# Hydrolysis of *p*-Methoxyphenoxy- and Methoxy- Triphenylsilane

By COLIN EABORN,* RUDOLF EIDENSCHINK, and DAVID R. M. WALTON
(*School of Molecular Sciences, University of Sussex, Brighton* BN1 9QJ)

*Summary* Contrary to a recent assertion, the base-catalysed hydrolyses of *p*-methoxyphenoxy- and methoxy-triphenylsilane in 60:40 MeCN–$H_2O$ are of first order in alkali in the concentration range 0·2—3·2 × $10^{-3}$ M.

SWAIN, Schowen, and their co-workers recently reported that the hydrolysis of *p*-methoxyphenoxytriphenylsilane (I), in 60:40 v/v MeCN–$H_2O$ is of second order in base at alkali concentrations below *ca.* 2 × $10^{-3}$ M but of first order above *ca.* 3 × $10^{-3}$ M, and that the hydrolysis of methoxy-

TABLE. Rate constants for hydrolysis of (I) and (II) in 60:40 v/v $MeCN{-}H_2O$

| | $Ph_3Si{\cdot}C_6H_4{\cdot}OMe$-*p* (I)[a] | | | $Ph_3SiOMe$ (II)[b] | |
|---|---|---|---|---|---|
| $10^3[OH^-]/M$[c] | $10^3k/s^{-1}$ [d] | $(k/[OH^-])/mol\ l^{-1}\ s^{-1}$ | $10^3[OH^-]/M$[e] | $10^3k/s^{-1}$ [f,g] | $(k/[OH^-])/mol\ l^{-1}\ s^{-1}$ |
| 0·20 | 6·2[g] | 31 | 0·20 | 1·52 | 7·6 |
| 0·40 | 12·0[g] | 30 | 0·30 | 2·53 | 8·4 |
| 0·80 | 26·5[g] | 33 | 0·40 | 3·34 | 8·3 |
| 1·60 | 51[h] | 33 | 0·80 | 6·5 | 8·1 |
| 3·20 | 105[h] | 33 | 1·60 | 12·0 | 7·5 |

[a] M.p. 76°; prepared as in ref. 2. [b] M.p. 56°; prepared[3] from C-tritiated methanol. [c] Aq. NaoH (6·4 μl) was injected into 2 ml of a mixture of water (3·97 ml) with 6·00 ml of a 5 × $10^{-4}$ M solution of (I) in MeCN; the base concentration is that calculated from the known concentration of injected alkali. [d] Observed first-order rate constant, measured spectrophotometrically (310 nm) at 24·7 °C. [e] Aq. NaOH (80 μl) was injected into a mixture of water (9·92 ml) with 15·0 ml of a 5 × $10^{-4}$ M solution of (II) in MeCN. [f] Observed first-order rate constant at 26·0 °C; rate measured as in ref. 4. [g] Derived from initial rate, since the products consume alkali. [h] Derived from first-order plots, since the consumption of base by the products can be neglected.

triphenylsilane (II), is of second order in base over the whole range of alkali concentration studied (0·3—2 × $10^{-3}$ M).[1] These observations and their interpretation had profound mechanistic implications not only for the reactions mentioned but also for a large number of other base-catalysed reactions of organosilicon compounds which were previously regarded as of first order in alkali, since they raised the possibility that such reactions might be of second order in alkali if they could be studied at sufficiently low (and possibly experimentally unrealistic) base concentrations.

We thought it improbable, (i) that a reaction between hydroxide ion and a negatively charged species such as $[Ph_3Si(OH)(OR)]^-$ would be very fast compared to that between hydroxide ion and the initial neutral species, as it would have to be to fit in with the observations and interpretations by Swain *et al.*; and (ii) that the mechanism of hydroxide-catalysed hydrolysis should be completely different from that of methoxide-catalysed methanolysis, as their work implied,[1] and so we re-examined the hydrolyses.

After purifying our acetonitrile by a standard procedure involving distillation from phosphorus pentoxide and then from potassium carbonate, we obtained results for (I) similar to those reported by Swain *et al.*, though there was a less marked dependence of the specific rate constant, $k/[OH^-]$, on the concentration of base taken, but this behaviour was due to an acidic (or acid-generating) impurity in the acetonitrile which was reducing the base concentration in the reaction medium by *ca.* 0·15 × $10^{-3}$ M. When allowance was made for this, or when the rates were based on measurement of the actual alkali concentration in the reaction mixture, the specific rate constant was independent of the alkali concentration over the whole range.

When we removed the acidic impurity by passing the acetonitrile through basic alumina (Woelm W200), we found satisfactory first-order dependence of the observed rate constant on the base-concentration for both (I) and (II) over a range rather wider than that used by Swain *et al.* (Table). [The specific rate constant for (I) is in satisfactory agreement with that obtained by Swain *et al.* at their highest base concentrations, at which acidic impurity would have the smallest effect.] It seems likely that Swain *et al.* used acetonitrile containing acidic impurity; although they reported that the hydrolysis of *p*-nitrophenyl acetate was of first order in base over the whole range used, we note that those experiments were performed by a different worker, who presumably used purer acetonitrile.

We conclude that the results obtained by Swain *et al.* were in error, and that the unusual mechanistic scheme they suggested need not at present be considered further.

We thank Professor A. G. Brook and Dr. R. A. Jackson for valuable discussions, and the Deutsche Forschungsgemeinschaft for the award of a Fellowship to R.E.

(*Received*, 19*th February* 1975; *Com.* 210.)

[1] C. G. Swain, K.-R. Pörshke, W. Ahmed, and R. L. Schowen, *J. Amer. Chem. Soc.*, 1974, **96**, 4700.
[2] R. L. Schowen and K. S. Latham, *J. Amer. Chem. Soc.*, 1967, **89**, 4677.
[3] H. Gilman and G. D. Lichtenwalter, *J. Amer. Chem. Soc.*, 1960, **82**, 3319.
[4] R. Baker, R. W. Bott, C. Eaborn, and P. W. Jones, *J. Organometallic Chem.*, 1963, **1**, 37.