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ARYL SUBSTITUENT EFFECTS UPON THE THERMAL ISOMERIZATION OF N-ALKYL OXAZIRIDINES TO NITRONES

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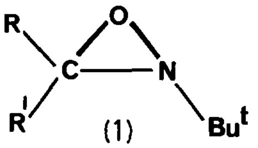
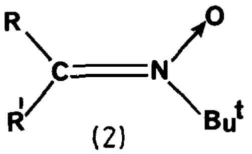
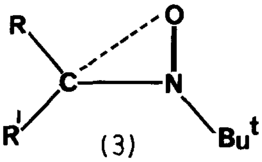
Summary. The results of a kinetic study of the thermal isomerization of oxaziridines derived from para-substituted C-arylaldimines and C-diarylketimines to the isomeric nitrones is reported.

The rearrangement of oxaziridines (1) to nitrones (2) has been the subject of two recent theoretical reports.[1,2] However, although it has long been known that 3-aryloxaziridines undergo this thermal rearrangement,[3] there is a paucity of quantitative experimental data apart from the original[3] pioneering investigation on 2-t-butyl-3-phenyloxaziridine. The present report is concerned with the rates of thermal rearrangement of various para-substituted 3-aryl- and 3,3-diaryl-oxaziridines. The rearrangements were followed by ^1H n.m.r. at 95° in toluene-d_8 solution using the methyl resonance of either toluene or hexamethyl benzene as internal reference for integration, and linear first order kinetic plots were obtained.

3-Aryloxaziridines gave the nitrones exclusively, but in the 3,3-diaryl series the initially formed nitrones eliminated 2-methylpropene at 95° to give the corresponding diaryloximes, as anticipated from earlier studies.[4,5]


(1)


(2)


(3)

The results shown in the table establish that the thermal rearrangement (1)→(2) is facilitated by electron donating substituents on the phenyl ring. The best Hammett correlations were obtained with σ_p^+ and the corresponding ρ^+ values are given in the table. Calculations on a model system using ab initio and semiempirical SCF methods indicate that the transition state for the thermal rearrangement of oxaziridine to nitrone resembles a distorted 90° twisted nitrone as depicted in (3).[1,2] Carbon-oxygen bond fission is quite well advanced ($C\hat{N}O$ = 90-100°), but rotation around the CN bond mainly occurs after the transition state (3).[1,2] The direction of the para-substituent effect in 3-phenyloxaziridines indicates that positive charge develops at C-3 in the transition state for rearrangement, though the magnitude of the ρ^+ values suggests that the positive charge development is modest. Semiempirical molecular orbital calculations on nitrones indicate that the imino carbon is negatively charged in both the ground and 90° twisted states.[6,7] Therefore the negative ρ values obtained in the present investigation would tend to suggest that the transition state is attained fairly early, i.e. during the initial C-O bond cleavage of the oxaziridine.

The ρ value for the series 2 compounds which possess two substituents might have been expected to be approximately twice that for series 1. Steric hindrance in series 2 compounds may prevent the aryl rings from adopting a coplanar confrontation which optimises conjugation. The second aryl ring present in series 2 compounds lowers the free energy barrier to rearrangement by ca. 1.5 kcal mol^{-1}. This effect could be attributed to electronic stabilization of the transition-state or to steric destabilization of the ground-state oxaziridines.

Table. Rate constants (k,sec^{-1}) and free energies of activation ($\Delta G^{\neq}$, kcal mol^{-1}) for thermal rearrangement of oxaziridines at 95°C in toluene-d_8

Series 1				Series 2			
R	R^1	10^5k	$\Delta G^{\neq}$	R	R^1	10^5k	$\Delta G^{\neq}$
4-$NO_2C_6H_4$	H	0.980	30.1	4-$NO_2C_6H_4$	4-$NO_2C_6H_4$	7.30	28.6
4-ClC_6H_4	H	3.20	29.2	4-ClC_6H_4	4-ClC_6H_4	17.1	28.0
4-FC_6H_4	H	3.11	29.3	4-FC_6H_4	4-FC_6H_4	16.0	28.1
C_6H_5	H	3.89	29.1	C_6H_5	C_6H_5	11.6	28.3
4-MeC_6H_4	H	7.15	28.6	4-MeC_6H_4	4-MeC_6H_4	29.3	27.6
4-$MeOC_6H_4$	H	17.0	28.0	4-$MeOC_6H_4$	4-$MeOC_6H_4$	85.4	26.8
4-$Me_2NC_6H_4$	H	1500.00	24.7				
	Hammett ρ^+	-1.27			Hammett ρ^+	-0.67	
	correlation coeff.	0.96			correlation coeff.	0.93	

References and Notes

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2. J. Sauer, Tetrahedron, 1979, 35, 2109.
3. M.F. Hawthorne and R.D. Strahm, J. Org. Chem., 1957, 22, 1263.
4. D.R. Boyd, D.C. Neill, and M.E. Stubbs, J.Chem.Soc., Perkin Trans. 2, 1978,30.
5. In addition to the oxime and 2-methylpropene, a small amount of other unidentified decomposition products were evident in the n.m.r. spectra (singlet signals at δ 1.19 and 1.39 in toluene-d_8).
6. W.B. Jennings, D.R. Boyd, and L.C. Waring, J.Chem.Soc.,Perkin Trans.2, 1976, 610.
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