Tetrahedron Letters Vol. 21, pp 1901 - 1902

0040-4039/80/0501-1901$02.00/0

REVERSIBLE PROTONATION OF A VINYL SELENIDE DURING ITS ACID CATALYZED HYDROLYSIS

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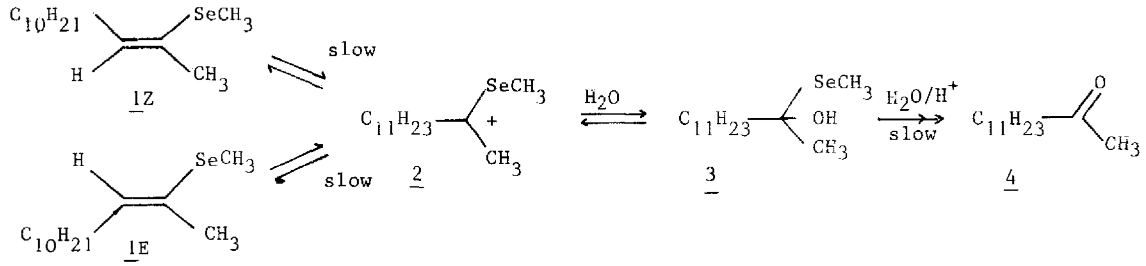
Partially reversible protonation is shown to occur in the course of the acid catalyzed hydrolysis of 2-methylseleno-2 tridecene 1 together with a significant lowering of the kinetic solvent isotope effect ($k_{H_2O^+}/k_{D_2O^+} = 1.4$).

Detailed investigations of the mechanism of hydrolysis of vinyl ether [1] and vinyl sulfides [2] have shown that these reactions proceed by rate determining and irreversible proton transfer from hydronium ion or general acid catalysts to the β carbon atom of the olefinic substrate. Therefore, these reactions are accompagnied by rather high limiting solvent isotope effects, usually $k_{H_3O^+}/k_{D_3O^+} \gtrsim 3$, in pure aqueous or mixed organic-aqueous solvents.

We wish to report here preliminary results we obtained for the acid catalyzed hydrolysis of a vinyl selenide, which show that proton transfer may not be the rate determining step in this reaction or at least that an other step exists on the reaction path which is as slow as protonation (Scheme).

SCHEME



Reversible protonation of a vinylic substrate is a rather unique observation and is of interest in connection with the problem of the stabilization of a cationic centre by an adjacent heteroatomic moiety. While the abilities of oxygen and sulfur to stabilize carbonium ions have been investigated experimentally [3] and theoretically [4], selenium has not yet received much attention[5,6].

In a large scale (i.e. 1 mM) experiment and in conditions similar to those used for the kinetic measurements, vinyl selenide 1 hydrolyzed smoothly to give 2-tridecanone 4 in very high yield (>90%) and free of any side-product.

Rates of this reaction were measured at 30°C, in 60/40 (v/v) dioxane/water mixtures and at various acid catalyst ($HClO_4$) concentrations. Logarithms of the observed pseudo first order rate constants correlate linearly with Hammett's acidity function (H_o) of the reaction medium with a slope of -1.2 ± 0.08.

Activation parameters for the hydrolysis of 2-methylseleno-2-tridecene cis (1Z) have been determined (at 1M $HClO_4$ in dioxane/water, 60/40 v/v) in the temperature range of 30-50°C :

$\Delta H^{\neq} = 54$ KJ M^{-1} (13 Kcal M^{-1}) and $\Delta S^{\neq} = -11 \pm 0.5$ e.u.

We have also measured kinetic solvent isotope effects in moderately acidic solutions (0.98 M HCl or DCl) and by using pure H_2O or D_2O or a 50/50 (v/v) mixture of them to make up the final dioxane/water (60/40) mixture. Surprisingly , the ratio of the observed rate constants in the isotopically pure solvents is $k_{H_3O^+}/k_{D_3O^+} = 1.4$ and $k_{H_3O^+}/k_{X=0.5} = 1.06$. (X being the H/D isotopic composition of the water fraction of the solvent).

Furthermore, in order to get more detailed insight into the reaction mechanism, we have prepared pure Z(cis) and E(trans) isomers of 1 and measured their rates of hydrolysis. Although the former reacts 1.3 times faster than the latter, at least partial isomerization during the reaction cannot be excluded.

Pure 1(Z) was hydrolyzed (dioxane/water 60/40 ; 0.3 M $HClO_4$; 20°C) for 3.5 hours and the resulting mixture subjected to gas chromatograhic analysis, which showed that the reaction proceeded only to about 25% conversion and most importantly that the unreacted vinyl selenide contained 37% of the trans isomer (1E).

Hydrolysis of a mixture of 1E and 1Z in the presence of heavy water (dioxane/D_2O 60/40 ; 0.8 M DCl ; 20°C ; 4 hrs) followed by mass spectrometric analysis indicated a 25% deuterium incorporation in the unreacted vinyl selenide. These findings demonstrate unambiguously that protonation of 1 is reversible to some extent and therefore the reaction sequence is more properly depicted as in the Scheme. The most striking feature of this scheme is that there appear to be two slow steps. Indeed, although reversible, step 1 → 2 must be slow since the observed solvent isotope effect is still normal. On the other hand, reversibility can only arise either because carbonium ion 2 is particularly well stabilized or because hemiselenoketal 3 is quite unreactive (probably due to extremely low proton basicity of the selenium atom [7]).

We are currently investigating the effect of varying vinyl selenide structure (that of the carbonyl and selenium moieties) on the rates and mechanisms of hydrolysis.

We thank Fonds National de la Recherche Scientifique, F.N.R.S., for financial support.

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3. See for example,J.K. Pau, M.B. Ruggera, J.K. Kim and M.C. Caserio, J. Amer. Chem.Soc., 100, 4242 (1978) and references cited for oxygen vs.sulfur stabilization of carbonium ions.

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5. Hydrolysis of selenoacetals (which should also involve an α-selenocarbonium ion)has been described recently from a synthetic point of view ; A.Burton, L.Hevesi, W. Dumont, A.Cravador and A. Krief, Synthesis, 877 (1979).

6. During the preparation of this manuscript appeared a work by R.A.Mc Clelland and M. Leung, J. Org. Chem., 45, 187 (1980) on the mechanism of hydrolysis of aryl vinyl selenides. Interestingly, these authors do not find reversible protonation.

7. Inferred from the fact that thioethers are less basic by a factor of 10^4 than oxygen ethers, see J.L. Jensen and W.P.Jencks ,J.Amer.Chem.Soc., 101, 1482 (1979) and references cited.

(Received in UK February 1980)