Cyclisation of Hex-5-en-2-one to the 2,5-Dimethyl-1-oxoniacyclopent-1-enyl Cation in Sulphuric Acid

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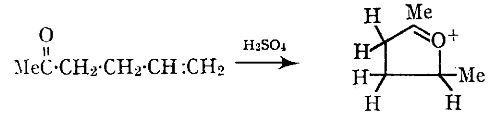
THE base strength of aliphatic ketones was determined by Edward[1] using u.v. techniques. The $\mathrm{p}K_{\mathrm{PH}^+}$ values of acetone and isopropyl methyl ketone in sulphuric acid are −7·2 and −7·1, respectively. Olah and his co-workers[2] demonstrated that protonation occurred on oxygen and did not destroy the carbonyl double-bond. From an analysis of the ^{1}H n.m.r. data they showed that in FSO_3H–SbF_5 protonated ketones are best represented by an oxonium resonance form with little contribution from a hydroxy-carbonium ion. The proton on oxygen exhibited *syn*- and *anti*-geometrical isomerism. Oxygen protonation was also demonstrated in several aryl and $\alpha\beta$-unsaturated ketones.[3]

When hex-5-en-2-one (I) was dissolved in 60, 70, 80, 90, and 98% sulphuric acid protonation on oxygen was not observed, but the 2-5-dimethyl-1-oxoniacyclopent-1-enyl cation (II) was generated quantitatively. The 100 Mc./sec. ^{1}H n.m.r. spectra of the acid solutions demonstrate the existence of (II) (see Figure) 6·58 (sextet, 5-H, *J* 7), 4·30 (t, 3-H, *J* 6·9), 3·47 (s, 2-Me), and 2·32 p.p.m. (d, 5-Me, *J* 6·5 Hz). The non-equivalent protons at C-4 appear as two multiplets centred at 3·27 and 2·69 p.p.m. This spectrum closely resembles that reported for 2-methyl-1-oxoniacyclopent-1-ene hexachloroantimonate recently prepared by Ward and Sherman[4] and definitely identifies (II).



(I) (II)

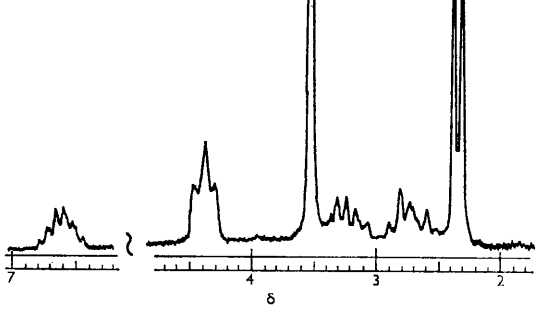
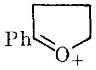


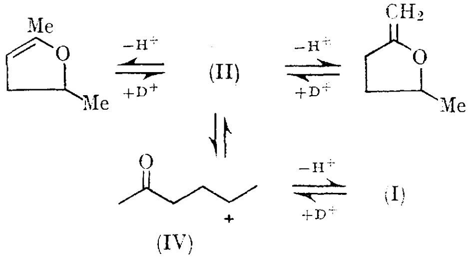
FIGURE. *The* 100 *Mc./sec.* ^{1}*H n.m.r. spectrum of ion* (II) *in* 96% *sulphuric acid*

The ease of and propensity towards cyclisation of (I) is probably the result of participation by the carbonyl oxygen during protonation at C-6. Other examples of related neighbouring-group effects are the greatly increased solvolysis rates of 4-chloro-[5] and 4-bromo-butyrophenone[6] compared with their corresponding n-butyl halides. In these examples participation by carbonyl oxygen which assists solvolysis by forming intermediate oxonium ion (III) was suggested. Ward and Sherman generated (III) by protonation of 4,5-dihydro-2-phenylfuran in trifluoroacetic acid.[4]



(III)

In 96% deuteriated sulphuric acid at 24° and 120° deuterium is only incorporated into the C-2 methyl group (δ3·47) and the C-3 methylene group [δ4·30 of (II.)] The C-2 methyl hydrogens were exchanged (34%) during 68 hr. at 24° and during 7 min. at 120° (65%). The C-3 methylene hydrogens were 43 and 78% exchanged under these conditions. The lack of exchange of the C-4 methylene and C-5 methyl protons demonstrates that equilibration of (II) to (I) does not occur in 96% deuteriated sulphuric acid, even at 120°. The observed H–D exchange is best explained by the direct removal of a proton from (II) by base (H_2O or HSO_4^-). Invoking exchange through an enolization of the acyclic alkyl ion (IV) requires this enolization to occur faster than equilibration of (IV) to (I) or reclosure of (IV) to (II). In both 96 and 80% deuteriated sulphuric acid the cyclisation of (I) to (II) initially incorporates only a single deuterium at the C-5 methyl group into (II). Thus, acid-catalysed enolization of (I) does not occur prior to carbon protonation and cyclization.



The ratio of C-3 methylene to C-2 methyl H–D exchange rates (1·26, 24° and 1·20 at 120°) illustrates the similarity of the transition-state energies for *endo*- and *exo*-double-bond formation from (II).

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[1] H. J. Campbell and J. T. Edward, *Canad. J. Chem.*, 1960, **38**, 2109.

[2] G. A. Olah, M. Calin, and D. H. O'Brien, *J. Amer. Chem. Soc.*, 1967, **89**, 3586; G. A. Olah and M. Calin, *J. Amer. Chem. Soc.*, 1968, **90**, 938.

[3] C. U. Pittman, jun., Ph.D. Thesis, The Pennsylvania State University, 1964; R. Stewart and K. Yates, *J. Amer. Chem. Soc.*, 1958, **80**, 6355.

[4] H. R. Ward and P. D. Sherman, jun., *J. Amer. Chem. Soc.*, 1968, **90**, 3813.

[5] D. J. Pasto and M. P. Serve, *J. Amer. Chem. Soc.*, 1965, **87**, 1515.

[6] S. Oae, *J. Amer. Chem. Soc.*, 1956, **78**, 4030.