and 5% of 7-*exo*-chloro-1-methylbicyclo[3.1.1]heptan-6-one (**17**). (The fourth unknown compound mentioned above appeared again in about 2% overall yield.)

Zinc–Acetic Acid Reduction of 7-*exo*-Chloro-5-methylbicyclo-[3.2.0]heptan-6-one (18). A mixture of 53 mg of bicycloheptanone **18** and 400 mg of zinc dust in 3 ml of acetic acid was stirred at room temperature for 3 hr. The solution was decanted into 100 ml of water and extracted with petroleum ether (30–60°). The extract was washed five times with water and dried over magnesium sulfate. Removal of the solvent gave 31 mg of 5-methylbicyclo-[3.2.0]heptan-6-one (**21**), identical in all major respects with an authentic sample.[20]

Zinc–Acetic Acid Reduction of 7-*endo*-Chloro-5-methylbicyclo-[3.2.0]heptan-6-one (19). A mixture of 38 mg of bicycloheptanone (**19**) and 250 mg of zinc dust in 2 ml of acetic acid was stirred at 60° for 2 hr. Work-up as above gave 21 mg of 5-methylbicyclo-[3.2.0]heptan-6-one (**21**) containing traces of starting material.

Acknowledgments. The authors are indebted to Mr. Logan C. Stone and Mr. Norbert E. Gilman for technical assistance. We are grateful to Dr. Roger E. Reavill and associates for the nmr spin decoupling experiments.

The Stereochemistry of Cyclopropylcarbinyl Rearrangements. Synthesis and Solvolysis of Cyclopropylcarbinyl-*1,1',1'-trans*-2,3,3-d_6 Methanesulfonate[1]

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Abstract: The stereochemistry of the three different rearrangement processes involving the cyclopropylcarbinyl cation was investigated under solvolysis conditions. The substrate employed, cyclopropylcarbinyl-*1,1',1'-trans*-2,3,3-d_6 mesylate (**1b**), contained only a single hydrogen atom as label, to facilitate pmr analysis of the solvolysis products (60% aqueous acetone, $CaCO_3$): cyclopropylcarbinol-d_6 (**2**), cyclobutanol-d_6 (**3**), and 1-buten-4-ol-d_6 (**4**). The cis-2 hydrogen of **1b** was distributed in these products as follows: in **2**, 77% at the cis-2 (and cis-3) and 23% at the carbinyl (1') positions; in **3**, 60% at the cis-2 (and cis-4) and 40% at the cis-3 positions; and in **4**, *ca.* 32% at the cis-1, *ca.* 30% at the 3, and *ca.* 38% at the 4 positions. Within experimental error all three rearrangement processes, the cyclopropylcarbinyl → cyclopropylcarbinyl, the cyclopropylcarbinyl → cyclobutyl, and the cyclopropylcarbinyl → allylcarbinyl, were completely stereospecific.

Not only is the cyclopropylcarbinyl cation unusually stable, it is also particularly rearrangement prone.[3–10] Three types of rearrangements are possible: ring expansion to give cyclobutyl products, ring opening to give allylcarbinyl products, and a degenerate cyclopropylcarbinyl–cyclopropylcarbinyl isomerization which can be detected by use of isotopic labels. Such labeling experiments further reveal that extensive methylene group scrambling occurs during formation of the cyclobutyl and allylcarbinyl products.[3–5] Very recently it has been possible to demonstrate the degenerate cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement by direct nmr observation of the stable cyclopropylcarbinyl cation in SbF_5–SO_2ClF solution at −80°.[8] On the nmr time scale, equilibration of the three methylene groups is so rapid that only a single signal (consisting of a pair of doublets, one for the three cis and one for the three trans protons) is observed.

Our paper is concerned with the stereochemistry of these three rearrangement processes with the parent cyclopropylcarbinyl cation. When our work was commenced in 1968 very little pertinent information was available. Subsequently, results from a number of laboratories on substituted cyclopropylcarbinyl and cyclobutyl derivatives have indicated all three types of rearrangements to be at least highly stereoselective.[4c,6,7,11] Experimental work on the parent cyclo-

(1) This work was supported by grants from the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society.

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(3) Reviews: Chapters by H. G. Richey, Jr., and by K. B. Wiberg, B. A. Andes, Jr., and A. J. Ashe in "Carbonium Ions," G. A. Olah and P. v. R. Schleyer, Ed., Vol. III, Interscience, New York, N. Y., in press.

(4) Extensive bibliographies may be found in previous papers from this laboratory: (a) P. v. R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, **88**, 2321 (1966); (b) P. v. R. Schleyer and V. Buss, *ibid.*, **91**, 5880 (1969); (c) P. v. R. Schleyer, P. LePerchec, and D. J. Raber, *Tetrahedron Lett.*, 4389 (1969); (d) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 6380 (1970). For additional work, see ref 5–10.

(5) Z. Majerski, S. Borčić, and D. E. Sunko, *Tetrahedron*, **25**, 301 (1969); *Chem. Commun.*, 1636 (1970); and unpublished results.

(6) (a) K. B. Wiberg and G. L. Nelson, *Tetrahedron Lett.*, 4385 (1969); (b) K. B. Wiberg, J. E. Hiatt, and K. Hseih, *J. Amer. Chem. Soc.*, **92**, 544 (1970); (c) K. B. Wiberg, and J. G. Pfeiffer, *ibid.*, **92**, 553 (1970); (d) K. B. Wiberg, V. Z. Williams, Jr., and L. E. Friedrich, *ibid.*, **92**, 564 (1970); (e) K. B. Wiberg, R. A. Fenoglio, V. Z. Williams, Jr., and R. W. Ubersax, *ibid.*, **92**, 568 (1970); (f) K. B. Wiberg and G. Szeimies, *ibid.*, **92**, 571 (1970); **90**, 4195 (1968); (g) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

(7) M. Julia and Y. Noël, *Bull. Soc. Chim. Fr.*, 3756 (1968). Also see M. Julia and Y. Noël, *ibid.*, 3749 (1968); M. Julia, Y. Noël, and R. Guégan, *ibid.*, 3742 (1968); M. Julia, S. Julia, and S.-Y. Tchen, *ibid.*, 1849 (1961); M. Julia, S. Julia, and R. Guégan, *ibid.*, 1072 (1960); S. F. Brady, M. A. Ilton, and W. S. Johnson, *J. Amer. Chem. Soc.*, **90**, 2882 (1968).

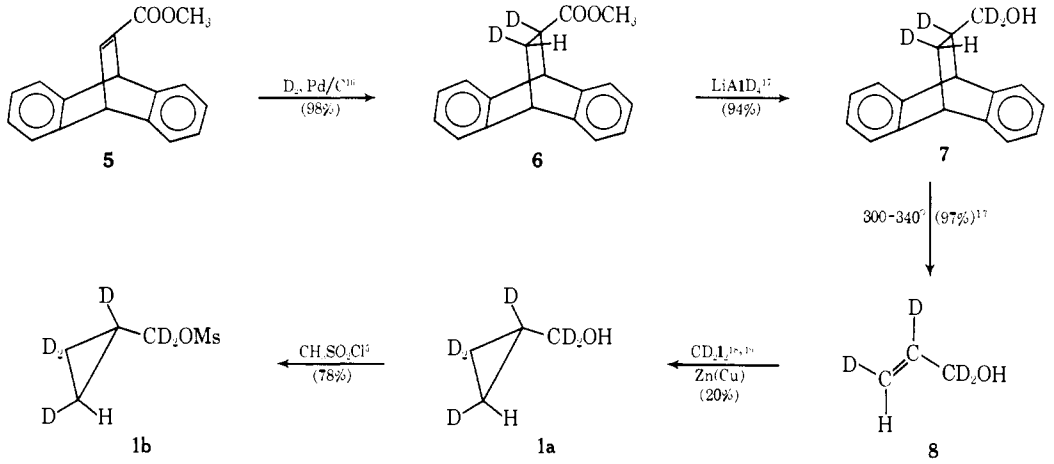
(8) G. A. Olah, D. P. Kelly, C. L. Jeuell, and R. D. Porter, *ibid.*, **92**, 2544 (1970).

(9) M. Saunders and J. Rosenfeld, *ibid.*, **92**, 2548 (1970).

(10) (a) J. C. Martin and B. R. Ree, *ibid.*, **91**, 5882 (1969); B. R. Ree and J. C. Martin, *ibid.*, **92**, 1660 (1970); (b) R. Maurin and M. Bertrand, *Tetrahedron Lett.*, 1307 (1970).

(11) (a) J. E. Baldwin and W. D. Fogelsong, *J. Amer. Chem. Soc.*, **90**, 4303, 4311 (1968); (b) I. Lillien, G. F. Reynolds, and L. Handloser, *Tetrahedron Lett.*, 3475 (1968); I. Lillien and L. Handloser, *ibid.*, 1035 (1969); (c) W. G. Dauben and E. I. Aoyagi, *Tetrahedron*, **26**, 1249 (1970); (d) M. Gašić, D. Whalen, B. Johnson, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 6382 (1967); D. Whalen, M. Gašić, B. Johnson, H. Jones, and S. Winstein, *ibid.*, **89**, 6384 (1967).

Scheme I. Outline of Synthesis Employed



propylcarbinyl system has led to the same conclusion.[6f,8] The direct nmr results of Olah, *et al.*,[8] show that cis and trans methylene protons retain their stereochemical integrity during CH_2 group equilibration in superacid solution.

The study of Wiberg and Szeimies[6f] is most closely related to our own work. The labeled cyclopropylcarbinyl cation was generated in an interesting way: by protolysis of bicyclobutane in acetic acid-*d* and in heavy water, a reaction believed to take place with stereospecific proton (deuteron) attachment.[6f,12] The cyclopropylcarbinyl acetate obtained with CH_3COOD showed the following deuterium distribution: 1′ position, 24 ± 2%; 1 position, 0%; trans-2 and -3 positions, 1 ± 3%; and cis-2 and -3 positions, 79 ± 1%. Quite similar results were obtained by protolysis in heavy water; the cyclopropylcarbinol so obtained was estimated to have deuterium at the 2 and 3 positions distributed 81 ± 2% cis and 0 ± 3% trans and the rest at the carbinyl group. Since mechanistic considerations indicated that the deuterium atom first became attached to the cis-2 position of the initially generated cyclopropylcarbinyl cation, the observation of deuterium at the carbinyl (1′) position of the product indicated that the cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement had taken place. Since very little, if any, deuterium was found in the trans-2 or -3 positions of the products, this rearrangement was indicated to be highly (80 or 82 to 100%) stereoselective.[13]

A much lower degree of stereoselectivity (68–80%)[13] was found in the cyclopropylcarbinyl acetate formed by acetolysis of 1-buten-4-yl-*cis*-1-*d* tosylate. The deuterium was distributed as follows: trans-2 and -3 positions, 17 ± 3%; cis-2 and -3 positions, 48 ± 3%; and 1′ position, 35 ± 3%.[6f]

These analyses were carried out by pmr integration. Unfortunately, the pmr spectra of cyclopropylcarbinol[14] and of cyclobutanol[15] in particular are very complex and the location and accurate integration (by difference) of the single deuterium atom introduced by the Wiberg–Szeimies method was difficult. In fact, analysis of the stereochemistry of the deuterium in the cyclobutyl products was impossible and no stereochemical results were reported either for the cyclopropylcarbinyl → allylcarbinyl rearrangement, since the cis and trans protons of the olefinic CH_2 group could not be distinguished with sufficient clarity.[6f] The use of a single deuterium atom as label also seriously reduced the accuracy of the estimate of selectivity during the cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement.[13]

We have used a different approach which largely circumvented these difficulties and permitted the study of the stereochemistry of *all three* rearrangement processes involving the cyclopropylcarbinyl cation. Instead of a single deuterium atom,[6f] we used *a single hydrogen atom as label* in molecules otherwise completely deuterated. This greatly facilitated proton magnetic resonance analysis. Also, the label distribution in our starting material, cyclopropylcarbinol-*1,1′,1′-trans-2,3,3-d*$_6$, could be determined accurately, unlike the situation with the Wiberg–Szeimies experiment,[6f] where the stereospecificity of the initial bicyclobutane protolysis had to be assumed since no direct check was possible.

Synthesis of Starting Material. The synthetic sequence used to prepare cyclopropylcarbinol-*1,1′,1′-trans-2,3,3-d*$_6$ (**1a**) is summarized in Scheme I. The initial steps were based on work of Hill and Newkome,[16] who showed that the Diels–Alder adduct of methyl propiolate with anthracene (**5**) could be reduced cleanly to **6** with deuterium gas and a palladium catalyst. Lithium aluminum deuteride reduction of **6**,[17] followed by pyrolysis of **7**[17] gave an excellent overall yield of allyl-*trans-1,2,3,3-d*$_4$ alcohol (**8**). Unexpectedly, the Simmons–Smith cyclopropanation of allyl alcohol proceeds poorly to give only low (*ca.* 20%) yields of cyclopropylcarbinol.[18] Use of CD_2I_2[19] in this reaction

(12) W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964).

(13) For the bicyclobutane protolysis experiments,[6f] the per cent deuterium at the 1′ position can be taken as a measure of the amount of cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement which has occurred. The stereoselectivity range for the reaction with CH_3COOD is thus: 100[1 − (1 ± 3/24 ± 2)] = 82–100%. The stereoselectivity range for the heavy water reaction is: 100[1 − (0 ± 3/17 ± 2)] = 80–100%. In the acetolysis of 1-buten-4-yl-*cis*-1-*d* tosylate, the deuterium at the 2 and 3 positions in the cyclopropylcarbinyl acetate product arose *via* cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement; the stereoselectivity range is indicated to be 100[1 − (17 ± 3)/(65 ± 3)] = 68–80%.

(14) K. B. Wiberg and D. E. Barth, private communication. The chemical shifts in cyclopropylcarbinol are δ 0.175 (C-2 and C-3 cis H's), 0.460 (C-2 and C-3 trans H's), 1.015 (H at C-1). See Figure 2. We are grateful to Professor Wiberg for supplying this information.

(15) K. B. Wiberg and D. E. Barth, *J. Amer. Chem. Soc.*, **91**, 5124 (1969).

(16) R. K. Hill and G. R. Newkome, *J. Org. Chem.*, **34**, 740 (1969). We thank Dr. Newkome for his advice.

(17) *Cf.* P. D. Bartlett and F. A. Tate, *J. Amer. Chem. Soc.*, **75**, 91 (1953).

(18) The major product is the formal of cyclopropylcarbinol. This reaction has been reported in detail; Z. Majerski and P. v. R. Schleyer, *J. Org. Chem.*, **34**, 3215 (1969).

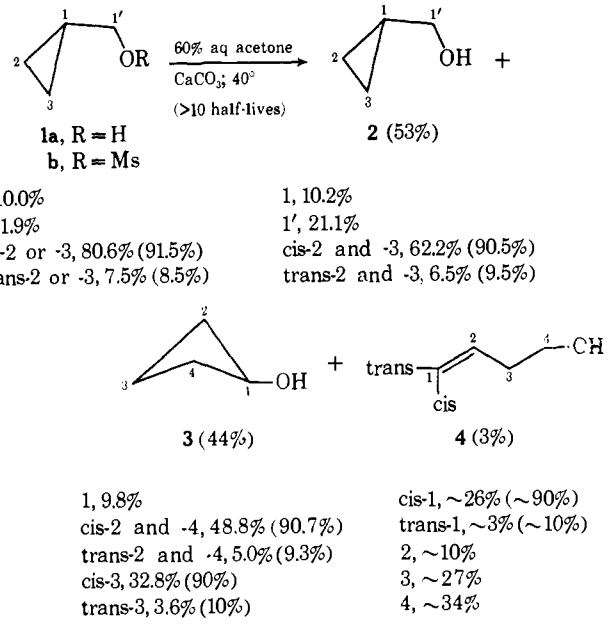


Figure 1. Quantitative pmr analysis of the proton signals from cyclopropylcarbinol-*1,1',1'-trans-2,3,3-d*$_6$ (**1a**) and the solvolysis products from the derived **1b**. The values given are the percentages of H at each position relative to the total carbon-bound H in each molecule (1.2 H atoms). The values in parentheses represent the cis–trans composition at key positions. Multiple pmr integration consistently resulted in reproducibilities better than ±0.5% in both instruments used except for the 3 position of **3** (±1%) and for **4**, where insufficient sample reduced the precision substantially.

with **8** gave the desired **1a** from which the methanesulfonate **1b** could be prepared according to the published method.[5]

The starting alcohol, **1a**, was not cleanly proton labeled. The reagents used to introduce deuterium contained small amounts of hydrogen and this reaction scheme may have permitted some further contamination. In fact, both **7** and **8** contained 0.1–0.2 atom of carbon-bound hydrogen as impurity. The actual alcohol synthesized, **1a**, was estimated by pmr to contain about 1.2 atoms of carbon-bound hydrogen. The percentage distributions of all the hydrogen in **1a** are given in Figure 1.

Mesylate **1b**, prepared from **1a**, was solvolyzed in 60% aqueous acetone in the presence of $CaCO_3$ at 40° for 6 min (>10 half-lives). The product alcohols, **2**, **3**, and **4**, were salted out with K_2CO_3; the final purifications were carried out by preparative glc. It was most convenient to isolate **2** and **3** together and **4** separately. The product composition, 53% **2**, 44% **3**, and 3% **4**, corresponded well to that found previously with unlabeled material under essentially the same conditions.[5]

The products are stable to reaction conditions employed. This was shown by treating unlabeled **2** (the most reactive of the three products)[20] with methanesulfonic acid in 60% aqueous acetone at 40° for 6–10 min in the presence of $CaCO_3$. No rearrangement to **3** or **4** was observed. Cyclobutyl methanesulfonate, known to be formed by return to the extent of about 10%, solvolyzes about 100 times slower than cyclopropylcarbinyl mesylate.[5] Therefore, under the reaction

(19) S. Winstein, E. C. Friedrich, R. Baker, and Y. Lin, *Tetrahedron, Suppl.*, No. 8 (II), 621 (1966).

(20) M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, 11, 171 (1960).

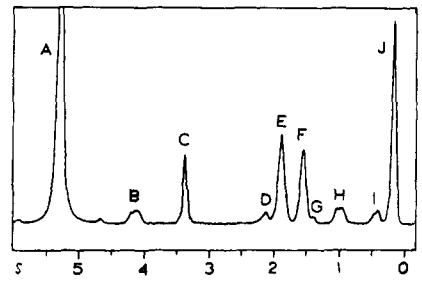


Figure 2. 60-MHz pmr spectrum of the mixture of **2** and **3**: A, -OH; B, **3** 1-H; C, **2** 1'-H; D, **3** trans-2(4)-H; E, **3** cis-2(4)-H; F, **3** cis-3-H; G, **3** trans-3-H; H, **2** 1-H; I, **2** trans-2(3)-H; J, **2** cis-2(3)-H.

conditions employed for **1b**, any cyclobutyl mesylate which formed should not have given rise to any significant amounts of solvolysis products.

The pmr spectrum of the mixture of **2** and **3** is shown in Figure 2. The signals for each of the positions in both compounds were well separated at 100 MHz, and nearly all were well separated even at 60 MHz. The availability of complete analyses of the pmr spectra of cyclopropylcarbinol[14] and of cyclobutanol[15] greatly facilitated the assignment summarized in Figure 2. The percentage composition in the product is given in Figure 1. This was determined by repeated pmr integration on two different days, using both 60- and 100-MHz instruments.

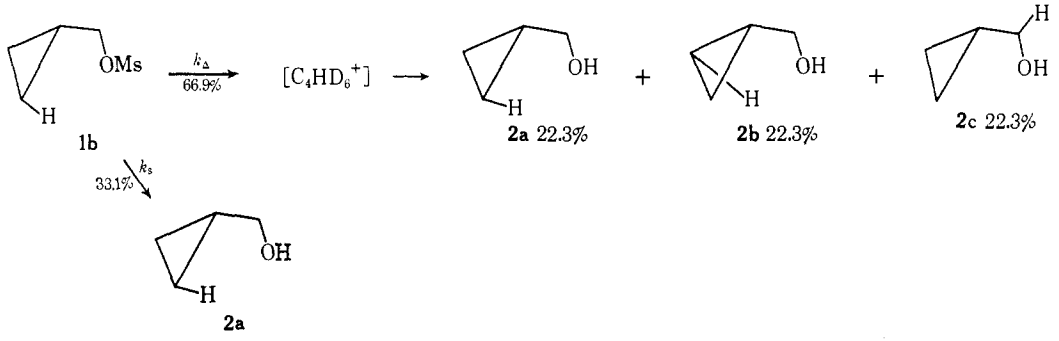
The results provide an internal check. The methine (1-proton) of **1** (10.0 ± 0.5%) should not scramble.[5,21] Well within experimental error, this expectation was confirmed by the methine proton composition of the products: **2** (1 position) 10.2 ± 0.5%, **3** (1 position) 9.8 ± 0.5%, and **4** (2 position) ~10%. These results further show that no significant change in deuterium content occurred during solvolysis.

The migration of the proton label in **1b** to the various positions in products **2** and **3** corresponded well to results previously found starting with cyclopropylcarbinyl-*1,1-d*$_2$ methanesulfonate under similar conditions.[5] Thus, in **3** the distribution of hydrogen at methylene groups was 59.6% at the 2 and 4 positions (29.8% each) and 40.4% at the 3 position. In **2**, 23.5% of the methylene-bound hydrogen appeared at the 1' position and the rest at the 2 and 3 positions (38.2% each). This result is important as it provides a quantitative estimate of the amount of cyclopropylcarbinyl → cyclopropylcarbinyl rearrangement which took place during this conversion of **1b** to **2**. The final product, **4**, had the following proton composition at the methylene groups: C_1, ~32%, C_3, ~30%, and C_4, ~38%.

The key results of interest to us were the stereochemical distribution (cis or trans) of the proton label at each position where differentiation can be made. *Within experimental error all of these trans/cis ratios in* **2**, **3**, *and* **4** *were identical with that in the starting material*, **1**. This shows that the cyclopropylcarbinyl → cyclopropylcarbinyl, the cyclopropylcarbinyl → cyclobutyl, and the cyclopropylcarbinyl → allylcarbinyl rearrangements all take place *stereospecifically*. Each of these cases will be discussed individually.

(21) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *J. Amer. Chem. Soc.*, 81, 4390 (1959).

Cyclopropylcarbinyl → Cyclopropylcarbinyl Rearrangement. The starting material, **1a**, had 1.9% H at the 1′ position, but in the product, **2**, this had increased to 21.1% while the trans/cis ratio at the 2 (and/or 3) positions remained essentially constant. This result suggests that the solvolysis took the following course, as far as the cyclopropylcarbinyl products are concerned

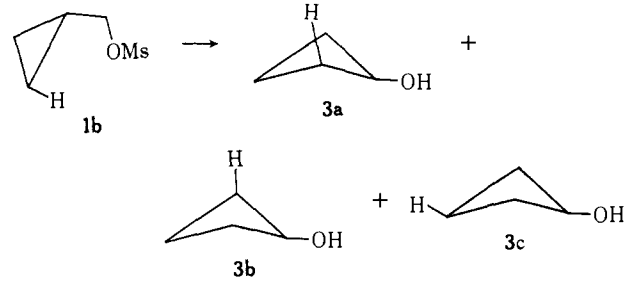


Because of symmetry (neglecting a possible very minor isotope effect) there is an equal probability of forming the two cyclopropylcarbinyl → cyclopropylcarbinyl rearrangement products, **2b** and **2c**. The labeling experiments indicate the formation of 22.3% **2c**;[22] therefore, 22.3% **2b**[22] must have been produced as well. It seems reasonable to ascribe the 66.9% of unrearranged **2a** to the operation of two mechanisms, k_Δ and k_s,[23] as indicated above. This assumption, which is not important as far as the interpretation of the stereochemical results is concerned, is based on the expectation that the cyclopropylcarbinyl → cyclopropylcarbinyl interconversion is rapid relative to solvent capture. Since 22.3% **2c** forms (and 22.3% **2b**) it is to be expected that 22.3% **2a** also arises *via* the same k_Δ route. According to this view, the excess **2a** observed is due to solvent attack (k_s) before rearrangement takes place.

The labeling results are complicated by the presence of a small amount of hydrogen (1.9%) at the 1′ position.[22] Upon rearrangement to **2**, **3**, or **4**, the portion of this hydrogen which rearranges would be expected to be distributed equally to cis and to trans positions. Thus, of the 1.9% 1′ hydrogen in **1**, 1.0% (67% 1.9%) should remain at the 1′ position in **2**, but 0.4% should be distributed to the cis-2 (and -3) and 0.4% to the trans-2 (and -3) positions. The trans/cis ratio at these positions should therefore be reduced from 91.5 ± 0.5%:8.5 ± 0.5% in **1** to 91.1 ± 0.5%:8.9 ± 0.5% in **2**. The actual percentages experimentally observed in **2**, 90.5 ± 0.5%:9.5 ± 0.5%, are identical with this value, within experimental error. Expressed in a different way, our results show that the cyclopropylcarbinyl → cyclopropylcarbinyl rearrangement occurred with 97.3 ± 4% (100[1 − [(91.1 ± 0.5) − (90.5 ± 0.5)]/(22.3 ± 0.5)]) stereoselectivity, the cis-2 (or -3) proton of **1** being transformed to the cis-3 (or -2) position of **2**.

Cyclopropylcarbinyl → Cyclobutyl Rearrangement. The cyclopropylcarbinyl → cyclobutyl rearrangement also proceeds stereospecifically, within experimental error, as revealed by a comparison of the raw cis/trans percentages for **1** and **3** (in parentheses) in Figure 1. When corrected for the 1.9% hydrogen at the 1′ position in the starting material (**1**), the agreement is practically perfect. It is known from an experiment using cyclopropylcarbinyl-*1′,1′-d*$_2$ mesylate that the 1′-methylene rearranges ~76% to the 2 and 4 and ~24% to the 3 position.[5] For this reason, the 1.9% hydrogen at C-1′ in **1** should distribute itself in **3** as follows: cis-2, cis-4, trans-2, and trans-4, each 0.35%; cis-3 and trans-3, each 0.25%. After correction for these amounts, the stereochemical label distributions became cis-2 (and -4), 91.8%, trans-2 (and -4), 8.2%; cis-3, 90.7%, trans-3, 9.3%. Taking the 2, 3, and 4 positions together, the corrected cis–trans distribution is 91.3% cis and 8.7% trans, virtually identical with the percentages in the starting material—**1**, 91.5% cis and 8.5% trans.

The course of the cyclopropylcarbinyl → cyclobutyl rearrangement, then, is as shown



Cyclopropylcarbinyl → Allylcarbinyl Rearrangement. Although the lack of material made our error limits larger, the cyclopropylcarbinyl → allylcarbinyl rearrangement also appears to proceed stereospecifically. In this case the nmr spectrum of 1-buten-4-ol had not been assigned previously. From the chemical shifts and coupling constants, it is easy to assign the 3- and 4-methylene signals and that for the 2-vinyl hydrogen (see Experimental Section for details). The only difficulty is differentiation of the 1-cis from the 1-trans signals. In **4** these signals are found at δ 5.02 (a 1:1:1 triplet) and 4.94 ppm (shoulder). This 0.08 ppm difference is similar to that found for similar molecules (propene 0.09 ppm, allyl alcohol 0.12 ppm, diallyl ether 0.08 ppm, 1-butene 0.07 ppm, 1-hexene 0.06 ppm);[24] in all these cases the protons at C-1 trans to the methylene groups are more shielded than the cis protons. For this reason we assign the 5.02 ppm signal of **4** to the C-1 proton cis to the methylene. This assignment is supported by the 1:1:1 triplet character of this signal

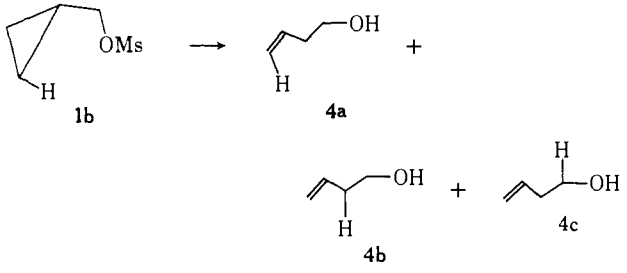
(22) In going from **1** to **2**, the per cent H at C-1′ increases from 1.9 to 21.1%, but 0.9% of the C-1′ hydrogen originally present rearranged. Therefore, the net increase at C-1′ in 2 was 21.1 − 1.0 = 20.1%. Methine hydrogen (10%) does not change; therefore, the percentage conversion of **1** to **2c** is 20.1/0.9 = 22.3%.

(23) *Cf.* P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *J. Amer. Chem. Soc.*, **92**, 2542 (1970); R. K. Crossland and K. L. Servis, *ibid.*, in press.

(24) F. A. Bovey, "NMR Data Tables for Organic Compounds," Vol. 1, Wiley, New York, N. Y., 1967, Compd no. 248, 261, 459, 946, and 1005.

(J_{HD} = 2.5 ± 0.2 Hz), due to coupling with the C-2 deuterium atom. Since H–H couplings are 6.514 times larger than corresponding H–D couplings,[25] this would correspond to a coupling of J = 16.3 ± 1.3 Hz in the hydrogen compound. In unlabeled 1-buten-4-ol, we determined the following values: $J_{H_2\text{-trans-}H}$ = 17.5 ± 0.2 Hz and $J_{H_2\text{-cis-}H}$ = 9.4 ± 2 Hz. Thus, J_{HD} = 2.5 ± 0.2 Hz found in **4** corresponds to the value expected for the 1-hydrogen cis to the methylene group. It should be added that labeled allyl alcohol (**8**) also shows a similar 1:1:1 triplet with the same coupling constant (J_{HD} = 2.5 ± 0.2 Hz) for coupling of the methine vinyl D to the H cis to the methylene group.

The cis–trans proton distribution at C_1 in **4** corresponds closely to that in **1**. Corrections for the 1.9% hydrogen at C_1 in **1** would make the agreement even better, but the uncertainty due to the experimental error is so large in this instance that the actual calculation is pointless.



We conclude that the transformation of the cis-2 (or -3) hydrogen in **1** to the cis (to the methylene) 1 position of **4a** is at least 90% stereoselective, and may well be stereospecific. The stereochemistry of the rearrangement of **1** to **4b** and to **4c** cannot be determined by our procedure.

Discussion

Our results show that all three rearrangement processes, cyclopropylcarbinyl → cyclopropylcarbinyl, cyclopropylcarbinyl → cyclobutyl, and cyclopropylcarbinyl → allylcarbinyl, occur stereospecifically (within experimental error), at least under our reaction conditions. In all three processes, the cis configuration of the hydrogen used as a label is preserved in the products: **1b** → **2a**, **2b**, **3a**, **3b**, **3c**, and **4a**.

In view of the extensive discussion in the literature,[8–11] and the available theoretical analyses[6f,g,26] regarding the detailed mechanistic interpretation of such processes, it will suffice here to present a summary description of our results.

Solvolysis of cyclopropylcarbinyl mesylate (**1b**) proceeds to a minor extent to give "excess" unrearranged cyclopropylcarbinol (**2a**). The remainder of the reaction involves stereospecific rearrangement.

(25) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon, New York, N. Y., 1969, p 142.

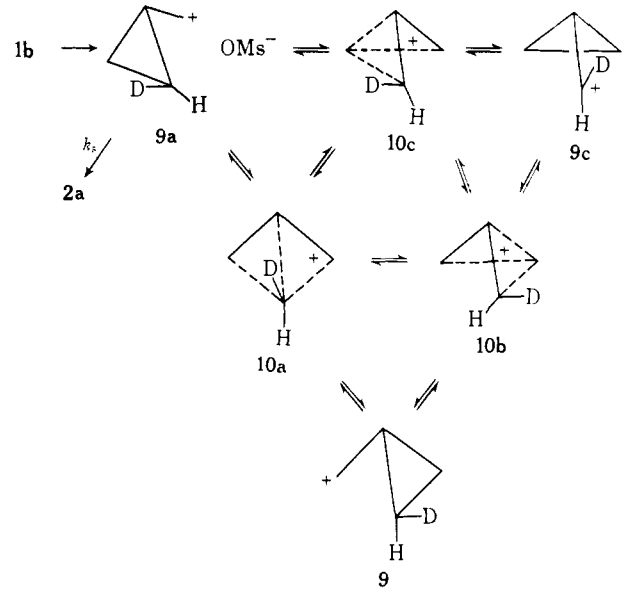
(26) (a) C. Trindle and O. Sinanoglu, *J. Amer. Chem. Soc.*, **91**, 4054 (1969); (b) H. Kollmar and H. O. Smith, *Tetrahedron Lett.*, 3133 (1970). Because of flaws which seem to be inherent in semiempirical molecular orbital methods when applied to small ring systems and bridged carbonium ions (R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 5350 (1969)), the relative energies of the various $C_4H_7^+$ species calculated in the latter paper should not be taken literally. They also do not correspond to expectations based on chemical evidence. These criticisms also apply to extended Hückel calculations (R. E. Davis and A. Ohno, *Tetrahedron*, **24**, 2063 (1968)) which suggested the cyclobutyl cation was a planar, classical species.

Solvolysis of cyclopropylcarbinyl derivatives has long been known by labeling studies to give cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl products in each of which the methylene groups are largely, but not completely, scrambled.[5,21] In the present work, the cyclopropylcarbinol was scrambled to the extent of ~67%, while, as expected, the cyclobutyl and allylcarbinyl products were methylene scrambled to a larger extent (~90%).

The first formed intermediate (**9a** or a solvated ion pair) from **1b** therefore is trapped before any rearrangement can take place; we have described this above as a k_s process (nucleophilic solvent attack).[23] Alternatively, it can be regarded that ion-pair **9a** allows much leakage, but to some extent collapses before rearrangement takes place.

In Scheme II, we have represented the cyclopropylcarbinyl cation in the preferred bisected geometry (**9**); in addition, solvation by leaving group and by sol-

Scheme II

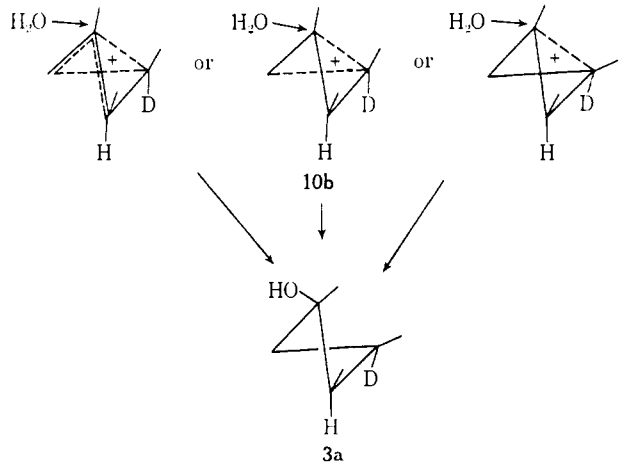


vent is expected. Interconversion of isomeric cyclopropylcarbinyl cations is shown to proceed *via* structure **10**[5,6f,11a] which may be intermediates of higher energy than **9**. The question of whether there are one or two (or more) intermediates on the cyclopropylcarbinyl–cyclobutyl energy surface has not yet been settled.[5] While the cyclopropylcarbinyl products arise from both **9** and **10**, it seems more difficult to ascribe the formation of the cyclobutyl products from **9**; **10** (*cf.* the puckered cyclobutyl cation of Wiberg)[6f] seems a more likely precursor. According to Wiberg[6f] the allylcarbinyl products may originate either from cyclopropylcarbinyl-type or cyclobutyl-type intermediates, depending on the circumstance. In the present instance, the degree of scrambling suggests (but does not require) a closer kinship of the allylcarbinyl with the cyclobutyl products.

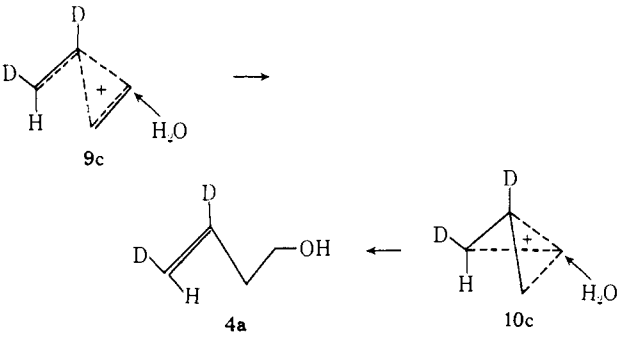
Whatever the number and nature of the transition states and intermediates, our work (and the literature) makes a number of points clear. The initially formed intermediate undergoes cyclopropylcarbinyl rearrangement at a rate comparable to (1) its capture by solvent, and (2) its rearrangement to cyclobutyl (and allylcarbinyl) products. Scrambling is extensive, but it is not complete. As is also known from previous work,[5]

hydride shifts do not occur. All processes take place with very high stereoselectivity, and no readily accessible pathway permitting cis ⇄ trans interconversion is possible. The cyclopropylcarbinyl → cyclopropylcarbinyl rearrangement, *e.g.*, **9a** ⇄ **9b** ⇄ **9c**, occurs with *clean* inversion (retention of the cis configuration). In principle, rotation of the C_1–C_1' bond in **9b** would lead to stereomutations. However, the barrier to such rotation in cyclopropylcarbinyl cations is known to be very high[4,8,27] and this rotation does not compete with the other processes.

Similarly, the cyclobutyl cation, if it is involved, *cannot* be a classical, planar species.[26b] Such a species, because of symmetry, would be attacked by solvent with equal facility from either cis or trans side. In contrast, we find only cis products at both the 2 (and 4) and at the 3 positions. Inversion at the methine position has taken place. It is already known that the reverse reaction, the solvolysis of cyclobutyl derivatives to give cyclopropylcarbinyl products, occurs with preferential inversion at the reaction site.[4c,11b] Direct observation of the $C_4H_7^+$ cation also excludes a planar cyclobutyl cation structure.[8]



The cyclobutyl-forming process is shown above as taking place *via* puckered cyclobutyl cation **10b**[5,6f] (two other formulations of this species are shown). This intermediate (or transition state) may be the same as that involved in the cyclopropylcarbinyl → cyclopropylcarbinyl rearrangement (*vide supra*). In terms of the relative positions of atoms, the structures of the bisected cyclopropylcarbinyl cation **9** and of the puckered cyclobutyl cation **10** are quite similar; interconversion between these species should be quite easy. It probably is significant that cyclopropylcarbinyl and cyclobutyl products dominate the kinetic-controlled products from solvolysis of cyclopropylcarbinyl and cyclobutyl derivatives.



The allylcarbinol is also formed with high (if not complete) stereoselectivity. This contrasts somewhat with the result of Wiberg[6f] in which the acetolysis of allylcarbinyl tosylate gave a much lower degree of stereoselectivity in the cyclopropylcarbinyl product. However, Wiberg's experiment was carried out in a less nucleophilic solvent at a much higher temperature and a less reactive starting material was used; it is not surprising that more opportunities for leakage were present.

Experimental Section

Pmr spectra were recorded on a Varian A-60A and/or HA-100 spectrometers in ~15% solution unless otherwise indicated. The pmr spectra of all cyclopropyl compounds were recorded with $CHCl_3$ instead of TMS as the internal standard. The quantitative pmr measurements were carried out at least twice on each of the instruments, five to ten times per determination. Mass spectra were taken on an AEI MS-9 high-resolution mass spectrometer.

Methyl 9,10-ethenoanthracene-11-carboxylate (5), prepared by a previously reported procedure,[16,28] had mp 177–178°; pmr in $CDCl_3$–CH_3, s, δ 3.74, 3 H; =CHC*H*, d, δ 5.27, J = 6.0 Hz, 1 H; =CC*H*, d, δ 5.72, J = 1.9 Hz, 1 H; arom *H*, m, δ 7.53–6.93, 8 H; =C*H*, 2 d, δ 7.92, J_1 = 6.0, J_2 = 1.9 Hz, 1 H.

Methyl 9,10-ethanoanthracene-11-carboxylate-*cis*-*11,12*-d_2 (6) was prepared by reduction of 82.9 g (0.316 mol) of **5** in anhydrous ethyl acetate solution (2.1 l.) with deuterium gas (Matheson, 99.9% *d*; ~7.8 l.) at atmospheric pressure.[16] Palladium on charcoal (10%; 2.1 g) was used as a catalyst: yield 82.5 g (98.2%); mp 114–116°; pmr in $CDCl_3$—CD*H*, broad d, δ 2.12, J ~ 2 Hz, 1 H; CH_3, s, δ 3.50, 3 H; CDHC*H*, d, δ 4.26, J = 2.5 Hz, 1 H; –CDC*H*, s, δ 4.62, 1 H; arom *H*, m, δ 7.35–6.85, 8 H.

9,10-Ethanoanthracene-11-methanol-*cis*-*11,12,11',11'*-d_4 (7). A suspension of 4.8 g (0.114 mol) of $LiAlD_4$ in 1.2 l. of dry ether was stirred mechanically and the ether was refluxed through a Soxhlet extractor containing 50.0 g (0.188 mol) of **6**. After 8 hr the gummy mass in the reaction flask was treated with sufficient 10% aqueous H_2SO_4 solution to dissolve the hydroxides. The ethereal layer was then washed once with 300 ml of 10% H_2SO_4, three times with 300 ml of 10% K_2CO_3, and twice with 300 ml of water, and dried over Na_2SO_4. The solvent was evaporated and the gummy residue crystallized from 1:1 pentane–ether mixture to give 43.4 g of white crystals. The pmr spectrum showed ~25% of unreacted starting material. The crude product was reduced again with 2.9 g (0.069 mol) of $LiAlD_4$ in 0.7 l. of dry ether as previously described. Recrystallization from pentane–ether gave 42.6 g (94.2%) of **7**: mp 108–110°; pmr in $CDCl_3$—C*H*D, broad d, δ 1.01, J ~ 2 Hz, ~1.1 H; O*H*, s, δ 1.70, 1 H; CHDC*H*, d, δ 4.16, J = 2.4 Hz, 1 H; –CDC*H*, s, δ 4.30, 1 H; arom *H*, m, δ 7.3–6.8, 8 H.

Propen-3-ol-*cis*-*1,2,3,3*-d_4 (8), obtained by pyrolysis[17] of 41.0 g (0.171 mol) of **7** (above) at 300–340°, was redistilled (95–97°) to give 10.3 g (97.1%) of **8** which was ≥98% chemically pure by glc (the major impurity was methyl acrylate-d_4): pmr in $CDCl_3$–O*H*, s, δ 3.8, 1 H; =CD*H*, 1:1:1 t, δ 5.15, J = 2.5 Hz, ~0.9 H, d, δ 5.15, J ~ 17 Hz, ~0.1 H; =C*H*–, broad d, δ ~5.9, J ~ 17 Hz, ~0.1 H.

Cyclopropylcarbinol-*1,1',1'-trans*-*2,3,3*-d_6 (1a) was prepared by a somewhat modified previously reported procedure.[18] Into a vigorously stirred mixture of 32.8 g of commercial Zn–Cu couple (Alfa Inorganics/Ventron), 0.2–0.3 g of iodine, and 260 ml of dry ether was added dropwise 102.3 g (0.38 mol) of CD_2I_2[19] (98.5% *d* by mass spectroscopy) over a 15-min period. The reaction mixture was heated by an ir lamp until the reaction started and was then stirred over a 40° oil bath. After 1 hr a solution of 10.2 g (0.165 mol) of **8** in 20 ml of dry ether was added dropwise for 15 min (strongly exothermic). The mixture was stirred for an additional 2 hr at 40°, cooled to 20°, and diluted with 200 ml of ether. A saturated aqueous solution of NH_4Cl was added dropwise until a

(27) D. S. Kabakoff and E. Namanworth, *J. Amer. Chem. Soc.*, **92**, 3234 (1970); 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, Jr., *ibid.*, **87**, 3000 (1965).

(28) W. R. Vaughan and K. M. Milton, *ibid.*, **74**, 5623 (1952).

black precipitate separated. The precipitate was washed with ether. The combined ether extracts were washed once with 150 ml of saturated NH_4Cl solution, three times with 150 ml of saturated K_2CO_3 solution, and twice with 150 ml of saturated NaCl solution, and dried over Na_2SO_4. The solvent was evaporated through a Vigreux column. The residue was fractionated through a 20 × 0.6 cm vacuum-jacketed column containing a 0.4 cm o.d. tube. The fraction collected at 100–130° was purified by preparative glc (25 ft Carbowax 20M at 112°) to give 2.6 g (20.2%) of **1a** which was ≥98% chemically pure by glc: pmr spectrum (in $CHCl_3$, ~80%) cis-2 (-3) *H*, s, δ 0.17, 1 H; trans-2 (-3) *H*, δ 0.43, 0.09 H; 1 H, broad, δ 1.00, 0.12 H; 1′-*H*, s, δ 3.38, 0.02 H; O*H*, s, δ 4.3, 1 H.

Cyclopropylcarbinyl-*1,1′,1′-trans*-2,3,3-d_6 methanesulfonate (1b), prepared from **1a** by a previously reported procedure[5] in 78% yield, was ~96% chemically pure by pmr (the major impurity was pyridine): pmr in $CDCl_3$—cis-2 and -3 *H*, broad s, δ 0.37, 1 H; trans-2 and -3 *H*, broad, δ 0.65, ~0.1 H; C*H*, broad, δ 1.2, ~0.1 H; CH_3, s, δ 2.98, 3 H.

Solvolysis of Cyclopropylcarbinyl-*1,1′,1′-trans*-2,3,3-d_6 Methanesulfonate (1b). **1b** (3.3 g, 21.1 mmol) was solvolyzed in a vigorously stirred suspension of $CaCO_3$ (1.6 g, 16 mmol) in 84 ml of 60% aqueous acetone at 40°. After 6 min (~10 half-lives), pH 6–7, 100 ml of pentane was added followed by anhydrous K_2CO_3 until a saturated water solution separated out. The aqueous layer was extracted twice with 30 ml of a 1:1 pentane–ether mixture. The combined extracts and the acetone solution were dried over Na_2SO_4. The solvents were evaporated (pentane and ether through a 60-cm Vigreux column, acetone through a 20 × 0.6 cm vacuum-jacketed column) and the residue (53% **2**, 44% **3**, and 3% **4** *via* glc on 20 ft 15% glycerol on Chromosorb P 45–60 at 80°) was fractionated by preparative glc (25 ft Carbowax 20M at 112°). Two fractions were collected: **4** (~90% chemically pure by glc analysis) and 1.2 g (78%) of a mixture of **2** and **3** (≥97% by glc; the major impurity was pyridine). The pmr spectrum of **4** (~30% in CCl_4; 25 μl tube) shows four broad singlets, =C*H*, δ 4.3, ~0.1 H; O*H*, δ 5.5, 1 H; CH_2, δ 7.81, ~0.3 H; CH_2OH δ 6.50, ~0.4 H, and a 1:1:1 triplet (J = 2.5 Hz) at δ 5.02 with a small shoulder (~10%, δ 4.94) which corresponds to the cis-1 and trans-1 hydrogen, respectively (~0.35 H). The pmr spectrum of the mixture of **2** and **3** (~90% in $CHCl_3$) is shown in Figure 2.

Control Experiment. Cyclopropylcarbinol was treated with an equivalent amount of methanesulfonic acid under the conditions described for the solvolysis of **1b**. No rearrangement was observed when $CaCO_3$ was present.

Acknowledgment. This research was supported by grants from the National Science Foundation and by the Petroleum Research Fund, administered by the American Chemical Society. The authors appreciate exchanges of information with Professor K. Wiberg.

Cyclopropanes. XXIX. The Stereochemistry of the 1-Methyl-2,2-diphenylcyclopropyl Radical in and out of Solvent Cage[1]

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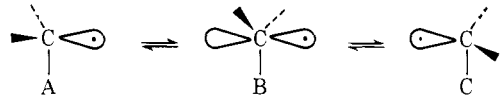
Contribution from the Department of Chemistry, Florida State University, Tallahassee, Florida 32306. *Received June 6, 1970*

Abstract: The 1-methyl-2,2-diphenylcyclopropyl radical (**4**) has been generated in solution from a variety of optically active precursors to yield cyclopropyl derivatives which were largely if not entirely racemized. However, when the radical **4** disproportionates within the solvent cage, the 1-methyl-2,2-diphenylcyclopropane (**3a**) obtained was found to be 31–37% optically pure (66–68% retention of configuration). Evidence to support the contention that the disproportionation occurred within a solvent cage will be presented.

The stereochemistry of free radicals and the question of their geometry have been the subject of a number of reviews.[2] The question whether a radical is bent and is undergoing a rapid inversion from one pyramidal form to another (A ⇄ C) or whether it is a planar mole-



cule (B) is a difficult one to answer since B is a transition state in the inversion process. To decide whether B is a transition state or a true intermediate is a difficult question to answer chemically. If a radical is planar, it would have a plane of symmetry and could not exist in optically active form. Therefore, one approach used to determine whether or not it is planar has been to prepare a radical from an optically active starting material. A number of examples have been studied,[2] and every case gave a racemic product. This result, however, can be explained in two ways. In the first explanation, the loss of optical activity in the product is due to the planar radical which cannot exist in optically active form. In the second, the loss of optical activity is ascribed to the fact that the rate of inversion of the radical is more rapid than the rate at which it reacts to form product. Even where optically active products are obtained, the results are not subject to a clear-cut explanation of the geometry of a radical. Skell and coworkers[3] have found that the bromination of optically active 1-chloro- or 1-bromo-2-methylbutane leads to optically active products, and they interpret these results in terms of halogen-bridged radicals. If a bridged radical is formed directly without ever proceeding through an open-chain radical, then clearly the optical activity in the product has no bearing whatever on the geometry of the open-chain radical.

(1) The support of this work by Public Health Service Research Grant No. CA 04065 from the National Cancer Institute is gratefully acknowledged.

(2) E. L. Eliel, "Stereochemistry of Carbon Compound," McGraw-Hill, New York, N. Y., 1962; C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957; W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966.

(3) P. S. Skell, *Chem. Soc. Spec. Publ.*, No. 19, 131 (1965).