Conformational Effects in the Rearrangements of Thermally Generated Oxygen Diradicals

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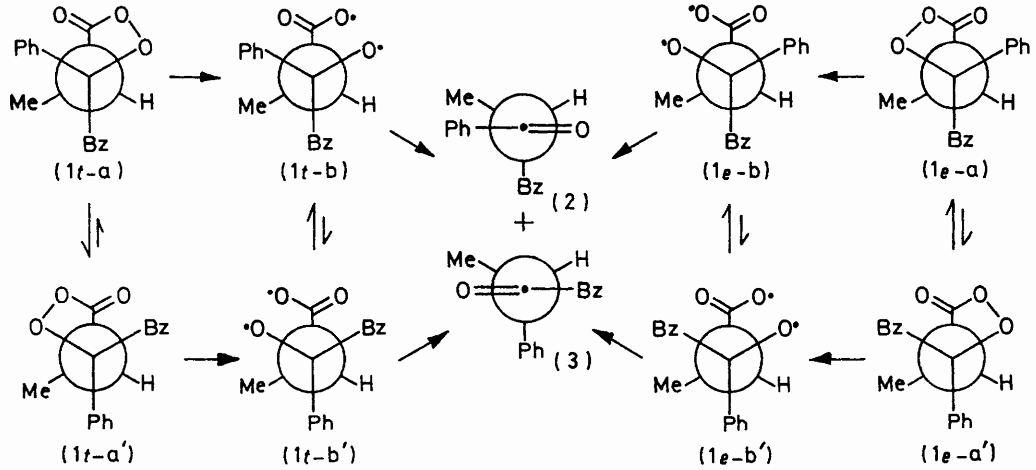
Summary *erythro*- and *threo*-4-Benzyl-3-methyl-4-phenyl-1,2-dioxolan-2-one on thermolysis at 125° in benzene affords 1,3-diphenyl-2-methylpropan-1-one (benzyl migration) and 1,3-diphenyl-3-methylbutan-2-one (phenyl migration) in a ratio of 12·2 ± 0·2 : 1 for the *threo*- and 21·0 ± 0·3 : 1 for the *erythro*-isomer.

We have demonstrated[1] that the thermolysis of β-peroxylactones proceeds *via* 2-oxo-1,5-dioxapentamethylene diradicals which decarboxylate to give rearrangement ketones by alkyl or phenyl migration. Replacement of a hydrogen at the α-carbon (the migration terminus) by an alkyl group introduces a steric interaction in the transition states which should alter alkyl migration with respect to phenyl migration, *i.e.*, the proportion of rearrangement ketones should be subject to conformation effects. Such effects have been amply demonstrated in carbonium ion[2] but not in diradical rearrangements. Recently Cvetanovic[3] invoked conformational effects in the rearrangement of 1-oxatrimethylene diradicals generated by addition of oxygen atoms to olefins; however, this interpretation has been challenged by Scheer and Klein[4] who prefer a non-diradical mechanism.



Scheme

The thermolysis of (**1*t***) and (**1*e***) at 125° C in benzene gave the rearrangement ketones (**2**) (benzyl migration) and (**3**) (phenyl migration) as major products (Scheme). They were identified by comparison of their g.l.c. retention times and their i.r. and n.m.r. spectra with the authentic materials. Quantitative g.l.c. analysis of the thermolysis products gave a benzyl : phenyl migratory aptitude [ratio of rearrangement ketones (**2**) and (**3**)] of 12·2 ± 0·2 : 1 for (**1*t***) and 21·0 ± 0·3 : 1 for (**1*e***). Clearly, a significant difference in the migratory aptitudes between benzyl and phenyl is discernible; however, in both the *erythro*- and *threo*-isomers the benzyl group migrates in preference to the phenyl group.

In the Scheme these results are interpreted in terms of a conformational effect on the rearrangement of the 2-oxo-1,5-dioxapentamethylene diradical.

Of the two rotamers (**1*e*-a**) and (**1*e*–a′**) of (**1*e***) the thermodynamically more stable one is (**1*e*–a**) since a lesser number of bulky groups are crowded together. Thus, in the reactant state rotamer (**1*e*–a**) is preferentially populated. On thermal activation, the peroxide bond is ruptured to produce the *erythro*-diradical of which rotamer (**1*e*–b**) is also thermodynamically more stable than (**1*e*–b′**). Consequently, in the intermediate state rotamer (**1*e*–b**) is preferentially populated and it is not surprising that benzyl migration predominates by a factor of 21.

For the *threo*-isomer, rotamers (**1*t*–a′**) and (**1*t*–b′**) are expected to be thermodynamically more stable than (**1*t*–a**) and (**1*t*–b**), respectively. Thus, in the intermediate state, rotamer (**1*t*–b′**) is preferentially populated and it would be expected that phenyl migration should outweigh benzyl migration, but in fact benzyl migration again predominated over phenyl migration by a factor of 12·2. However, in all cases examined[1] alkyl migration is preferred over phenyl migration for the 2-oxo-1,5-dioxapentamethylene diradical. This implies that rearrangement of rotamer (**1*t*–b′**) is, for electronic reasons, kinetically unfavourable compared to (**1*t*–b**). Consequently, (**1*t*–b′**), instead of suffering a phenyl 1,2-shift, rotates into the thermodynamically less stable (**1*t*–b**) rotamer in which the benzyl group is aligned for kinetically favoured migration.

While a conformational effect is clearly evident in the rearrangement of the thermally generated oxygen diradicals, for (**1*e***) and (**1*t***) the α-methyl substituent is not sufficiently obstructing to overcome the electronically favoured benzyl migration. Presumably a t-butyl substituent at the α-carbon (the migration terminus) might be sufficiently large enough to freeze the (**1*t*–b**) rotamer and thus provoke a preferential phenyl 1,2-shift.

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