the thianthrene cation radical also occurred and gave the same oxidized products or product distribution of singlet oxygen. Cf. C. S. Foote, Abstracts of Joint Seminar on Chemi- and Bio-energized Processes, São Paulo, Brazil, 1978, p 42. Singlet oxygen is quenched by superoxide ion; so the detection of it by chemical trapping is less effective. Cf. W. C. Danen and R. L. Arudi, *J. Am. Chem. Soc.*, **100**, 3944 (1978), and references therein.

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(18) The singlet state of thianthrene is 2.48 eV,[20] but the energy of annihilation, ΔH°, is ~1.84 eV according to[19] $\Delta H^\circ = eE^\circ(A/A^-\cdot) - eE^\circ(D/D^+\cdot) + 0.16$ eV where $E^\circ(A/A^-\cdot)$ for oxygen is −0.75 V vs. SCE and $E^\circ(D/D^+\cdot)$ for thianthrene is +1.25 V vs. SCE.

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(21) Although singlet oxygen was generated, diphenyl sulfide and thianthrene were not oxidized by singlet oxygen under the conditions. Cf. M. Matsumoto and K. Kuroda, Abstracts of Symposium on Photochemistry, Sendai, Japan, 1977, p 4; ref 12.

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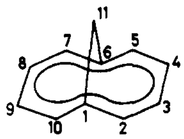
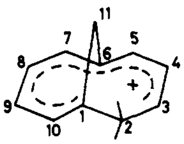
Aromatic Protonation. 6.[1] The Rearranged Ion of Monoprotonated 1,6-Methano[10]annulene. Evidence for the Presence of a Cyclopropylcarbinyl Cation Moiety

Sir:



1



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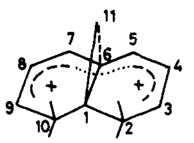


3

The protonated aromatic hydrocarbon 1,6-methano[10]-annulene (**1**)[2] is, in view of its methano bridge, a potential source of cyclopropylcarbinyl cations. We reported that treatment of **1** with FSO_3H-SbF_5-SO_2ClF at −120 °C yields the stable monocation **2**, but that, on raising the temperature to −60 °C, the dication **3**, containing the cyclopropyldicarbinyl dication moiety **4**, is formed.[1] A decade ago Winstein and Warner reported on the monocation **2**, using FSO_3H, and briefly indicated a slow rearrangement to another species at −60 °C.[3] We now report on the rearrangement of **2** to the stable cation **5**, containing the cyclopropylcarbinyl moiety **6**. Addition of **1** in SO_2ClF to a solution of FSO_3H-SO_2ClF (1:1 v/v) at ca. −100 °C in an NMR tube resulted in an orange-colored solution of **2**. At −60 °C ion **2** rearranges slowly (in ~1 h) to ion **5** (dark red), as was established by NMR spectroscopy. The ^1H and ^{13}C NMR spectra of **5** are shown in Figure 1, and the chemical shifts, coupling constants, and assignments[4] are compiled in Table I.

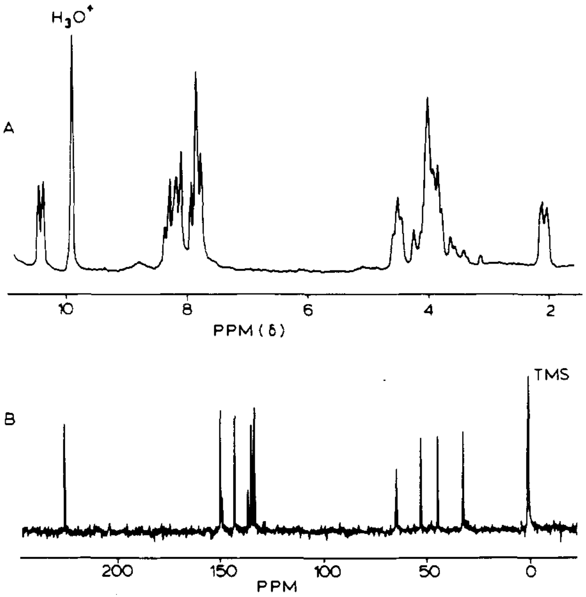
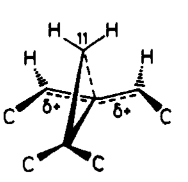


Figure 1. ^1H NMR (100 MHz) spectrum (A) and ^{13}C proton noise decoupled NMR spectrum (B) of ion **5** in FSO_3H-SO_2ClF at −60 °C.



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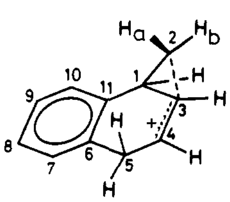

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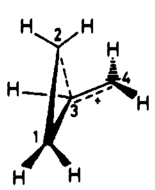
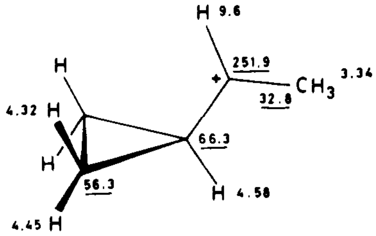


6

Both the ^1H and ^{13}C NMR spectra show three types of signals, viz., the aliphatic ones, those of a disubstituted benzene moiety,[5] and one of the carbocationic center. Comparison of the aliphatic ^1H and ^{13}C NMR data with those of, e.g., the bisected ions **7**[6] and **8**[7] reveals the presence in **5** of a cyclopropylcarbinyl cation moiety.



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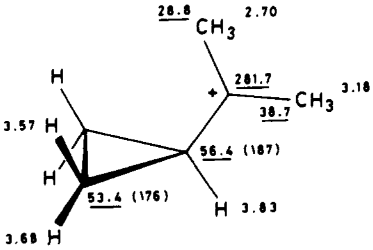

8

The rearrangement of **2** to **5** may be rationalized in terms of ring closure (in **2**) between C(1) and C(6) after which the bridge methano group wanders over the "naphthalenium" skeleton probably via a [1,2] and subsequent [1,4] sigmatropic shift (see Scheme I), although two subsequent [1,3] shifts cannot be ruled out a priori. Quenching of the ion solution of

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Table I. ^1H and ^{13}C NMR Parameters of **5**[a]

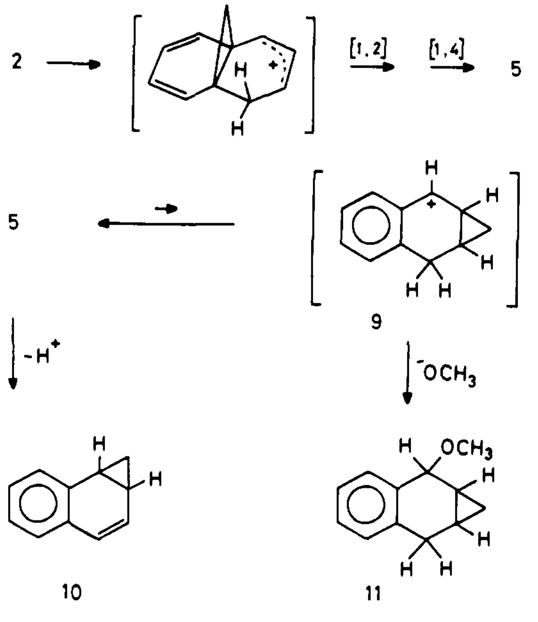
position	$\delta_{^1H}$	$\delta_{^{13}C}$
1	4.0 (m)	43.7 (d, 177)
2a	2.55 (d, t; ≈10, 2)	63.5 (t, 172 ± 2)
2b	4.50 (t, m; ≈8, 2)	
3	4.0 (m)	51.7 (d, 191.6)
4	10.38 (d, 7)	221.2 (d, 168.0)
5	4.0 (m)	31.3 (t, 132.4)
6		146.3 (s)
7	7.77 (d, 7)	132.2 (d, 166.3)
8	8.23 (t, d; 7, 1.5)	146.8 (d, 165.4)
9	7.82 (t, 7)	130.8 (d, 169.0)
10	8.11 (d, 7)	140.1 (d, 169.0)
11		133.8 (s)

[a] ^1H and ^{13}C chemical shifts are in parts per million from external Me_4Si (capillary). Multiplicities (s = singlet, d = doublet, t = triplet, m = multiplet) and coupling constants (J_{HH} and $^1J_{CH}$ in hertz) are in parenthesis.

5 in sodium bicarbonate buffered methanol at −78 °C afforded **10** (13%) and **11** (87%).[8] This may be explained by assuming an equilibrium between ion **5** and the ^1H NMR undetected ion **9**[9] (thus present for at most 5%), which is therefore very far to the side of **5**, vide infra. Because of the low basicity of the methoxide, the proton abstraction from **5**, yielding **10**, will be slow, whereas the nucleophilic attack on **9**, resulting in the formation of **11**, is considered to be rapid (see Scheme I).

A close examination of the NMR characteristics of the aliphatic signals of **5**, of which the cyclopropylcarbinyl cationic moiety (**6**) has a fixed geometry, reveals the following for this structural element. Firstly, the H(4) resonance shows a vicinal coupling with H(3) ($J = 7$ Hz), but not with the H(5) hydrogens ($J < 1$ Hz). This may be interpreted in terms of a more or less flat "naphthalenium" skeleton; i.e. C(5), C(4)H, C(3), and C(1) are in one plane. Secondly, C(2) is deshielded relative to both C(1) and C(3), and H(2b) is deshielded relative to both H(1) and H(3); therefore it can be argued that position 2 carries some positive charge. [H(2a) is observed at high field (δ 2.04) because of shielding by the benzene ring]. Thirdly, the smaller $^1J_{CH}$ value of C(2) H_2 (172 ± 2 Hz) compared with C(1) H (177 Hz) and the large value of 191 Hz for C(3) H indicates both some weakening of the C(2)-C(3) bond and some double-bond character of the C(3)-C(4) linkage. Finally, it is of interest to note that H(2a) has a vicinal coupling with H(1) of ~10 Hz and with H(3) of ~2 Hz, whereas H(2b) has a vicinal coupling with both H(1) and H(3) of 7-8 Hz [the geminal coupling constant for C(2) H_2 is only ~2 Hz]; these phenomena indicate an increase of the H(1)-C(1)-C(2)-H(2a) dihedral angle, and are also in line with the suggested partial positive charge at C(2) and the coupled weakening of the C(2)-C(3) bond.

Scheme I



The proposed geometry of the moiety **6** in ion **5** compares with the conformation of the cyclopropylcarbinyl cation ($C_4H_7^+$), which was recently calculated to be only 0.5 kcal mol^{-1} higher in energy than the (most stable) bisected form.[10]

Further and more detailed work on the cyclopropylcarbinyl cation moieties present in ions resulting from protonated annulenes is currently in progress.

Acknowledgment. We thank Professor E. Vogel (Cologne) for a sample of 1,6-methano[10]annulene and for stimulating our present investigations and Mr. C. Kruk for assistance in obtaining the NMR data.

References and Notes

(1) Part 5: Lammertsma, K.; Cerfontain, H. *J. Am. Chem. Soc.* in press.

(2) (a) Vogel, E.; Roth, H. D. *Angew. Chem.* **1964,** *76,* 145. (b) Vogel, E.; Klug, W.; Breuer, A. *Org. Synth.* **1974,** *54,* 11. (c) Lammertsma, K.; Cerfontain, H. *J. Am. Chem. Soc.* **1978,** *100,* 8244, and references cited thereln.

(3) Warner, P.; Winstein, S. *J. Am. Chem. Soc.* **1969,** *91,* 7785.

(4) The assignments were facilitated by (i) the use of the double resonance technique for the ^1H NMR data, (ii) the use of the long range couplings ($^3J_{CH}$) obtained from the fully proton coupled gated noise ^{13}C NMR spectrum, and (iii) comparison of the NMR data with those of the homologues of **5**, obtalned from several methyl substituted 1,6-methano[10]annulenes, the data of which will be reported in the full paper.

(5) The spread in ^{13}C chemlcal shifts suggest a certain degree of interaction between the carbocationic center at C(4) and the benzene ring.

(6) Olah, G. A.; Jeuell, C. L.; Kelly, D. P.; Porter, R. D. *J. Am. Chem. Soc.* **1972,** *94,* 146.

(7) Olah, G. A.; Spear, R. J.; Hiberty, P. C.; Hehre, W. J. *J. Am. Chem. Soc.* **1976,** *98,* 7470.

(8) The assignments were based on ^1H and ^{13}C NMR data and an exact mass determination of the mixture of the products.

(9) Because of the large amount of **11** obtained after quenching, it might be argued that the ion observed by NMR is actually **9** instead of **5.** Such a view is, however, ruled out on the basis of (i) the NMR data (Table I) and (ii) a comparison of these data with those of the homologous ions obtained from the methyl substituted 1,6-methano[10]annulenes (see note 5). For example, 2-Me-**2** rearranges to 1-Me-**5** and not to Me-**9**, as was concluded from, e.g., the presence of the ^1H NMR doublet at δ 9.98, assigned to H(4).

(10) Levi, B. A.; Blurock, E. S.; Hehre, W. J. *J. Am. Chem. Soc.* **1979,** *101,* 5537.

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Formation of Methane and Ethane by Reduction of Carbon Monoxide Coordinated through Both Carbon and Oxygen on $Mg[CpFe(CO)_2]_2 \cdot 4THF$

Sir:

Facile catalytic hydrogenation of carbon monoxide would supply a very important step in the conversion of coal into other fuel sources. Considerable interest and activity in the homogeneous reduction of CO has been shown in recent years, although catalytic systems have been elusive. In our examination of reactions of carbon- and oxygen-coordinated CO, we have found that the CO coordinated in this manner can be reduced to mixtures of methane and ethane under mild conditions on the complex $Mg[CpFe(CO)_2]_2 \cdot 4THF$.

Homogeneous reductions of carbon monoxide to methane,[1-3] mixtures of alkanes,[4,5] methanol,[6] and a mixture of linear alcohols[7] have been observed. Only in Bercaw's zirconium system is there an understanding of the steps of the