chloromethyl cation, β-CD, and phenolates as a stable species. Instead, the regulation of the mutual conformation between phenolates and the trichloromethyl cation can be achieved by β-CD only in the transition state, also through noncovalent interactions.

Comparison of Selective Catalysis by CDs in Carboxylation with That in Formylation. As shown above, one of the functions of β-CD in the selective carboxylation is the regulation of the mutual conformation between phenolates and the trichloromethyl cation. This is identical with the function of β-CD in the selective syntheses of 4-hydroxybenzaldehydes from phenols and chloroform.[12] There, β-CD regulates the mutual conformation between phenolates and chloroform (and thus that between phenolates and the active species, dichlorocarbene), resulting in the reaction at the para position in high selectivity.

In the present selective carboxylation, β-CD additionally functions as a trapping and protecting agent for the active species. Thus, only a small amount of β-CD is required for the selective catalyses to proceed efficiently. In the selective formylation, however, the molar ratio of chloroform to β-CD must be carefully controlled below unity throughout the reaction, so that almost all of the chloroform is in the complexing state with β-CD.[12] Otherwise, the reaction involving free chloroform takes place competitively with the β-CD-catalyzed reaction, resulting in a decreased selectivity. This difference is due to the fact that the inclusion of the trichloromethyl cation in the cavity is much more favorable than the inclusion of dichlorocarbene in the cavity.

Acknowledgment. The authors would like to thank Makoto Yoshida for his technical assistance. This work is partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education in Japan. The support by the Kawakami Foundation is also ackowledged.

Registry No. Phenol, 108-95-2; 2-methylphenol, 95-48-7; 3-methylphenol, 108-39-4; 4-methylphenol, 106-44-5; 4-hydroxybenzoic acid, 99-96-7; 4-hydroxy-3-methylbenzoic acid, 499-76-3; 4-hydroxy-2-methylbenzoic acid, 578-39-2; 2-hydroxybenzoic acid, 69-72-7; copper, 7440-50-8; copper sulfate, 7758-98-7; β-CD, 7585-39-9; α-CD, 10016-20-3; γ-CD, 17465-86-0; hexakis(2,6-di-*O*-methyl)-α-CD, 51166-72-4; heptakis(2,6-di-*O*-methyl)-β-CD, 51166-71-3; CCl_4, 56-23-5; $^+CCl_3$, 27130-34-3.

cis-1-Methylcyclopropylcarbinyl Cation. Preparation and Facile Interconversion with the 1-Ethylallyl Cation

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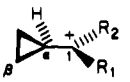
Abstract: The preparation of the previously unknown *cis*-1-methylcyclopropylcarbinyl cation **3** is reported. Cation **3** rearranges rapidly at −100 °C to the stable trans isomer, but instead of a direct rotation of the Cα–Cl bond, **3** finds a lower energy route involving at least seven intermediates, including the observable 1-ethylallyl cation **5**.

Of the simple "bisected" cyclopropylcarbinyl cations **1–4**, only



1, $R_1 = R_2 = H$

2, $R_1 = H$, $R_2 = CH_3$

3, $R_1 = CH_3$; $R_2 = H$

4, $R_1 = R_2 = CH_3$

the cis secondary ion **3** is unreported. However, the obvious precursers of **3**, e.g., 1-cyclopropylethanol, are reported[1] to yield only the trans ion **2** on addition to strong acids and this, and other evidence, strongly suggests that **2**, is the thermodynamically preferred member of this $C_5H_9^+$ pair.

The existance of **3**, as distinct from the trans isomer **2**, would seem to depend only on the magnitude of the rotation barrier about the C1–Cα bond, also an unknown experimental quantity. In Table I, we have tabulated what is presently known concerning the apparent C1–Cα rotation barriers in **1–4**. Barriers calculated by MO procedures are also listed and in the single case where a comparison with experimental can be made, the agreement is quite good. It is sufficient to note at this point that were the rotation barrier is **3** 19 kcal/mol, this would readily permit the observation of **3** ($t_{1/2}$ ca. 1 h at −21 °C).

Table I. C1–Cα Rotation Barriers for Cyclopropylcarbinyl Cations 1-4

cation	designation	experimental barrier, E_a, kcal/mol	calculated barrier,[a] ΔE, kcal/mol
1	primary	⩾11.4[b]	26.3
2	secondary	?	20.8
3	secondary	?	19.0
4	tertiary	13.7[c]	13.2

[a] See ref 2. The data for **3** were calculated subsequently by using the same procedure. [b] This ion is stable to about −60 °C.[1] The absence of line broadening ($k < s^{-1}$) at this temperature was used to calculate a minimum $\Delta G^{\ddagger}$. [c] Reference 3.

This paper reports on the first preparation of **3**, the subsequent rearrangement of **3** to **2**, and the fact that the **3** → **2** rearrangement does not, as assumed above, take place by a direct C1–Cα bond rotation, involving instead the 1-ethylallyl cation as a key observable intermediate. This in turn allows one to study certain mechanistic aspects of the little investigated cyclopropylcarbinyl ⇄ allyl cation interconversion process.

Results

Cyclopropylcarbinyl–cyclobutyl cation interconversions are known to be highly stereospecific, and this suggests that a cyclobutane system would be a logical precurser to **3**. In fact, we

(1) Olah, G. A.; Kelly, D. P.; Jeuell, G. L.; Porter, R. D. *J. Am. Chem. Soc.* **1970**, *92*, 2544.
(2) Schmitz, L. R.; Sorensen, T. S. *J. Am. Chem. Soc.* **1982**, *104*, 2605.
(3) Kabakoff, D. S.; Namanworth, E. *J. Am. Chem. Soc.* **1970**, *92*, 3234.

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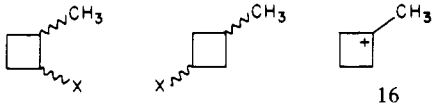
chose for completeness to try two different precursers, the 2-methyl-1-X **14** and the 3-methyl-1-X **15** systems, where X is a

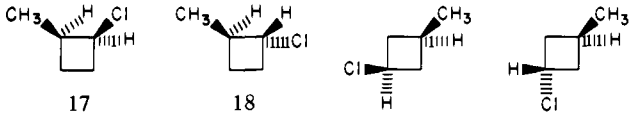


14 15 16

leaving group. The major worry was that under superacid preparative conditions, one might get 1,2- or 1,3-hydrogen shifts, thereby leading irreversibly to the tertiary 1-methylcyclobutyl cation **16**.[4] In this regard, system **15** would appear to be a safer choice since one needs either a 1,3-hydrogen shift or two 1,2 shifts before **16** would be formed.[5]

The key to the possible stereospecific formation of **3** involves choosing the correct geometric isomers of **14** and **15**. Although the solvolysis results on **15** (X = OBs) are not very encouraging,[6] the work of the Wiberg[7] and Schleyer[8] groups on the parent cyclobutyl–cyclopropylcarbinyl system, using isotopic labels, indicates complete rearrangement stereospecificity. In order to prepare cation **3**, one can predict from this work that the cis geometry in both **14** and **15** would be required.

Chlorides are ideal cation precursors under SbF_5–SO_2ClF ionizing conditions, leading us to prepare the previously unreported *cis*- and *trans*-2-methyl-1-chlorocyclobutanes **17** and **18** and *cis*-



17 18 19 20

and *trans*-3-methyl-1-chlorocyclobutanes **19** and **20**. Both sets were obtained as mixtures from modified Hunsdiecker reactions.[9] The pair **17** and **18** were readily separated by preparative GLC on a number of liquid supports but **19** and **20** were unresolved on all common phases. They were eventually completely separated on a polyphenyl ether (six ring) column. Geometric assignments for each pair were based on ^1H NMR coupling constants and chemical shifts (see Experimental Section). For **17–18**, the high retention isomer has the cis structure, whereas for **19–20**, the reverse occurs.

Ionization Studies. The addition of *cis*-3-methylcyclobutyl chloride **19** to SbF_5–SO_2ClF (1:4) at −80 °C gave cleanly the *trans*-cyclopropylcarbinyl cation **2**, as shown by comparing the ^1H NMR spectrum to that of authentic **2**. This clearly indicated that either **3** was not being formed or that the **3** → **2** rearrangment was much faster than expected. A positive point was that no 1-methylcyclobutyl cation **16** was formed under these conditions.

On the chance that **3** was formed initially but had rearranged, the preparation was carried out at −135 °C using SbF_5–SO_2Cl-F–SO_2F_2 (1:3:1) solvent. Measured at −125 °C, one sees the relatively clean[10] formation of a new cation, identified as **3** by both ^1H and ^{13}C NMR spectroscopy (data for **2** and **3** are compared in Table II). One sees the effects of the well-known shielding by the cyclopropyl ring; in **2**, the C1 proton is 1.29 ppm higher field than in **3**, whereas the methyl group in **3** is upfield by 0.34 ppm. Similar effects are noted in the ^{13}C spectrum, and these differences agree well with data for similar cis and trans isomers in the nortricyclylcarbinyl cation system.[11] In terms of coupling constants, cation **2** shows a 13-Hz coupling for the Hα–H1 pair vs. ca. 8 Hz for **3** (trans and cis vicinal coupling, respectively).

Table II. ^1H[a] and ^{13}C[b] NMR Data for Cations **2**, **3**, and **5**

cation	H1	Hα	Hβ (cis)	Hβ (trans)	CH_3
2	8.78[c]	3.75[d]	3.51[e]	3.73[e]	2.57[f]
3	10.07	3.75[d]	3.75[e]	3.87[e]	2.23[h]

cation	C1	Cα	Cβ	CH_3
2	252.2	66.7	59.9	32.7
3	257.5	65.3	66.1	26.4

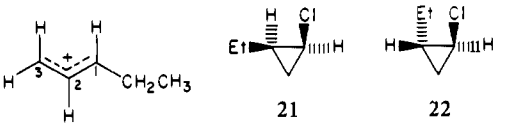
cation	H1	H2	H3 (syn)	H3 (anti)	CH_2	CH_3
5	10.14[i]	7.81[j]	8.19[k]	8.46[l]	3.45[m]	1.07[n]

cation	C1	C2	C3	CH_2	CH_3
5	258.0	146.5	199.6	46.4	9.0

[a] Externally referenced to Me_4Si-dimethyl ether-d_6 and then corrected (+0.15 ppm correction) to external Me_4Si in SO_2ClF solvent. [b] Referenced to internal $CFCl_3$ = 117.9 ppm. [c] d, q, J = 13 and 5.4 Hz. [d] These peaks are partially obscurred by β-protons and were located by decoupling experiments. [e] Multiplet structure; the assignment could possibly be interchanged. [f] d, J = 5.4 Hz. [g] d, q, J = ca. 8 and 6.2 Hz. [h] d, J = 6.2 Hz. [i] d, t, J = 16 and ca. 3 Hz. [j] d, d, d, J = 16, 16, and 8 Hz. [k] d, J = 8 Hz. [l] d, J = 16 Hz. [m] Broad. [n] t, J = 6 Hz.

Ionization of *cis*-2-methyl-1-chlorocyclobutane **17** at −135 °C led to identical results, whereas ionization of either of the trans chlorides **18** or **20**, at this same temperature, led only to the trans cation **2**.

Warming solutions of the cis ion **3** to −80 °C for 1 h results in the complete conversion of **3** into **2**, confirming the results found in the initial preparation attempts. However, if the **3** → **2** rearrangement is followed by NMR spectroscopy, one sees the appearance of a third cation, identified as the previously unknown *E*- (or *anti*-) 1-ethylallyl cation **5**. The ^1H and ^{13}C data are



5 21 22

completely consistent with this structure,[12] but for added proof, the cation was prepared independently from the ionization of *cis*- or *trans*-1-chloro-2-ethylcyclopropane **21** and **22**.[13] In the cation **3** → **2** rearrangement, **5** builds in concentration and eventually reaches an equlibrium population with **3**, K = **3**/**5** = 1.25 ± 0.1, based on an integration of the respective methyl resonances. Both **3** and **5** then decrease together as more and more **2** is formed. Conversely, starting with **5**, both **2** and **3** are formed and one reaches the same **3**/**5** equilibrium. Cation **5** is an intermediate in the **3** → **2** conversion, although the above kinetic data are probably not accurate enough to unequivocally yield this evidence (however, see later discussion of H–D exchange work).

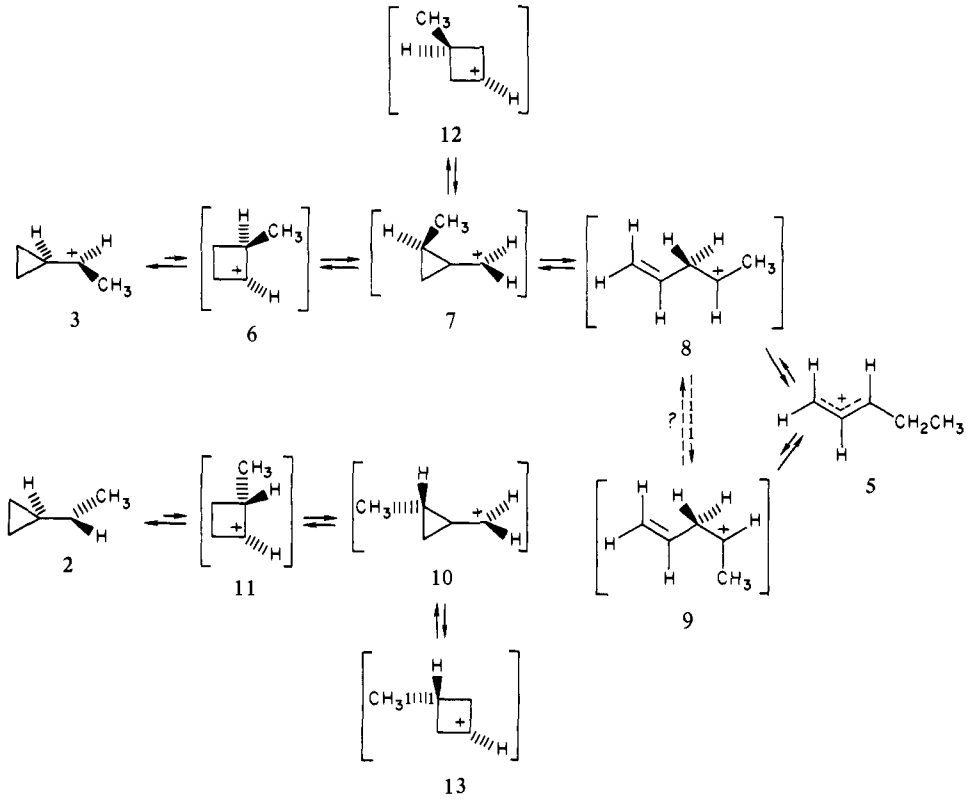
The eventual formation of **2** is virtually complete but careful ^1H NMR studies suggest that **2** and **3** (or **5**) ultimately also reach an equilibrium, where K = **2**/**3** is ca. 50. For kinetic purposes, however, the rearrangement can be treated as

$$3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 5 \xrightarrow{k_2} 2$$

One can use several simplifications to help unravel the rather complex rate law involved here, and computer simulation of the time–concentration data eventually yields the following rate constants at −100 °C: $k_1 = 7 \times 10^{-4}$ s^{-1}, $\Delta G^{\ddagger}$ = 12.5 kcal/mol;

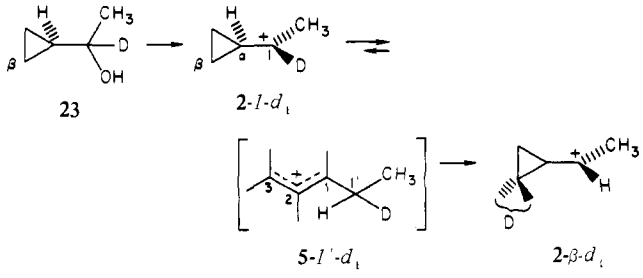
(4) Saunders, M.; Rosenfeld, J. *J. Am. Chem. Soc.* **1970**, *92*, 2548. Cation **16** is reported to yield cation **2** at about −25 °C.
(5) From the recent work of Staral and Roberts (Staral, J. S.; Roberts, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 8020), there is reason to believe that 1,2 shifts would be relatively slow.
(6) Lillien, I.; Handloser, L. *J. Am. Chem. Soc.* **1971**, *93*, 1682.
(7) Wiberg, K. B.; Szeimies, G. *J. Am. Chem. Soc.* **1970**, *92*, 571.
(8) Majerski, Z.; Schleyer, P. v. R. *J. Am. Chem. Soc. 1971*, **93**, 665.
(9) Becker, K. B.; Geisel, M.; Grob, C. A.; Kuhnen, F. *Synthesis* **1973**, 493.
(10) In the best cases, less than 10% of the trans isomer **2** is produced.
(11) Schmitz, L. R.; Sorensen, T. S. *J. Am. Chem. Soc.* **1982**, *104*, 2605.
(12) Olah, G. A.; Mayr, H. *J. Am. Chem. Soc.* **1976**, *98*, 7333.
(13) The trans isomer **22** is expected to yield the *E* (or anti) geometry while **21** might have given the *Z* isomer. See: Schleyer, P. v. R.; Su, T. M.; Saunders, M.; Rosenfeld, J. C. *J. Am. Chem. Soc.* **1969**, *91*, 5174. However, only **5** is produced from either **21** or **22**, although the reaction is far from clean.

Scheme I



$k_{-1} = 9 \times 10^{-4}$ s^{-1}, $\Delta G^{\ddagger} = 12.4$ kcal/mol; $k_2 = 3.5 \times 10^{-4}$ s^{-1}, $\Delta G^{\ddagger} = 12.7$ kcal/mol.

Hydrogen–Deuterium Exchange Studies. In order to provide further evidence that **5** is indeed the key intermediate in the **3** → **2** reaction, i.e., further evidence that **2** and **3** (or **5**) form a populated, but lopsided, equilibrium mixture, and to aid in looking at the overall mechanism of the **2** or **3** ⇄ **5** process, we have studied cation **2**-*1*-d_1, prepared from the corresponding alcohol.



A mechanism involving the transformation of **2**-*1*-d_1 back to a small (essentially unobservable) steady-state concentration of the 1-ethylallyl cation **5**-*1'*-d_1 and then the reverse process beginning with deuterium migration in **5**-*1'*-d_1 would lead to deuterium appearing in the β-cyclopropyl position of **2**, e.g. **2**-β-d_1. The rate for this process should be approximately $(3.5 \times 10^{-4})/50 = 7 \times 10^{-6}$ s^{-1}, $\Delta G^{\ddagger} = 14.0$ kcal/mol, at −100 °C (ignoring kinetic isotope effects and statistical factors). Experimentally, one finds a rate constant of ca. 2×10^{-3} s^{-1} at −70 °C, $\Delta G^{\ddagger} = 14.2$ kcal/mol, in good agreement. It is significant for discussions on the overall rearrangement mechanism that deuterium appears at an equal rate in *both* the cis and trans β-positions. There is no evidence for deuterium appearing either at Cα or in the methyl group and, furthermore, no evidence for significant equlibrium isotope effects between the C1 and Cβ positions when one eventually reaches equilibrium (see Figure 1).

Discussion

Thermodynamic Aspects. Cations **3** and **5** provide the first case in which allyl and cyclopropylcarbinyl cations are actually in equilibrium ($\Delta\Delta G = 80 \pm 20$ cal/mol). These species would

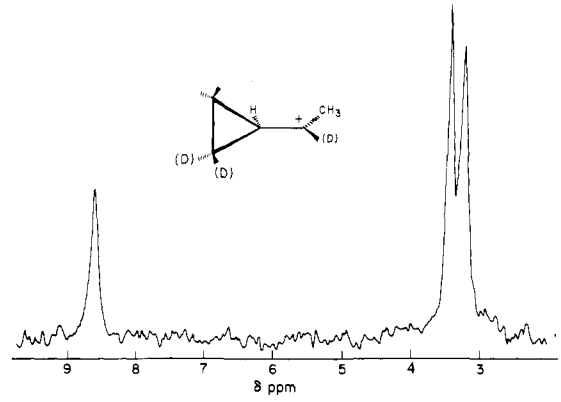


Figure 1. Starting with the *trans*-1-methylcyclopropylcarbinyl cation **2**-*1*-d_1, in which deuterium is only at C1, one sees by ^{2}H NMR spectroscopy at −70 °C a rapid reaction to transfer this deuterium to *either* β-position of the cyclopropane ring, eventually forming the equilibrium mixture shown above (^{2}H spectrum with ^{1}H decoupling).

therefore serve as an excellent test of the ability of MO calculations to model the energy differences of simple solution carbocations whose overall structure are quite different.

The energy difference between the cis and trans isomers **2** and **3** (K = ca. 50) is $\Delta\Delta G = 1.5$ kcal/mol. A recent MO calculation[2] (STO/3G-MNDO geometry) gives 1.8 kcal/mol, in reasonable agreement.

Kinetic and Mechanistic Aspects. The complete mechanism of the **3** → **2** rearrangement involves one observable intermediate **5** and probably six "high-energy" intermediates (Scheme I). The preparation of **3** from chloride **17**, involving cation **6**, and the preparation of **3** from chloride **19**, involving cations **12**, **7**, and **6**, shows that the barrier leading to **5** is considerably higher than those giving **3**. As well, the **12** → **7** → **6** → **3** processes must be completely stereospecific. A similar situation exists for the preparation of **2** from precursors **18** and **20**. A possible energy profile is shown in Figure 2.[14] One can only speculate on the

(14) For a previous discussion see: Mayr, H.; Olah, G. A. *J. Am. Chem. Soc.* **1977**, *99*, 510.

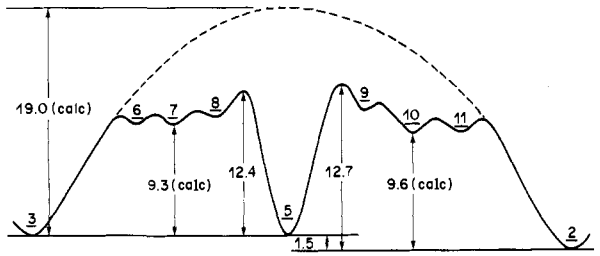
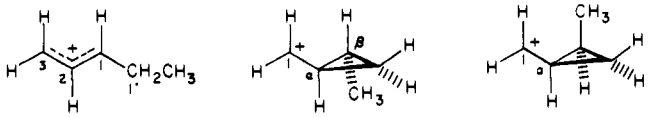


Figure 2. Energy profile for the isomerization of the *cis*-1-methylcyclopropylcarbinyl cation **3** to the trans isomer **2**. The dashed line represents the calculated barrier height for isomerization via a simple 180° rotation of the C1–Cα bond.

height of the barrier from **3** to **6**, but the **6** → **7** barrier would likely be quite small[15] and with little energy difference between the cations. MO calculations give ΔE for **3** and **7** as 9.3 kcal/mol. A similar situation exists for **2**, **10**, and **11**. One can also add to this figure the $\Delta G^{\ddagger}$ data derived in the present work. Overall, leaving out cations **8** and **9** for the present, the profile shown in Figure 2 seems internally fairly consistent with the experimental observations.

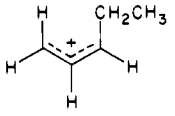
The key reaction in the **3** → **2** rearrangement concerns the transformation of **5** into either **7** or **10**, since this partitioning provides the only connection between the left- and right-hand manifolds in Figure 2.

If one compares the structure of **5** with **7** and **10**, one notes some similarities in overall atom positions but also some distinct differences, as shown below:



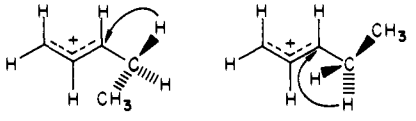
5 **10** **7**

It seems reasonable that the relative orientation of the H2 and H3 protons in **5**, and the H1 and Hα protons in **7** or **10**, would be retained, since their overall geometry is similar. The bond being cleaved in **7** (or **10**) is the Cα–Cβ (CH_3) bond, the remaining βCH_2 group, after migration of *one* of the protons, destined to become C1 of the allyl cation. There are, in theory, two possible allyl cations that could be formed, the syn isomer **21** and the



experimentally observed anti isomer **5**. Since there is no evidence that **21** is involved here, pathways involving this cation are not considered further.

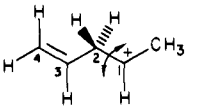
The key step in the partitioning of **5** into **7** or **10** is best shown by leaving for a moment the cyclopropylcarbinyl cleavage discussion and instead to start working from the other end. The hydrogen migrating in **5** should be approximately colinear with the allyl cation π-orbitals, and this leads to two rotamers, **5A** and



5A **5B**

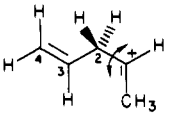
5B. An identical set involving the other prochiral hydrogen are also present. One can make an argument for rotamer **5A** leading to **10** and conversely for **5B** giving **7** (inversion at the migrating center and bonding to C2 (Cα) opposite to the migrating hydrogen). It would also appear that rotamer **5B** is slightly more stable than **5A** and this could account for the small preference found for the **5** → **7** process (0.3 kcal/mol). However, it is easy to see why one can get a crossover between **3** and **2** at this stage.

In Scheme I or as shown in Figure 2, we have placed an intermediate in the reaction path between **5** and **7** and between **5** and **10**. There are three main reasons for doing this: (1) In spite of the similarities in atom positions noted previously, there are major changes in position and hybridization involving the β-cyclopropyl carbons and the ethyl group. (2) These allyl ⇌ cyclopropylcarbinyl cation transformations seem to require a methyl substituent in the β-position of the cyclopropyl ring. For example, the direct cleavage of either **2** or **3**, which would produce the 1,3-dimethylallyl cation, is not observed. Instead, the pathway going uphill from **2** (or **3**) to **10** (or **7**) and then cleavage to a less stable allyl cation is much preferred. This suggests that the β-cyclopropyl carbon (becoming "primary" in the former cleavage and "secondary" in the latter) develops a large positive charge at some point in the reaction, and this seems to us better accommodated by postulating a homoallylic-type intermediate rather than simply having a totally concerted process. (3) The strongest evidence for this intermediate comes from the H–D exchange studies on **2**-*1*-d_1. A totally concerted reaction from **5** to **10** would in all probability lead to a stereospecific incorporation of deuterium at only one β-position of **2** or at least differing rates. To get randomization of the label,[16] consider the homoallylic-type intermediates **8** and **9**. All that is required is that the methyl group



8

(drawn in a symmetric orientation)



9

(drawn in a symmetric orientation)

on C1 loses any specific orientation with respect to either of the C2 methylene protons (one having just migrated), and the easiest way to accommodate this is to postulate the existance of an intermediate like **8** or **9**, with a lifetime long enough to oscillate the C1–C2 bond through a symmetrical arrangement (either transition-state or ground-state structure).[17] It is also possible that complete 180° rotation could occur, leading to the interchange of these homoallylic cations, and we have indicated this possibility with a dashed line in Scheme I. However, this process is not needed to rationalize the data. In Figure 2, we show the barrier from **8** (or **9**) to **7** (or **10**) as smaller than the ones from **9** or **10** to **5** because of previous work on homoallylic cations in which this partitioning reaction has been studied.[19]

The facile rearrangement of **3** to **2**, which finds a lower barrier than the obvious rotation mechanism, serves again to emphasize the very facile nature of carbocation rearrangements. A similar

(15) In the parent cyclopropylcarbinyl–cyclobutyl system, both cations seem to be present, but no NMR line broadening, due to slowing the interchange reaction, is observed down to as low as −132 °C. This places $\Delta G^{\ddagger}$ at less than 4 kcal/mol. Staral, J. S.; Yavari, I.; Roberts, J. D.; Prakash, G. K. S.; Donovan, D. J. Olah, G. A. *J. Am. Chem. Soc.* **1978**, *100*, 8016.

(16) Deuterium would also appear on C3 of **5** (via **12** or **13**) but this reaction should be stereospecific and there is no low energy barrier that interchanges the syn and anti protons on C3, i.e., which would randomize the label.

(17) In the parent C4 system, calculations[18] have failed to locate a potential surface minimum for the homoallyl cation. However, a secondary or tertiary species should be much more stable. We have, however, no evidence that the ground-state structure is symmetrical, as shown in **8** and **9**. Also, in solvolyses of the parent system, homoallylic products are formed stereospecifically,[8] indicating that the free ion is probably not involved.

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case is found in 2-norbornyl cation chemistry, where an endo-3,2-hydrogen or methyl shift is preferentially accomplished by a multistep process rather than the simple shift.[20]

Experimental Section

***cis*- and *trans*-3-Methyl-1-chlorocyclobutanes 19 and 20.** *N*-Chlorosuccinimide (13.44 g, 0.10 mol), 3-methylcyclobutanecarboxylic acid, as a mixture of the cis and trans isomers[21] (2.0 g, 1.8×10^{-2} mol), and 10 mL of a 5:1 mixture of *N,N*-dimethylformamide–glacial acetic acid were added to a 100-mL three-neck round-bottom flask provided with tandem water condensers terminating in an air lock connected to a gas volume measuring device. The soupy yellow mixture was degassed for 20 min under argon and then 7.5 g (1.7×10^{-2} mol) of lead tetraacetate was added and the mixture degassed for a further 15 min. The mixture was heated until the very exothermic reaction was initiated (≈57 °C). After 1.5 min, gas evolution ceased and the residue was extracted 7 times with 20-mL portions of pentane. The combined pentane extracts were washed 3 times each with dilute perchloric acid, 10% sodium carbonate, and water. After drying over magnesium sulfate, most of the pentane was removed on a spinning band column. The remaining 3 mL was distilled in a small apparatus, collecting **19** and **20** at about 80 °C/700 mm, 1.43 g of 74% pure **19** and **20** (60% yield). The ratio of **19** and **20** was close to 1:1.

Pure **19** and **20** were separated by preparative GLC [20 ft × $^1/_4$ in. column, 10% polyphenyl ether (six ring) on Chromosorb W-AW-DMCS, 60–80 mesh]. Under these conditions the peaks are partially resolved. Chloride **19** was obtained pure from a side cut of the first peak and **20** from a cut of the higher retention peak.

***cis*-3-Methyl-1-chlorocyclobutane 19**: ^{1}H NMR δ 4.216 (d, t, J = 7–7.5 and 8.5 Hz, H1), 2.75 (complex, H2 trans to Cl), 2.09 (complex, H3), 1.94 (complex, H2 cis to Cl), 1.135 (d, J = 6.3 Hz, CH_3); ^{13}C NMR δ 48.7 (C1), 42.8 (C2 and C4), 25.3 (C3), 21.9 (CH_3); MS calcd mass for $^{12}C_5{}^1H_9{}^{35}Cl$ 104.0393, found 104.0417.

***trans*-3-Methyl-1-chlorocyclobutane 20**: ^{1}H NMR δ 4.519 (d, t, J = 7, 7 Hz), H1), 2.63 (complex, H3), 2.44 (complex, H2 cis to Cl), 2.21 (complex, H2 trans to Cl), 1.13 (d, J = 6.8 Hz, CH_3); ^{13}C NMR δ 52.5 (C1), 40.9 (C2 and C4), 25.5 (C3), 20.8 (CH_3); MS calcd mass for $^{12}C_5{}^1H_9{}^{35}Cl$ 104.0393, found 104.0394.

***cis*- and *trans*-2-Methyl-1-chlorocyclobutanes 17 and 18.** These were prepared essentially as described for **19** and **20**, from a cis–trans mixture[22] of 2-methylcyclobutanecarboxylic acid. The exothermic reaction was initiated at a somewhat higher temperature (≈ 65 °C). A mixture of **17** and **18** was obtained by distillation, bp ca. 100 °C, 55% yield. The ratio of **17** to **18** was close to 1:2.

Pure **17** and **18** were easily separated by preparative GLC. By use of the same column as above, **17** and **18** are completely resolved, with **1** the longer retention product.

***cis*-2-Methyl-1-chlorocyclobutane 17**: ^{1}H NMR δ 4.55 (d, d, d, J = 7.5, 7.5 Hz, H1), 2.68 (complex, H2), 2.3 and 2.46 (both complex, H4 protons), 2.00 (complex, H3 trans to Cl), 1.67 (complex, H3 cis to Cl), 1.175 (d, J = 7.1 Hz, CH_3); ^{13}C NMR δ 57.3 (C1), 36.5 (C2), 24.6 (C3), 31.65 (C4), 16.0 (CH_3); MS calcd mass for $^{12}C_5{}^1H_9{}^{35}Cl$ 104.0393, found 104.0403.

***trans*-2-Methyl-1-chlorocyclobutane 18**: ^{1}H NMR δ 3.86 (d, d, d, J = 7.5, 7.5, 7.5 Hz, H1), 2.48 (complex, H2), 2.08 and 2.36 (both complex, H4 protons), 2.08 (complex, H3 cis to Cl), 1.32 (complex, H3 trans to Cl), 1.07 (d, J = 6.7 Hz, CH_3); ^{13}C NMR δ 58.6 (C1), 43.9 (C2), 24.4 (C3), 31.3 (C4), 18.5 (CH_3); MS calcd mass for $^{12}C_5{}^1H_9{}^{35}Cl$ 104.0393, found 104.0387.

***cis*- and *trans*-2-Ethyl-1-chlorocyclopropanes 21 and 22.** The synthesis of **21** and **22** has been reported by Closs but no physical data were given.[23] These were separated by preparative GLC using the same column as for separating **19** and **20**, with the trans isomer being the shorter retention product.

***trans*-2-Ethyl-1-chlorocyclopropane 22**: ^{1}H NMR δ 2.73 (d, d, d, J = 3.5, 3.5, 7 Hz, H1), 1.33 and 1.25 (each d, q, J = 6, 7 Hz, nonequivalent CH_2 of ethyl), 1.13 (complex, H3 cis to Cl), 0.67 (complex, H3 trans to Cl), 0.87 (complex, H2), 0.99 (t, J = 7 Hz, CH_3); ^{13}C NMR δ 32.6 (C1), 25.5 (CH_2 of Et), 24.4 (C2), 15.6 (C3), 12.8 (CH_3); MS calcd mass for $^{12}C_5{}^1H_9{}^{35}Cl$ 104.0393, found 104.0393.

***cis*-2-Ethyl-1-chlorocyclopropane 21**: ^{1}H NMR δ 3.15 (d, d, d, J = 7, 7, 4 Hz H1), 0.85–1.15 (complex pattern of area 2, H2 and H3 trans to Cl), 0.43 (complex, H3 cis to Cl), 1.52 (d, q, J = 7, 7, Hz, CH_2 of ethyl); 1.06 (t, J = 7 Hz, CH_3; ^{13}C NMR δ 34.1 (C1), 22.3 (CH_2 of Et), 19.2 (C2), 14.5 (C3), 13.6 (CH_3); MS calcd mass for $^{12}C_5{}^1H_9{}^{35}Cl$ 104.0393, found 104.0393.

1-Cyclopropylethanol-*1*-d_1 (23) was prepared by reduction of the ketone with lithium aluminum deuteride: ^{2}H NMR δ 3.27, no other peaks and no ^{1}H peak at this position.

Structure Assignments. ^{1}H NMR spectra were simulated by using the LAME program on the XL-200 spectrometer. Extensive decoupling experiments were also employed to simplify the analysis. Chlorides **19** and **20**: spectra are consistent with the Cl occupying an equatorial position in both cases. The vicinal couplings to the >CHCl proton are in the range 7–8.5 Hz in both cases (aa and ae coupling constants). The vicinal couplings to the >$CHCH_3$ proton differ in the two isomers, ca. 8.5 and 4–4.5 Hz. Therefore, the latter feature is assigned to the trans isomer **20** (ee coupling). This assignment is consistent with chemical shift data, where the methyl group shields the protons cis to itself. Chlorides **17** and **18**: once again one of the vicinal couplings to the >$CHCH_3$ proton is in the range 4–4.5 Hz (ee), which in this case implies the cis structure **17**. The chemical shift data are also consistent.

Preparation of the Cations. These were prepared by a general procedure that has been described in detail.[24] Proton and ^{2}H spectra were obtained on a Varian XL-200 spectrometer and ^{13}C spectra on a Bruker WH-90. Locking procedures, temperature calibration, etc. have been described.[24]

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Registry No. 2, 27861-45-6; **2**-*1*-d_1, 87863-07-8; **5**, 79096-95-0; *cis*-**17**, 56180-89-3; *trans*-**18**, 56180-91-7; *cis*-**19**, 56180-90-6; *trans*-**20**, 56180-92-8; *cis*-**21**, 87863-05-6; *trans*-**22**, 87863-06-7; **23**, 35300-15-3; *cis*-3-methylcyclobutanecarboxylic acid, 87863-08-9; *trans*-3-methylcyclobutanecarboxylic acid, 87863-09-0; cyclopropyl methyl ketone, 765-43-5; *cis*-2-methylcyclobutanecarboxylic acid, 57705-60-9; *trans*-2-methylcyclobutanecarboxylic acid, 57705-61-0.

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