Fully Reversible Carbon Protonation in the Hydrolysis of Keten Selenoacetals

By HENRI WAUTIER, STÉPHANE DESAUVAGE, and LASZLO HEVESI*
(Facultés Universitaires Notre-Dame de la Paix, Department of Chemistry, 61, rue de Bruxelles, B-5000 Namur, Belgium)

Summary Kinetic solvent isotope effects [$k(H_3O^+)/k(D_3O^+) < 1$] and deuterium incorporation (*ca.* 100%) during acidic hydrolysis of keten selenoacetals establish that these reactions proceed through a pre-equilibrium carbon protonation step.

THE acid-catalysed hydrolysis of vinylic substrates such as vinyl ethers,[1] vinyl sulphides,[2] alkyn-1-yl sulphides,[3] *N*-vinyl amides,[4] and keten acetals[5] implies rate-limiting proton transfer from the catalyst to the β-carbon atom of the vinylic moiety. A similar mechanism also pertains for a great variety of olefin hydration reactions.[6] The only known exception to this general behaviour was the rather peculiar example reported by Vitullo and his co-workers.[7] We discovered recently[8] that nearly all vinyl selenides hydrolyse by a partially reversible, slow protonation step.[9] We now report the occurrence of complete reversibility of the carbon protonation step during hydrolysis of some keten selenoacetals. These compounds hydrolyse smoothly in the presence of mineral acids in aqueous organic solvents to produce essentially the corresponding selenocarboxylic esters. In most cases small amounts of seleno-orthoesters are also produced.

As a typical example, 1,1-bis(methylseleno)dodec-1-ene (5×10^{-4} mol) was allowed to react in 10 ml of dioxan–1 M aqueous $HClO_4$ (60:40) at room temperature for 72 h. Simple work-up and t.l.c. purification (SiO_2, pentane as eluant) yielded 10 mg (6%) of unchanged starting material, 22 mg (10%) of 1,1,1-tris(methylseleno)dodecane, and 100 mg (77%) of *Se*-methyl dodecaneselenoate. After prolonged reaction times or at higher temperatures the resulting selenoesters hydrolyse further to carboxylic acids.

However, under the conditions of our kinetic measurements [HCl or DCl, dioxan–water (60:40); low substrate concentrations and short reaction times] the only important reaction is the conversion of the keten selenoacetals into the selenoesters.†

Evidence for the completely reversible protonation of the title compounds stems from measurements of kinetic solvent isotope effects and from deuterium incorporation into the unchanged keten selenoacetals during their hydrolysis. The results of these experiments are in the Table. In all cases inverse solvent isotope effects are observed [$k(H_3O^+)/k(D_3O^+) < 1$] and for compounds (**3**) and (**4**) the values are similar to those generally found for specific acid-catalysed reactions proceeding through pre-equilibrium protonation.[10] The results of the deuterium incorporation experiments closely parallel the solvent isotope effects. Indeed, as shown in the last column of the Table, when hydrolysis-reaction mixtures are quenched with base a long time before completion of the reaction, and analysed in a mass spectrometer, it is found that, with the exception of 1,1-bis-

---

† The easy oxidation of methaneselenol to dimethyl diselenide prevents formation of seleno-orthoesters.

TABLE. Kinetic solvent isotope effects[a] and deuterium incorporation[b] for the hydrolysis of keten selenoacetals.

Substrate	[HCl] or [DCl]/ mol l^{-1}	$k(H_3O^+)/s^{-1}$	$k(D_3O^+)/s^{-1}$	$k(H_3O^+)/k(D_3O^+)$	% Deuterium incorporation
(**1**) $MeCH{=}C(SeMe)_2$	1·26	$3{\cdot}5 \times 10^{-3}$	$4{\cdot}82 \times 10^{-3}$	0·73	60[c]
(**2**) $MeCH{=}C(SePh)_2$	1·26	$8{\cdot}81 \times 10^{-6}$	$11{\cdot}2 \times 10^{-6}$	0·79	100[d]
(**3**) $PhCH{=}C(SeMe)_2$	1·26	$1{\cdot}21 \times 10^{-4}$	$3{\cdot}18 \times 10^{-4}$	0·38	100[e]
(**4**) $PhCH{=}C(SePh)_2$	2·77	$5{\cdot}76 \times 10^{-6}$	$14{\cdot}5 \times 10^{-6}$	0·40	100[f]

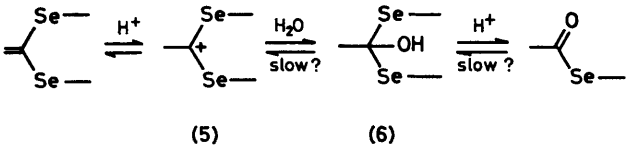
[a] Pseudo-first-order rate constants were determined in dioxan–water (60:40 v/v) mixtures at 30 °C. [b] Determined by mass spectrometry as described in ref. 8. [c–f] After 50, 15, 25, and 60% conversion respectively.

(methylseleno)prop-1-ene (**1**), all the unchanged keten selenoacetals are completely deuteriated. In some cases 100% incorporation is observed even at an early stage of the reaction [after 15 and 25% conversion of compounds (**2**) and (**3**), respectively].

The above two series of results clearly establish that most of the keten selenoacetals undergo a rapid pre-equilibrium protonation at the olefinic β-carbon atom during hydrolytic reactions. Although similar conclusions were arrived at recently for one specific keten dithioacetal,[11] we think our results disclose more clear-cut examples of this unusual behaviour.‡

Obviously, then, the hydrolysis reaction of these keten selenoacetals must have a rate-limiting step other than the initial protonation of the olefinic β-carbon atom. This could either be hydration of the α-bis(methylseleno)-carbonium ion (**5**) (Scheme) as suggested for the sulphur analogue[11] or decomposition of the bis(methylseleno)-hemiorthoester (**6**).

At present, we are not able to give a definite answer to this question. If however account is taken of the great rate difference between the methylseleno- and phenylseleno-derivatives [a factor of about 2500 for compound (**1**) *vs.* compound (**2**), Table], one would prefer the decomposition of (**6**) as the rate-determining step. Indeed, it seems reasonable that the selenium atom of the phenylseleno-group in (**6**) should be considerably less basic than that of the methylseleno group.§



SCHEME

Intermediates (**5**) [which probably will allow the generation of (**6**)] can now be prepared in a stable form[12] and we are currently investigating the kinetics of their independent breakdown.

We are indebted to 'Fonds National de la Recherche Scientifique (FNRS)' of Belgium for financial support.

(*Received, 8th April* 1981; *Com.* 409.)

---

‡ We have measured deuterium incorporation in the case of ββ-bis(methylthio)styrene studied in ref. 11 and found that *ca.* 67% of the recovered starting material contained one deuterium atom after *ca.* 60% conversion. Moreover, the reported secondary isotope effect (k_H/k_D = 1·38, ref. 11) can also be interpreted as resulting from a rate-determining sp^2 to sp^3 hydridization change of the β-carbon atom.

§ It is noteworthy in this respect that for vinyl selenides under very similar conditions the rate ratio for MeSe/PhSe derivatives is only about 15 (see ref. 8).

[1] See for example, D. M. Jones and N. F. Wood, *J. Chem. Soc.*, 1964, 5400; A. Ledwith and H. J. Woods, *J. Chem. Soc. B*, **1966**, 753; A. J. Kresge and Y. Chiang, *ibid.*, 1967, 53; *ibid.*, 1968, 58.

[2] T. Okuyama, N. Nakada, and T. Fueno, *Tetrahedron*, 1976, **32**, 2249; R. A. McClelland, *Can. J. Chem.*, 1977, **55**, 548; T. Okuyama, M. Masago, N. Nakada, and T. Fueno, *Tetrahedron*, 1977, **33**, 2379; W. Drenth and H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, 1960, **79**, 1002.

[3] W. F. Verhelst and W. Drenth, *J. Org. Chem.*, 1975, **40**, 130.

[4] V. M. Csizmadia, K. M. Koshy, K. C. M. Lan, R. A. McClelland, V. J. Nowlan, and T. T. Tidwell, *J. Am. Chem. Soc.*, 1979, **101**, 974.

[5] V. Gold and D. C. A. Waterman, *Chem. Commun.*, 1967, 40; A. Kankaanperä and H. Tuominen, *Suomen. Kem.*, 1967, **340**, 271; V. Gold and D. C. A. Waterman, *J. Chem. Soc. B*, 1968, 839, 849.

[6] V. J. Nowlan and T. T. Tidwell, *Acc. Chem. Res.*, 1977, **10**, 252.

[7] J. D. Cooper, V. P. Vitullo, and D. L. Whalen, *J. Am. Chem. Soc.*, 1971, **93**, 6294.

[8] J. L. Piquard and L. Hevesi, *Tetrahedron Lett.*, 1980, **21**, 1901; L. Hevesi, J. L. Piquard, and H. Wautier, *J. Am. Chem. Soc.*, 1981, **103**, 870.

[9] Exceptions to this were also reported: R. A. McClelland and M. Leung, *J. Org. Chem.*, 1980, **45**, 187.

[10] See for example, E. H. Cordes and H. G. Bull, *Chem. Rev.*, 1974, **74**, 581.

[11] T. Okuyama and T. Fueno, *J. Am. Chem. Soc.*, 1980, **102**, 6590.

[12] L. Hevesi and S. Desauvage, to be published.