Evidence Against the Reported Direct Observation of a Bishomocyclopropenyl Cation

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Summary Protonation of bicyclo[3.1.0]hexan-3-ols yields cyclopentenyl cations and not bishomocyclopropenyl cations, as reported.

BOTH the reported[1] direct observation of the bishomocyclopropenyl cation (**1a**),† at 25 °C, from dissolution of isothujol (**2a**) in strong acids, and a later related communica-

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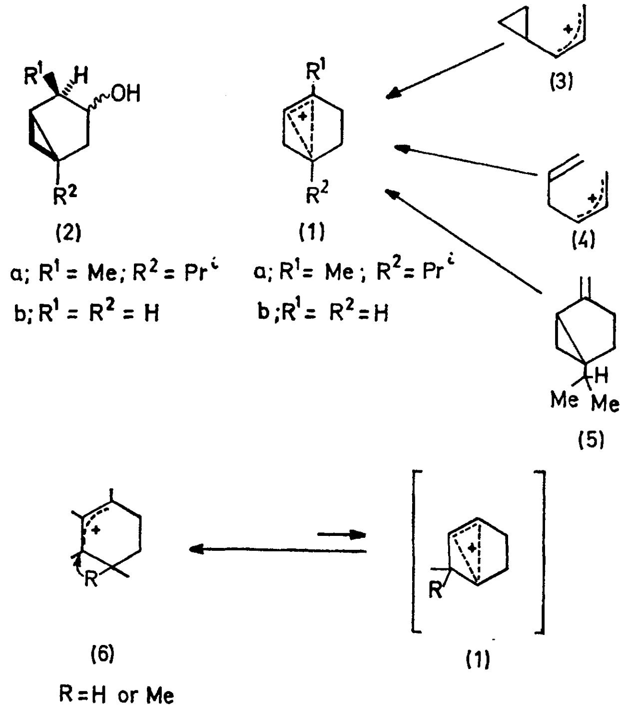
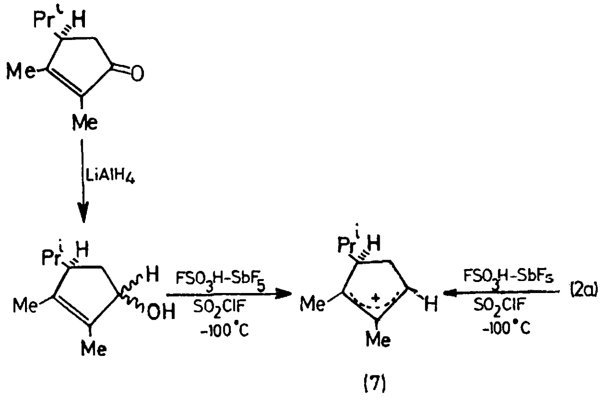
† Strictly, cation (**1**) is neither a bishomocyclopropyl[3] nor a bishomocyclopropenyl cation either. It could be described as a homoallylic or cyclopropylcarbinyl system.

tion[2] claiming the direct observation of the parent cation (**1b**), seem surprising, for several reasons: (i) the ion (**1**) system is postulated as a short-lived intermediate in both the cyclization of the cyclopropylallyl[3] (**3**) and hexa-1,5-dienylium[4] cations (**4**), but has never been directly observed,



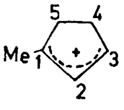
SCHEME 1

even at temperatures as low as −100 °C. (ii) Protonation of appropriate precursors, *e.g.* sabinene[5] (**5**) and others[6], which logically might give (**1**), have invariably yielded cycloallyl cations, *e.g.* (**6**), even at very low temperatures.

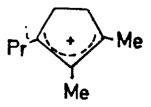


SCHEME 2

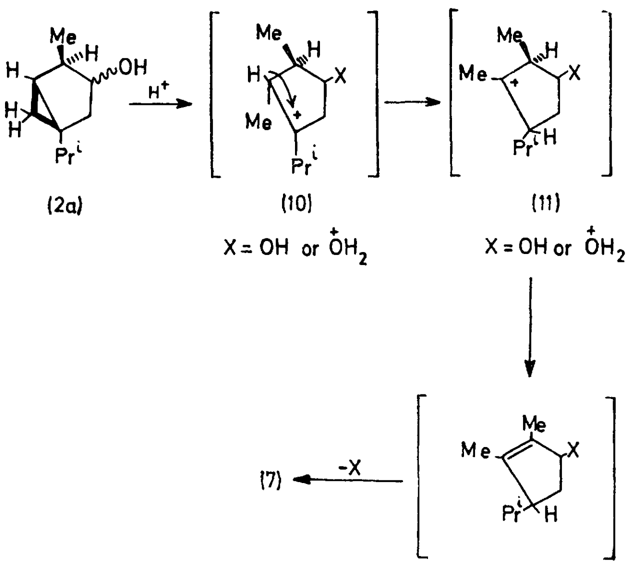
(iii) Rate studies[7] involving these cycloallyl cations have shown that a hydride or methyl migration leading to (**1**) as a high-energy intermediate can occur at temperatures as low as −70 °C (Scheme 1). The reverse reaction starting from (**1**) will therefore be even faster, accounting for observations (i) and (ii).



(**8**)



(**9**)



SCHEME 3

Accordingly, we have reinvestigated the original reports[1,2] (reporting only ^{13}C n.m.r. spectral observations) and find that the cation formed from isothujol (**2a**)‡ is in fact the 2,3-dimethyl-4-isopropylcyclopentenyl cation (**7**), not (**1a**). The structure of (**7**) was confirmed by an unequivocal synthesis (Scheme 2). The ^{1}H and reassigned ^{13}C n.m.r. assignments are in the Table.

TABLE

N.m.r. chemical shifts[a]

^{13}C Resonances for (**7**)[b] :	263·0, C(3); 221·3, C(1); 159·5, C(2); 69·2,[c] C(4); 45·7[c], C(5); 34·3[c] C(3)-Me; 26·0, 22·6, 16·4, 12·3, unassigned Me's and isopropyl-C.
^{13}C Resonances for (**8**) :	264·0, C(1); 225·0, C(3); 148·6, C(2); 51·1,[c] C(5); 46·9,[c] C(4); 28·2, C(1)-Me.
^{1}H Resonances for (**7**)[d] :	0·2, 3-H;[e] 6·0—6·6 br, 4- and 5-H; *ca.* 6·9, C(1)-Me; 7·67, C(2)-Me; 8·66 and 9·34, both d, *J* 7 Hz, nonequivalent isopropyl Me.[f]

[a] In 1 : 1 SbF_5–FSO_3H, diluted with *ca.* 2 vol. of SO_2ClF. [b] In p.p.m. downfield from external Me_4Si dissolved in $(CD_3)_2CO$ lock solvent. [c] Assignment tentative. [d] τ scale, relative to internal Me_4N^+ = τ 6·90. [e] In pure FSO_3H, obscured by solvent peak otherwise. [f] Characteristic of cyclopentenyl cations with a C(4)-Prⁱ group (T. S. Sorensen, *J. Amer. Chem. Soc.*, 1967, **87**, 1585; *Canad. J. Chem.*, 1967, **45**, 1585).

A reinvestigation of the supposed parent ion (**1b**) reveals the ^{13}C n.m.r. peaks reported for (**1b**) to be virtually identical in position to those found for authentic 1-methylcyclopentenyl cation (**8**), which has previously been reported as

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‡ A mixture of the epimeric alcohols from reduction of isothujone with $LiAlH_4$ was used (D. V. Banthorpe and H. ff. S. Davis, *J. Chem. Soc.* (*B*), 1968, 1356).

the product formed from alcohol (**2b**) in strong acids.[8] The further rearrangement of (**7**) into the allyl cation isomer (**9**) (the stable end-product ion previously reported by both Norin[9] and Whittaker[1]) is predictable, as is the observed variation in rate for this reaction, depending on the strength of the acid solvent system used.[10] A plausible mechanism for the formation of (**7**) is shown in Scheme 3, but it is still not clear why deprotonation occurs *via* intermediate cation (**11**) rather than the initially expected ion (**10**).

The formation of observable carbocations in strong acid solutions can be generally regarded as a logical extension to more conventional solvolyses, except that one now has a solvent system of very low nucleophilicity, and, in many cases, high polarity. A major exception to this generalization occurs in cases where an acid-labile functional group (*e.g.* alkene, alkyne, cyclopropane) is present in addition to the leaving group. If heterolysis of the leaving group occurs *before* acid attack on the labile group, this group is given a meassure of 'charge protection,' since attack would now lead to doubly charged species. However, as in the present case, the reverse situation can occur and the cyclopropane ring in (**2a**) appears to be cleaved before heterolysis of the C–OH bond. Thus, the ultimate course of the reaction differs from that found in conventional solvolyses.

We thank the National Research Council of Canada for financial support.

(*Received, 2nd October* 1975; *Com.* 1127.)

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