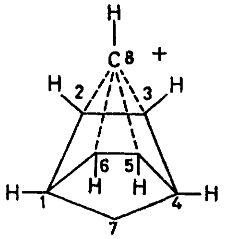
A Bishomo Square-pyramidal Carbonium Ion

By Anthony V. Kemp-Jones, Nobuo Nakamura, and Satoru Masamune*
(*Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada* T6G 2E2)

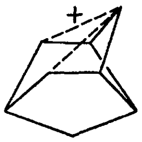
Summary The charge-delocalized cation (**1**) has been generated from two precursors which have been prepared *via* unique double bond participation of a cyclopropyl cation in solvolysis.

In view of the interest[1,2] shown in the recent experimental work on the $(\text{CH})_5^+$ species,[3] we record the preparation of the cation (**1**), structurally related to cation (**2**).[3a,b]

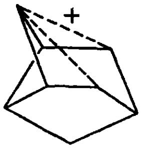
A reasonable precursor for cation (**1**) is compound (**3**). The reported synthesis[4] of (**3**) is multi-step and of low overall yield and therefore we have developed an alternative route leading to precursors for (**1**). The mixture of esters (**4**) and (**5**) previously reported[5] was heated with 1% $[Rh(CO)_2Cl]_2$ at 65° for 2—3 days. This caused isomerization of (**4**) to a saturated compound assumed to be (**6**) by analogy with the behaviour of the parent hydrocarbon.[6] Compound (**5**) was separated from the mixture of (**5**) and (**6**) by means of $AgNO_3$ and hydrolysed to give acid (**7**) m.p. 113—115° in 12% yield, based on ethyl diazoacetate used. Compound (**7**) was converted into the urea (**8**) (81%) m.p. 213—215° (decomp.) by standard methods[7,8] and then to the nitrosourea (**9**), m.p. 80° (decomp.) (35—45%) with sodium nitrite in acetic acid.[8] Reaction of (**9**) with $NaHCO_3$ in aqueous tetrahydrofuran[8,9] provided in 60—70% yield a *ca.* 1 : 1 mixture of two alcohols, one of which was shown to be (**3**) by comparison of spectra with those of (**3**) prepared earlier.[4] The other alcohol, also saturated, is likely to possess structure (**10**). Formation of (**3**) and (**10**) from (**9**) implies participation of the double bond in ionisation of cyclopropyl diazonium ion (**11**), a process rarely precedented.[9]



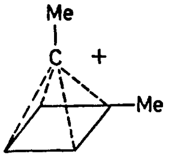
(1)



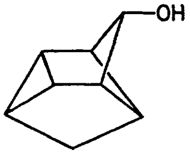
(1a)



(1b)



(2)



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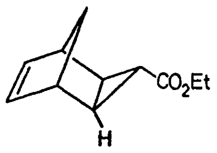

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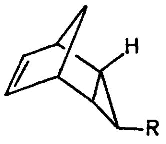
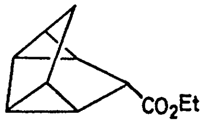
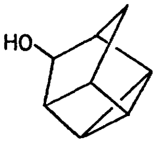


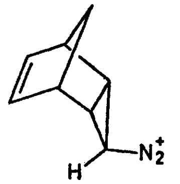
(5) R = CO_2Et
(7) R = CO_2H
(8) R = $NHCONH_2$
(9) R = $N(NO)CONH_2$



(6)



(10)



(11)

Conversion of alcohols (**3**) and (**10**) into the corresponding chlorides with thionyl chloride and addition of the resulting chlorides to a mixture of SbF_5 and SO_2ClF at −120° provided a solution, the ^1H n.m.r. spectrum of which at −80° showed three singlets at δ (ext. Me_4Si) 3·84, 3·37, and 1·80, in a ratio of 44 : 23 : 30, consistent with formation of (**1**). The observed signals can be attributed to 2-, 3-, 5-, 6-H, 1-, and 4-H, and 7-H with 8-H overlapping, respectively.† The proton decoupled ^{13}C n.m.r. spectrum of (**1**) showed four lines at δ Me_4Si 41·7(t),‡ 30·4(d), 29·0(d), and 2·4(d) having relative intensities of 1 : 4 : 2 : 1. Thus the δ 41·7 peak is assigned to C-7, the δ 30·4 peak to C-2, -3, -5 and -6, the δ 29·0 peak to C-1 and C-4, and the δ 2·4 peak to C-8. These assignments are consistent with the absorption of 8-H at δ 0·76 and C-8 at δ 4·6 in octamethyl-(**1**)[10] and with the spectrum of the cation derived from ionisation of tricyclo[3,2,0,0^{2,7}]heptan-4-yl chloride.[11] Quenching the solution of (**1**) with NaOMe in MeOH gave a 60% yield of a 1 : 1 mixture of the methoxy-compounds corresponding to (**3**) and (**10**). These were independently prepared by reaction of (**9**) with $NaHCO_3$ in MeOH. Decomposition of the cation was evident at −60° and complete at −40°.

The spectra of (**1**) are in principle consistent with the presence of rapidly equilibrating trishomocyclopropenyl cations (**1a** $\rightleftarrows$ **1b**). Our studies of the parent[12] and substituted[13] trishomocyclopropenyl cations may provide further information on this point.

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† We have numbered this cation arbitrarily (see formula). The width at half height of the three signals at −80° was 3·8, 4·2, and 2·5 Hz, respectively, which suggests the presence of a small coupling. The widths were essentially the same at −60°. A referee commented on the lack of coupling in the spectrum. Lack of information about the precise geometry and the nature of electron delocalization in this system precludes a firm prediction of the coupling constants. [For a theoretical prediction of unusual bond angles in square pyramidal $(CH)_5^+$, see ref. 2b.] However, we note that small coupling constants for the relevant protons (0—4 Hz) are not totally unexpected (*e.g.*, see the norbornene system: L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance in Organic Chemistry," Pergamon Press, Oxford, 1969, p. 289).

‡ The letter in brackets after each figure indicates whether the peak became a doublet (d) or triplet (t) in the off-resonance spectrum.

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