Two- and Threefold Degenerate Rearrangements in Di- and Trimethylcyclopropylcarbinyl Cations[1]

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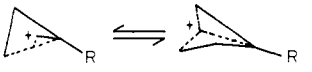
Abstract: A series of secondary di- and trimethylcyclopropylcarbinyl cations were prepared in stable ion media and were investigated by ^{13}C NMR spectroscopy. Whereas β,1-dimethylcyclopropylcarbinyl and α,β,1-trimethylcyclopropylcarbinyl cations undergo fast twofold degenerate rearrangements on the NMR time scale, the β,β',1-trimethylcyclopropylcarbinyl cation shows threefold degeneracy. The degenerate equilibrium in all three systems could not be frozen even at −140 °C, indicating the activation energy barrier for the process to be below 5 kcal/mol. All three cations are of classical carbocation nature as indicated on the basis of the additivity of chemical shift analysis. On the other hand previously studied parent cyclopropylcarbinyl and α-methylcyclopropylcarbinyl cations are equilibrating bridged ions. It is important to recognize that the nature of classical and nonclassical ions cannot be differentiated in the context of static vs. equilibrating ions.

The structure of cyclopropylcarbinyl and cyclobutyl cations and their equilibria have been extensively investigated[2] both under solvolytic and stable ion conditions. The parent cyclopropylcarbinyl and α-methyl cyclopropylcarbinyl cations **1** and **2** have

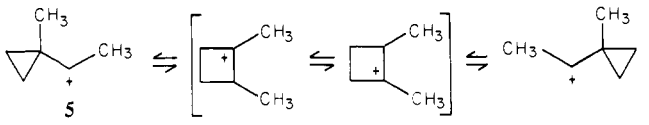
$$[C_4H_7]^+ \qquad [C_5H_9]^+$$
$$\mathbf{1} \qquad \mathbf{2}$$

been shown[3,4] to have bridged ground-state structures **3** and **4** in



3, R = H
4, R = CH_3

the stable ion media, although they undergo rapid degenerate cyclopropylcarbinyl–cyclobutyl cation equilibrium even at very low temperatures on the NMR time scale. Subsequently we have shown[5] that introduction of additional methyl substituent as in the case of α,1-dimethylcyclopropylcarbinyl cation **5** resulted in



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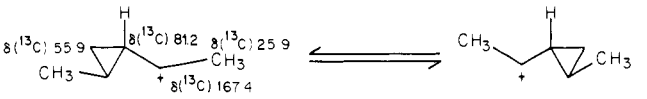
a classical carbocation with substantial charge delocatization into the cyclopropane ring. The cation **5** showed below −107 °C static nature, above which it underwent twofold degenerate equilibration through the unpopulated (in the Boltzman distribution) 1,2-dimethylcyclobutyl cation 6. From this study[5] the barrier for 1,2-hydrogen shift in 1,2-dimethylcyclobutyl cation 6 was estimated to be about 8.6 kcal/mol. We wish to report now a ^{13}C NMR spectroscopic study of the long-lived β,1-dimethylcyclopropylcarbinyl,α,β,1-trimethylcyclopropylcarbinyl, and β,β',1-trimethylcyclopropylcarbinyl cations **7**, **8**, respectively, and **9**, which also show degenerate behavior.

Results and Discussion

β,1-Dimethylcyclopropylcarbinyl Cation. Ionization of trans-β,1-dimethylcyclopropylcarbinol in SbF_5/SO_2ClF solution at −78 °C resulted in a light yellow solution. The 20-MHz ^{13}C NMR spectrum of the solution at −80 °C (Figure 1) showed four absorptions at $\delta(^{13}C)$ 167.4 (d, J_{C-H} = 177.6 Hz), 81.2 (d, J_{C-H} = 192.1 Hz), 55.9 (t), and 25.9 (q). The observed chemical shifts and multiplicities indicate that the formed β,1-dimethylcyclopropylcarbinyl cation **7** is undergoing fast twofold degenerate rearrangement on the NMR time scale, resulting in averaged methyl, carbocation center and β-methine signals.



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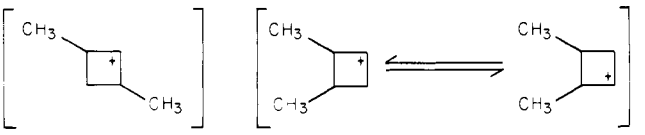
Attempts to freeze the fast equilibration process by lowering the temperature to −140 °C did not broaden the methyl signals significantly, although the averaged cationic center peak at $\delta(^{13}C)$ 167.4 merged into the base line at −108 °C. The above result seem to indicate that the equilibration process is occurring with an activation energy barrier below[6] 5 kcal/mol. The observed facile rearrangement process in all probability occurs through an unpopulated puckered 2,4-dimethylcyclobutyl cation **10** as an



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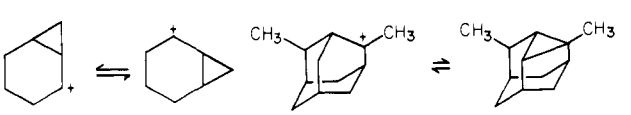
intermediate or a transition state. The involvement of the 2,3-dimethylcyclobutyl cation **11** is clearly ruled out on the basis of the observed symmetry. Moreover, there is significant activation energy barrier for the degenerate hydride shifts[5,7] in cyclobutyl cations. It is interesting to note that if the cyclopropylcarbinyl framework is embodied in a rigid skeleton the activation energy barrier increases substantially as was observed in the case of the 2-bicyclo[5.1.0]heptyl[8] and the 2,8-dimethyl-8,9-dehydro-2-adamantyl cations **12** and **13**.



12, $\Delta G^{\ddagger}$ = 8.5 ± 0.5 kcal/mol 13, $\Delta G^{\ddagger}$ = 7.4 ± 0.5 kcal/mol

The classical carbocation nature of the ion **7** is evident from the observed ^{13}C NMR chemical shifts. Applying the additivity

(1) Stable Carbocations. 238. For part 237, see G. A. Olah, G. K. S. Prakash, and A. Husain, *Angew. Chem., Int. Ed. Engl.*, in press.

(2) For reviews see: (a) G. Richey in "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, 1972, Chapter 25; (b) K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe, ref 5a, Vol III, Chapter 26; (c) J. Haywood-Farmer, *Chem. Rev.*, **74**, 315 (1974); (d) H. C. Brown, "The Nonclassical Ion Problem", Plenum Press, New York, 1977, Chapter 5.

(3) J. S. Staral, I. Yavari, J. D. Roberts, G. K. S. Prakash, D. J. Donovan, and G. A. Olah, *J. Am. Chem. Soc.*, **100**, 8016–8018 (1978).

(4) G. A. Olah, G. K. S. Prakash, D. J. Donovan, and I. Yavari, *J. Am. Chem. Soc.*, **100**, 7085–7086 (1978) and references cited therein.

(5) G. A. Olah, D. J. Donovan, and G. K. S. Prakash, *Tetrahedron Lett.*, 4779–4782 (1978).

(6) Attempts to freeze the process at −130 °C on a 50-MHz ^{13}C NMR instrument were also not successful.

(7) J. Staral and J. D. Roberts, *J. Am. Chem. Soc.*, **100**, 8014–8016 (1978).

(8) G. A. Olah, G. K. S. Prakash, and T. N. Rawdah, *J. Org. Chem.*, **45**, 965–969 (1980).

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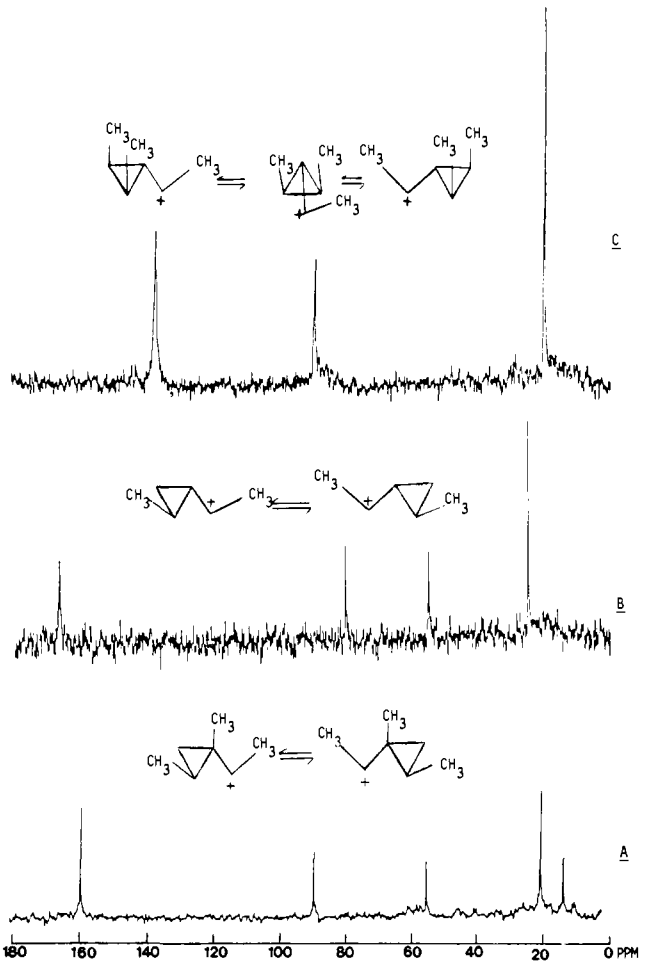
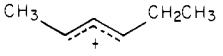


Figure 1. Proton decoupled ^{13}C NMR spectra of equilibrating (A) α,β,1-trimethylcyclopropylcarbinyl cation **8**, (B) β,1-dimethylcyclopropylcarbinyl cation **7** and (C) β,β',1-trimethylcyclopropylcarbinyl cation **9** at −80 °C.

of chemical shift analysis,[10] ion **7** clearly falls into the classical category. Warming the ion solution to −40 °C resulted in irreversible rearrangement into the 3-hexen-2-yl cation[11] **14**.



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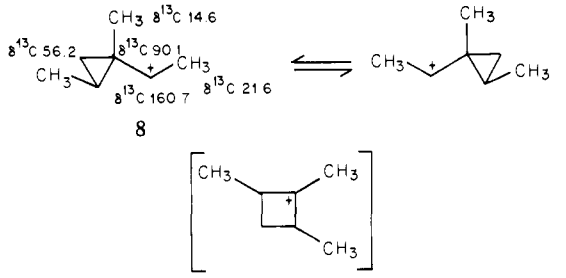
α,β,1-Trimethylcyclopropylcarbinyl Cation. Having studied the facile nature of twofold degenerate rearrangements in cations **5** and **7**, we also explored the effect of additional methyl substituent on the process. The α,β,1-trimethylcyclopropylcarbinyl cation **8** prepared from *cis*-α,β,1-trimethylcyclopropylcarbinol in SbF_5/SO_2ClF solution at −78 °C showed five ^{13}C NMR absorptions at −80 °C (Figure 1). The peaks were observed at $\delta(^{13}C)$ 160.7 (d, J_{CH} = 173.3 Hz), 90.1 (s), 56.2 (t), 21.6 (q), and 14.6 (q). The ^{13}C NMR chemical shift data clearly indicate the twofold degenerate rearrangement process occurring in cation **8**. Lowering the temperature down to −140 °C did not appreciably broaden peaks at $\delta(^{13}C)$ 90.1, 56.2, 21.6, and 14.6, respectively. However, the averaged cationic center at $\delta(^{13}C)$ 160.7 merged into the base line at −100 °C. This behavior indicates that the activation energy



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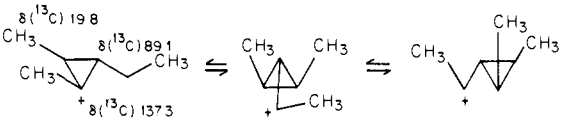
barrier for the observed twofold degenerate rearrangement is also below[6] 5 kcal/mol. Again, the most reasonable pathway involves the puckered 1,2,4-trimethylcyclobutyl cation as an unpopulated intermediate or a transition state for the observed degenerate process. The activation energy barrier, in this case due to apical methyl substitution,[8] must be significantly lower than in the previous ion.[7] The classical carbocationic nature of ion **8** is also evident from the chemical shift additivity analysis.[10] The cation at −50 °C irreversibly decomposes to a mixture of closely related allylic ions.[12]

β,β',1-Trimethylcyclopropylcarbinyl Cation. Realization of the facile twofold degenerate nature of the α,β,1-trimethylcyclopropylcarbinyl cation **8**, we extended our study to prepare the β,β',1-trimethylcyclopropylcarbinyl cation, to observe a potentially threefold degenerate equilibrating ion. Ionization of *cis*-β,β',1-trimethylcyclopropylcarbinol in SbF_5/SO_2ClF solution at −78 °C resulted in a light brown solution, whose ^{13}C NMR spectrum at −80 °C (Figure 1) showed only three peaks at $\delta(^{13}C)$ 137.3 (d, J_{C-H} = 163.7 Hz), 89.1 (d, J_{C-H} = 181.2 Hz), and 19.8 (q). The observation of only three peaks clearly indicate the occurrence of threefold rapid degenerate equilibration process in the cation **9** on the NMR time scale at −80 °C. Attempts to freeze the process even at −140 °C[6] were not possible, indicating similar low barrier to the previously discussed two twofold degenerate systems. Again one can postulate an unpopulated puckered 2,3,4-trimethylcyclobutyl cation **16** as an intermediate or a transition state.



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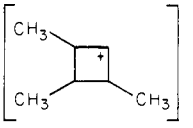

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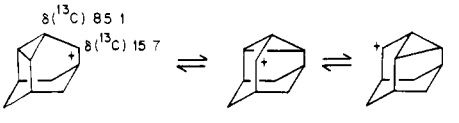
It is interesting that there is no interconversion between isomeric cations **9** and **8**. Additivity of chemical shift analysis[10] again shows the classical carbocation nature of the ion **9**. The presently investigated threefold degenerate ion **9** could be compared to the previously studied 8,9-dehydro-2-adamantyl cation **17**,[13] which also undergoes fast threefold degenerate rearrangement. It is



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instructive to note that alkyl substituion on the parent cyclopropylcarbinyl cation **1** results in classical carbocations still undergoing fast degenerate cyclopropylcarbinyl–cyclobutyl cation rearrangements. Upon warming the cation **9** to −30 C results in

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(10) (a) P. v. R. Schleyer, D. Lenoir, P. Mison, G. Liang, G. K. S. Prakash, and G. A. Olah, *J. Am. Chem. Soc.*, **102**, 683–961 (1980). (b) Applying additivity of chemical shift analysis,[10a] the total chemical shift difference for cations **7**, **8**, and **9** are 398, 375, and 410 ppm, respectively. The sum of total chemical shifts for the model hydrocarbons 1-ethyl-2-methylcyclopropane, 1-ethyl-1,2-dimethylcyclopropane, and 1-ethyl-2,3-dimethylcyclopropane were estimated to be 125, 150, and 150 ppm, respectively.

(11) The ^{13}C NMR shifts of the allylic ion **14** at $\delta(^{13}C)$ 235.4 (s), 230.3 (s), 144.0 (d), 38.4 (t), 28.7 (q), and 7.9 (q).

(12) The structures of allylic ions obtained as a mixture from ions **8** and **9** were difficult to assign on the basis of the ^{13}C NMR data.

(13) G. A. Olah, G. Liang, K. A. Babiak, T. M. Ford, D. L. Goff, T. K. Morgan, Jr., and R. K. Murray, Jr., *J. Am. Chem. Soc.*, **100**, 1494 (1978).

the irreversible formation of mixture of closely related allylic cations.[12]

Conclusion

In conclusion rapid two and threefold degenerate equilibration processes were demonstrated in secondary cyclopropylcarbinyl cations which are of classical carbocation nature. In contrast the primary cyclopropylcarbinyl cations[3,4] are equilibrating nonclassical cations. The nature of classical and nonclassical ions thus cannot be differenciated in the context of static vs. equilibrating ions[14] as both of these type of ions can belong to either categories as demonstrated for example in case of studied cyclopropylcarbinyl cations.

Experimental Section

β,1-Dimethylcyclopropyl- and α,β,1-trimethylcyclopropyl methanols were prepared by the Simmons–Smith reaction on *trans*-3-penten-2-ol and *trans*-3-methyl-3-penten-2-ol in diethyl ether solutions. The *cis*-β,β′,1-trimethylcyclopropyl methanol was prepared by the addition (*cis*-β,β′-dimethylcyclopropyl)magnesium bromide to acetaldehyde in ether solution which was obtained as a mixture of isomers. The isomeric alcohols were directly used for ionization. All compounds gave satisfactory physical and spectral data.

Preparation of Carbocations. The appropriate cation precursor dissolved in SO_2ClF, precooled at −78 °C (dry ice–acetone bath temperature) is slowly added with vigrous stirring to a freshly prepared solution of a fourfold excess of SbF_5 in SO_2ClF maintained at −78 °C in a 10-mm NMR tube. This procedure affords approximately 10–15% solution of the ion.

^{13}C NMR spectroscopic studies were carried on a Varian Associates Model FT-80 spectrometer equipped with a variable-temperature broad-band probe. The chemical shifts are in parts per million from external capillary tetramethylsilane.

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Registry No. **7**, 80243-99-8; **8**, 80244-00-4; **9**, 80244-01-5; **12**, 72610-47-0; **13**, 73882-17-4; **14**, 80244-02-6; β,1-dimethylcyclopropylcarbinol, 19293-90-4; α,β,1-trimethylcyclopropylcarbinol, 67074-42-4; β,β′,1-trimethylcyclopropylcarbinol, 80244-03-7.

(14) H. C. Brown, "The Nonclassical Ion Problem", Plenum Press, New York-London, 1977, pp 89–91.

Stereochemical Control in the Intramolecular Diels–Alder Reaction. 2. Structural and Electronic Effects on Reactivity and Selectivity

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Abstract: The cyclization reactions of a series of triene lactones activated by electron-withdrawing groups at the terminus of the chain have been investigated. The 4 + 2 cycloadducts resulting from intramolecular Diels–Alder cycloaddition were characterized and the stereochemistry determined. The effects of varying the structure of the electron-withdrawing groups and the substitution patterns of the dienophile on the rate and stereoselectivity were examined. In all cases studied, trans-hydrindene systems were produced exclusively, although the rates of the cyclization varied dramatically. This effect was interpreted on the basis of steric inhibition of resonance in the dienophile. The effects of geminal substitution in the connecting chain were also examined, and it was found that the stereochemical outcome was not altered but a rate enhancement of ~4× occurred, presumably due to a decrease in the $\Delta S^{\ddagger}$ for cyclization. This effect was interpreted in terms of a buttressing due to the geminal substitution which favorably influenced the population of conformers properly disposed to undergo cycloaddition.

The development of intramolecular analogues of electrocyclic and cycloaddition reactions as tools for the stereospecific synthesis of complex molecules has received considerable attention recently.[2,3] A number of nicely conceived examples of the use of the intramolecular Diels–Alder protocol for the preparation of complex systems have now appeared.[4] Furthermore, a growing body of data regarding the stereochemical consequences and other features of this reaction is being acquired with the intention of developing a coherent picture of the factors affecting reactivity and stereoselectivity in these processes, and of probing the scope and limitations of the process for a variety of synthetic applications.[5]

In order for the intramolecular Diels–Alder reaction to become an accepted basic strategy for the construction of complex mol-

(1) Fellow of the Alfred P. Sloan Foundation 1976–1980. Recipient of an NIH Career Development Award (Grant CA-00702). Address correspondence to this author at the University of Rochester.

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(4) A few recent examples: (a) Snowden, R. L. *Tetrahedron Lett.* **1981**, *22*, 97, 101. (b) Wilson, S. R.; Misra, R. N. *J. Org. Chem.* **1980**, *45*, 5079. (c) Ichihara, A.; Kimura, R.; Yamada, S.; Sakamura, S. *J. Am. Chem. Soc.* **1980**, *102*, 6353. (d) Pyne, S. G.; Hensel, M. J.; Byrn, S. R.; McKenzie, A. T.; Fuchs, P. L. *Ibid.* **1980**, *102*, 5960. (e) Martin, S. F.; Tu, C.; Chou, T. *Ibid.* **1980**, *102*, 5274. (f) Taber, D. F.; Saleh, S. A. *Ibid.* **1980**, *102*, 5085. (g) Schmitthener, H. F.; Weinreb, S. M. *J. Org. Chem.* **1980**, *45*, 3372. (h) Roush, W. R.; Gillis, H. R. *Ibid.* **1980**, *45*, 4283. (i) Tietze, L.-F.; Kiedrowski, G. V. *Tetrahedron Lett.* **1981**, *22*, 219.

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