Thermal Rearrangements of Some α-Aroyl Epoxides into Dioxoles

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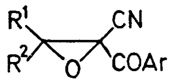
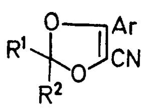
Summary Thermal rearrangement of α-cyano-α-oxo-epoxides quantitatively affords the corresponding dioxoles, which are formed by initial cleavage between the two carbon atoms of the starting epoxide ring.

Several examples of thermal rearrangements of vinylaziridines into Δ^2- or Δ^3-pyrrolines have been reported,[1] and more recently it has been shown that thermolysis of vinyl epoxides gives rise to dihydrofurans *via* carbonyl ylides.[2] A similar isomerization has been observed with aziridines substituted by oxo,[3] ester, amide, or nitrile groups,[4,5] but there are no reports of similar reactions of α-oxo-epoxides.

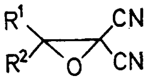
We have shown that thermolysis of epoxides αα-disubstituted with two electron-withdrawing groups gives carbonyl ylides which can be trapped by various dipolarophiles.[6–9] These results suggest that the thermolysis of α-oxo-epoxides (**1**) may be similar to that of α-oxo-aziridines; thermolysis of (**1**) provides, in fact, a new route to the dioxoles (**2**).



(1)



(2)



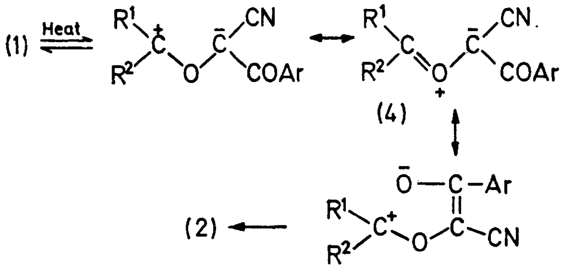
(3)

R^1 = Ph or *p*-ClC_6H_4, R^2 = H or Ph, Ar = Ph or *p*-MeC_6H_4

The new epoxides (**1**) were prepared[10] by Grignard reaction of ArMgBr with the dicyano-epoxides (**3**), and were thermolysed in boiling toluene under nitrogen. The dioxoles (**2**) were obtained in quantitative yield and gave satisfactory elemental analyses.

The structures (**2**) were based on n.m.r., u.v., and i.r. spectra. It is of interest that the i.r. spectra contain bands due to a conjugated nitrile group and also medium intensity absorptions which may be attributed to a cyclic acetal [1018—1093 and 1308 cm^{-1} (Nujol)][6,11] but lack C=O absorption bands.

It has been established that epoxides gem-disubstituted with electron-withdrawing groups give carbonyl ylides,[7–9] and so, as with α-oxo-aziridines,[3] it is reasonable to suppose that isomerization of the epoxides (**1**) proceeds *via* a stabilised 1,3-dipolar intermediate (Scheme).



Scheme

1,3-Dipolar cycloadditions are very sensitive to steric effects, *e.g.*, gem-dicyano-epoxides substituted by two phenyl groups undergo 1,3-cycloadditions to only a limited extent,[9] so it is likely that steric effects would not be so important in the intramolecular cyclisation leading to (**2**).

Isomerization of the diphenyl epoxides (**1**; $R^1=R^2=Ph$) is faster than that of the monoaryl epoxides (**1**; $R^2=H$) (Table), which suggests that the rate determining step is

Table

Preparation of dioxoles (**2**)

Dioxoles (2)	R^2	Time[a]	M.p. (°C)
Ar = Ph			
R^1 Ph	H	24 h	77—78
R^1 *p*-ClC_6H_4	H	24 h	79—80
R^1 Ph	Ph	1 h	118—119
Ar = *p*-MeC_6H_4			
R^1 Ph	H	24 h	74—75
R^1 *p*-ClC_6H_4	H	24 h	
R^1 Ph	Ph	1 h	127—128

[a] Time required for quantitative isomerization.

formation of the carbonyl ylide (**4**). A second phenyl group may stabilize the 1,3-dipolar intermediate and so favour its formation.

It is thus not surprising that 1,3-dipolar cycloaddition was not observed, even when the epoxides (**1**) were thermolysed in presence of a good dipolarophile such as *p*-nitrobenzaldehyde;[7] the dioxole (**2**) was then formed, by the intramolecular process.

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