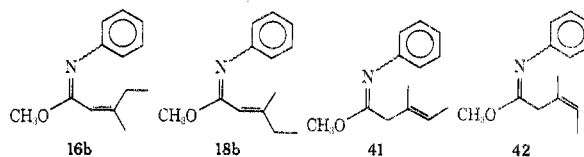


- (14) N. Schamp, N. De Kimpe, and W. Coppens, *Tetrahedron*, **31**, 2081 (1975).
- (15) N. De Kimpe, N. Schamp, and W. Coppens, *Bull. Soc. Chim. Belg.*, **84**, 227 (1975).
- (16) N. De Kimpe and N. Schamp, *Tetrahedron Lett.*, 3779 (1974).
- (17) N. De Kimpe and N. Schamp, *Bull. Soc. Chim. Belg.*, **83**, 507 (1974).
- (18) D. Cantacuzène and M. Tordeux, *Tetrahedron Lett.*, 4807 (1971).
- (19) R. H. de Wolfe and W. G. Young, *Chem. Rev.*, **56**, 786 (1956).
- (20) A. Streitwieser, "Solvolytic Displacement Reactions", McGraw-Hill, New York, N.Y., 1962.
- (21) C. Vernon, *J. Chem. Soc.*, **423**, 4462 (1954).
- (22) R. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1970.
- (23) N. Turro, *Acc. Chem. Res.*, **2**, 25 (1969).
- (24) H. Quast, E. Schmitt, and R. Frank, *Angew. Chem.*, **83**, 728 (1971).
- (25) H. Quast and W. Rissler, *Angew. Chem.*, **85**, 411 (1973).
- (26) F. Greene, R. Camp, V. Abegg, and G. Pierson, *Tetrahedron Lett.*, 4091 (1973).
- (27) R. Camp and F. Greene, *J. Am. Chem. Soc.*, **90**, 7349 (1968).
- (28) D. Sclove, J. Pazos, R. Camp, and F. Greene, *J. Am. Chem. Soc.*, **92**, 7488 (1970).
- (29) J. Liebman and A. Greenberg, *J. Org. Chem.*, **39**, 123 (1974).
- (30) E. Ullman and W. Fanshawe, *J. Am. Chem. Soc.*, **83**, 2379 (1961).
- (31) F. Greene and J. Pazos, *J. Org. Chem.*, **34**, 2269 (1969).
- (32) J. Sheehan and I. Lengyel, *J. Am. Chem. Soc.*, **86**, 746 (1964).
- (33) W. Adam, J.-C. Liu, and O. Rodriguez, *J. Org. Chem.*, **38**, 2269 (1973).
- (34) J. Deyrup and R. Greenwald, *Tetrahedron Lett.*, 5091 (1966).
- (35) H. U. Hostettler, *Helv. Chim. Acta*, **49**, 2417 (1966).
- (36) N. Turro, S. Edelson, J. Williams, and T. Darling, *J. Am. Chem. Soc.*, **90**, 1926 (1968).
- (37) K. Srinivasan and J. Boyer, *J. Chem. Soc., Chem. Commun.*, 379 (1974).
- (38) C. Marvel and F. Hager, "Organic Syntheses", Collect. Vol. I, Wiley, New York, N.Y., 1948, p 248.
- (39) J. Johnson and F. Hager, "Organic Syntheses", Collect. Vol. I, Wiley, New York, N.Y., 1948, p 351.
- (40) W. Coppens and N. Schamp, *Bull. Soc. Chim. Belg.*, **81**, 643 (1972).
- (41) S. O. Lawesson et al., *Recl. Trav. Chim. Pays-Bas*, **83**, 462 (1964).
- (42) The NMR spectrum of **13a** (obtained from preparative gas chromatography or distillation in vacuo) showed a complex pattern of methoxy peaks at δ 3.2–3.4 ppm, which immediately collapsed to a single peak on addition of a few drops of 2 N HCl; this trituration with acid resulted in the spectrum of the appropriate dimethoxymethyl ketone, i.e., 1,1-dimethoxy-4-methyl-2-pentanone (**34a**), in pure form.
- (43) In general cis α,β -unsaturated imidates **15** were converted into a mixture of cis and trans α,β -unsaturated esters **38** and **39**, while trans imidates **15'** were transformed into exclusively trans α,β -unsaturated esters **39**. Contrary to the immediate hydrolysis of dimethoxymethylketimines, the α,β -unsaturated imidates were hydrolyzed in a slower way. In a typical standardized experiment, *trans*-methyl *N*-phenyl-4-methyl-2-penten-imidate (**15'a**) was dissolved in CCl_4 and treated with excess 2 N HCl (in an undegassed and unsealed NMR tube). The emulsion was shaken regularly, followed by NMR measurement of the organic layer. Compound **15'a** showed a half-life period of 105 min at 35°C.
- (44) The imidates were most probably existing in the *Z* form (i.e., the one with the aryl group cis with respect to the methoxy group) based on accepted concepts of steric considerations, although a recent paper, concerning *E/Z* isomerism (syn/anti) of saturated imidates, reported that steric influences as well as dipole interactions play a role in the determination of the equilibrium.⁴⁵
- (45) C. O. Meese, W. Walter, and M. Berger, *J. Am. Chem. Soc.*, **96**, 2259 (1974).
- (46) The mass spectrum of **13a** clearly supports the structure: expulsion of a dimethoxymethyl radical ($\text{CH}_2\text{OCH}=\text{OCH}_3$) provides the base peak *m/e* 160. Also the dimethoxymethyl cation *m/e* 75 is typical for this compound. Contrary to this observation, the corresponding O analogues, 1,1-dimethoxy-2-alkanones, are characterized by the base peak *m/e* 75 ($\text{CH}_2\text{OCH}=\text{O}^+\text{CH}_3$)¹⁷.
- (47) (a) E. Abderhalden, *Hoppe-Seyler's Z. Physiol. Chem.*, **251**, 164 (1938); (b) L. A. Yanovskaya and V. F. Kucherov, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, **7**, 1341 (1964); *Chem. Abstr.*, **61**, 11887 (1964).
- (48) All cis *N*-aryl α,β -unsaturated imidates **15** showed the unresolved AB part (NMR, 60 MHz, CCl_4) of the ethylenic protons at δ 5.3–5.6 ppm (**ABX** or **ABX₂**). Since the structural assignment of **15a** and **15c** was fully established, the correspondence of spectral analysis, especially the typical AB line pattern, allowed us to determine the cis *N*-aryl α,β -unsaturated imidates **15** by analogy.
- (49) The δ values of the β -methyl groups allowed us to distinguish cis and trans isomers **16** and **18**. Similar to α,β -unsaturated carbonyl compounds^{50,51} the methyl group cis with respect to the carbon-nitrogen double bond in α,β -unsaturated imidates resonated at lower field than when trans, the cis methyl group being deshielded because of the anisotropy of the C=N function.
- (50) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, Elmsford N.Y., 1969.
- (51) H. Günther, "NMR Spektroskopie", Georg Thieme Verlag, Stuttgart, 1973.
- (52) R. B. Wagner, *J. Am. Chem. Soc.*, **71**, 3214 (1949).
- (53) These four isomeric compounds were characterized by their mass spectrum, obtained by GC-MS coupling (Varian 1200, AEI MS 30 OV₁ capillary column 150 m, temperature 80 \rightarrow 160°C, 0.5°C/min). The observation that β,γ -unsaturated imino esters were more volatile than the α,β -unsaturated isomers and that cis isomers were more volatile than trans isomers allowed us to classify the imino esters as follows (increasing volatility with percent amount in parentheses): **18b** (45%) < **16b** (15%) < **41** (28%) < **42** (12%).



Solvolytic Rearrangement of Quadricyclyl-7-carbinol¹

William G. Dauben* and John W. Vinson

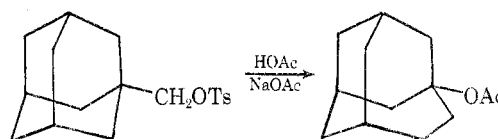
Department of Chemistry, University of California, Berkeley, California 94720

Received July 29, 1975

Quadricyclyl-7-carbinol was synthesized from 7-benzyloxymethylnorbornenone via 7-benzyloxynorbornadiene. The triflate ester of the carbinol upon solvolysis in buffered trifluoroethanol rearranged via a cyclopropylethyl carbonium ion pathway. This result indicates that the energy gained by rearrangement from a primary to a secondary carbonium ion to form a quadricyclooctyl system is insufficient to overcome the strain engendered in the new ring system.

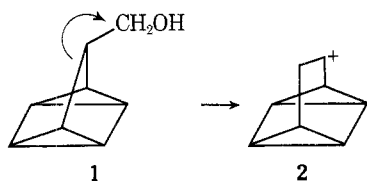
Much work has been reported on the solvolysis of strained ring systems,² and the usual result has been the formation of less strained ring systems. A problem which has been less thoroughly investigated is the use of carbonium ion rearrangements to incorporate strain into the ring system. Considerable energy can be released when a less stable primary carbonium ion rearranges to the highly stabilized tertiary carbonium ion, and it should be possible to salvage some of this energy in the form of higher skeletal strain. One such case of such energy salvage is found in the solvolysis of 1-adamantylcarbinyl tosylate.³ In this case, the stabilization energy gained in going to the tertiary car-

bonium ion outweighs the increased skeletal strain of the homoadamantyl ring system.



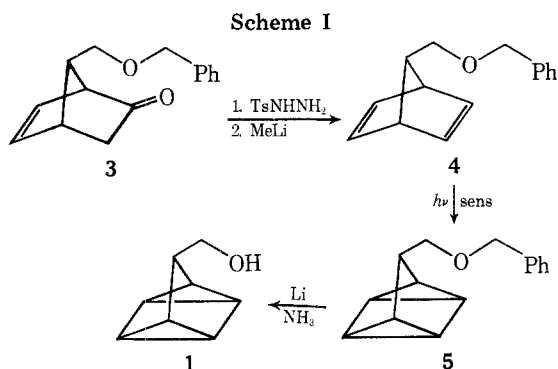
It is well known that an adjacent cyclopropyl ring can stabilize a carbonium ion,⁴ but a less investigated problem is how early in the process of rearrangement does the assistance of a neighboring group take effect. A compound that

has the potential of providing answers to both the questions of introduction of strain by rearrangement and participation of stabilizing groups in the process of rearrangement is quadricyclyl-7-carbinol (1). Solvolysis of the sulfo-



nate ester of 1 would give an ion theoretically capable of a myriad of rearrangements. Of special interest is the most obvious rearrangement, a 1,2-alkyl shift. In this rearrangement an intermediate with a highly stabilized cyclopropylcarbinyl structure would be formed from the unstabilized primary cation, but the rearranged structure 2 is very highly strained. The strain of 2 is evident both from molecular models and from the extreme thermal lability of compounds with the same skeleton.⁵ A minimum of 8 kcal/mol would be gained by rearrangement from a primary to a secondary cation, and even more if the cyclopropyl ring can participate in the rearrangement step.⁵ The question raised is whether the stabilization gained is sufficient to overcome the concomitant increase in ring strain introduced by the rearrangement to the quadricyclooctane skeleton.

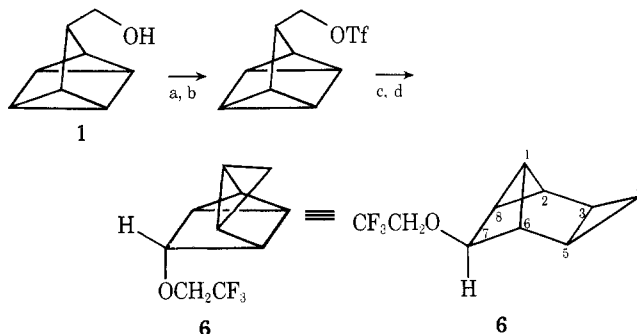
Compound 1 was synthesized by the route shown in Scheme I. It was found that the *p*-toluenesulfonate ester



and the *p*-bromobenzenesulfonate ester of 1 upon acetolysis in sodium acetate buffered acetic acid at 60 and 100° gave an intractable mixture of ten or more products. This multitude of products formed in the acetolysis was apparently due to attack of the solvent on the strained quadricyclooctane system, itself.

A manageable solvolysis product mixture was obtained by solvolysis of the highly reactive trifluoromethanesulfonate ester⁶ in the nonacidic, nonnucleophilic solvent trifluoroethanol.⁷ The triflate of 1 was prepared by reaction of the lithium salt of 1, prepared with *n*-butyllithium in benzene, with triflic anhydride. Solvolysis of the triflate in trifluoroethanol with 1 equiv of triethylamine, to scavenge the acid produced in the reaction, led to a mixture of five products. One of these products comprised 80% of the product mixture, and it was obtained in a pure state by preparative gas chromatography; the other four products ranged from 1 to 7% of the mixture, and they could not be resolved into pure compound on preparative gas chromatography.

The major solvolysis product was assigned structure 6 on the basis of spectral evidence. The mass spectrum showed a parent ion at *m/e* 204, consistent with 6; the infrared spectrum displayed no absorptions for olefinic bonds, suggesting a quadricyclic structure. The NMR spectrum also had no resonance bands higher than δ 5.0, a feature also indi-



a, BuLi; b, $(\text{CF}_3\text{SO}_2)_2\text{O}$; c, Et_3N ; d, $\text{CF}_3\text{CH}_2\text{OH}$

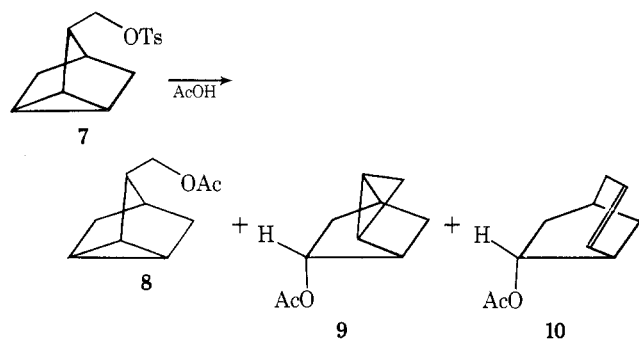
cating the absence of olefinic hydrogens. There were eight resolved signals in the NMR spectrum, as described in Table I. The two-proton quartet at δ 3.88 is characteristic

Table I
NMR Resonances of Compound 6

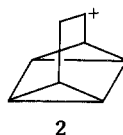
δ	Protons	Assignment	Coupled to protons
0.20	2	C-4	C-3, C-5; $J = 2.8$ Hz
0.92	1	C-5	C-3, C-4, C-6 ($J = 1.0$ Hz)
1.37	2	C-2, C-3	C-1, C-3, C-4, C-6, C-8
1.80	1	C-1	C-2, C-6, C-8
1.86	1	C-8	C-1, C-2, C-7
2.88	1	C-6	C-5 ($J = 1.0$ Hz), C-2 ($J = 0.4$ Hz), C-1, C-7
3.88	2	CH_2CF_3	Fluorine ($J = 8.8$ Hz)
4.03	1	C-7	C-6 ($J = 3.4$ Hz), C-8 ($J = 1.8$ Hz)

of the trifluoroethyl group. The two-proton multiplet at δ 0.2 is assigned to the two secondary cyclopropyl protons on C-4. The doublet of doublets integrating for one proton at δ 4.03 is assigned to the proton on the carbon bearing the trifluoroethyl group, and the doublet of multiplets at δ 2.88 is ascribed to the proton on the tertiary noncyclopropyl carbon, C-6. The remaining protons were assigned by extensive homonuclear decoupling, as summarized in Table I, except that carbons 2 and 3 could not be distinguished owing to overlapping of their signals. The stereochemistry of the cyclopropyl ring at C-3 and C-5 is assigned exo for two reasons. First, the most plausible mechanism suggests such an arrangement. Second, a coupling constant of 1 Hz between the protons on C-5 and C-6 is in line with a large dihedral angle relationship. Inspection of models of the exo and endo ring fused isomers show a dihedral angle of 55° for the exo and 15° for the endo; using the Karplus⁸ equation these values suggest coupling constants of 2.5 and 7.5 Hz, respectively. An enlarged CCH angle at C-5, due to the cyclopropyl ring, could cause a reduction of the predicted coupling constants, but the magnitude is not known.⁹ In view of the fact that the exo stereochemistry is mechanistically predicted, it is assumed that bond angle changes would not reduce the coupling constant sufficiently to indicate an endo stereochemistry. All other coupling constants are consistent with the assigned structure 6.

The solvolysis of 1 involves a cyclopropylethyl carbonium ion, and a close analogy to it is to be found in the solvolysis of 7.¹⁰ In the latter case, the major products were 8, 9, and 10, and the primary difference in these two systems is that in the case of 7, the product 9 only comprises 35% of the reaction mixture whereas 6 makes up 80% of the products from 1. Consideration of other possible results of the Wagner–Meerwein rearrangement of 1, in analogy to 7, shows that all such detectable products should be olefinic. Not only should 2 continue to rearrange by one or more cyclopropylcarbinyl-homoallyl openings, but if trapped as 2,



the observed product should be a bicyclooctadiene in view of the known lability of the quadricyclooctyl system 2.⁵



Olefinic materials account for less than 2% of the reaction mixture. The stabilization that is obtained by conversion of primary to a secondary carbonium thus is insufficient to overcome the increase in strain engendered in such a simple 1,2 shift. With such a shift ruled out, the more obscure cyclopropylethyl carbonium ion rearrangement becomes the main path of the rearrangement process.

Experimental Section

7-Benzyloxymethylnorbornadiene (4). A solution of 27.8 g (0.12 mol) of 7-benzyloxymethylnorbornenone (3)¹¹ and 22.7 g (0.12 mmol) of *p*-toluenesulfonylhydrazine in 100 ml of THF was heated under reflux for 12 hr. TLC with 25% ether-pentane on silica gel G indicated the absence of ketone (R_f 0.7) and the presence of tosylhydrazone (R_f 0.05). The solution was diluted with 400 ml of benzene, and the mixture distilled until the distillation temperature reached 80°. The residue was cooled to 0° and treated with 153 ml (5.49 g of methyl lithium, 0.25 mol) of 5.07% methyl lithium solution. The addition was done slowly with a syringe; foaming occurred during the first part of the addition. A Gilman test of the solution after the addition was complete was positive.

The orange solution was stirred under nitrogen at room temperature for 6 hr, 150 ml of water was added, and the organic layer separated. The extract was washed with water and saturated NaCl solution, filtered through $MgSO_4$, and concentrated at reduced pressure. The residue was Kugelrohr distilled to yield 10.62 g (41%) of 4: NMR δ 2.74 (tr of m, 1), 3.24 (d, $J = 8$ Hz, 2), 3.35 (sextet, $J = 2$ Hz, 2), 4.30 (s, 2), 6.45 (tr, $J = 2$ Hz, 2), 6.70 (tr, $J = 2$ Hz, 2), 7.14 (s, 5); ir 3080, 2980, 2970, 2850, 1080 cm^{-1} ; mass spectrum m/e 212, 145, 91.

Anal. Calcd for $C_{15}H_{16}O$ (212.29): C, 84.87; H, 7.60. Found: C, 84.66; H, 7.73.

7-Benzyloxymethylquadricyclane (5). A solution of 10.8 g (0.048 mol) of 7-benzyloxymethylnorbornadiene (4) and 250 mg of triphenylene in 840 ml of benzene was irradiated with Vycor-filtered light from a Hanovia 450-W lamp for 6 hr. The benzene was rotary evaporated, and the residue chromatographed on 500 g of silica gel. The triphenylene was eluted with twelve 200-ml fractions of 10% benzene-pentane and the 7-benzyloxymethylquadricyclane with three 200-ml fractions of 10% ether-pentane: yield 7.47 g (73%); NMR δ 1.2–1.6 (m, 6), 2.74 (tr of m, 1), 3.39 (d, 2), 4.40 (s, 2), 7.25 (s, 5); ir 3030, 2850, 1090 cm^{-1} .

Anal. Calcd for $C_{15}H_{16}O$ (212.29): C, 84.87; H, 7.60. Found: C, 84.61; H, 7.37.

Quadricyclyl-7-carbinol (1). A solution of 7.25 g (34.2 mol) of 7-benzyloxymethylquadricyclane in 500 ml of ammonia (distilled from blue sodium-ammonia solution) and 500 ml of THF was

stirred at -78° and 0.47 g (2 equiv) of lithium wire was added in 1-cm long pieces. The mixture was allowed to reflux for 90 min and an additional 50 mg of lithium added (blue color remained). To the solution was carefully added 200 ml of water and 200 ml of ether; the ammonia was allowed to evaporate. The residue was chromatographed on 800 g of silica gel with 10–30% ether-pentane. The most polar fraction was quadricyclyl-7-carbinol, crude yield 4.02 g (96%), and the material recrystallized from pentane: yield 1.92 g (47%); mp 42.0–43.5°; NMR δ 1.20–1.60 (m, 6), 2.65 (tr of m, $J = 7$ Hz, 1), 3.56 (d, $J = 7$ Hz, 2), 4.26 (s, 1, variable with concentration); ir 3330, 3075, 2920, 1230, 1030 cm^{-1} ; mass spectrum m/e 122, 91.

Anal. Calcd for $C_8H_{10}O$ (122.17): C, 78.65; H, 8.25. Found: C, 78.66; H, 8.09.

Quadricyclyl-7-carbinyl Triflate. A solution of 221 mg of the carbinol in 10 ml of anhydrous benzene was cooled to 0° and allowed to react with 0.84 ml of a 2.27 *M* butyllithium solution. At 0°, 525 mg (1.8 mmol) of triflic anhydride was weighed into the solution, with swirling. A gelatinous precipitate of lithium triflate formed within 1 min and the precipitate was removed by centrifugation. The benzene was rotary evaporated to yield the crude triflate, which decomposed on attempted purification. The crude product had the following spectral properties: NMR δ 1.2–1.8 (m, 6), 2.95 (tr of m, 1), 4.45 (d, 2); ir 3080, 2940, 1740, 1410, 1240, 1140, 930 cm^{-1} ; mass spectrum m/e 254, 105, 91.

Trifluoroethanolysis of 7-Quadricyclylcarbinyl Triflate. A solution of 450 mg of crude triflate and 250 mg of triethylamine in 10 ml of trifluoroethanol was allowed to stand at room temperature for 20 hr, at which time the NMR spectrum of an aliquot indicated the absence of triflate (doublet at δ 4.46). The solution was diluted with aqueous sodium bicarbonate solution and with pentane. The pentane layer was removed and the aqueous trifluoroethanol solution extracted three times with pentane. The combined extracts were washed with saturated NaCl solution, dried ($MgSO_4$ and $NaHCO_3$), and the solvent removed as samples studied. The mixture was analyzed by VPC (6 ft \times 0.125 in., 10% Carbowax 600–10% KOH, 80°).

The major product (80%) was the only one of the six products which could be isolated. The NMR spectral data are given in the text; mass spectrum m/e 204, 139, 105, 91, 78, 77.

Registry No.—1, 56817-37-9; 3, 56817-38-0; 4, 56817-39-1; 5, 56817-40-4; 6, 56817-42-6; quadricyclyl-7-carbinyl triflate, 56817-41-5; triflic anhydride, 358-23-6.

References and Notes

- (1) This work was supported by Grant No. GP-8700, National Science Foundation.
- (2) W. G. Dauben and L. N. Reitman, *J. Org. Chem.*, **40**, 835, 841 (1975); W. L. Dilling and J. A. Alford, *J. Am. Chem. Soc.*, **96**, 3615 (1974), and earlier papers; W. G. Dauben and D. L. Whalen, *ibid.*, **93**, 7244 (1971), and earlier papers; W. Lotsch and A. S. Kende, *Angew. Chem., Int. Ed. Engl.*, **10**, 559 (1971); J. C. Barborak and R. Pettit, *J. Am. Chem. Soc.*, **89**, 3080 (1967); P. v. R. Schleyer, J. J. Harper, G. C. Dunn, V. J. D. Pasquo, and J. R. E. Hoover, *ibid.*, **89**, 698 (1967); for a general review see R. C. Fort, Jr., in "Carbonium Ions", Vol. 4, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1973, Chapter 32; R. E. Leone, J. C. Barborak, and P. v. R. Schleyer, *ibid.*, Chapter 33.
- (3) J. E. Nordlander, S. P. Jindal, P. v. R. Schleyer, R. Fort, Jr., J. J. Harper, and R. D. Nicholas, *J. Am. Chem. Soc.*, **88**, 4475 (1966).
- (4) H. G. Richey, Jr., in "Carbonium Ions", Vol. 3, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1972, Chapter 25; K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe, III, *ibid.*, Chapter 26.
- (5) H. Prinzbach, G. Phillipposian, and U. Scheidegger, *Helv. Chim. Acta*, **53**, 857 (1970), and earlier papers; S. F. Nelson and J. P. Gillespie, *Tetrahedron Lett.*, 3259, 5059 (1969); R. S. H. Liu, *ibid.*, 1409 (1969).
- (6) A. Streitwieser, Jr., C. L. Wilkins, and E. Kiehlmann, *J. Am. Chem. Soc.*, **90**, 1598 (1968).
- (7) W. S. Trahanovsky and M. P. Doyle, *Tetrahedron Lett.*, 2155 (1968).
- (8) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).
- (9) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, Elmsford, N.Y., 1969, p 286.
- (10) J. A. Berson, D. Wege, G. M. Clarke, and R. G. Bergmann, *J. Am. Chem. Soc.*, **91**, 5601 (1969), and earlier papers; R. R. Sauers and J. A. Beisler, *J. Org. Chem.*, **32**, 569 (1967); K. B. Wiberg and G. R. Wenzinger, *ibid.*, **30**, 2278 (1965).
- (11) E. J. Corey, T. Ravindranathan, and S. Terashima, *J. Am. Chem. Soc.*, **93**, 4326 (1971).