Solvent Effects on the Rates of Hydrolysis of Phosphonium Ylides and Salts

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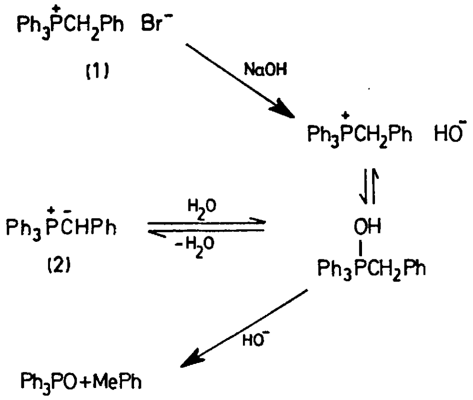
Summary The rate of hydrolysis of triphenylbenzylphosphonium hydroxide, produced from the bromide or the corresponding ylide, may be increased by a factor of $> 10^6$ by reducing the water content of the medium.

The necessity to avoid the presence of water in the preparation of phosphonium ylides is well known. Its presence leads to the rapid formation of the same phosphine oxides and hydrocarbons as are formed in the slower alkaline hydrolysis of the corresponding salts.[1]



The rates of hydrolyses of triphenylbenzylphosphonium bromide (**1**) and the corresponding ylide (**2**) have been measured in aqueous tetrahydrofuran (Table). The bromide (**1**) was hydrolysed by alkali (1 equiv.) and the reaction followed by conventional conductimetric and back titration methods. The ylide (**2**), in dry tetrahydrofuran, was mixed rapidly† with an equal volume of aqueous tetrahydrofuran and the hydrolysis was followed by measuring the amount of toluene produced or the disappearance of ylide.‡ The difference in rates for the salts and the ylides is small and can be accounted for by a salt effect. The results support the generally accepted similarity of

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† Mixing within 20 ms was achieved using the mixing device on a stopped flow apparatus. Rapid mixing was essential to minimise dielectric constant gradients.

‡ When the medium contained 1% water the production of toluene corresponded to the disappearance of ylide which could be monitored conveniently using stopped-flow equipment.

the mechanisms of hydrolyses of salts and ylides (see Scheme).[1]

TABLE. Rates of hydrolyses of the salt (**1**) and ylide (**2**) in aqueous tetrahydrofuran

% H_2O in tetrahydrofuran	Ylide (0·035M) $t_{\frac{1}{2}}$/s	Salt (0·025M) $t_{\frac{1}{2}}$/s
60		2400
50	420	480
40	50	120
30	5	8
20	3	[a]
10	$<0{\cdot}02$	
1	2	

[a] The rate of alkaline hydrolysis of the salt in tetrahydrofuran containing 20% water or less was too fast to give consistent results using conductimetric or back titration methods.

Thus the apparent faster hydrolyses of ylides, which are prepared in media of low polarity and usually hydrolysed in the same media, compared to the alkaline hydrolyses of the corresponding salts in highly aqueous media, is due to a solvent effect.§

The rate of hydrolysis increases by $> 10^5$ as the water content of the medium is reduced from 60 to 10%. The rate increase in low polarity media should be particularly useful for the hydrolysis of alkali-resistant salts. We are studying the effect of low polarity media on the stereospecificity of the hydrolysis. Some loss of stereospecificity may occur if the five-co-ordinate intermediate is sufficiently long lived to undergo ligand rearrangement.

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§ Hydrolysis is extremely fast even when an ethereal solution of ylide is poured into excess of water. This is due to slow mixing and the hydrolysis is complete before the polarity of the medium surrounding the ylide has significantly increased.

[1] Careful analysis of the products confirmed the identical nature of the products of ylide and salt hydrolysis. See also D. Coffman and C. S. Marvel, *J. Amer. Chem. Soc.*, 1929, **51**, 3496; D. Seyferth and G. Singh, *ibid.*, 1965, **87**, 4156; H. J. Bestmann, H. Haberlein, and I. Pils, *Tetrahedron*, 1964, **20**, 2079; K. Issleib and R. Lindner, *Annalen*, 1966, **699**, 40.