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IONIC DECOMPOSITION OF 2-ALKOXY-2-PROPYL PER-p-NITROBENZOATES

BAEYER-VILLIGER-TYPE REACTIONS OF A KETAL AND AN ORTHOESTER [1]

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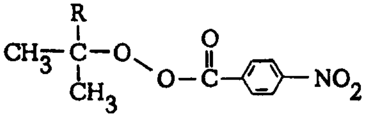
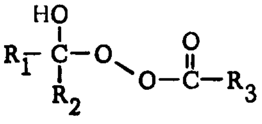
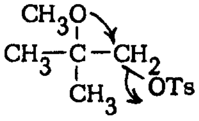
AS part of a general investigation of ionic decomposition of peresters of type I, the two peresters with R = OMe (Ia) and R = OEt (I-b) were studied. These were of interest as models for the intermediate adduct II[3] in the Baeyer Villiger reaction of ketones with peracids. The results of this study, reported in the present Communication, have significance for the mechanistic interpretation of the Baeyer-Villiger reaction and help suggest new modifications and extensions of this type of reaction.



Ia; R = OCH_3
Ib; R = OC_2H_5



II



III

The 2-methoxy- and 2-ethoxy-2-propyl hydroperoxides were obtained in satisfactory yields by ozonization of tetramethylethylene in methanol or ethanol, respectively.[4] Acylation with p-nitrobenzoyl chloride in pyridine

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[1] Research supported by the National Science Foundation.

[2] United States Rubber Company Foundation Fellow in Chemistry, 1960-1961.

[3a] M.F. Hawthorne, W.D. Emmons and K.S. McCallum, *J. Amer. Chem. Soc.* **80**, 6393 (1958); [b] W. von E. Doering and E. Dorfman, *Ibid.* **75**, 5595 (1953); [c] A.G. Davies, *Organic Peroxides* p. 151. Butterworth, London, Washington (1961).

[4] R. Criegee and G. Lohaus, *Liebigs Ann.* **583**, 6 (1953).

gave rise to pale yellow crystalline peresters: Ia, m.p. 64-66° (Found: C, 52.05; H, 4.96. Calc. for $C_{11}H_{13}O_6N$: C, 51.77; N, 5.13); Ib, m.p. 71-73° (Found: C, 53.41; H, 5.71. Calc. for $C_{12}H_{15}O_6N$: C, 53.50; H, 5.62). These peresters are very much more reactive in ionic decomposition than t-butyl per-p-nitrobenzoate,[5] methyl acetate and p-nitrobenzoic acid being produced quantitatively from the methoxy perester Ia in methanol. Dimethyl ether was also detected, but not determined.

Ionic decomposition of peresters Ia and Ib proceeded with good first order kinetics in methanol, the first order rate constants obtained by titration of developed acid being summarized in Table 1. Rate constants based on less accurate active oxygen titrations were closely similar. The sequence of relative rates of ionic decomposition of the peresters I in methanol at 25° is as follows for the various R groups:[5] Me, 1 < Et, 49 < OMe, 1.3 x 10^3 < OEt, 2.1 x 10^3 < i-Pr, 3.2 x 10^3 < C_6H_5,[6] 1.3 x 10^5 < t-Bu, 2.5 x 10^5. Rate of ionization climbs steeply, not only as the migrating group is changed from Me to t-Bu,[7] but also as a non-migrating alkoxyl

TABLE 1

Solvolysis Rate Constants for Peresters Ia and Ib

R	Solvent	Temp. ($^{\circ}$C)	k[a] (sec^{-1})
OMe	MeOH	75.00	1.61 x 10^{-3}
OMe	MeOH	50.00	1.02 x 10^{-4}
OEt	MeOH	25.00	6.50 x 10^{-6}
OEt	MeOH	50.00	1.40 x 10^{-4}
OEt	EtOH	50.00	9.17 x 10^{-5}

[a] Based on developed acid titer; theoretical acid infinity titers were observed; average deviation in k less than 2 per cent.

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[5] E. Hedaya, unpublished work.

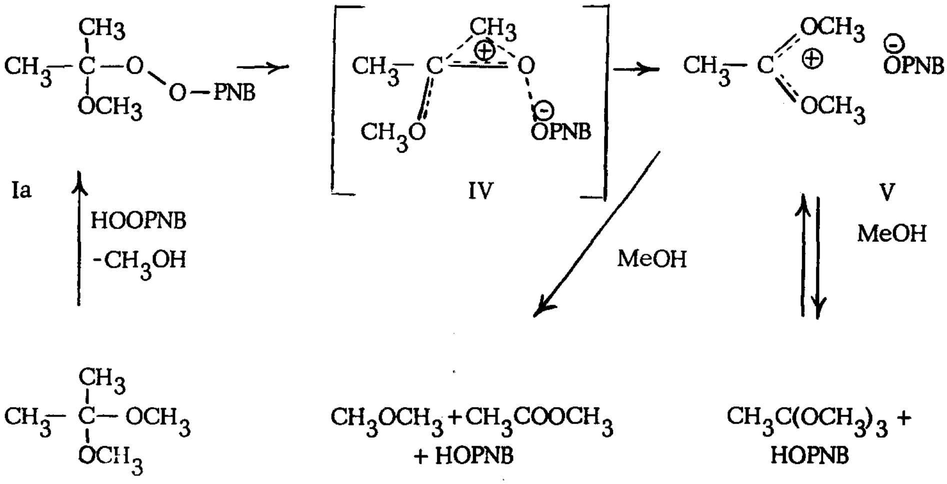
[6a] K. Nelson, unpublished work; [b] P.D. Bartlett and J.L. Kice, Private communication.

[7] S. Winstein and T.G. Traylor, *J. Amer. Chem. Soc.* **77**, 3747 (1955), footnote 18.

group is substituted for methyl. Correcting for inductive retardation by a methoxyl group,[8] we see that rate enhancement due to alkoxyl is approximately the same as that for phenyl or t-Bu.

It is interesting to compare the effect of methoxyl in ionization of perester Ia with that in anchimerically accelerated ionization of 2-methoxy-2-methyl-1-propyl toluenesulfonate[9] (III). In the latter case, rate enhancement due to methoxyl is much smaller than for the perester and anchimeric acceleration involves migration of methoxyl rather than methyl.

The most probable mechanism of ionic decomposition of the 2-methoxy-2-propyl perester Ia involves the dimethoxy carbonium ion V formed via transition state IV. While kinetic control of products would be expected to give methyl orthoacetate from ion V in methanol, it was found that the orthoester does not survive. Under the reaction conditions in the presence of one equivalent of p-nitrobenzoic acid, methyl orthoacetate was converted quantitatively to methyl acetate without consumption of acid. Evidently, even though ion V may equilibrate with orthoester and acid, it goes irreversibly to methyl acetate.



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[8] S. Winstein, C.F. Lindegren and L.L. Ingraham, *J. Amer. Chem. Soc.* **75**, 147 (1953).

[9] S. Winstein, C.F. Lindegren and L.L. Ingraham, *J. Amer. Chem. Soc.* **75**, 155 (1953).

Further evidence for equilibration between di-alkoxy carbonium ion intermediates and orthoesters under the conditions for ionic decomposition of peresters Ia and Ib is the composition of the ester products obtained in methanol and ethanol as solvent. Thus, as summarized in Table 2, decomposition of the methoxy-perester Ia in ethanol instead of methanol leads very predominantly to ethyl acetate instead of methyl acetate. Consistently, treatment of methyl orthoacetate with p-nitrobenzoic acid in ethanol leads to the same mixture of ethyl and methyl acetates. The switch in ester product due to the change in alcohol solvent is also shown by the ethoxy-perester Ib. This perester, which should give rise to an α-methoxy-α'-ethoxycarbonium ion intermediate, gives rise very predominantly to methyl acetate in methanol, but ethyl acetate in ethanol.

TABLE 2[a,b]

Percent Composition of Ester Products from Peresters and Orthoesters

Compound	MeOH		EtOH	
	MeOAc	EtOAc	EtOAc	MeOAc
Ia, R = OCH_3	100	-	93	7
$CH_3C(OCH_3)_3$	100	-	93	7
Ib, R = OEt[c]	97	3	99	1
$CH_3C(OEt)_3$	(96)[d]	(4)[d]	-	-

[a] Decompositions carried out with ca. 0.05 M peresters for 10 half-lives at 75°. Orthoesters were treated identically except for addition of one equivalent of p-nitrobenzoic acid.

[b] In control experiments the esters proved to be stable under all reaction conditions.

[c] 84 per cent yield of ester product in MeOH; 95 per cent yield of ester product in EtOH.

[d] Approximate values.

Since rate of ionization of the intermediate II is expected to be similar to that of the analogous alkoxy-peresters such as Ia and Ib, the high reactivity of peresters Ia and Ib furthers our understanding of reactivity in the Baeyer-Villiger reaction. In the latter reaction, rate is controlled by an unfavorable position of equilibrium in the addition of peracid to ketone and a favorable reactivity of the adduct II, due in part to the rate-enhancing effect of the non-migrating hydroxyl group.

An alternative way to generate alkoxy-peresters like Ia and Ib would appear to be provided by an exchange reaction between a ketal and a peracid. This suggests the interesting possibility of using ketals instead of carbonyl compounds in the Baeyer-Villiger reaction. Actually, when one equivalent of acetone dimethyl ketal was stirred with ca. one equivalent of peracid in benzene acidified with a trace of sulfuric acid catalyst, a 47 per cent yield (VPC) of methyl acetate was obtained in 24 hr at room temperature. A second alkoxyl group in an ester like Ia or Ib would be expected to cause a further large increase in ionization rate and such peresters can be formulated to arise from an exchange reaction between an orthoester and a peracid. On this basis, reaction of orthesters with peracids related to the unknown Baeyer-Villiger type reaction of ordinary esters becomes conceivable. Thus, when methyl orthoacetate was treated with one equivalent of per-p-nitrobenzoic acid in benzene, a 48 per cent yield (VPC) of dimethyl carbonate was obtained. Although these results are preliminary and no attempt has been made to optimize the conditions, it is already clear that modifications and extensions of the Baeyer-Villiger reaction, of the type illustrated here, may have considerable usefulness.