^{13}C Nuclear Magnetic Resonance Study of the Cation formed from *cis*-Bicyclo[3,1,0]hexan-3-ol

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Summary In solution in SbF_5–HSO_3F–SO_2 at −57°, *cis*-bicyclo[3,1,0]hexan-3-ol yields a bishomocyclopropyl cation of moderate thermal stability.

WE have recently[1] shown that in solution in SbF_5–HSO_3F–SO_2 at −50°, 4β-H-thujan-3α-ol (I) forms the cation (III) which slowly rearranges to (IV). Formation of (III) *via* (II) is probable, though we did not detect (II) directly. This result is in contrast to the observation[2] that the unsubstituted alcohol, *cis*-bicyclo[3,1,0]hexan-3-ol (V), yields only (VIII) in SbF_5–HSO_3F–SO_2ClF at −60°, suggesting that both the ions (VI) and (VII) are unstable under the conditions employed.

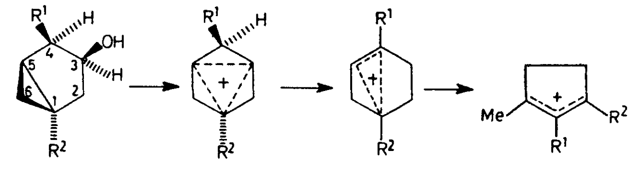
TABLE

^{13}C Chemical shifts
(δ values downfield from Me_4Si)

Substrate	C-1	C-2	C-3	C-4	C-5	C-6
Bicyclo[3,1,0]hexan-3-one	12·4	40·9	217·0	40·9	12·4	13·6
(V)	16·4	34·4	79·4	34·4	16·4	10·1
trans-Bicyclo[3,1,0]-hexan-3-ol	16·4	22·0	81·1	22·0	16·4	10·1
(VII)	262·0	28·3[a]	47·0[a]	148·1	223·5	50·8

[a] These assignments may be interchanged.

Formation of the ion (VI) by treatment of the chloride of (V) with SbF_5–SO_2ClF at −120° has been claimed,[3] this ion rearranging at −40° to an unidentified ion. We now report observation of (VII), an ion of moderate thermal stability, thus removing the apparent anomaly of different reactions of two essentially similar substrates.



(I), R^1=Me,R^2=Pr^i
(V), R^1=R^2=H

(II), R^1=Me,R^2=Pr^i
(VI), R^1=R^2=H

(III), R^1=Me,R^2=Pr^i
(VII), R^1=R^2=H

(IV), R^1=Me,R^2=Pr^i
(VIII), R^1=R^2=H

Treatment of the alcohol (V) with SbF_5–HSO_3F–SO_2 at −72° yielded the ion (VII) whose ^{13}C n.m.r. spectrum is reported in the Table. This ion was stable for several hours at −57°. Repetition of the experiment with HSO_3F–SO_2 yielded the same ion, (VII), which, after removal of the SO_2, was stable for 15 min at room temperature, but decomposed to an unidentifiable mixture when kept at room temperature for 18 h. The ion (VII) is clearly of comparable stability to the substituted version, (III).

Our data are consistent with the results obtained by Freeman and his co-workers[4] on the acid-catalysed addition of methanol to bicyclo[3,1,0]hex-2-ene, and suggest that the reaction sequence which we proposed for the substituted system[1] is equally applicable to the unsubstituted system.

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