Isomeric 1,2,3,4,5,6-Hexamethylbicyclo[3,1,0]hexenyl Cations and their Thermal Rearrangements

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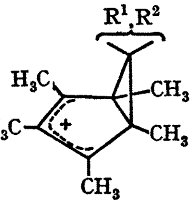
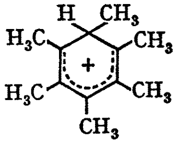
Winstein and his co-workers have recently published two interesting communications[1,2] concerning penta-, hexa-, and hepta-methylbicyclo[3,1,0]hexenyl cations (I—III). We report here on our investigations on such ions.

There are two possible stereoisomeric forms of the 1,2,3,4,5,6-hexamethylbicyclo[3,1,0]hexenyl cation (II); one with an "inside" and the other with an "outside" 6-methyl group. One of the two possible isomers was obtained by Childs and Winstein[2] by photochemical transformation of hexamethylbenzenonium ion (IV) in FSO_3H at −78°. This isomer (IIa) shows in its n.m.r. spectrum singlets at τ 7·43 (2- and 4-CH_3), 7·93 (3-CH_3), 8·23 (1- and 5-CH_3) and a doublet at τ 8·77 (6-CH_3). We have obtained the same isomer by reaction of 1-α-chloroethylpentamethylcyclopenta-2,4-diene (V)[3] with an equimolar amount of $AlCl_3$ in CH_2Cl_2 at −60°. The n.m.r. spectrum of the resulting solution is very similar to that mentioned above and shows the methyl-group singlets at τ 7·38, 7·96, and 8·28, the doublet for the 6-methyl group at τ 8·84, and the quartet for the C-6 proton† at τ 6·13 (*J* 6·5—7·0 Hz.), the ratio of signal intensities being 6 : 3 : 6 : 3 : 1. Quenching the solution in methanol at −60° gives the chloride (V) as the major product.

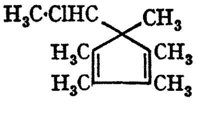
A rather different n.m.r. spectrum has been obtained for the solution prepared by dissolving olefin (VI)[4] in $ClSO_3H$ (or FSO_3H) at −70°. The low-temperature (−60°) spectrum of the $ClSO_3H$ solution consists of methyl singlets



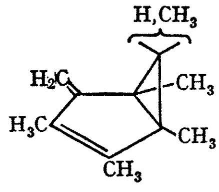
(I) $R^1=R^2=H$
(II) $R^1=H, R^2=CH_3$
(III) $R^1=R^2=CH_3$



(IV)



(V)



(VI)

at τ 7·43 (2 x CH_3), 8·11 (1 x CH_3), 8·37 (2 x CH_3), a doublet at τ 8·66 (1 x CH_3), and a quartet at τ 6·82 (the proton coupled with the protons of the last-mentioned methyl group,

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† This signal was not detected by Childs and Winstein (ref. 2).

J 6·5 Hz.). Quenching the $ClSO_3H$ solution in methanol at −60° results (as in the previous case) in formation of the chloride (V). We believe that protonation of the olefin (VI) leads to the second possible stereoisomer of the ion (II). The chemical behaviour of this isomer (IIb) differs substantially from that of (IIa)

Warming the CH_2Cl_2 solution of (IIa) above −40° results in the irreversible conversion of (IIa) into (IV), which can easily be followed by the changes in n.m.r. spectrum; the sharp signals of ion (IIa) disappear (without appreciable broadening) and the averaged methyl group signal of ion (IV) develops (*cf.* ref. 2). In contrast to this, when the temperature of a solution of (IIb) is raised, the signals for the five methyl groups on the cyclopentenyl ring broaden (at *ca.* −40°), coalesce (at *ca.* −20°; 60 Mc./sec.) and turn into a sharp singlet (τ 7·47) at 0°. At the same time the shape and the position of the doublet at τ 8·66 and of the quartet at τ 6·82 remain unchanged. These changes in the n.m.r. spectrum of (IIb) are reversible in the temperature range −60 to 0° and are apparently due to migration of the cyclopropyl $CH{\cdot}CH_3$ fragment around the cyclopentenyl ring ("cyclopropane merry-go-round"[1]). This type of fivefold degenerate rearrangement in bicyclo[3,2,0]hexenyl cations has been predicted by Swatton and Hart[5] and was recently observed by Childs and Winstein[2] for cation (II).

Our results lead to the conclusion, that the ratio of the rates of fivefold degenerate rearrangement and ring-opening of bicyclo[3,1,0]hexenyl cations is sensitive not only to the state of substitution of the cyclopropane C-6 atom,[2] but also to the steric arrangement of substituents at this atom (in the case of two different substituents). Taking into account the positions of the quartets for the C-6 protons in the n.m.r. spectra of the ions (IIa) and (IIb), we believe that (IIa) is the ion with the "inside" 6-methyl group and (IIb) the one with the "outside" 6-methyl group.

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[1] R. F. Childs, M. Sakai, and W. Winstein, *J. Amer. Chem. Soc.*, 1968, **90**, 7144.

[2] R. F. Childs and S. Winstein, *J. Amer. Chem. Soc.*, 1968, **90**, 7146.

[3] L. A. Paquette and G. R. Krow, *Tetrahedron Letters*, 1968, 2139.

[4] Olefin (VI) was prepared from the chloride (V) by the method of W. Schäffer and H. Hellmann, *Angew. Chem.*, 1967, **79**, 566.

[5] D. W. Swatton and H. Hart, *J. Amer. Chem. Soc.*, 1967, **89**, 5075.