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BEHAVIOR OF p-DIMETHYLAMINO-α-BROMOSTYRENE AND ITS DIMER IN DIOXANE-WATER.

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Abstract - Monomeric p-dimethylamino-α-bromostyrene undergoes S_N1 increasingly slowly in 60 to 91% dioxane. Reaction is catalyzed by $HClO_4$, NaOH and $NaClO_4$. Dimer II reverts to monomer I in 91% dioxane. There is only a small solvent effect on the solvolysis rate of II.

At UV concentration in H_2O, pH > 3, p-dimethylamino-α-bromostyrene, I, reacts so rapidly that only products of its solvolysis were detectable at the first spectral scan.[1] In accordance with the assigned S_N1 mechanism,[2] solvolysis was greatly slowed in dioxane-H_2O solutions.[3] In 91.2% dioxane, the UV change, probably giving some III, was unclean and still not complete in 31 days. Similar results were obtained in 80% dioxane. However, in 74.8 and 59.5% dioxane a fairly clean first order spectral change to that of III occurred (Table I).

Table I. First Order Rate Constants for Hydrolysis of p-Dimethylamino-α-bromostyrene[a]

Wt. % Dioxane	$k_{obsd}(sec^{-1})$	Wt. % Dioxane	$k_{obsd}(sec^{-1})$
0[b]	6×10^{-1}	74.8	6.3×10^{-4}
59.5	6.9×10^{-3}	91.2	very slow[c]

[a] At 21°, except 25° in H_2O; [b] Ref. 1; [c] Incomplete in 31 days.

It appeared possible that in solvents of high dioxane content an acid-catalyzed hydration-elimination could be detected. Since both initial and transition states of acid-catalyzed hydrolysis are mono-cationic, it should not be slowed in dioxane - H_2O nearly as drastically as the S_N1 solvolysis. Indeed, low concentrations of $HClO_4$ catalyzed clean hydrolysis to III in both 91.2 and 80% dioxane. However, this appears to be a salt effect since $NaClO_4$ produced a similar result (Table II). Reversible hydration followed by rate-controlling solvolysis of the hydrate was ruled out by nmr studies in acidic 91.2% d_8-dioxane-D_2O which showed that vinyl proton exchange did not precede acetophenone formation.

Low concentrations of NaOH or NaOH-$NaClO_4$ also accelerated reaction (Table II). The product was largely the acetylene IV in the basic solutions.

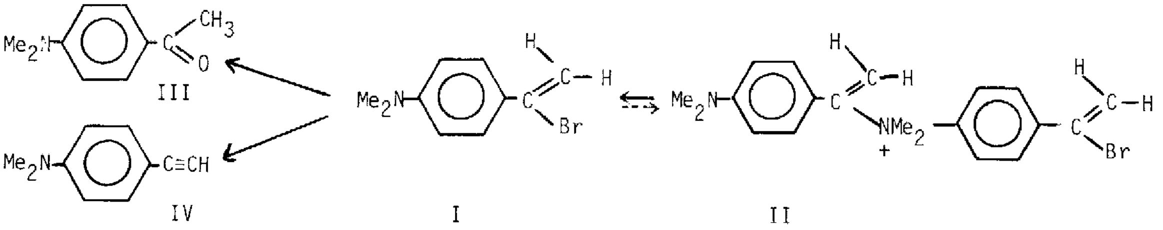

Table II. Effect of $HClO_4$, $NaClO_4$ and NaOH on the Reaction of Compound I at 21°

Solvent	$[HClO_4]$	$[NaClO_4]$	[NaOH]	$k_{obsd} \times 10^5 sec^{-1}$
91.2% dioxane[a]	0	0	0	extremely slow
	9.1×10^{-4}	0	0	1.0
	9.1×10^{-3}	0	0	3.0
	0	9.1×10^{-3}	0	3.6
	4.55×10^{-3}	4.55×10^{-3}	0	1.9
79.7% dioxane[a]	0	0	0	very slow
	1.0×10^{-3}	0	0	30.
91.2% dioxane[b]	0	0	9.1×10^{-3}	1.9
	0	4.5×10^{-3}	4.5×10^{-3}	4.1
	0	8.2×10^{-3}	9.1×10^{-4}	4.4

[a] The product was the acetophenone, λ_{max} 325, ε 20,000; [b] The product was largely the acetylene.

Behavior of the Dimer II - In water, the dimeric compound II is the intial extremely rapidly formed solvolysis product of p-N,N-dimethylamino-α-bromostyrene when either method A or B of the adjoining paper is used to prepare a UV solution.[1] This dimerization was shown to be local, i.e., to occur while I is being dispersed. Dimerization of I in solution (prepared by mixing a 0.1 M. $HClO_4$ solution of I with an equal volume of 0.1 M. NaOAc) also was observed when the initial monomer concentration was $\sim 3 \times 10^{-5}$ M, but not at a monomer concentration of 3×10^{-6} M. Interestingly enough, the reverse reaction of de-dimerization, II → I, is preferred in the solvent 91.2% dioxane.

Preparation of a $3\text{-}5 \times 10^{-5}$ molar solutions of the dimer II in 91.2% dioxane (λ_{max} 270, 8000) involved first introducing I into H_2O (1 vol.) by method A of the adjoining paper,[1] followed immediately by dioxane (10 vols). The spectrum underwent a clean first order change to that of monomer, I (λ_{max} 307, ε 15,000) contaminated slightly by the acetophenone, III.[3] That I was the product was verified by acidification of the solution to 9.1×10^{-3} M. $HClO_4$ after the first event, II → I, was complete. That is, the spectral changes upon acidification duplicated those of monomer I introduced directly into the same solution, yielding III with the same isoabsorptive points and first order rate constant, 3.6×10^{-5} sec.$^{-1}$.

The rate constant for II → I in 91.2% dioxane (2.5×10^{-3} sec^{-1}) was not much different than for solvolysis II → III in 9% dioxane (6×10^{-3} sec^{-1}). The small solvent effect on the rate is in accordance with transition and initial states both being mono-cationic. The interesting feature of the solvolysis of II in 91.2% dioxane is the capture of the vinyl cation by Br^- ($[Br^-] = 3.5 \times 10^{-5}M$) instead of by water, present in very much higher concentration, 4.9M. Evidently, dimer was reacting in the form of its ion pair, and the vinyl cation was captured by the nearby Br^- before the ions could diffuse apart.

References and Notes

1. W. M. Schubert and David C. Green, Tetrahedron Lett.
2. For a thorough review of S_N1 reactions of vinyl derivatives, see P. J. Stang, Z. Rappoport, M. Hanack and L. R. Subramanian "Vinyl Cations", Academic Press, 1979.
3. For a similar solvent effect on the solvolysis of t-butyl chloride, see A. H. Fainberg and S. Winstein, J. Amer. Chem. Soc., 78, 2770 (1956).

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