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Nitrenium Ions from Hydroxylamine Derivatives. A Comparison of the Transition State for Heterolytic Cleavage of the N–O *versus* C–O Bond

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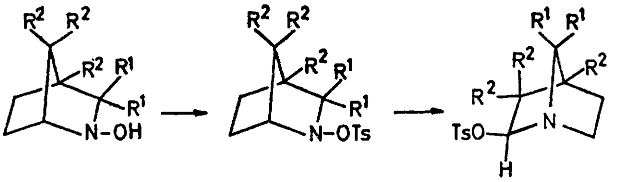
Summary A ρ-value of $+0{\cdot}68$ has been determined for the methanolysis of a series of piperidin-1-yl benzoates, in comparison with value of *ca.* $+1{\cdot}35$ for ρ determined for methanolysis of a series of 1-phenylcyclohexyl benzoates, indicating that the transition state for heterolytic cleavage of an N–O bond to generate a nitrenium ion occurs earlier in the bond breaking process than for heterolytic cleavage of a C–O bond to produce a tertiary carbonium ion.

THE growing interest of theoretical[1] and synthetic[2] organic chemists in the reactions of nitrenium ions[3] has dictated the need for a more thorough knowledge of basic nitrenium ion chemistry. We now report our results relative to both the practical and theoretical aspects of the generation of nitrenium ions from appropriately substituted dialkylhydroxylamines.†

By analogy with carbonium ion chemistry, the conversion of dialkylhydroxylamines into the corresponding tosylates should provide a simple route to nitrenium ions. This idea was supported by the investigation of Biehler and Fleury,[2] who prepared (1a) (R^1 = strong electron-withdrawing substituents) and studied its solvolytic activity. They found that (1a) rearranged readily to (2a) at 25° in aqueous dioxan, but was stable at room temperature in nonpolar media. We have found that, in the absence of such electron-withdrawing groups, the initially formed sulphonate esters are extremely unstable. Attempts to prepare (1b) from (3b) resulted in the isolation of only (2b), even at very low temperatures in relatively nonpolar solvents. For this reason, we investigated the use of benzoate anions as leaving groups in the generation of nitrenium ions.

In order to evaluate the effect of various benzoate anions as leaving groups, we studied the methanolysis of the piperidin-1-yl benzoates listed in the Table. Despite the good pseudo-first-order kinetics obtained conductometrically, the rates were anomalous in that all of the compounds appeared to solvolyse at about the same rate. A product analysis revealed that two competing reactions were occurring, one, which gave a nitrenium ion (4) and a benzoate anion (5), and a second, which produced *N*-hydroxypiperidine (6) and the appropriate methyl benzoate (7)



(3) (1) (2)

a; R^1=CN,R^2=H b; R^1=H,R^2=Me

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† C. F. Wilcox and K. K. Pohl have studied the solvolysis of *NN*-dialkylhydroxylamine derivatives in ethanol-water. We wish to thank Professor Wilcox for informing us of his unpublished results.

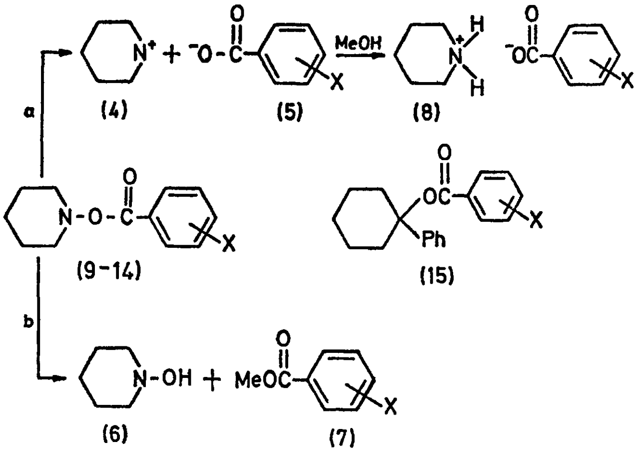
via a simple transesterification reaction. In methanol, the conversion of (4) into (8) was readily rationalized in terms of a singlet to triplet interconversion of the nitrenium ion, followed by hydrogen abstraction.‡§ The Table also lists the ratio of products obtained in these solvolyses. Use of the ratio of piperidine to *N*-hydroxypiperidine allowed us to determine the partial rate factors, k_N, for path a (Table). A plot of log k_N against σ gave a ρ value of $+0{\cdot}68$ (correlation coefficient 0·995) which is somewhat less than the value of $+1{\cdot}37$ determined for the ionization of *para*-substituted benzoic acids in methanol.[5] For a more suitable comparison, we prepared and solvolysed (15) (X = same substituents as in 9—14). A plot of log k against σ for the rates of methanolysis of (15) gave a ρ value of $+1{\cdot}34$ (correlation coefficient 0·969) This value correlates quite well the ρ value of $+1{\cdot}34$ obtained for the ionic rearrangement of perbenzoates.[6] In contrast, homolytic cleavages exhibit a negative ρ value, as in the unimolecular free-radical decomposition of benzoyl peroxide ($\rho = -0{\cdot}38$)[7] and of t-butylperbenzoate esters ($\rho = -0{\cdot}90$).[8] The positive ρ value observed for the methanolysis of (9—14) to yield (5) and (8) strongly supports the ionic nature of the bond cleavage involved in path a.

TABLE

*Methanolysis rates and products of piperidin-*1*-yl benzoates at* 50°

	$k \times 10^6\,s^{-1}$	k_{rel}	Ratio of (8) : (6)[a]	Ratio of (5) : (7)[b]	Partial rate factor ($\times 10^6\,s^{-1}$) for nitrenium ion formation[c]	$k_{N\,rel}$
(9) (X=4-MeO) ..	23·5 ± 0·5	1·16	10:90	10:90	2·36	1·0
(10) (X=4-Me) ..	15·5 ± 0·3	0·76	18:82	15:85	2·80	1·2
(11) (X=4-H) ..	20.4 ± 0·5	1·00	22:78	25:75	4·50	1·9
(12) (X=4-Cl) ..	16·2 ± 0·3	0·79	38:62	39:61	6·15	2·6
(13) (X=4-NO_2) ..	13·7 ± 0·2	0·67	86:14	83:17	11·8	5·0
(14) [X=3,5-$(NO_2)_2$]	43·8 ± 0·7	2·14	86:14	85:15	37·6	15·9

[a] Combined yields 88—96%. [b] Combined yields 82—90%. [c] Partial rate factors (k_N) were determined by multiplying the overall rates (column 2) by the ratio of (8) : (6) (column 4).



The smaller ρ value observed for the generation of nitrenium ions from (9—14) indicated to us that the transition state for ionization of an N–O bond occurs earlier in the bond-breaking process than the transition state for ionization of a comparable C–O bond. This is presumably related to the weaker nature of the N–O bond (48 kcal/mol) relative to the C–O bond (78 kcal/mol).[9] Synthetically, 3,5-dinitrobenzoates of *NN*-dialkylhydroxylamines offer particular advantage because these esters solvolyse readily and tend to minimize the side reaction due to transesterification.

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‡ Examples of such singlet to triplet interconversions have recently been well established.[4] Lee and Morokuma[1] have recently calculated that the singlet nitrenium ion should be separated from the triplet nitrenium ion by about 45 kcal/mole, with the triplet being the ground state.

§ Methanolysis of *N*-chloropiperidine also yields piperidine (P. G. Gassman and J. E. Trent, unpublished results).

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