Suprafacial Alkyl 1,2-Shift in the Rearrangement of Thermally Generated Oxygen Diradicals

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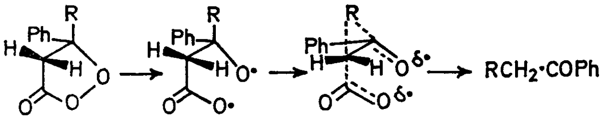
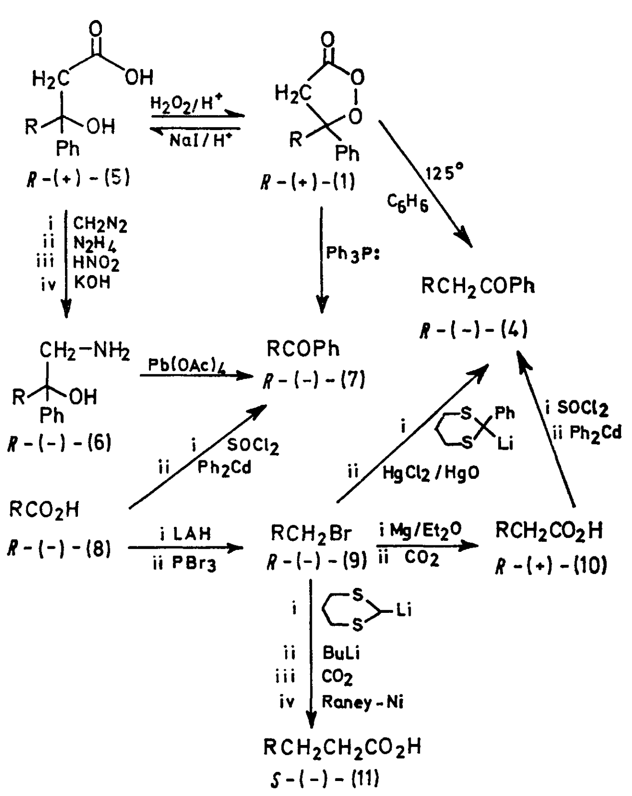
Summary In the rearrangement of 2-oxopropane-1,2-dioxy diradicals, generated *via* thermolysis of β-peroxy-lactones, an asymmetric alkyl substituent is shown to migrate with quantitative retention of configuration.

IN view of the concerted mechanism suggested for the rearrangement of the diradical (**2**),[2] generated by thermolysis of the peroxy-lactones (**1**) an asymmetric alkyl group is expected to migrate with retention or inversion, depending on whether an sp^3 hybrid or a $2p$ orbital at the migrant centre participates.[3] There is ample evidence that alkyl 1,2-shifts in carbonium ions proceed with retention (suprafacial shift),[4] while to the best of our knowledge no stereochemical studies on the migration of asymmetric alkyl groups in radicals and carbanions have been reported. β-Peroxy-lactones provide a unique opportunity for the examination of the stereochemical fate of asymmetric alkyl migrants in the thermal rearrangement of diradicals, and we now report on the thermolysis of the optically active peroxylactone (**1**).



(1) (2) (3) (4)

The synthesis, thermolysis, and configurational assignments of (**1**) are outlined in the Scheme. The acid (**5**) was prepared in 92% yield [m.p. 192—194° (decomp.)] by saponification of the corresponding ethyl β-hydroxy-ester, which was obtained by Reformatsky reaction of the propanone (**7**). The acid (**5**) was resolved with quinine to give



R = CHMe–CH_2–Ph throughout

SCHEME

R-(+)-(**5**) [m.p. 160—160·5°; α_D^{24} 5·14° (c 22·0 in THF)]. Peroxy-lactone R-(+)-(**1**) [α_D^{25} 28·3° (c 12·8 in C_6H_6)] was obtained (59%) as a colourless oil. Thermolysis of R-(+)-(**1**) at 125° in benzene for 24 h gave the R-(−)-butanone (**4**), m.p. 42—44° after g.l.c. (90%). The specific rotations of two separately decomposed samples of R-(+)-(**1**) were α_D^{29} −12·6° (c 3·72 in C_6H_6) and α_D^{25} −13·1° (c 2·84 in C_6H_6), respectively.

The optical purity of hydroxy-acid R-(+)-(**5**) was established to be 99% by correlation with ketone R-(−)-(**7**), which was prepared from the R-(−)-propionic acid (**8**) by treatment of its acid chloride with diphenylcadmium. Furthermore, treatment of peroxy-lactone R-(+)-(**1**) with aqueous NaI in acetone regenerated hydroxy-acid R-(+)-(**5**), m.p. 159—160°, without loss of optical purity. Therefore, the peroxy-lactone is also at least 99% optically pure R-(+)-(**1**). The optical purity of ketone R-(−)-(**4**) was shown to be 100% by correlation with the R-(−)-propionic acid (**8**). Consequently, the asymmetric alkyl migrant in diradical (**2**) suffers a suprafacial 1,2-shift with complete retention of configuration.

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