Isomerization of Cyclohexenyl Cations

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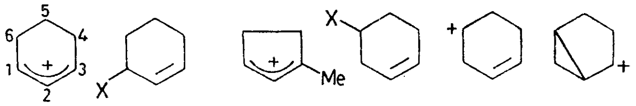
Summary Contrary to the literature data, the cyclohexenyl cation (I) rearranges to the 1-methylcyclopentenyl cation (IV) in FSO_3H–SbF_5 (4:1) at −20 °C; the rate of ring contraction is much slower than the published rate of intramolecular H/D scrambling for labelled (I).

THE cyclohexenyl cation (I) was described by Olah as the product of ionization of 3-chloro- (IIa) or 3-hydroxy-cyclohexene (IIb) in super-acid at −70 °C.[1] He also reported that (I) was stable up to 0 °C and showed no tendency toward rearrangement to the 1-methylcyclopentenyl cation (III).[1] On the other hand, it was reported that (III) was formed directly at −70 °C from the homoallylic precursor IV[1] [presumably *via* the cation (V)[2]]. In order to accommodate these observations it was necessary to conclude that hydride transfer (I) ⇌ (V) cannot occur in (I) under these conditions. However, this is at variance with the behaviour of the cyclopentenyl cation which undergoes an intramolecular exchange of hydrogen atoms,[3] as well as with the known[4] tendency of polysubstituted cyclohexenyl cations toward ring contraction.† In addition, it was reported that (I) labelled with deuterium undergoes isotope scrambling at −65 °C,[5] a process presumably involving 1,2-hydride shifts. {An alternative mechanism, involving 2-bicyclo[3.1.0]hexyl cations (VI) as intermediates[6] scrambles positions 1, 3, 4, 5, and 6, but leaves intact the hydrogen or deuterium bonded to C-2. Therefore, this mechanism alone cannot account for the described[5] H/D scrambling}.



(I) (II) (III) (IV) (V) (VI)

(a) X = Cl; (b) X = OH

In the hope of resolving these discrepancies, we reinvestigated the formation and behaviour of the ion (I). It was formed from (IIa) or (IIb) in super-acid at −94 to −80 °C. However, it rearranged to (III) with a measurable rate even at −20 °C. [The same ion (III) was obtained in our experiments from *trans*-1,2-dichlorocyclohexane[1] at −50 °C].‡

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† A rationalization for the different behaviour of (I) was given (ref. 1).

‡ The precursors were extracted into the super-acid from dilute solutions in Freon 11. The ions exhibited the same n.m.r. spectra as described. ref. 1. The rates were measured for 0·7M solutions in FSO_3H–SbF_5 (4:1) with *ca.* 12% SO_2FCl. The activation parameters are somewhat approximate values, as the rate constants are uncertain by *ca.* ± 10% at −18·70 °C and ±15% at −3·10 °C.

The isomerization could be monitored by the integration of the n.m.r. spectrum during the transformation.§ The first-order rate constants determined at two temperatures (k $6{\cdot}7 \times 10^{-6}$ s^{-1} at $-18{\cdot}70 \pm 0{\cdot}25$ °C and 6×10^{-5} s^{-1} at $-3{\cdot}10 \pm 0{\cdot}20$ °C) allowed the calculation of the activation parameters: $\Delta H^{\ddagger}$ 18·7 kcal mol^{-1}; $\Delta S^{\ddagger}$ $-8{\cdot}5$ cal K^{-1} mol^{-1}.

The rate of the isomerization (I) $\rightarrow$ (III) is 50—100 times slower than the rate of hydride shift in the cyclopentenyl cation.[3] More interesting, the value of the rate for (I) $\rightarrow$ (III) calculated for -50 °C is about 10^4 times slower than the rate of the H/D scrambling in (I).[5] This suggests that the rate-determining step for ring contraction occurs after the hydride shift, which is in contradiction with the reported[1] total absence of (I) in the ionization of (IV) [*via* (V)].¶

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§ The area ratio for the peak of (I) at δ 2·50 (2H) to the peaks at 8·37 [for (I)] and 8·38 [for (III)] (constant at 1H) changed from 2 to 0. At the same time, the peak of (I) at δ 3·91 (4H) was replaced by the peaks of (III) at δ 3·62 and 4·12 (combined 7H).

¶ It is possible that the reaction of (IV) described in ref. 1 does not involve ionization of the C–X bond, but a much more exothermic protonation of the double bond, followed by ring contraction. In fact, extensive polymerization was reported for (IVa)[1] (see also S. Masamune, M. Sakai, A. V. Kemp-Jones, and T. Nakashima, *Canad. J. Chem.*, 1974, **52**, 855). Similarly, it was shown[1,2] that bicyclo [3.1.0]hexan-3-ol undergoes protonolysis of the three-membered ring, rather than heterolysis of the C–O bond, in super-acid.

[1] G. A. Olah, G. Liang, and Y. K. Mo, *J. Amer. Chem. Soc.*, 1972, **94**, 3544. (Several acid systems based on antimony pentafluoride were employed.)

[2] For a discussion of the possible electronic structures for (V), see P. A. Buttrick, C. M. Y. Holden, and D. Whittaker, *J.C.S. Chem. Comm.*, 1975, 534 and references therein. The claims (see also ref. 4b) that ion (V) or (VI) is stable enough to be detected in super-acid solution at low temperature have now been refuted: T. S. Sorensen, *J.C.S. Chem. Comm.*, 1976, 45.

[3] From the published data (M. Saunders and R. Berger, *J. Amer. Chem. Soc.*, 1972, **94**, 4049) a value $k = 6{\cdot}6 \times 10^{-3}$ s^{-1} at 0 °C ($\Delta H^{\ddagger}$ 17·26 kcal mol^{-1}, $\Delta S^{\ddagger}$ $-5{\cdot}15$ cal K^{-1} mol^{-1}) can be calculated.

[4] (a) N. C. Deno and R. R. Lastomirsky, *J. Amer. Chem. Soc.*, 1968, **90**, 4085; N. C. Deno and J. J. Houser, *ibid.*, 1964, **86**, 1741; T. S. Sorensen, *ibid.*, 1969, **91**, 6398; T. S. Sorensen and K. Ranganayakulu, *ibid.*, 1970, **92**, 6539; (*b*) C. M. Holden and D. Whittaker, *J.C.S. Chem. Comm.*, 1974, 353.

[5] G. Seybold, P. Vogel, M. Saunders, and K. B. Wiberg, *J. Amer. Chem. Soc.*, 1973, **95**, 2045.

[6] R. Cone, R. P. Haseltine, P. Kazmeier, and T. S. Sorensen, *Canad. J. Chem.*, 1974, **52**, 3320.