**1,2,5-Trimethylcyclopentanol** was prepared from 2,5-dimethylcyclopentanone and $CH_3MgI$. 2,5-Dimethylcyclopentanone (12.6 g) gave 7.0 g (48%) of 1,2,5-trimethylcyclopentanol, bp 45° (4.5 mm) [lit.[22] bp 176.6° (749 mm)].

**1,2,3-Trimethylcyclopentene.** 1,2,5-Trimethylcyclopentanol (2 g) was added to $ZnCl_2$ (2 g) and the mixture was heated to 160°. The olefin (bp 121°)[23] was distilled from the reaction mixture as it formed giving 1.5 g (87.2%).

**Acknowledgment.** Support of this work by grants from the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

(22) A. V. Koperina and B. A. Kazanskii, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 302 (1968).

(23) W. A. Noyes and C. E. Burke, *J. Amer. Chem. Soc.*, **34**, 174 (1912).

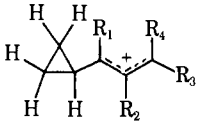
# The Preparation and Reactions of Cyclopropylallyl Cations

**T. S. Sorensen* and K. Rajeswari**

*Contribution from the Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada.* *Received November 16, 1970*

**Abstract:** Cyclopropylallyl cations rearrange at measurable rates to give a variety of cyclohexenyl and cyclopentenyl cations. The reaction was studied in three different acid solvents, $H_2SO_4$, $FSO_3H$, and $FSO_3H$–$SbF_5$, the "acidity" increasing greatly in the order given. The exact products are quite different in each solvent and a mechanism is proposed to account for the product cations actually observed.

The 3-cyclopropylallyl cations (Ia–c) can all be directly observed at moderately low temperatures (*e.g.*, −50°). However, at higher temperatures each disappears by a clean first-order kinetic process.

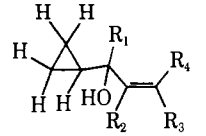


Ia, $R_1 = R_3 = R_4 = CH_3$; $R_2 = H$
b, $R_1 = R_2 = R_3 = CH_3$; $R_4 = H$
c, $R_1 = R_2 = R_3 = R_4 = CH_3$

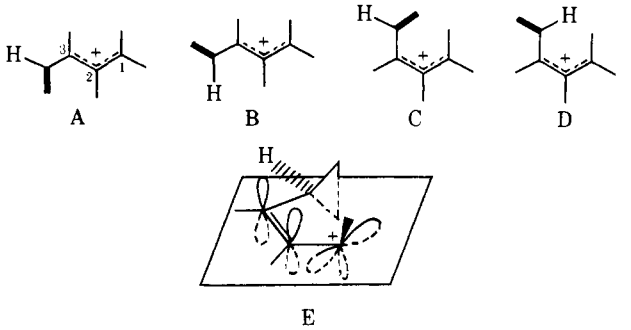
In this paper, we present a detailed study of this system, including the characterization of the cyclopropylallyl cations, rate measurements in three different acid solvents, the measurement of activation parameters, and a complete product characterization study.

Ions of type I have been reported only in cases where the allylic system is part of a five- or six-membered ring, *i.e.*, cyclopropyl-substituted cyclopentenyl or cyclohexenyl cations.[1] These ions, in marked contrast to those studied in this work, are "stable" at room temperature in concentrated acid solvents.[2]

**The Cyclopropylallyl Cations.** Each cyclopropylallyl cation was prepared from the corresponding alcohol (IIa, b, c) and a strong acid solvent in the usual way. Three different strong acid solvents, $FSO_3H$, $H_2SO_4$, and $FSO_3H$–$SbF_5$ (1:1 or 4:1), these covering a wide range of "acid strength," were used. All reactions have been carried out *in situ*, in most cases employing 10% w/v[3] solutions. Table I lists the nmr assignments for the three ions Ia–c. The cyclopropyl ring protons appear as broad peaks partially obscured by the methyl resonances and no attempt has been made to analyze these. Only in Ib is it possible to easily assign the protons of the allyl portion. In Ia, the assignment is based partly on a comparison of the spectrum with that from Ib and partly on an analysis of the reversible temperature dependence of the chemical shifts of the protons, tabulated in Table II. Relative to three separate reference signals, one methyl resonance shifts to higher fields as the temperature increases, one shifts to lower fields, and one remains constant. In addition, the C2 proton shifts strongly to higher fields. To interpret this temperature effect one must consider the possible conformations of the ion. With a cyclopropyl ring in a bisected conformation, there are four possibilities, arbitrarily labeled A, B, C, and D.[4] One



IIa, $R_1 = R_3 = R_4 = CH_3$; $R_2 = H$
b, $R_1 = R_2 = R_3 = CH_3$; $R_4 = H$
c, $R_1 = R_2 = R_3 = R_4 = CH_3$



E

(1) N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *J. Amer. Chem. Soc.*, **87**, 4533 (1965).

(2) The term "stable," as used in this paper, means that the ions have an extended existence at 25° in the order of days or weeks.

(3) Weight of alcohol in grams per volume of acid in milliliters.

(4) It is questionable whether any of the conformations of Ia or Ic are completely planar because of the steric repulsion of the two "upright" substituents.

Table I. Nmr Spectra of the Cyclopropylallyl Cations in $FSO_3H$ Solvent

| Ion | Temp, °C | $R_1$ ($CH_3$) | $R_2$ (H or $CH_3$) | $R_3$ ($CH_3$) | $R_4$ (H or $CH_3$) | Cyclopropane ring |
|---|---|---|---|---|---|---|
| Ia | −20 | 7.44[a] | 2.53 | 7.63 | 7.30 | 6.6–7.2 |
| Ib | −10 | 7.51 | 7.75 | 7.595 (d) $J$ = 7 Hz | 1.62 (q) $J$ = 7 Hz | 6.4–7.3 |
| Ic | −30 | 7.58 or 7.62 | 7.84 | 7.58 or 7.62 | 7.40 | 6.3–7.35 |

[a] In $\tau$ units relative to internal tetramethylammonium cation = 6.90, ref 2. Similar chemical shifts were found in $H_2SO_4$ solvent, and also in the case of Ib, in 4:1 $FSO_3H$–$SbF_5$ solvent.

Table II. Temperature Dependence of the Nmr Spectrum of Ia in $FSO_3H$ Solvent

| Temp, °C | $R_2$ (H) | $R_1$, $R_3$, $R_4$ ($CH_3$) | | |
|---|---|---|---|---|
| −80 | 2.41[a] | 7.31 | 7.33 | 7.48 |
| −60 | 2.46 | 7.30 | 7.34 | 7.46 |
| −40 | 2.49 | 7.30 | 7.35 | 7.45 |
| −20 | 2.53 | 7.30 | 7.36 | 7.44 |
| 0 | 2.57 | 7.30 | 7.37 | 7.43 |
| +15 | 2.58 | 7.30 | 7.37 | 7.43 |
| +30 | 2.59 | 7.30 | 7.38 | 7.43 |

[a] In $\tau$ units relative to internal tetramethylammonium cation = 6.90, with secondary references of internal acetone = 6.98 and the *tert*-butyl group of the 1-*tert*-butyl-3-methylcyclopentenyl cation = 8.50. These three internal references do not change in relative position as the temperature is changed.

can immediately reject symmetrical conformations, *e.g.*, E, in which one end of the "allyl" system has been twisted 90°, since only two separate methyl resonances would be observed. For this same reason, the rotation of the two C1 methyl groups about the C2–C1 bond axis must be slow on the nmr time scale. Although not directly measurable, it seems reasonable to suppose that the rather analogous rotation about the C3–C2 bond axis, leading to interconversions between A and C or B and D, would also be slow. On the basis of steric repulsions, *e.g.*, conformer C, and the preference of transoid structures in extending conjugation (into the cyclopropane ring), the two most probably "bisected" conformers would be A and B. The temperature-dependent chemical shifts observed for Ia can then be rationalized if one assumes (a) that conformer B is the more stable and (b) that protons in the face of the cyclopropyl ring will be shielded. A similar procedure has, for example, been used in the analysis of the vinylcyclopropane nmr spectrum[5] and the appreciable shielding effects of a cyclopropyl ring are clearly shown in the nmr spectrum of the cyclopropyldimethylcarbonium ion.[6] The conformers A and B must be rapidly interchanging on an nmr time scale except at low temperatures (< −80°) where, for example, the C2 proton signal begins to broaden appreciably.

Neither ion Ib nor Ic shows appreciable temperature dependent chemical shifts and we believe that only conformer B is important in these cases, the steric repulsion between the C2 methyl group and the cyclopropyl group destabilizing conformer A. The assignment of protons in Ic has been made by the closest matching of observed resonances with those of Ia and Ib without attempting to distinguish the closely separated peaks at $\tau$ 7.58 and 7.62.

There is no indication that the chemical shift positions (and by analogy the conformations) are in any way dependent on the acid solvent used.

The chemical shifts of the methyl groups at C1 and C3 are much higher than those in simple methyl-substituted allyl cations, as expected,[1] but no attempt is made to picture this charge delocalization in the formulas.

In conclusion, we believe these ions exist preferentially in all of the acid solvents in conformation B with, on an nmr time scale at −50°, slow rotation about C3–C2[7] and rapid rotation about C3-cyclopropyl.

**Rate Studies.** The rate constants for the rearrangement of Ia–c, both as a function of temperature and acid solvent, are given in Table III. In each case, a reference signal ($CH_3NO_2$) was used as a standard peak area with which to measure the disappearance of the cyclopropylallyl cations (see Experimental Section). In a 1:1 $FSO_3H$–$SbF_5$ solvent system it was not practical to measure the actual rate of rearrangement of I because this solvent becomes very viscous at the low temperatures needed in this measurement. Suitable inert diluents could probably be added; however, it was observed that in a 4:1 $FSO_3H$–$SbF_5$ mixture, identical products were observed in each case and in two cases, crude kinetics could also be obtained.

Several points may be made which will be relevant in discussing the mechanism of the reaction. (1) The rate of rearrangement of Ia–c is of the same order of magnitude in $H_2SO_4$ and $FSO_3H$ but faster in 4:1 $FSO_3H$–$SbF_5$ and even faster still in 1:1 $FSO_3H$–$SbF_5$. (2) At the same temperature, using the measured activation energy data, the relative values of $k$ are 1:24:330 for Ia, Ib, and Ic, respectively. (3) The rate is fractionally faster in $FSO_3H$ compared to $H_2SO_4$. This same relative order has been observed previously[8] in another observable unimolecular cation–cation rearrangement.

**Product Study.** The nature of and the relative amounts of the product ions from the cyclopropylallyl cation rearrangements are completely dependent on the particular acid solvent system used in the study and hence will be described separately for each solvent system. A census of the product ions produced depends very much on the time elapsed at which one looks at the reaction since many of the earliest products are unstable. The identification of the products is accomplished in most cases by the usual comparison with authentic samples and of perhaps even more use in the case of unstable ions, by noting the character-

(5) G. R. De Mare and J. S. Martin, *J. Amer. Chem. Soc.*, **88**, 5033 (1966).

(6) C. U. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 2998 (1965).

(7) The stereochemistry at C3 in the ions is undeveloped in the alcohol precursers. Ion formation is assumed to occur through heterolysis of a protonated hydroxy function and this probably leads directly to conformer A or B.

(8) T. S. Sorensen, *J. Amer. Chem. Soc.*, **91**, 6398 (1969).

Table III. Rates and Activation Parameters for the Rearrangement of the Cyclopropylallyl Cations

| Ion | Solvent | Temp,[a] °C | $k$,[b] sec$^{-1}$ | $\Delta H^{\pm}$ [c] | $\Delta F^{\pm}$ [c] | $\Delta S^{\pm}$, eu |
|---|---|---|---|---|---|---|
| Ia | $FSO_3H$ | 0 | $9.2 \times 10^{-5}$ | | | |
| | | 6.2 | $1.3 \times 10^{-4}$ | | | |
| | | 14.2 | $4.8 \times 10^{-4}$ | | | |
| | | 20.2 | $1.0 \times 10^{-3}$ | | | |
| | | 29.6 | $2.1 \times 10^{-3}$ | 17 | 21.5 | −15 |
| | $H_2SO_4$ | 13.95 | $4.0 \times 10^{-4}$ | | | |
| | $FSO_3H$–$SbF_5$ (4:1) | *Ca.* −70 | Very fast | | | |
| Ib | $FSO_3H$ | −22.0 | $7.5 \times 10^{-5}$ | | | |
| | | −16.0 | $1.6 \times 10^{-4}$ | | | |
| | | −9.7 | $5.2 \times 10^{-4}$ | | | |
| | | −4.7 | $9.7 \times 10^{-4}$ | | | |
| | | 0.1 | $1.7 \times 10^{-3}$ | 19 | 19.5 | −2 |
| | $H_2SO_4$ | −9.7 | $3.8 \times 10^{-4}$ | | | |
| | $FSO_3H$–$SbF_5$ (4:1) | *Ca.* −10 | *Ca.* $1 \times 10^{-3}$ | | | |
| Ic | $FSO_3H$ | −49.8 | $7.2 \times 10^{-5}$ | | | |
| | | −43.8 | $1.7 \times 10^{-4}$ | | | |
| | | −39.4 | $2.9 \times 10^{-4}$ | | | |
| | | −32.2 | $7.9 \times 10^{-4}$ | | | |
| | | −27.1 | $1.7 \times 10^{-3}$ | 15 | 18 | −9 |
| | $FSO_3H$–$SbF_5$ (4:1) | *Ca.* −90 | *Ca.* $4 \times 10^{-4}$ | | | |

[a] ±0.1°. [b] *Ca.* ±5% based on the scatter from repeated determinations. [c] kcal/mol (±1).

Table IV. Nmr Data for All New Ions in $FSO_3H$ Solvent

| Ion | C1 | C2 | C3 | C4 | C5 | C6 | Other |
|---|---|---|---|---|---|---|---|
| IV[a] | 1.20 b[b] | 7.80 | 7.08 (d) $J$ = 3 | 8.59 | 8.10 (t) $J$ = 6 | 6.79 v.b. | |
| V[c] | 7.29 | 7.87 | 7.29 | 8.625[d] (d) $J$ = 7 | 8.13–8.40 (m) | 6.81 v.b. | |
| XII[e] | 8.48 | 7.58 | 0.33 b | 6.22 or 6.60 b | 6.22 or 6.60 b | | |
| XIII[f] | *g* | 8.62 | 0.11 b | g | g | | |
| XIV[h] | 8.63 (d) $J$ = 6 | 7.86 | 7.17 (t) $J$ = 3 | 6.58 b | 6.58 b | | *i* |
| XVI[j] | 1.11 b | 7.75 | 7.02 b | 8.505[d] (d) $J$ = 7 | 7.6–7.9 (m) | 6.4–7.0 v.b. | |
| XVII[k] | 7.24 | 7.81 | 7.24 | 6.7–6.9 (t) ? | 8.05 (qn) $J$ = 6 | 6.7–6.9 (t) ? | |
| XVIII[l] | 6.99 | 7.74 | 1.23 b | 8.57[d] (d) $J$ = 7 | *g* | *g* | |
| XIX[m] | 8.54 (d) $J$ = 6.5 | 7.69 | *g* | 6.30 or 6.53 b | 6.30 or 6.53 b | | i<br>*o* |
| XXIII[n] | *g* | 2.13 (d) $J$ = 4.5 | −0.11 (d) $J$ = 4.5 | 8.83 and 8.89 both (d) $J$ = 6 | 6.3–6.5 b (m) | | |
| XXIV[p] | 6.93 b | 2.20 (d) $J$ = 8.2 | 0.76 b (d) $J$ = 8.2 | 6.63 or 6.82 b | 8.83 | 6.63 or 6.82 b | |
| XXV[q] | 6.86 and/or 7.01 b | 2.20 | 6.86 or 7.01 b | 6.54 (d) $J$ = 6 | 4.42 b (m) | 8.26 (d) $J$ = 6 | |
| XXVII[r] | 7.00 b | 2.27 | 7.00 b | 6.06–6.22 v.b. | 4.2–4.8 (m) | 4.2–4.8 (m) | |

[a] 2,3,4,4-Tetramethylcyclohexenyl. [b] ±0.01 ppm, v.b. = very broad, b = broad, (d) = doublet, (t) = triplet, (qt) = quartet, (qn) = quintet, (m) = multiplet of peaks with undetermined coupling constants, $J$ in hertz, all peak positions relative to tetramethylammonium cation = τ 6.90. [c] 1,2,3,4-Tetramethylcyclohexenyl. [d] The C4 proton is obscured by C6 protons. [e] 1-*tert*-Butyl-2-methylcyclopentenyl. [f] 1-Methyl-2-*tert*-butylcyclopentenyl. [g] Could not be determined with certainty. [h] 1,2-Dimethyl-3-isopropylcyclopentenyl. [i] The methine proton of the isopropyl group is obscured by C4 and C5 protons. [j] 2,3,4-Trimethylcyclohexenyl. [k] 1,2,3-Trimethylcyclohexenyl. [l] 1,2,4-Trimethylcyclohexenyl. [m] 1-Isopropyl-2-methylcyclopentenyl. [n] 1-Methyl-4-isopropylcyclopentenyl. [o] The chemical shift of the methine proton of the isopropyl group could not be determined. [p] 1,5,5-Trimethylcyclohexenyl. [q] 1,1,3-Trimethyl-5-fluorosulfatohex-1,2,3-enyl cation. [r] 1,1,3-Trimethylhex-5-en-1,2,3-enyl cation.

istic decay patterns (rates and products) of these ions. The following description is a running commentary starting with the earliest observed products.

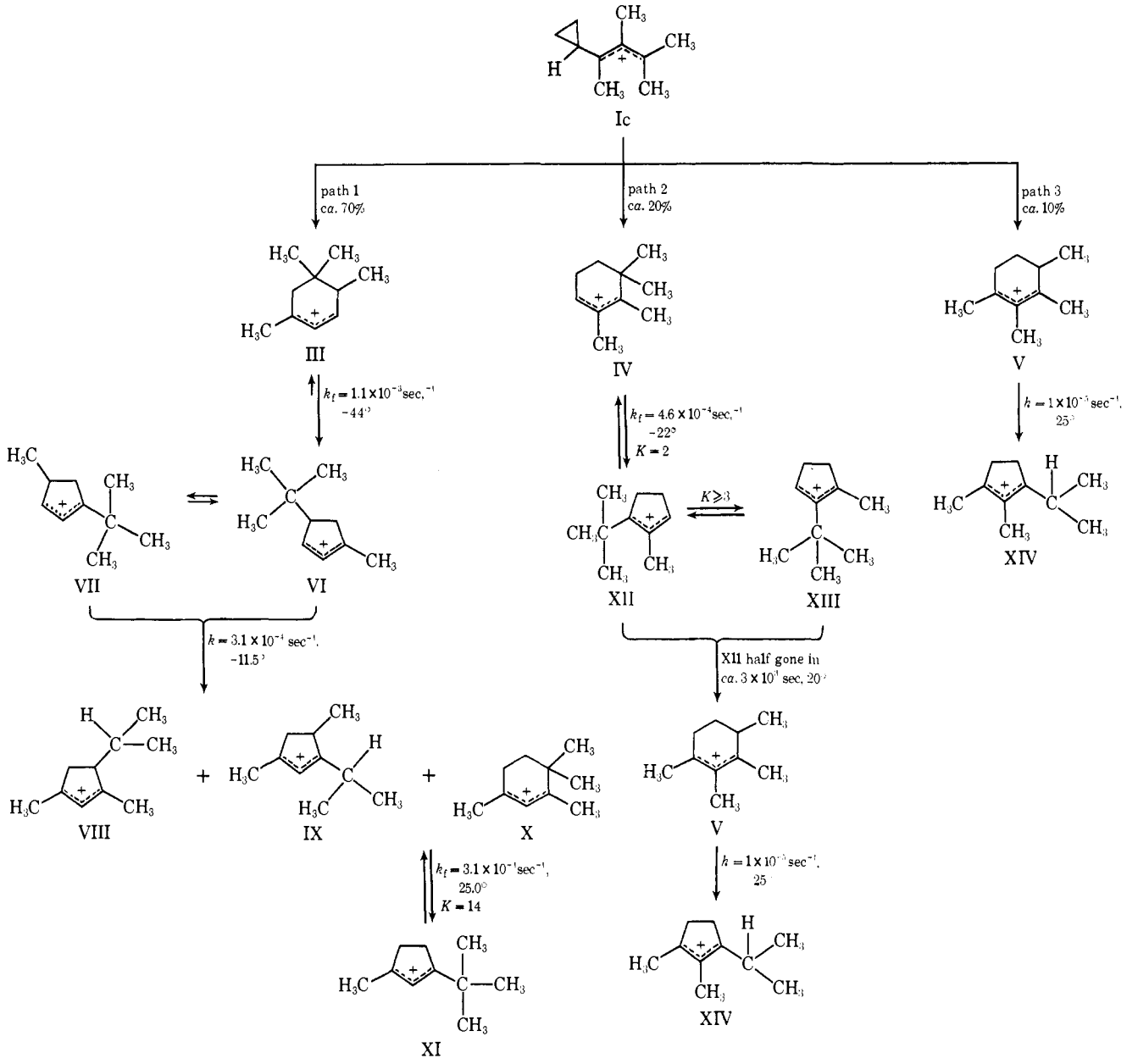
**The Tetramethyl System Ic. Fluorosulfonic Acid Solvent.** This cation in the title solvent most dramatically illustrates the great complexity of the rearrangement products. Scheme I depicts the complete sequence leading to the final, room temperature "stable" (2) ions.

The first observable products are III, IV, and probably V. The path 1 decay series involving II has previously been reported.[9,10] Ion III never appears as a major species in the spectra; however, this is expected since this ion is known[9] to decompose at a rate faster than that measured for the rearrangement of Ic. Employing consecutive first-order kinetics, the calculated value of III/Ic (initial) × 70/100 after 43% reaction is 0.08, in rough agreement with the measured value of 0.16. The daughter decay product VI is actually the

(9) T. S. Sorensen and K. Ranganayakulu, *J. Amer. Chem. Soc.*, **92**, 6539 (1970).

(10) The amount of X formed, relative to VIII and IX, has now been found to be concentration dependent and, for example, using 10% w/v solutions, the ratio is 2:3, while with a 2% solution, the ratio is 1:4. A base-catalyzed ($FSO_3^-$) reaction must be involved here.

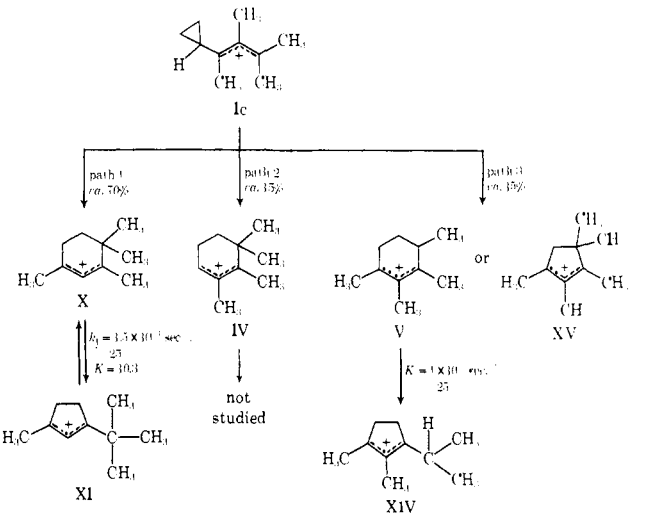
**Scheme I**




early major observable product of the reaction. The decay series involving IV has been elucidated in this work, aided by the independent synthesis of XII, V, and XIV. The nmr spectra of all new product ions are given in Table IV. The formation of XIII almost certainly represents a "deadend" pathway but serves to complicate the kinetics relating to the formation of V, since XIII and V are produced at competitive rates. The third reaction pathway corresponds to the direct formation of V. This identification is not regarded as conclusive and is based on the appearance of nmr peaks at $\tau$ 7.87 and 7.29, identical with the C2 and C1–C3 methyl groups, respectively, of authentic V. In addition, there is absorption in the product spectrum in the region characteristic of the C4 methyl group of V. These separate resonances cannot readily be shown to belong to the same ion and, in particular, an absorption at about $\tau$ 7.87 is a common feature of a great many ions with a C2 methyl group.

**Sulfuric Acid Solvent.** The complete sequence for this solvent is shown in Scheme II. The initial products

**Scheme II**

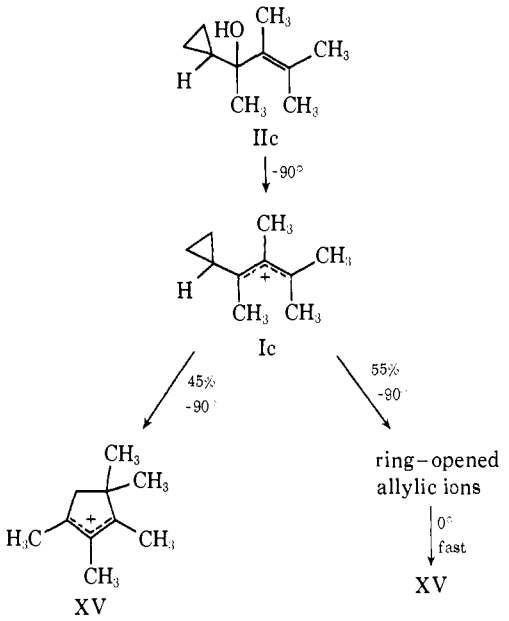



are X, IV, and possibly V or XV or both. The second

pathway appears to be the same as that observed in $FSO_3H$ solvent and we have not investigated the subsequent reactions of IV. The product nmr spectrum has some absorption at $\tau$ 7.86 (represented as path 3) and by analogy to the $FSO_3H$ solvent case, one might tentatively assign the same structure (V); another possibility is XV, a known ion.[11] The major product (path 1) is, however, X, and this subsequently equilibrates with XI.[8] The major, room temperature "stable," product is thus XI.

**$FSO_3H$–$SbF_5$ (1:1 or 4:1) Solvent.** In the 1:1 solvent mixture, the only ion observed at −40° was XV,[12] a known species.[11] For the 4:1 solvent mixture, the complete sequence is given in Scheme III. When the

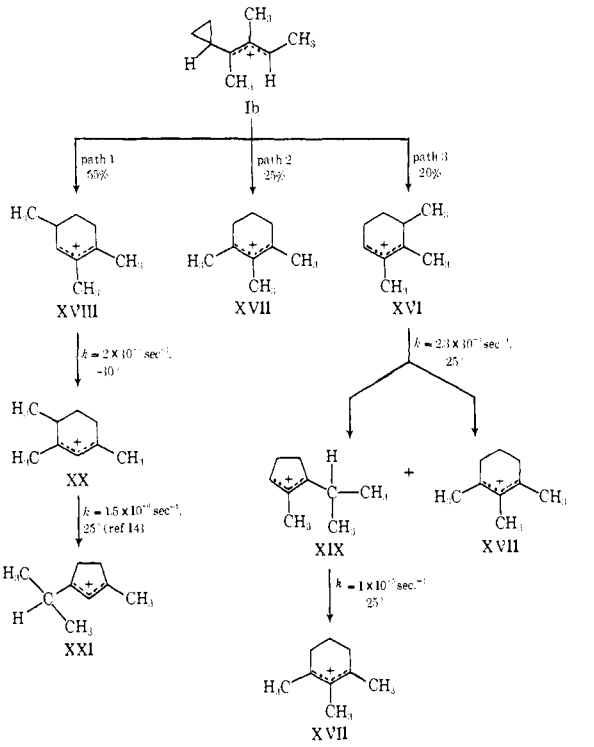
**Scheme III**




alcohol IIc was added to the 4:1 solvent at −90°, the initial spectrum contained Ic, XV, and ring-opened ions. Even at this temperature, however, Ic disappears quite rapidly. The transformation of the ring-opened ions into XV takes place at a much higher temperature. The evidence for ring-opened structures is based on the following data: (1) major nmr absorption at $\tau$ 6.94 and 7.75, characteristic of methyl groups at the C1, C3, and C2 positions, respectively, of allylic cations;[11] (2) major absorption occurring in the spectrum in the $\tau$ 4.83–5.25 region is completely uncharacteristic of purely hydrocarbon allylic cations but seems reasonable for a methylene or methine proton on a carbon atom also substituted by oxygen (*e.g.*, a fluorosulfate ester). Several possible structures are discussed in the Mechanism section. There is also a large nmr peak in the $\tau$ 8.33 (broad) region which remains unassigned.[13]

**The 1,2,3-Trimethyl System Ib. $FSO_3H$ Solvent.** Scheme IV depicts the complete sequence for this ion in $FSO_3H$ solvent. The "stable" products are XXI and XVII. The identity and decay sequence for XVI (path 3) is based on an independent synthesis of XVI. The identity of XVIII is based on the observed nmr

**Scheme IV**




spectrum and the unequivocal identification of the daughter decay product XX.[14] Applying consecutive first-order kinetics to path 1, one can calculate a value for

$$\text{XVIII} \xrightarrow{k} \text{XX}$$

of $2 \times 10^{-3}$ sec$^{-1}$ at −10°. The build-up of XVIII in the reaction is substantial and is reflected in the close magnitude of the two rate constants involved. A similar kinetic treatment can be made for Ib → XVI → XIX and XVII, except that both rate constants can be directly measured since XVI was independently synthesized. The ratio of XVI/Ib (original) × 20/100 is experimentally 0.4 at a time corresponding to 37% disappearance of Ib; the theoretical value based on the two measured rate constants is 0.37. The ratio of XIX to XVII formed in the rearrangement of XVI is, as expected, concentration dependent ($FSO_3^-$ catalysis) and favors the formation of XIX at low carbonium ion concentrations (*e.g.*, at 2% w/v concentration the ratio of XIX/XVII is 45:55). The "stable" product of this pathway is ion XVII, however, and since most of these processes are probably reversible, XIX is eventually converted to XVII, logically by way of XVI. The amount of rearrangement proceeding *via* path 2 is somewhat difficult to measure since the peaks from ion XVII are partially obscured by the cyclopropylallyl (1b) cation signals and later on in the rearrangement, when Ib is absent, some of ion XVII has already been produced from path 3.

**$H_2SO_4$ Solvent.** Scheme V depicts the complete sequence. The two major pathways appear to be the same as those found in $FSO_3H$ solvent, except, as expected of the stronger base, paths 2 and 3 in $FSO_3H$ solvent lead very rapidly in $H_2SO_4$ to the same ion (XVII). In addition, we suspect the presence of *ca.*

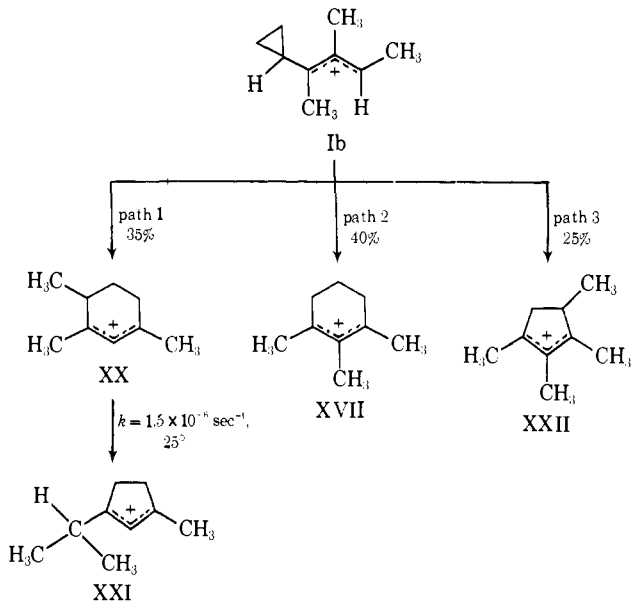
(11) N. C. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *J. Amer. Chem. Soc.*, **85**, 2995 (1963).

(12) A small amount of unidentified absorption is present at $\tau$ 6.98 and 7.52–7.66.

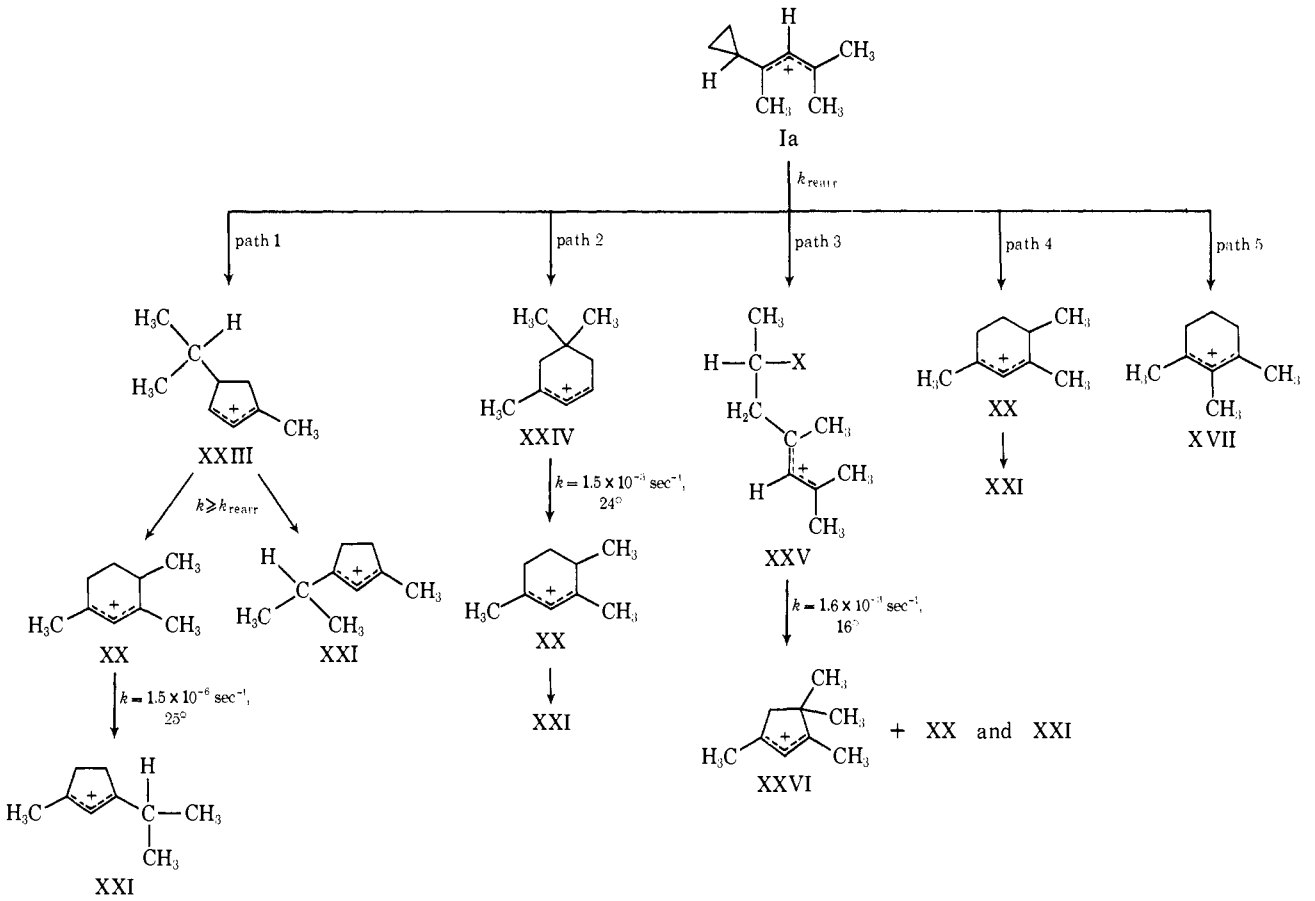
(13) Other minor peaks occur at $\tau$ 2.07, 2.50, 5.75 6.05, 7.55–7.67, 8.47, and 8.80.

(14) N. C. Deno and R. R. Lastomirsky, *J. Amer. Chem. Soc.*, **90**, 4085 (1968).

Scheme V



Scheme VI



only ion XXII is formed.[17] Using the 4:1 solvent, one observes only the cyclopropylallyl cation at low temperatures. Rearrangement of this ion becomes rapid at −10° (see Table III), and the major product is XXII, 85%, with minor amounts of XVII and XX, 15%, also observed. There are no observable ring-opened products produced.

**The 1,1,3-Trimethyl System Ia. $FSO_3H$ Solvent.** The complete product sequence, insofar as it can be measured, is shown in Scheme VI.

This system is quite obviously very difficult to unravel. The early major product is XXIII with smaller amounts of XXIV, XXV, XX, and XVII. For example, after about 50% of Ia has disappeared, the relative ratios are 3:0.5:0.75:2:1 with XXI and XXVI already present (1 and 0.75). At the point where all of Ia has disappeared, XXIII, XXIV, and XXV have also virtually disappeared. The relative amounts of XX, XXI, XXVI, and XVII are now about 3:4:1.5:1.5. The identity of XXIII is made on the basis of several very characteristic nmr peaks (C2 and C3 protons and the isopropyl group at C4). We have not been able to

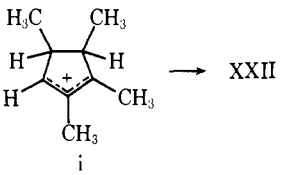
25% of the cyclopentenyl cation XXII in the product spectrum. Unfortunately, most of the characteristic peaks of this known ion[15] are overlapped completely by XVII and XX, and it is only by comparing relative peak areas that one can infer the presence of this ion.[16]

**$FSO_3H$–$SbF_5$ Solvent.** In the 1:1 solvent at −40°, calculate the rate of disappearance of XXIII using a consecutive rate equation since the products of the reaction are not known with certainty, except that XXI

(15) T. S. Sorensen, *Can. J. Chem.*, 42, 2768 (1964).

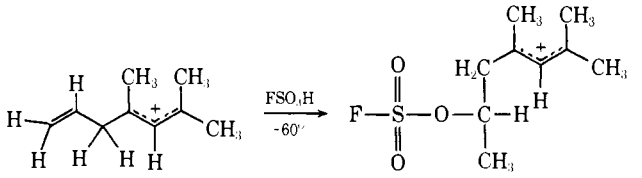
(16) For example, the C-2 proton/C4 methyl group ratio is considerably less than the theoretical expected for XX alone, and indicating some extra area due to a split methyl group, as in XXII.

(17) Small amounts of ion i may be initially present.



i

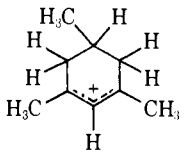
and probably XX are obvious candidates. Path 2 is a very minor one and the identity of and the sole rearrangement product of XXIV has been made on the basis of a comparison with authentic XXIV. Path 3 also represents a rather minor one and the identity of XXV is based on a synthesis of the ion XXVII which can be observed at −80° (Table IV). At somewhat higher temperatures (−60°), ion XXV is rapidly formed,[18] where X most likely represents a fluorosulfate group. The further rearrangement of XXV then



XXVII XXV

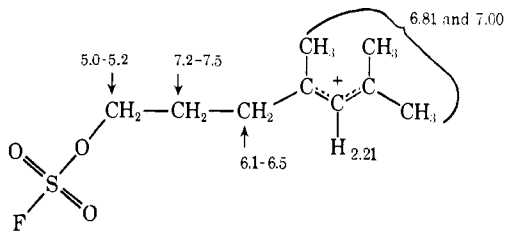
leads mainly to XXVI, a known ion.[15] Paths 4 and 5 are uncomplicated and the chief difficulty lies in deciding how much XX is produced directly from Ia since this ion also comes from the rearrangement of XXIV and probably XXIII.

**$H_2SO_4$ Solvent.** In sulfuric acid, ions XXVI, XVII, XX, and XXI are all produced as first observable products, the relative amounts being about 1:0.75:1:1. In addition, an unidentified ion is present and represents about 15% of the total. This ion is characterized by a C2 proton at $\tau$ 2.27 and very broad absorption in the $\tau$ 5.36–5.70 region. The ion is probably a ring-opened species and on warming the solution to 25°, it disappears. There is also about 10% of yet another ion present, provisionally identified as XXVIII by comparing the product spectrum to the spectrum of authentic XXVIII.



XXVIII

**$FSO_3H$–$SbF_5$ Solvent.** In the 1:1 solvent at −40°, only ion XXVI is produced. In the 4:1 solvent at −70°, the main product is again XXVI (75%), with about 25% of a ring-opened ion to which the structure XXIX is assigned on the basis of the observed nmr spectrum (see formula XXIX) and the fact that this ion leads only to XXVI at higher temperatures (fast at −20°). At room temperature, therefore, ion XXVI



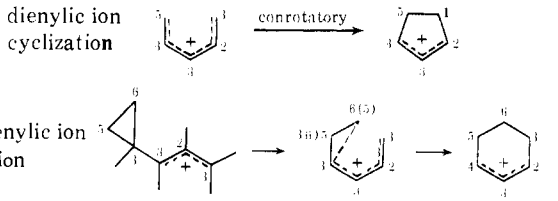

XXIX

is again the sole product.

(18) Small amounts of XXIII and XXIV are also formed.

**The Mechanism.** In energy terms, the "driving force" for these reactions is the *ca.* 30 kcal/mol of ring strain energy inherent in the cyclopropane ring. The resulting energy cascade then leads to ever more stable cations.

The operationally most simple mechanism for giving a closed ring allylic ion would be to break the C4–C5(C6) bond in the cyclopropane ring and join C5(C6) to C1. This naive picture has a reasonable mechanistic parallel in the well-known dienylic cation cyclization[19] if one regards the present reactions as proceeding through a homodienylic ion transition or intermediate prior to the final link-up of C5(C6) and C1. However, neither the

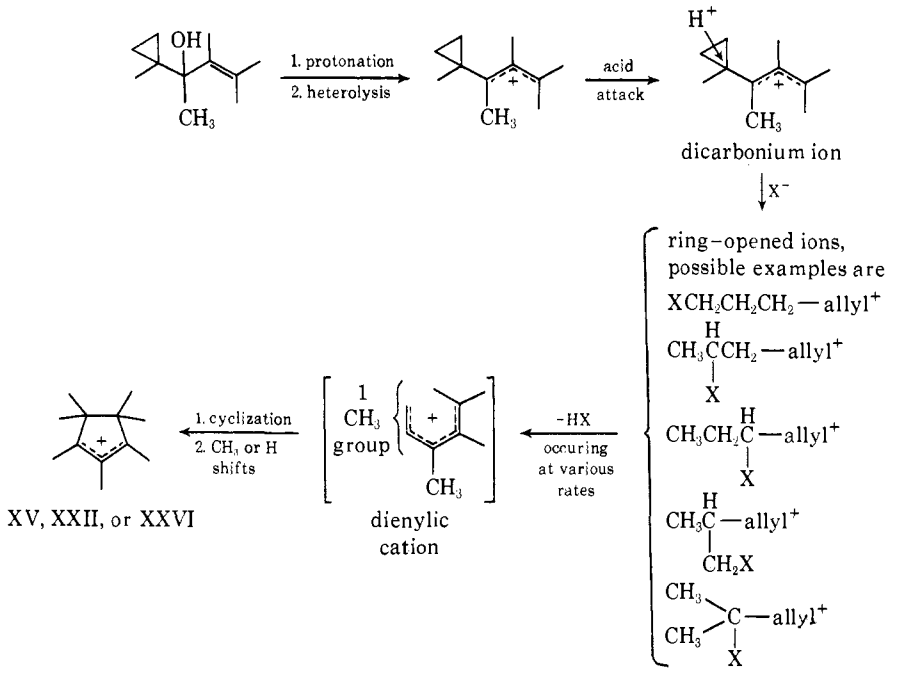



major product of each reaction nor the multiplicity of reaction products can possibly be explained by this mechanism. In considering a "family tree" as depicted, for example, in Scheme I, the first problem lies in deciding at what ancestral product the branching begins. To start with, we believe that the $FSO_3H$–$SbF_5$ solvent reactions are unrelated mechanistically to those occurring in $FSO_3H$ or $H_2SO_4$ solvent and represent a divergent path commencing at the cyclopropylallyl cation itself. This conclusion is based on (1) the completely different products produced compared to those found in $FSO_3H$ or $H_2SO_4$ solvent, (2) the much faster rearrangement rate of the cyclopropylallyl cations in $FSO_3H$–$SbF_5$ solvent, the rate increasing as the ratio of $SbF_5$ is increased, (3) the appearance in the product nmr spectrum of intermediary ions which can be in some cases rationalized as ring-opened products, and (4) the product ions themselves, XV, XXII, and XXVI, are exactly those predicted to be formed from ring-opened cations, *i.e.*, dienylic ions or incipient dienylic ions;[15] indeed, we regard the presence of XV, etc., as diagnostic of this kind of pathway. A reasonable picture of this mechanism is depicted in Scheme VII. The dienylic cation cyclization would be expected[15] to be extremely fast for all of the possible dienylic ions which might be produced from Ia–c and they are thus not observable themselves. The rearrangement of Ib is much slower compared to Ia and Ic, consistent with the argument that Ib, having a less stable allyl system, will involve more participation of the cyclopropane ring and hence will be attacked by acid more slowly (see ref 2).

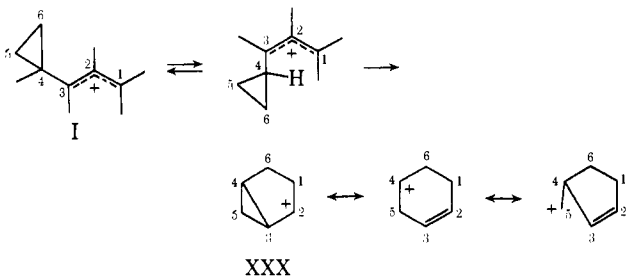
Most of the reaction pathways proceeding in $H_2SO_4$ and $FSO_3H$ solvent are assumed to proceed initially through a common rate-determining transition state, since the rates of the two reactions are very similar. A reaction intermediate which successfully rationalizes both the ultimate formation of the observed product ions and their diversity, is a bicyclo[3.1.0]hexyl cation (XXX), which is most simply formed by breaking the C5–C6 bond in I and joining one end to C1, the other to C3. Descriptively this corresponds to adding the allyl ion across the C5–C6 bond of the cyclopropane ring,

(19) P. H. Campbell, N. W. K. Chiu, K. Deugau, I. J. Miller, and T. S. Sorensen, *J. Amer. Chem. Soc.*, 91, 6404 (1969), and references contained therein.

**Scheme VII.** Mechanism in $FSO_3H$–$SbF_5$ Solvent

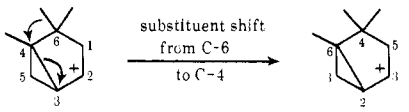



however, not necessarily in a concerted process. This ring closure would necessitate an initial trans → cis isomerization of the cyclopropylallyl cations and would explain why ions incapable of this are stable, *i.e.*, cyclopropyl-substituted cyclopentenyl or cyclohexenyl cations.[1] It seems very unlikely that this trans → cis

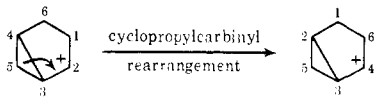



isomerization process could be rate determining.[20]

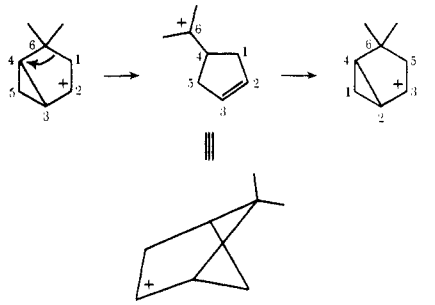
The 2-bicyclo[3.1.0]hexyl cation intermediate is proposed to undergo several degenerate (in the absence of substitution) rearrangements: (1) a shift of a group at C6 to C4 (this results in the new numbering of the carbon atoms as shown)[21]



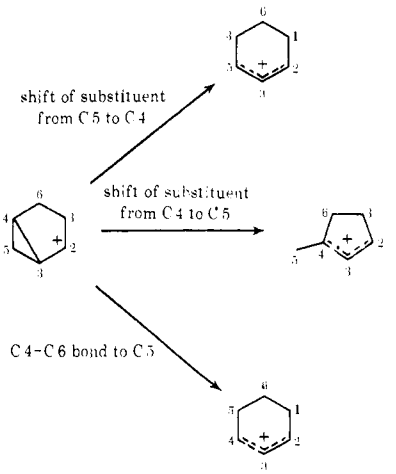

(2) a degenerate cyclopropylcarbinyl rearrangement (this results in yet another "renumbering" of the carbon atom skeleton as shown)




(3) where C6 is dialkyl substituted, a ring contraction leads to the symmetrical ion **XXXI**, perhaps better written as a 2-bicyclo[2.1.1]hexyl cation. On ring expansion in the opposite way, the following renumbering occurs.



Each 2-bicyclo[3.1.0]hexyl cation has potentially at least three ways in which to rearrange to the more stable allylic cation. There is good evidence that in

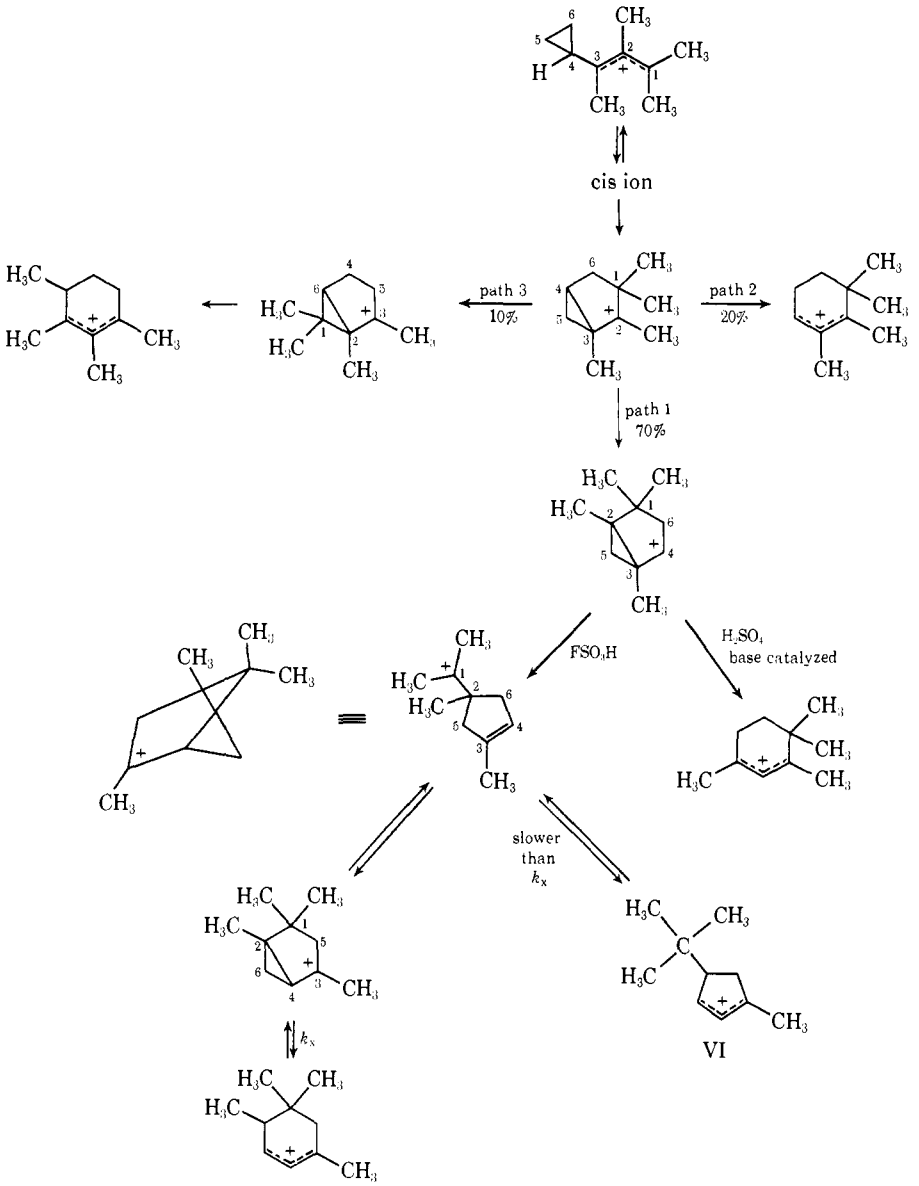



certain cases all three paths for the rearrangement of a 2-bicyclo[3.1.0]hexyl cation can operate in the same system.[9] In this study, however, we have not found

(20) Unpublished results from this laboratory show that a cyclopropylallyl cation containing an α-methyl group undergoes the rearrangement reaction at an enormously increased rate. This is inconsistent with a transition state involving a trans → cis isomerization.

(21) The numbering system used is derived from the original cyclopropylallyl cation and is not related to the proper nomenclature of this cation.

**Scheme VIII**



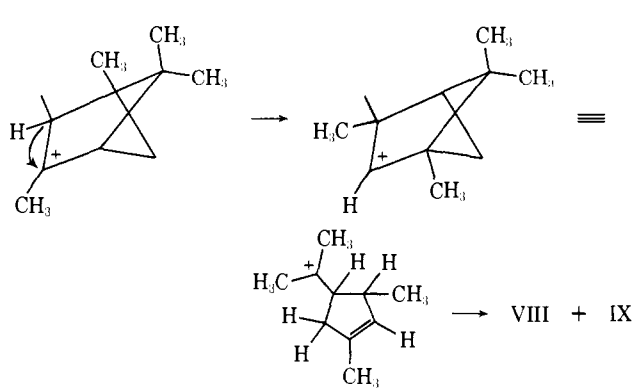

any products which necessitate invoking a C4–C5 substituent shift (leading to a cyclopentenyl cation). In those cases where C4 and C5 are substituted by hydrogen, both remaining mechanisms lead to the same product. Employing these intermediates, one can now rationalize the reaction sequence of Ic (Scheme VIII).

The same sort of reactions can be used to rationalize the products produced from Ia and Ib, employing the guideline that the 2-bicyclo[3.1.0]hexyl cation "degenerate" rearrangements should either remain the same with respect to or *increase* methyl substitution at the active centers (C2, C4, and C5 in the original numbering system).

Most of the reactions occurring in the subsequent decay series are either acid–base reactions of a known type or involve a cyclopentenyl–cyclohexenyl cation interconversion, again a known type[8,14] in which the mechanism has been recently investigated.[9] The mechanism of several of the decay reactions is not, however, evident, for example, the rearrangement of VI into VIII, IX, and X. In Scheme VIII, the major ion, VI, is proposed to come from a 2-bicyclo[2.1.1]hexyl cation intermediate and it is possible, by means of the usual norbornyl-type rearrangement processes, to produce a mechanism leading to VIII and IX (see also ref 10).[22]

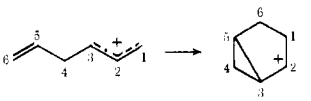
A third mechanistic pathway for the rearrangement of the cyclopropylallyl cations is indicated on the basis

(22) For example



of the probable identification, in the $H_2SO_4$ solvent spectra, of cyclopentenyl cations diagnostic of a dienylic cation–cyclization genesis, in fact identical in structure with the ions produced in $FSO_3H$–$SbF_5$ solvent. The most probable explanation would involve a base-catalyzed opening of the cyclopropane ring, a precedented type of reaction.[1] It should be emphasized that this particular pathway in 96% $H_2SO_4$ is a relatively minor one.

In some cases at least, the 2-bicyclo[3.1.0]hexyl cation is readily accessible, as a presumed intermediate, from the rearrangement of hex-5-en-1,2,3-enyl cations.[23] In fact, this rearrangement is much more rapid than the cyclopropylallyl rearrangement and will



probably allow one to intercept some of the intermediates which are not observed in the latter case.

In summary, the rearrangement of Ia–c in $FSO_3H$–$SbF_5$ involves acid-catalyzed ring opening and leads almost entirely to cyclopentenyl cations derived from dienylic cations (or incipient dienylic cations). A minor pathway of the $H_2SO_4$ solvent reactions leads to these same cyclopentenyl cations and may represent a base-catalyzed ring opening. The acid occupying a middle acidity–basicity range, $FSO_3H$, in general causes neither of the above processes and allows the cations to undergo an internal structural rearrangement. In the most part, the same is true for $H_2SO_4$ solvent; however, certain base-catalyzed shunts become available to the rearranging ion and thus, in some cases, very different end products are produced. The preceding mechanisms obviously cannot be considered as proven but any further information can at least be tested against the proposals put forth here.

## Experimental Section

**Preparation of the Ions.** In sulfuric acid solvent, the ions were prepared by the usual solvent extraction technique while with $FSO_3H$ and $FSO_3H$–$SbF_5$, the liquid alcohols were added directly to the acid from a microliter hypodermic needle, keeping the acid at Dry Ice temperature. The sulfuric acid was 96.7% and ratios for $FSO_3H$–$SbF_5$ given in the text refer to molar ratios. All nmr measurements of the ions were carried out with a Varian HA-100 spectrometer using the acid solvent as a lock signal. Peak area measurements were made either on the basis of peak heights, where the shape of the peaks were identical, or by tracing and weighing the peaks.

**Rate Studies.** The cyclopropylallyl cation rearrangement kinetics were performed in the nmr tubes, employing a constant-temperature cryostat, and analyzing the reaction by quenching the samples in Dry Ice–Acetone and measuring the nmr spectra at a temperature well below that used for the kinetics. The methyl group of nitromethane was found to be a suitable reference signal from which relative peak heights could be measured. Nitromethane slowly decomposes in $FSO_3H$ but the rate is slow enough not to affect our results. The C2 proton was followed in Ia, the C1 proton in Ib, and the lowest field methyl group in Ic. For the subsequent decay reactions, a variety of peaks were used in the kinetics. The paramount consideration, of course, is that the peak be free from interference by other ions. Fortunately, the C2 proton or methyl resonances are always sharp, reasonably variable in chemical shift and mostly singlets, and were most often used.

**Synthetic Procedures.** All nmr spectra of neutral compounds (*ca.* 10% solutions) were measured in carbon tetrachloride, tetramethylsilane = $\tau$ 10. Infrared spectra were measured as films or chloroform solutions using a Perkin-Elmer Model 337 spectrophotometer. The purity of all of the compounds except the alcohols (most of which dehydrated) were verified by glc analysis. All boiling points are uncorrected.

**Ethyl 2,3-Dimethyl-3-hydroxybutyrate.** This alcohol was prepared in 63% yield according to literature procedures.[24] Nmr analysis showed $\tau$ 5.87 (2 H, quart., $J$ = 7), 7.59 (1 H, quart., $J$ = 7), 6.95 (OH), 8.73 (3 H, t, $J$ = 7), 8.82 (3 H), 8.85 (3 H), 8.835 (3 H, d, $J$ = 7).

**2,3-Dimethyl-2-butenoic Acid.** A 100-g sample (0.625 mol) of the above ester was dissolved in 900 g of 96% sulfuric acid at 0° with stirring. The mixture was allowed to stand for 2 hr at this temperature and then poured into 2 kg of ice, vigorously stirring during the addition. The solid was filtered and washed several times with ice-cold water. Recrystallization from petroleum ether gave 55.5 g (78%) of the pure acid: mp 69.5–70° (lit.[24] 70°). Nmr analysis showed $\tau$ −2.38 (1 H), 7.88 (3 H), 8.15 (6 H).

**2,3-Dibromo-2,3-dimethylbutanoic Acid.** The above acid was dissolved in the minimum quantity of chloroform and bromine added dropwise at 25° till the bromine color persisted. The solvent was allowed to evaporate and the residual white powder used directly in the next step. A sample recrystallized from petroleum ether had mp 221–222° (lit.[25] 222°).

**2-Bromo-3-methyl-2-butene.** This compound was prepared from the above acid using the sodium carbonate procedure described by Farrell and Bachman:[25] yield 66%; bp 113–114° (660 mm) (lit. bp 118–120° (760 mm)). Nmr analysis showed $\tau$ 7.75 (3 H, quart., $J$ = 2). 8.15 (3 H, quart., $J$ = 2), 8.25 (3 H, slightly broadened singlet, $J$ < 1).

**2-Cyclopropyl-4-methyl-3-penten-2-ol (IIa).** Isobutenyl bromide,[26] 13.5 g (0.1 mol), in 50 ml of dry ether was added dropwise to a finely cut suspension of 1.4 g-atoms of lithium (1% sodium) (0.2 g-atom) in 100 ml of dry ether at 0°, under argon and with stirring. When metallation was complete, cyclopropyl methyl ketone, 8.4 g (0.1 mol), in 50 ml of ether was added with stirring at 0°. After the addition was complete, the reaction mixture was stirred for an additional 2 hr and then filtered through a glass wool plug. The resulting solution was then worked up in the usual manner, care being taken to keep the wash solutions slightly basic by adding sodium bicarbonate to them. The product was distilled through an 18 in. spinning band column, employing a 10:1 reflux ratio, to yield 12 g (86%) of product: bp 80–82 (12 mm) (lit.[27] bp 80–85° (24 mm); nmr analysis gave $\tau$ 4.85 (1 H, septet, $J$ = 1.5, 8.15 (3 H, d, $J$ = 1.5), 8.31 (3 H, d, $J$ = 1.5), 8.78 (3 H), 8.90 (1 H, OH), 9.17 (1 H, quint., $J$ = 7.2), 9.70 (4 H, unequal doublets, $J$ = 7.2).

**2-Cyclopropyl-3-methyl-3-penten-2-ol (IIb).** This alcohol was prepared in the same way as IIa, employing 2-butenyllithium (9:1 mixture of the cis and trans isomers, respectively).[28] From 8.4 g (0.1 mol) of cyclopropyl methyl ketone, there was obtained 9.8 g (70%) of the title product, bp 76–77° (12 mm). *Anal.* Calcd for $C_9H_{16}O$: C, 77.1; H, 11.5. Found: C, 76.56; H, 11.96. Nmr analysis showed the presence of both cis and trans isomers in the approximate ratio found for the bromobutene starting material. For the cis isomer, $\tau$ 4.42 (1 H, quart., $J$ = 6.2), 8.35 (3 H), 8.40 (3 H, d, $J$ = 6.2, each doublet slightly split again), 8.83 (3 H), multiplets centered at *ca.* 9.0, 9.63, and 9.8 for the cyclopropyl protons.

**2-Cyclopropyl-3,4-dimethyl-3-penten-2-ol (IIc).** This alcohol was prepared in the same way as IIa, employing 3-methyl-2-butenyllithium (7.45 g, 0.05 mol, of 2-bromo-3-methyl-2-butene and 0.7 g, 0.1 g-atom, of lithium). From 4.2 g (0.05 mol) of cyclopropyl methyl ketone, there was obtained 5.0 g (65%) of the title product, bp 88° (12 mm). *Anal.* Calcd for $C_{10}H_{18}O$: C, 77.89; H, 11.74. Found: C, 77.90; H, 11.89.

**3,5,5-Trimethylcyclohex-2-en-1-ol.** This alcohol was prepared in 90% yield from 5.0 g (0.0357 mol) of isophorone and 0.7 g (0.02 mol) of lithium aluminum hydride in ether solvent: bp 82–84° (9 mm) (lit.[29] bp 79.5–81.5° (8 mm)).

(23) Unpublished results from this laboratory.

(24) (a) W. H. Perkin, Jr., *J. Chem. Soc.*, **69**, 1479 (1896); (b) R. L. Shriner in "Organic Reactions," Vol. I, Wiley, New York, N. Y., p 17.

(25) J. K. Farrell and C. B. Bachman, *J. Amer. Chem. Soc.*, **57**, 1281 (1935).

(26) E. A. Braude and E. A. Evans, *J. Chem. Soc.*, 3324 (1955).

(27) French Patent 1,310,528 (1963); *Chem. Abstr.*, **60**, 427e (1964).

(28) (a) A. S. Dreiding and R. J. Pratt, *J. Amer. Chem. Soc.*, **76**, 1902 (1954); (b) F. G. Bordwell and P. Landis, *ibid.*, **79**, 1593 (1957).

(29) I. Alkonyi, *Ber.*, **96**, 1873 (1963).

**2,3,4-Trimethylcyclohex-2-en-1-ol.** This alcohol was prepared by reducing 2,3,4-trimethylcyclohex-2-en-1-one[30] with lithium aluminum hydride in ether, bp 84–85° (9 mm). Nmr analysis showed $\tau$ 6.18 (1 H, very broad and unresolved), 7.29 (1 H, broad and unresolved), 8.38 (6 H), 8.98 (3 H, d, $J$ = 6.8), and a very complex region from 7.9 to 9.0 for the methylene protons.

**1,2,3,4-Tetramethylcyclohex-2-en-1-ol.** This alcohol was kindly supplied by Mr. K. A. Ananthanarayan of this department.

**4,6-Dimethylhepta-1,5-dien-4-ol.** The preparation of this alcohol has been reported.[31]

**1-Isopropyl-2,3-dimethylcyclopent-2-en-1-ol.** A solution of 1.281 g (0.0116 mol) of 2,3-dimethylcyclopent-2-en-1-one[32] in 10 ml of pentane was added to a stirred, ice-cold solution of isopropyllithium (8–9 ml of 1.8 $M$ in pentane). The reaction was worked up in the usual manner[33] and the residue was dissolved in pentane and added to a second portion of isopropyllithium (8–9 ml). The reaction was again worked up and distillation of the residue gave 1.01 g (56%) of product, bp 36–40° (0.15 mm). As usual with these alcohols, some dehydration occurred during the distillation (nmr analysis) and a satisfactory C, H analysis was not obtained. This dehydration product yields the same carbonium ion as the alcohol and is of no consequence. Nmr analysis showed a complex region from $\tau$ 7.0 to 8.5 for the methylene and methine protons, 8.40 (3 H, broad), 8.49 (3 H, t, $J$ = 1.8), 8.85 (1 H, OH), 9.08 and 9.37 (6 H, both d, $J$ = 7.0).

**5-Carbethoxy-2,2-dimethyloctane-3,6-dione.** A solution of the sodium enolate of ethyl 3-oxopentanoate[34] was prepared in the usual order of addition from 36 g (0.25 mol) of ethyl 3-oxopentanoate, 200 ml of absolute ethanol, and 6.25 g-atoms (0.272 mol) of sodium. This solution was heated to reflux and 60 g (0.335 mol) of 1-bromo-3,3-dimethylbutan-2-one[35] was added dropwise over a period of 2 hr. The solution was refluxed a further 3 hr and cooled. Water was added to dissolve the precipitated salt and most of the ethanol removed on a rotary evaporator. The resulting mixture was extracted with three 300-ml portions of ether and the ether dried over magnesium sulfate. Removal of the ether gave a residue (63.5 g). Distillation gave a considerable forerun of the unreacted bromo ketone and then a main product: bp 134–135° (8 mm), yield 35.0 g (60%). *Anal.* Calcd for $C_{13}H_{22}O_4$: C, 64.43; H, 9.15. Found: C, 64.42; H, 8.89. Nmr analysis showed $\tau$ 5.88 (2 H, quart., $J$ = 7.2), 6.07 and 6.20 (1 H, both d, $J$ = 6.2), 6.91, 7.03, 7.13, (2 H, AB part of ABX system), 7.37 (2 H, quart., $J$ = 7.2), 8.73 (3 H, t, $J$ = 7.2), 8.87 (9 H), 8.95 (3 H, t, $J$ = 7.2).

**3-*tert*-Butyl-2-methylcyclopent-2-en-1-one.** A solution of 32.5 g (0.135 mol) of 5-carboethoxy-2,2-dimethyloctane-3,6-dione in 150 ml of methanol, 100 ml of water, and 25.0 g of sodium hydroxide was heated to reflux. After a few minutes, sodium carbonate begins to precipitate (bumping!). After 2 hr, the solution was cooled and the salt removed by filtration and washed with 50 ml of methanol. An additional 50 g of sodium hydroxide was added to the filtrate together with a further 100 ml of water and the mixture was refluxed for 40 hr in a closed atmosphere. Water (500 ml) was then added and the cold mixture extracted twice with two 250-ml portions of ether. The wet ether layer was evaporated on a rotary evaporator and the residue treated with 100 ml of water and 200 ml of ether. The ether layer was again separated and washed with 100 ml of water, back-extracting the wash layer with an additional 100 ml of ether. The combined ether extracts were dried over magnesium sulfate. Removal of the ether gave 18.5 g of residue which was distilled through a spinning band column to give a main fraction, bp 96° (8 mm), yield 11.0 g (54%), of the title compound. The rest of the crude material remains as a high boiling residue. *Anal.* Calcd for $C_{10}H_{16}O_2$: C, 78.83; H, 10.59. Found: C, 78.96; H, 10.08. Nmr analysis showed $\tau$ 7.33–7.97 (4 H, complex series of peaks), 8.23 (3 H, t, $J$ = 1.8), 8.76 (9 H).

**3-*tert*-Butyl-2-methylcyclopent-2-en-1-ol.** Prepared in 80% yield from 1.0 g (0.0066 mol) of the above ketone and 0.2 g of lithium aluminum hydride (0.006 mol) in ether; bp 94–95° (8 mm). *Anal.* Calcd for $C_{10}H_{18}O$: C, 77.89; H, 11.74. Found: C, 77.95; H, 12.37. Nmr analysis showed $\tau$ 5.5–5.7 (1 H, broad and unresolved); 7.6–8.0 (4 H, broad and unresolved); 8.21 (3 H, broad, partially resolved triplet), 8.88 (9 H).

**1,3,5-Trimethylcyclohex-2-en-1-ol.** This alcohol was prepared in 70% yield from 0.6 g (0.005 mol) of 3,5-dimethylcyclohex-2-en-1-one and 3 ml of 2.16 $M$ methyllithium (0.0065 mol) solution, in ether solvent, bp 81° (8 mm).

**Acknowledgments.** The authors wish to thank the National Research Council of Canada for generous support.

(30) P. C. Mukharji, *J. Indian Chem. Soc.*, **33**, 99 (1956).
(31) T. S. Sorensen, *Can. J. Chem.*, **42**, 2781 (1964).
(32) D. Varech, C. Ouannes, and J. Jacques, *Bull. Soc. Chim. Fr.*, 1662 (1965).
(33) T. S. Sorensen, *J. Amer. Chem. Soc.*, **89**, 3782 (1967).
(34) A. Brändström, *Acta Chem. Scand.*, **5**, 820 (1951).
(35) J. H. Boyer and D. Straw, *J. Amer. Chem. Soc.*, **74**, 4506 (1952).

# Cyclopropane in Photochemistry. I. Photochemistry of 4,4-Dicyclopropylcyclohexenone

**Roger C. Hahn* and Gerald W. Jones[1]**

*Contribution from the Department of Chemistry, Syracuse University, Syracuse, New York 13210.* *Received November 5, 1970*

**Abstract:** Irradiation of 4,4-dicyclopropylcyclohexenone (**5**) in *tert*-butyl alcohol affords only 6,6-dicyclopropylbicyclo[3.1.0]hexan-2-one (**6**) and 3-(dicyclopropylmethyl)-2-cyclopentenone (**10**). The absence of detectable amounts of cyclopropyl migration products is rationalized most readily in terms of a reacting excited state having radical character.

One of the more pronounced mechanistic dichotomies in photochemistry is the behavior of 4,4-dimethylcyclohexenone (**1**) and 4,4-diphenylcyclohexenone (**3**) on irradiation. Whereas **1** reacts predominantly *via* breakage of the 4,5 bond and rebonding of the 2,4 and 3,5 carbon atoms, respectively,[2] **3** undergoes predominant 4,3-phenyl migration, without attendant skeletal rearrangement.[4]

(1) National Science Foundation Trainee, 1965–1968.
(2) O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Lett.*, 2049 (1963). The general transformation of 4-substituted cyclohexenones and cyclohexadienones to 6-substituted bicyclo[3.1.0] systems, in which C-3 and C-4 appear to exchange places, has been termed a type A rearrangement.[3]
(3) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. Staley, and M. Semmelhack, *J. Amer. Chem. Soc.*, **88**, 1965 (1966).
(4) H. E. Zimmerman and K. G. Hancock, *ibid.*, **90**, 3749 (1968), and references therein.