Thermolysis of 1,2-Dioxolanes†

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Summary The 1,5-dioxapentamethylene diradical (**2**), generated in the thermolysis of 1,2-dioxolanes (**1**), suffers cyclization into epoxides (**3**), rearrangement into ketones (**4**), and fragmentation into ketones (**5**) as major transformations.

WHILE the thermolysis of 5-membered ring cyclic peroxides such as the 1,2,4-trioxolanes (ozonides),[1] the 4-aza-1,2-dioxolanes,[2] the 4-thia-1,2-dioxolanes,[3] and the 3-keto-1,2-dioxolanes (β-peroxylactones),[4] has been reported in recent years, it is surprising that the structurally simpler 1,2-dioxolanes (**1**) have not been studied so far. We present preliminary but novel results on the thermolysis of 3,3,5,5-tetrasubstituted derivatives of (**1**).

TABLE

	(1)				(3)	(4)	(5)
	R^1	R^2	R^3	R^4	Cyclization (%)	Rearrangement (%)	Fragmentation (%)
(**1a**)	Me	Me	Me	Me	37	14	16
(**1b**)	Me	Me	Me	Ph	15	32	21
(**1c**)	Me	Ph	Me	Ph	6	40	27
(**1d**)	Me	Ph	Ph	Ph	7	43	28
(**1e**)	Ph	Ph	Ph	Ph	0	78	14

The 1,2-dioxolane (**1a**—**e**) were all readily prepared by acid-catalysed cyclization of their respective diols with concentrated hydrogen peroxide,[5] and were characterized by their i.r., n.m.r., and mass spectra, as well as lithium aluminium hydride reduction back to their diols. On heating of 1·0M-solutions of (**1**) in benzene at 180—200° for 24—30 h, the major thermo-products (see Table) were epoxides (**3**) (cyclization), ketones (**4**) (rearrangement), and ketones (**5**) (fragmentation), all identified by comparison of g.l.c. retention times and i.r. spectra with the authentic materials. Control experiments confirmed the thermal stability of all products under the thermolysis conditions. Quantitative g.l.c. analysis of the thermolysis mixtures using the internal standard technique, gave the product composition in the Table, accounting for 96—99% product balance if involatile residue is included. In the case of (**1a**) 17% alcohol was formed by hydrogen abstraction.

An interesting trend in cyclization *vs.* rearrangement is immediately apparent in the Table, *i.e.* the more phenylation the greater the amount of rearrangement and the smaller the amount of cyclization (*cf.* systems **1a**, **1c**, and **1e**). Furthermore, for the unsymmetrical systems (**1b**) and (**1d**) the ability for deketonization (ratio of $R^1R^2C{=}O : R^1R^4C{=}O$ as a measure of leaving group ability) is 0·5, 1·0, and 1·5, for acetone, acetophenone, and benzophenone respectively. Moreover, for these unsymmetrical systems

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the amounts of methyl *vs.* phenyl 1,2-shift (the ratio Me : Ph as a measure of migratory aptitude) are 1·3 and 2·5 in favour of methyl migration for (**1b**) and (**1d**) respectively. For comparison, the Me : Ph ratio is 5·6 in the thermolysis of β-methyl-β-phenyl-β-peroxypropiolactone, where carbon dioxide is the leaving group.[4]

In the thermolysis of β-peroxylactones we have shown[4] that no epoxide is formed and by means of stereolabelling and kinetic experiments it was concluded that the 1,5-dioxa-2-oxopentamethylene diradical is the precursor to the thermoproducts. Analogous to the β-peroxylactones, our preliminary product data for the thermolysis of 1,2-dioxolanes are most economically accommodated in terms of a mechanism in which the cyclization and rearrangement products are principally derived from the 1,5-dioxapentamethylene diradical (**2**) rather than deketonization to the 1-oxatrimethylene diradical (**6**), which subsequently cyclizes rearranges, or fragments into the observed products (see Scheme).

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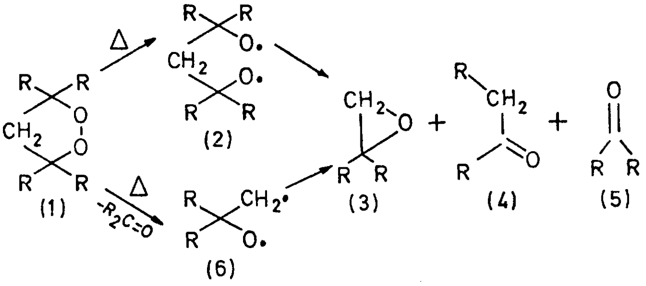

SCHEME

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