(13) Aldehyde substrates were carefully purified by repeated fractional distillations and were run through an activated alumina column.
(14) GLC conditions: 8-ft columns packed with 10% Carbowax 20M on Chromosorb GNAW or 10% OV-101 on Chromosorb G.
(15) A. R. Sanger, *J. Chem. Soc., Dalton Trans.*, 120 (1977); M. C. Hall, B. T. Kilbourn, and K. A. Taylor, *J. Chem. Soc. A*, 2539 (1970).
(16) L. Vaska and D. L. Catone, *J. Am. Chem. Soc.*, **88**, 5324 (1966).
(17) J. A. J. Jarvis, R. H. B. Mais, P. G. Owston, and K. A. Taylor, *Chem. Commun.*, 906 (1966).
(18) L. Vaska, L. S. Chen, and W. V. Miller, *J. Am. Chem. Soc.*, **93**, 6671 (1971).
(19) W. Strohmeier and E. Hitzel, *J. Organomet. Chem.*, **87**, 353 (1975).
(20) W. Strohmeier and P. Pföhler, *J. Organomet. Chem.*, **108**, 393 (1976).

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Concerning the Structure and Modes of Degenerate Rearrangement of the Nonclassical 1-Methylcyclobutyl and Related Carbocations

Sir:

The structure of the 1-methylcyclobutyl cation (**1**) is of dispute.[2] Based on ^{1}H and ^{13}C NMR spectroscopic studies by Saunders and Rosenfield,[3] as well as by Olah et al.,[4] in which the methylene groups were found to be completely averaged at the lowest temperature studied (ca. -80 °C), it was concluded that ion **1** is best represented as a set of rapidly equilibrating bisected σ-delocalized 1-methylcyclopropylcarbinyl cations (**3**) equilibrating through the classical 1-methylcyclobutyl cation (**2**). In earlier work, Olah et al.[4a] have also

$$[C_5H_9]^+$$
1

2   **3**

4
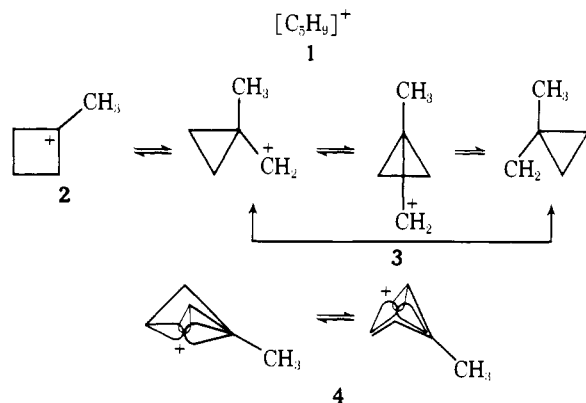
considered the equilibrating σ-delocalized bicyclobutonium ion (**4**) like structure.

Sorensen and Kirchen[2] have recently reinvestigated ion **1** by NMR spectroscopy at considerably lower temperatures (ca.

-158 °C). In both the ^{1}H and ^{13}C NMR spectra, the methylene peaks broadened and decoalesced into two separate peaks without affecting the chemical shifts associated with the other two carbon atoms. Similar behavior was also reported for the 1-propylcyclobutyl cation (**5**). From the new, very low temperature observations, Sorensen and Kirchen rightly ruled out the previously suggested[3,4] equilibrating cyclopropylcarbinyl-1-methylcyclobutyl structures (**2** $\rightleftharpoons$ **3**). They claimed

5   **6**   **7**
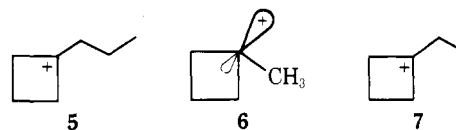
to have frozen out the static classical 1-methylcyclobutyl cation and suggested that, at higher temperatures, methylene scrambling occurs via equilibration through unpopulated cyclopropylcarbinyl cations (**3**). Since the carbocationic center in **1** as already reported[4] by us is highly shielded (by 170 ppm) compared with that in typical sp^2-hybridized static carbocations such as the 1-methylcyclopentyl cation and other tertiary cycloalkyl cations, Sorensen and Kirchen suggested an sp^3-hybridized 1-methylcyclobutyl cation structure (**6**) for an unstrained tertiary cycloalkyl cation.

The suggestion of such an unusual sp^3-hybridized classical carbocation structure **6** called for reinvestigation. We have repeated Sorensen and Kirchen's low temperature ^{13}C NMR work on ion **1** and also carried out low temperature studies at a higher field (63 MHz for carbon). The results for ion **1** were comparable with those of Sorensen and Kirchen. The 1-ethyl- and 1-propylcyclobutyl cations (**7** and **5**) also behave similarly to ion **1** at -150 °C, but rearrange to substituted cycloalkyl cations at temperatures as low as -130 °C. Whereas the 1-phenylcyclobutyl cation (**8**) as reported previously by us is a

8, X = H
9, X = 4-CF$_3$
10, X = 3,5-(CF$_3$)$_2$
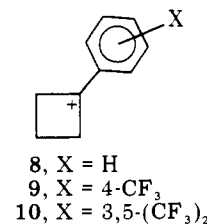
static classical carbocation, the 4-trifluoromethylphenylcyclobutyl cation (**9**) and 3,5-bis(trifluoromethyl)phenylcyclobutyl cation (**10**) were found, upon raising the temperature, to equilibrate through the related, but practically unpopulated (in the Boltzmann distribution) cyclopropylcarbinyl cations which average the methylene carbons similar to ion **1**. The ^{13}C NMR shifts of the carbocation centers of ions **10** and **9** at -60 and -34 °C are $\delta(^{13}$C) 286.4 and 284.1, respectively. The averaged methylene peaks are observed at $\delta(^{13}$C) 37.8 for **9**

Table I. ^{13}C NMR Chemical Shifts^a of Substituted Cyclobutyl Cations

ion	temp, °C	C$^+$	C$_\alpha$	C$_\beta$	methyl	additional groups
1	-74	163.09	48.69	48.69	25.37	
	-156.4	162.08	72.72	-2.83	25.83	
8	-70	271.67	44.95	17.47		Ci, 138.48; Co, 142.28; Cm, 133.17; Cp, 157.40
5	-121	164.41	45.99	45.99	12.68	α^1-CH$_2$, 39.27; β^1-CH$_2$, 19.01
7	-130	166.43	merged in the base line		13.00	α^1-CH$_2$, 36.46
10	-60	286.42	39.64	39.64		Ci, 146.42; Cp, 140.50; Co, 137.70; and Cm, 137.29 (J_{C-C-F} = 35.7 Hz); -CF$_3$, 122.90 (J_{C-F} = 273.4 Hz)
	-123.4	290.11	50.47	17.88		identical with those at -60 °C
9	-114	285.29	47.36	16.86		Ci, 139.69; and Cp, 152.13 (J_{C-C-F} = 34.7 Hz); Co, 142.62; Cm, 129.67; and -CF$_3$, 122.80 (J_{C-F} = 278.0 Hz)
	-34	284.13	37.76	37.76		identical with those at -60 °C

^{a} Shifts from external capitallary Me$_4$Si in SbF$_5$/SO$_2$ClF solutions.

at −34 °C and 39.6 for **10** at −60 °C. Ions **9** and **10** could be frozen out to the static substituted phenylcyclobutyl cations at −114 and −123 °C, respectively. Under these conditions ions **9** and **10** compare well with the classical phenylcyclobutyl cation (**8**), which does not show temperature dependence. The ^{13}C NMR data are tabulated in Table I.

The observed NMR data for the ion **1** are in our view not in accordance with a classical 1-methylcyclobutyl cation (**6**) containing an sp^3-hybridized carbenium center. Rather, they indicate a σ-delocalized 1-methylcyclopropylcarbinyl cation containing two different methylene groups ($\delta(^{13}$C) 72.7 and −2.83), one of which is highly shielded suggesting a five-coordinated carbon. All available structural and theoretical studies on carbocations mitigate against the existence of a relatively unstrained sp^3-hybridized classical carbocation. Unstrained trivalent carbocations contain a close to planar carbocation center which displays an extremely deshielded ^{13}C NMR chemical shift. In strained and thus nonplanar carbocations such as **11, 12,** and **13,**[5-7] the ^{13}C NMR shifts of the

11   **12**   **13**
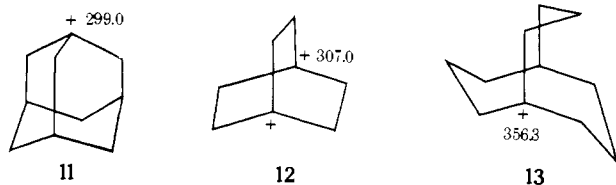
carbocation center are still highly deshielded ($\geq \delta(^{13}$C) 300). Thus, if an sp^3-like trivalent carbocation center would indeed exist in ion **1** (as suggested in structure **6**), the ^{13}C NMR shift would be expected to be more highly deshielded than the observed shift of $\delta(^{13}$C) 163.

The observed spectrum of **1** at −156 °C is thus not that of a frozen out static ion, but of either a degenerate set of σ-delocalized nonplanar bicyclobutonium like ions[3b] such as **4,** rapidly interconverting through a symmetrical σ-delocalized puckered species **15** which renders the β-methylene carbon pentacoordinated, or the symmetrical ion **15** itself. The clas-

15
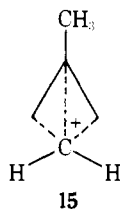
sical 1-methylcyclobutyl cation (**2**) or the bisected σ-delocalized 1-methylcyclopropylcarbinyl cations (**3**) which scramble the methylene carbons at higher temperatures ($\geq$ −140 °C) do not contribute to the NMR chemical shifts and, thus, must be at least 2 kcal/mol higher in energy than ions **4.** The energy barrier of 5.6 kcal/mol frozen out by Sorensen[2] must be thus between **4** and **3,** or **4** and **2,** with **3** or **2** being unstable reaction intermediates whose formation from the stable state **4** permits equilibration of the methylene groups.

The five coordinated β-methylene carbon in **4** resonates at $\delta(^{13}$C) −2.83. This kind of highly deshielded carbon has been observed in nonclassical pyramidal cations.[8]

The significant point to be made is that, if equilibration occurs between degenerate highly σ-delocalized unsymmetrical nonclassical ions (i.e., **4**) through a symmetrical nonclassical ion (**15**) via low energy barriers, for all practical purposes such systems would show symmetrical nature in the NMR spectra. Thus, the double energy minima would be indistinguishable from a single minimum, as the interconversions would take place through a very low energy barrier, i.e. $\leq$2 kcal/mol. This is also the case with the 2-norbornyl cation,[9] but again the question is not possible equilibration between classical ions vs.

the symmetrical, bridged nonclassical ion, ruled out by direct, spectroscopic studies of the long-lived ion, but of possibly still-equilibrating nonclassical σ-delocalized, but somewhat unsymmetrical, ions (double minima) vs. the symmetrical nonclassical ion (single minimum).[9] These are becoming by necessity indistinguishable by usual studies. It is important to recognize that σ-delocalized nonclassical ions are not necessarily static symmetrically bridged species, contrary to claims made to this effect.[10]

References and Notes

(1) Stable Carbocations. 217. Part 216: Olah, G. A.; Donovan, D. J.; Prakash, G. K. S. *Tetrahedron Lett.* in press.
(2) Kirchen, R. P.; Sorensen, T. *J. Am. Chem. Soc.* **1977,** *99,* 6687–6693.
(3) Saunders, M.; Rosenfield, J. *J. Am. Chem. Soc.* **1970,** *92,* 2548–2549.
(4) (a) Olah, G. A.; Jeuell, C. L.; Kelly, D. P.; Porter, R. D. *J. Am. Chem. Soc.,* **1972,** *94,* 146–156. (b) Olah, G. A.; Spear, R. J.; Hiberty, P. C.; and Hehre, W. J. *ibid.* **1976,** *98,* 7470–7475.
(5) Olah, G. A.; Liang, G.; Mateescu, G. D. *J. Org. Chem.* **1974,** *39,* 3750–3754.
(6) Olah, G. A.; Liang, G.; Schleyer, P. v. R.; Engler, E. M.; Dewar, M. J. S.; Bingham, R. C. *J. Am. Chem. Soc.,* **1973,** *95,* 6829–6831.
(7) Olah, G. A.; Liang, G.; Schleyer, P. v. R.; Parker, W.; Watt, C. I. F. *J. Am. Chem. Soc.,* **1977,** *99,* 966–968.
(8) Hogeveen, H.; Kwant, P. W. *Acc. Chem. Res.,* **1975,** *8,* 413–420.
(9) Olah, G. A. *Acc. Chem. Res.,* **1976,** *9,* 41–52.
(10) Brown, H. C. "The Non-classical Ion Problem", Plenum Press: New York, N.Y., 1977; Chapter 15, p 285.

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Direct Conversion of Nitro Compounds to Thiols[1]

Sir:

In recent years methods for the synthesis of a wide range of highly branched aliphatic and alicyclic tertiary nitro compounds have been devised.[2,3] As a consequence any reaction which results in the replacement of a nitro group by another group is of considerable interest. One such process—replacement by hydrogen—has been reported.[3]

The present communication describes another new reaction—the replacing of a nitro group by the mercapto group. When a tertiary nitro compound is treated with a solution of sodium sulfide and sulfur in Me$_2$SO at 25 °C smooth conversion to a mixture of the corresponding thiol and dialkyl polysulfides occurs; on subjecting this mixture to the action of amalgamated aluminum at 0 °C the polysulfides are converted to the thiol. Equation 1 is illustrative and Table I summarizes our results; yields refer to pure, isolated products.
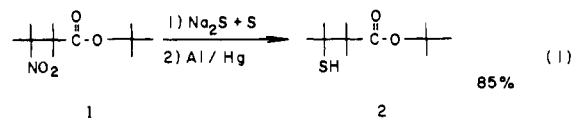
Precisely what reagent is responsible for the initial transformation of eq 1 is not known. Sodium sulfide is ineffective; it reacts very slowly with tertiary nitro compounds and gives little, if any, of the desired product. But, if elemental sulfur is added to the sodium sulfide so that for each sulfide ion there is one sulfur atom, i.e., so that the gross composition is Na$_2$S$_2$,