sh), 892 (w), 857 (w) cm^{-1}; nmr (220 MHz) singlet at δ 1.92 (3 H), complex multiplet from δ 1.73 to 1.57 (1 H), complex multiplet from δ 0.73 to 0.63 (2 H), complex multiplet from δ 0.60 to 0.41 (4 H), complex multiplet from δ 0.23 to 0.18 (2 H).

5-Acetoxyspirohexane (11): ir (CCl_4) 3075, 2995, 2980, 2935, 2850 (w). 1747, 1450 (sh), 1420, 1373, 1358, 1343, 1230, 1186, 1100, 1043, 1000, 953 (w), 900 (w), 882 (sh) cm^{-1}; nmr (220 MHz) quintet (J = 7 Hz) at δ 5.10 (1 H), doublet (J = 7 Hz) at δ 2.28 (4 H), singlet at δ 1.96 (3 H), symmetrical multiplet from δ 0.48 to 0.39 centered at δ 0.43 (4 H); exact mass 140.08430 (calcd 140.08372).

Unknown (14): ir (CCl_4) 3070 (w), 3050 (w), 2970, 2932, 2915, 2855, 1740, 1657 (w), 1430 (broad), 1370, 1352, 1298, 1240, 1190, 1075, 1045, 1018, 975, 880 cm^{-1}; nmr (220 MHz) doublet (J = 3 Hz) at δ 5.22 (1 H), doublet (J = 3 Hz) at δ 4.85 (1 H), complex multiplet from δ 2.7 to 2.5 (2 H), complex multiplet from δ 2.4

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to 2.1 (2 H), singlet at δ 2.00 (3 H), singlet at δ 1.70 (2 H), complex multiplet from δ 1.61 to 1.50 (1 H).

3-Acetoxy-2-cyclopropylpropene (13): ir (CCl_4) 3090, 3010 (broad), 2935 (broad), 2880 (w), 1750 1646 (w), 1430 (w), 1320, 1227, 1040, 1015, 930 (sh), 905 (sh), 886 cm^{-1}; nmr (220 MHz) singlet at δ 4.87 (1 H), singlet at δ 4.75 (1 H), singlet at δ 4.45 (2 H), singlet at δ 2.01 (3 H), complex multiplet from δ 1.36 to 1.21 (1 H), complex multiplet from δ 0.73 to 0.57 (2 H), complex multiplet from δ 0.52 to 0.41 (2 H); exact mass 140.0834 (calcd 140.0837).

α,α-Dideuterio-1-spiropentylcarbinol (8-d_2). To a suspension of 0.25 g (0.0007 mol) of lithium aluminum deuteride in 10 ml of anhydrous ether was added 0.50 g (0.0036 mol) of ethyl carbethoxyspiropentane. After allowing to stir for 15 min, a freshly prepared, saturated solution of anhydrous sodium sulfate was added slowly until a white precipitate was obtained. The solid was filtered and washed three times with tetrahydrofuran. The washings were combined and the solvent was removed. Repeated injections on a 5 ft × 0.25 in. 20% SE-30 column (T_c = 120°, F_c = 100 ml/min) gave 0.25 g (0.0025 mol) of the deuterated methanol, **8-d_2**.

The following spectral data for **8-d_2** were recorded: ir (neat) 3300, 3010, 2950, 2930 (sh), 2180, 2070, 1640 (w), 1400, 1310, 1160, 1110, 1090, 1050, 1020, 995, 960, 940 (w), 895 (w), 880, 885 (w), 825 cm^{-1}; nmr (60 MHz) broad singlet centered at δ 4.5 (1 H), complex multiplet from δ 1.47 to 1.27 (1 H), non-first-order triplet (ratio of peaks 0.8:1:0.8, J = 4 Hz) at δ 0.95 (1 H), complex eight-line multiplet from δ to 0.85 to 0.45 (5 H); exact mass 100.0806 (calcd 100.0857).

α,α-Dideuterio-1-spiropentylcarbinyl Tosylate (10-d_2). The alcohol **8-d_2** (0.12 g, 0.0012 mol) was dissolved in 0.2 ml of pyridine, cooled to 0°, and added dropwise to a solution of 0.25 g of *p*-toluenesulfonyl chloride dissolved in 2 ml of pyridine, also kept at 0°. After 2.5 hr, the reaction was quenched with ice. The reaction mixture was taken up in 50 ml of ether and the ethereal solution was washed twice with 50-ml portions of ice-cold 5% hydrochloric acid, once with 50 ml of cold water, and once with 50 ml of saturated sodium bicarbonate solution. After drying over anhydrous magnesium sulfate, the solvent was removed to give 0.20 g (0.0008 mol) of clear oil which was used without further purification.

The following spectral data for **10-d_2** were recorded: ir (neat) 3040, 2960, 2940, 2900, 2840, 2230 (w), 2130 (w), 1910 (w), 1725 (w), 1600, 1490 (w), 1440 (w), 1360, 1300 (w), 1290 (w), 1210 (w), 1190, 1180, 1120, 1100, 1070, 1040 (sh), 1030, 1000, 940 (broad), 885 (sh), 855, 815 (m), 790 (sh), 740 cm^{-1}; nmr (60 MHz) doublet (J = 8 Hz) at δ 7.67 (2 H), doublet (J = 8 Hz) at δ 7.25 (2 H), singlet at δ 2.42 (3 H), complex multiplet from δ 1.60 to 1.20 (1 H), complex multiplet from δ 1.26 to 0.83 (1 H), complex multiplet from δ 0.83 to 0.50 (5 H).

Acetolysis of α,α-Dideuteriospiropentylcarbinyl Tosylate (10-d_2). The acetolysis of **10-d_2** was accomplished in the manner previously described for the acetolysis of **10**. Glpc revealed that after removal of solvent the residue contained at least seven compounds. However, due to the small amount of material available only the three major components could be collected and purified by preparative glpc on a 12 ft × 0.25 in. 20% SE column (T_c = 120°, F_c = 80 ml/min). The following spectral data were recorded.

2′,2′-Dideuterio-1-cyclopropylcyclopropyl acetate (12-d_2): nmr (220 MHz) singlet at δ 1.95 (3 H), symmetrical multiplet centered at 1.67 (1 H), broad singlet with fine splitting at δ 0.71 (2 H), broad singlet with fine splitting at δ 0.58 (2 H), symmetrical multiplet centered at δ 0.49 (1 H), symmetrical multiplet centered at δ 0.24 (1 H).

5-Acetoxy-4,4-dideuteriospirohexane (11-d_2): nmr (220 MHz) triplet (J = 7 Hz) at δ 5.10 (1 H), doublet (J = 7 Hz) at δ 2.30 (2 H), singlet at δ 1.98 (3 H), broad singlet with fine splitting at δ 0.46 (4 H).

3-Acetoxy-2-(2′,2′-dideuteriocyclopropyl)propene (13-d_2). This material was obtained contaminated with **11-d_2** and so integration of the cyclopropyl proton region of **13** was not possible. However, the terminal methylenes, δ 4.87 and 4.75, and the acetoxy bearing methylene at δ 4.45 integrated for one, one, and two protons, respectively, with respect to the acetoxy protons at δ 2.01.

***medial,syn*-4-Methyl-1-spiropentylcarbinyl Tosylate (18)**. *medial,syn*-4-Methyl-1-spiropentylcarbinol[11] was treated with *p*-toluenesulfonyl chloride to give the tosylate **18** in the manner described for forming the tosylate **10** from **8**. After removal of the solvent the following spectral data for **18** were recorded: ir (neat) 3020 (sh), 2930, 2850 (sh), 1600, 1480 (w), 1440, 1350, 1300 (w), 1280 (w), 1210 (w), 1190, 1180, 1090, 1040 (w), 1020, 940, 885, 835, 815, 790, 780 (sh) cm^{-1}; nmr (60 MHz) ($CDCl_3$) doublet (J = 8 Hz) at δ 7.90 (2 H), doublet (J = 8 Hz) at δ 7.45 (2 H), apparent doublet of doublets (J = 7 Hz and J = 4 Hz) at δ 4.03 (2 H), singlet at δ 2.49 (3 H), complex multiplet from δ 1.90 to 1.20 (2 H), broad singlet from δ 1.1 to 0.85 with fine splitting (5 H), triplet (J = 4 Hz) at δ 0.58 (1 H), complex multiplet from δ 0.43 to 0.30 (1 H).

Acetolysis of *medial,syn*-4-Methyl-1-spiropentylcarbinyl Tosylate (18). The tosylate **18** was solvolyzed in glacial acetic acid in the manner described for the acetolysis of **10**. Glpc indicated that the residue, after solvent removal, was a mixture of at least seven compounds in the ratio of 1:2:26:9:3:2:4. The compounds were separated and purified by passing through a 12 ft × 0.25 in. 20% LAC-2-R-446 column (T_c = 100°, F_c = 75 ml/min). The following spectral data were recorded. Thd compounds are listed in order of elution from the glpc column.

5-Acetoxy-4-methylene-1-hexene (2%): ir (CCl_4) 3077 (w), 2981, 2931 (w), 1736, 1636, 1426 (w), 1366, 1235, 1103 (sh), 1075, 1055 (sh), 1028, 988 (sh), 940 (w), 910, 895 (w) cm^{-1}; nmr (220 MHz) multiplet from δ 5.85 to 5.64 (1 H), quartet (J = 7 Hz) at δ 5.20 (1 H), singlet with fine splitting at δ 5.07 (1 H), singlet with fine splitting at δ 5.01 (2 H), singlet with δ 4.83 (1 H), doublet with fine splitting (J = 7 Hz) at δ 2.76 (2 H), singlet at δ 1.98 (3 H), doublet (J = 7 Hz) at δ 1.29 (3 H).

***medial,syn*-4-Methyl-1-spiropentylcarbinyl acetate (18, OTs = OAc) (4%)**: ir (CCl_4) 3056 (w), 2984, 2950, 2922 (sh), 2893, 2865 (w), 1735, 1440 (w), 1375, 1360, 1272 (sh), 1230, 1085 (sh), 1023, 960 (w) cm^{-1}; nmr (220 MHz) symmetrical eight-line multiplet from δ 3.96 to 3.79 (2 H), singlet at δ 1.98 (3 H), complex nine-line multiplet from δ 1.51 to 1.36 (1 H), doublet (J = 3 Hz) at δ 1.08 (3 H), complex multiplet from δ 1.01 to 0.82 (3 H), complex multiplet with appearance of a triplet with 4 Hz between lines, at δ 0.62 (1 H), complex multiplet from δ 0.42 to 0.36 (1 H).

***syn*-5-Acetoxy-1-methylspirohexane (19-s) (52%)**: ir (CCl_4) 3052 (w), 2982, 2951, 2924, 2864 (w), 1740, 1448 (w), 1422 (w), 1368, 1347 (w), 1238, 1189 (w), 1108, 1080, 1030, 1005 (w) cm^{-1}; nmr (220 MHz) quintet (J = 7 Hz) at δ 5.11 (1 H), complex multiplet from δ 2.33 to 2.09 (4 H), singlet at δ 1.96 (3 H), doublet (J = 7 Hz) at δ 0.93 (3 H), complex multiplet from δ 0.73 to 0.55 (2 H), complex multiplet from δ 0.08 to 0.03 (1 H); exact mass 154.0995 (calcd 154.0994).

3-Acetoxy-2-cyclopropyl-1-butene (20) (18%): ir (CCl_4) 3085, 3005 (sh), 2983, 2935, 2875 (w), 1735, 1641, 1448, 1425, 1367, 1235, 1077, 1058, 1032, 1018, 948, 935, 895, 868 (w), 840 (w) cm^{-1}; nmr (220 MHz) quartet (J = 7 Hz) at δ 5.25 (1 H), singlet with fine splitting at δ 4.84 (1 H), singlet with fine splitting at δ 4.60 (1 H), singlet at δ 1.98 (3 H), doublet (J = 7 Hz) at δ 1.35 superimposed on a complex multiplet from δ 1.37 to 1.20 (total 4 H), complex multiplet from δ 0.71 to 0.59 (2 H), complex multiplet from δ 0.48 to 0.39 (2 H); exact mass 154.1002 (calcd 154.0994).

Unknown (6%): ir (CCl_4) 3075 (w), 2973, 2935, 2876 (w), 2850 (sh), 1737, 1654, 1445, 1428, 1371, 1365, 1235, 1183 (w), 1155, 1120 (w), 1077 (w), 1043 (sh), 1017, 958, 883 cm^{-1}; nmr (220 MHz) broad singlet with fine splitting at δ 5.16 (1 H), broad singlet at δ 4.87 (1 H), broad singlet at δ 4.77 (1 H), complex multiplet from δ 2.60 to 2.35 (3 H), singlet at δ 1.97 (3 H), complex multiplet from δ 1.89 to 1.75 (2 H), doublet (J = 7 Hz) at δ 1.0 (3 H); exact mass 154.0995 (calcd 154.0994).

Unknown (4%): ir (CCl_4) 3036 (w), 2968, 2931, 2915, 2853, 2840 (w), 1734, 1430 (w), 1418 (w), 1370, 1355, 1240, 1198, 1165, 1043, 1015, 968 (w) cm^{-1}; nmr (220 MHz) symmetrical multiplet from δ 5.34 to 5.21 (1 H), symmetrical multiplet from δ 5.09 to 5.0 (1 H), complex multiplet from δ 2.6 to 2.45 (1 H), complex multiplet from δ 2.35 to 2.19 (3 H), singlet at δ 1.95 superimposed on a multiplet from δ 2.0 to 1.77 (total = 5 H), a complex six-line multiplet from δ 1.62 to 1.52 with the appearance of a partially resolved doublet of triplets (J = 7 Hz and J = 3 Hz) (3 H); exact mass 154.0997 (calcd 154.0994).

1-Acetoxy-2-cyclopropyl-2-butene (21) (8%): ir (CCl_4) 3082 (w), 2006, 2930 (w), 2914 (w), 2957 (w), 1738, 1655 (w), 1440 (broad) (w), 1398 (w), 1370, 1353, 1222, 1042, 1015, 952 cm^{-1}; nmr (220 MHz) quartet (J = 7 Hz) at δ 5.59 (1 H), singlet at δ 4.21 (2 H), singlet at δ 1.97 (3 H), doublet (J = 7 Hz) at δ 1.75 (3 H), symmetrical multiplet from δ 1.53 to 1.36 (1 H), complex multiplet from δ 0.71 to 0.60 (2 H), complex multiplet from δ 0.54 to 0.44 (2 H); exact mass 154.0994 (calcd 154.0994).

***proximal*-and *medial,anti*-4-Methyl-1-spiropentylcarbinols (22-p and 22-m,a) (OTS = OH)**. A mixture of *proximal*- and *medial,anti*-1-carbethoxy-4-methylspiropentane (ratio ~0.8:1)[11] was reduced with lithium aluminum hydride to give the corresponding mixture of alcohols **22**-p and **22**-m,a (OTS = OH) in the manner

previously described for the reduction of **9** to **8**. The spectral data agreed with that reported[11] if their spectra of the separate compounds were superimposed on one another for comparison with the spectra recorded for the mixture.

proximal- **and** *medial,anti-***4-Methyl-1-spiropentylcarbinyl Tosylates (22-p and 22-m,a).** A mixture of the tosylates **22** was prepared from the corresponding alcohols in the manner described for the preparation of **10** from **8.**

After removal of the solvent the following spectral data for **22-p** and **22-m,a** were obtained: ir (neat) 3020 (w), 2970, 2930, 2900, 2850, 1595, 1490 (w), 1460, 1400 (sh), 1360, 1340 (sh), 1300 (w), 1290 (w), 1210 (w), 1190, 1180, 1130 (w), 1090, 1050, 1020, 940, 835, 820, 795, 775 cm^{-1}; nmr (100 MHz) complex multiplet from δ 4.26 to 3.76 (2 H), singlet at δ 2.43 (3 H), complex multiplet from δ 1.68 to 0.30 (9 H), the positions of the aromatic ring protons were not recorded because the HA-100 was locked on chloroform.

Acetolysis of *proximal-* **and** *medial,anti-***4-Methyl-1-spiropentylcarbinyl Tosylates.** A mixture of the tosylates **22-p** and **22-m,a** was solvolyzed in acetic acid at room temperature in the manner described for the acetolysis of **10.** After removal of the solvent, glpc indicated that the residue contained at least seven compounds. The four major components (ratio 8:2:1:2) were collected by preparative glpc on a 12 ft × 0.25 in. 20% LAC-2-R-446 column (T_c = 100°, F_c = 75 ml/min). The following spectral data were recorded. The compounds are listed in order of elution from the glpc column.

syn- **and** *anti-***5-Acetoxy-1-methylspirohexane (19-s and 19-a) (54%):** ir (CCl_4) 3056 (w), 2985, 2930, 2900 (sh), 2870 (w), 2850 (w), 1735, 1441, 1420 (w), 1367, 1347, 1230, 1188 (w), 1105, 1080, 1030, 888 (w) cm^{-1}; nmr (220 MHz) quintet (J = 7 Hz) at δ 5.11 (1 H), quintet (J = 7 Hz) at δ 4.99 (1 H), complex multiplet from δ 2.43 to 2.03 (8 H), singlet at δ 1.96 (6 H), overlapping doublets one (J = 7 Hz) centered at δ 0.96 and the other (J = 7 Hz) centered at δ 0.94 (total 6 H), complex multiplet from δ 0.73 to 0.45 (4 H), complex multiplet from δ 0.08 to −0.06 (2 H); exact mass 154.0992 (calcd 154.0994).

3-Acetoxy-2-cyclopropyl-1-butene (20) (18%): ir (CCl_4) 3085, 3003 (sh), 2981, 2932, 2970 (w), 1735, 1638 (w), 1442, 1422 (w), 1365, 1233, 1074, 1055, 1030, 1015, 945, 932, 892 cm^{-1}; nmr (220 MHz) quartet (J = 7 Hz) at δ 5.26 (1 H), broad singlet with fine splitting at δ 4.83 (1 H), broad singlet with fine splitting at δ 4.60 (1 H), singlet at δ 1.98 (3 H), doublet (J = 7 Hz) at δ 1.35 superimposed on a complex multiplet from δ 1.41 to 1.23 (total 4 H), complex multiplet from δ 0.72 to 0.62 (2 H), complex multiplet from δ 0.48 to 0.40 (2 H); exact mass 154.0992 (calcd 154.0994).

Unknown (9%): ir (CCl_4) 3035 (w), 2970, 2931 (sh), 2858, 1733, 1429, 1415 (w), 1368, 1353, 1308 (w), 1237, 1192, 1169, 1064 (sh), 1038, 1015, 969, 893 (w), 835 (w) cm^{-1}; nmr (220 MHz) complex multiplet from δ 5.35 to 5.20 (1 H), complex multiplet from δ 5.16 to 5.05 (1 H), complex multiplet from δ 2.52 to 2.44 (1 H), complex multiplet from δ 2.31 to 2.21 (2 H), complex multiplet from δ 2.21 to 2.14 (1 H), singlet at δ 1.95 (3 H), complex multiplet from δ 1.88 to 1.73 (2 H), complex multiplet from δ 1.61 to 1.52 (3 H); exact mass 154.0992 (calcd 154.0994).

1-Acetoxy-2-cyclopropyl-2-butene (21) (15%): ir (CCl_4) 3085 (w), 3006, 2932, 2915, 2858 (w), 1740, 1655 (w), 1440 (w), 1372, 1357, 1225, 1032, 1018, 954 cm^{-1}; nmr (220 MHz) quartet (J = 7 Hz) at δ 5.59 (1 H), singlet at δ 4.20 (2 H), singlet at δ 1.96 (3 H), doublet (J = 7 Hz) at δ 1.74 (3 H), complex multiplet from δ 1.51 to 1.38 (1 H), complex multiplet from δ 0.71 to 0.60 (2 H), complex multiplet from δ 0.71 to 0.60 (2 H), complex multiplet from δ 0.54 to 0.44 (2 H); exact mass 154.0986 (calcd 154.0994).

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Cyclization of 5-Hexenyl Radicals[1]

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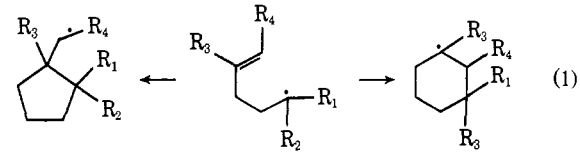
Abstract: The 5-hexenyl radical and its five 1- and 5-methyl-substituted derivatives have been generated by the radical chain reaction of the appropriate bromide and tributyl- or triphenylstannane. Cyclization to cyclopentylmethyl and cyclohexyl radicals competes with reaction of the uncyclized radical with stannane. Analysis of product yields as a function of stannane concentration and failure to detect open chain or cyclohexane products in the reaction of three cyclopentylmethyl bromides with stannanes or silanes indicate that cyclizations are irreversible under our conditions. At a given stannane concentration yields of cyclized products and ratios of six- to five-membered ring products both increase with temperature (40–100°) and with 1 substitution, while 5 substitution also increases the five- to six-membered ring ratio. Combination of our results with absolute rate data of Carlsson and Ingold indicates that 1 substitution slightly retards the rate of radical cyclization to cyclopentylmethyl products but increases the rate of cyclization to cyclohexyl products by a factor of at least 20. Accordingly, rather subtle steric effects as well as energetics determine the rate and direction of ring closure.

The cyclization of 5-hexenyl radicals has been the subject of a number of papers during the past 10 years[3] and is of interest because its ease and direction vary strikingly with radical structure. With highly substituted radicals (*e.g.*, R_1 = COOR, R_2 = CN) Julia has obtained chiefly cyclohexyl derivatives,[4] while several workers have observed that the unsubstituted



(1)

5-hexenyl radical cyclizes almost exclusively to the cyclopentylmethyl radicals[5] and a number of intermediate cases give both types of product.[3] The closure

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