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THE α, 1-DIMETHYLCYCLOPROPYLCARBINYL CATION[1]

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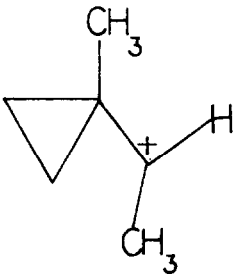
We wish to report the preparation and temperature dependent ^{1}H and ^{13}C NMR spectroscopic study of the α, 1-dimethylcyclopropylcarbinyl cation (1).[2a] At low temperatures (< - 100°C) ion 1 is a static carbocation, whereas at -70°, it undergoes equilibration through the 1,2-dimethylcyclobutyl cation (2).[2b] At -39°, 1 irreversibly rearranges to the 1,1,3-trimethylallyl cation (3).[2,4] The spectrum is totally reversible below -39°.

The α, 1-dimethylcyclopropylcarbinyl cation (1) is prepared from the corresponding α, 1-dimethylcyclopropylcarbinol[2c] via ionization with antimony pentafluoride in SO_2ClF solution at -78°. At -107°, the proton decoupled ^{13}C NMR spectrum of 1 comprises five absorptions (Table 1). This spectrum is consistent with that of a static secondary cyclopropylcarbinyl cation.[3] By raising the temperature to -96°, the carbocation center, the apical carbon and both methyl absorptions began to broaden while the methylene signal remains sharp. At -84°,



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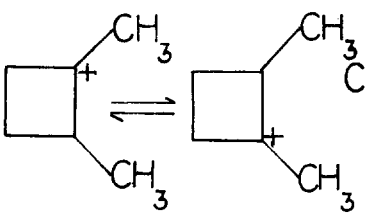

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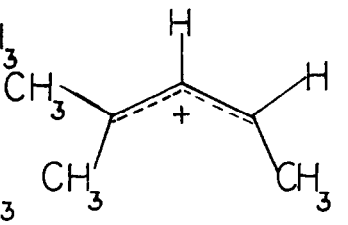

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only the methylene carbons' signal is observed,[3c] the other absorptions being merged into the baseline. Upon warming the solution to -73°, the average of the methyl groups' signal appears. At -39°, 1 irreversibly rearranges to the 1,1,3-trimethylallyl cation (3).[4] The averaged absorption of the carbocation and the apical carbon is not observed prior to the rearrangement of 1 to 3 since the chemical shift differences between these carbons is much larger than that of the methyl groups.

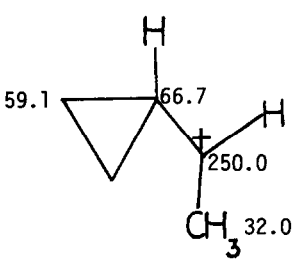
The 60 MHz ^{1}H NMR spectrum at -100° shows absorptions consistent with the α, 1-dimethylcyclopropylcarbinyl cation, structure 1. Warming the solution to -70°, the methyl groups coalesce, while the ^{1}H NMR chemical shifts of the other absorptions remain unaltered. A similar behavior is observed in the 80 MHz spectra.

Table 1. The ^{1}H and ^{13}C NMR Data of α, 1-Dimethylcyclopropylcarbinyl Cation 1 in SO_2ClF/SbF_5 Solution.

Ion	Temperature °C	H-C$^+$	C	CH_2	C$^+$-CH_3	CH_3
1	^{13}C NMR Data[a]					
	-119°	210.5	88.9	55.6	23.8	16.2
	J_{CH}	169.9(d)	--	176.7(t)	131.5(q)	131.5(q)
	-107°	209.5	89.4	55.3	23.6	16.2
	-96°	210.0	89.9	56.4	24.5	17.4
	-73°	--		56.1	20.8	20.8
	-39°	--		56.1	20.9	20.9
	^{1}H NMR Data[a]					
	-94°	8.4	--	4.3,3.9	3.1	2.5
	-50°	8.4	--	4.3,3.9	2.8	2.8

a - shifts are from external capillary TMS.

Both the ^{1}H and ^{13}C NMR data show that the α, 1-dimethylcyclopropylcarbinyl cation is a static secondary carbocation at low temperatures. Its NMR spectra and structure are similar to those reported for the parent methylcyclopropylcarbinyl cation (4)[2,3,5] with significant differences in the ^{1}H and ^{13}C NMR chemical shifts. The carbenium center of 1 is deshielded by 40.0 ppm relative to that of 4, whereas the apical carbon of 1 is deshielded by 22.7 ppm. This indicates that the apical carbon of 1 in comparison to 4 is stabilizing more charge due to the substituent effect of a methyl group. It is interesting to note that the methylene carbons of 1 are shielded by 3.5 ppm relative to that of 4. If the methylene shifts are corrected for a β substituent effect of the methyl group the value increases to 12.5 ppm.[6,7] This shows that methyl substitution at the C_1 position stabilizes the carbocation center by increasing the degree of σ-delocalization, resulting in a more positive apical carbon. The relative shielding of the methylene groups is due to the lesser electron density at the carbocation center. The same conclusion is reached by comparing the two tertiary carbocations 5 and 6.[2,3]



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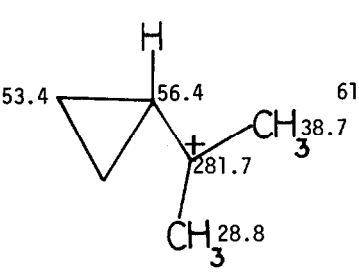

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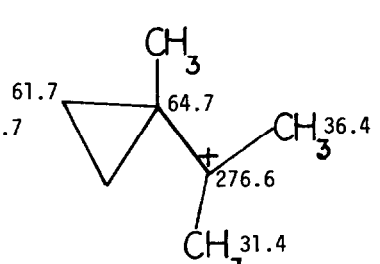

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A methyl group bonded to the carbocation center localizes charge better than the one at the neighboring apical carbon.

The temperature dependent behavior of 1 suggests that there are two degenerate ions involved, which equilibrate through an energetically high lying species, which does not contribute to the observed NMR parameters. The obvious choice for the higher lying species is the 1,2-dimethylcyclobutyl cation (2), but the exact nature of 2 could not be deduced from the present study as it does not contribute to the NMR parameters. Consequently, ion 1 is at least 2 kcal more stable than ion 2.

No similar temperature dependent behavior could be observed for 6 as it does not show any temperature dependent behavior up to -40°, above which it decomposes, When an attempt was made to generate ion 6 in $HSO_3F:SbF_5$ (1:1), only the formation of the 1,1,4,4-tetramethylally cation[4,8] was observed. An equilibrating system, such as 2, may be energetically unfavorable as ion 6 is a tertiary one.

The difference between carbocations 4 and 1 and 5 and 6 can be rationalized in terms of enhanced σ-delocalization due to the 1-methyl substituent.[8] However, the analogy cannot be applied to either the 1-methylcyclopropyl or to the parent cyclopropylcarbinyl cations. Similar observations have been made for the methyl substituted bicyclo (2.2.1) heptyl and the bicyclo (2.1.1) hexyl cations and their corresponding parent secondary ions.[9,10,11] The structural problem of the parent cyclopropylcarbinyl cations is discussed elsewhere.[12,13]

Acknowledgement:

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References and Notes

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2. a) Ion 1 below -107° is clearly static (non-exchanging) as five signals are observed in the proton decoupled ^{13}C NMR spectrum. Ion 1 could exist in two conformations, and tentatively the structure of ion 1 is assigned with the methyl groups trans to each other. A free rotation across C-$\overset{+}{C}$H bond at such a low temperature is unlikely in view of our previous studies on the secondary parent 1-methylcyclopropylcarbinyl cation.[2c,13] Methyl substitution at the 1-position should only increase the rotational barrier.

b) A simple equilibrium between 1 and 2 without a degenerate hydride shift in 2 is ruled out as an averaged methyl signal is observed for the methyl groups at temperatures above -73°.

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c) An approximate energy barrier for the hydride migration in the cation 2 with respect to the cation 1 was estimated from the coalescence temperature of the methyl signals both in ^{13}C and ^{1}H NMR spectra as:

$\Delta G^{\neq}$ = 8.9 ± 0.5 kcal/mole from the ^{13}C NMR spectrum with T_c at -80°.
$\Delta G^{\neq}$ = 8.6 ± 0.5 kcal/mole from the ^{1}H NMR spectrum with T_c at -95°.

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7. The corresponding cyclopropylcarbinols' ^{13}C NMR spectra were measured at room temperature (37°). The β-substituent effect of the 1-methyl groups is 9.4 ± 0.2 ppm for the methylene carbons.

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