Tandem 1,5-Hydrogen Transfer and Decarbonylation in the Flash Vacuum Pyrolysis of 5-Vinyl-3-methyl-1,2-dioxane

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Intramolecular 1,5-transfer of a primary hydrogen atom is the dominant behaviour in dioxyl diradicals formed by flash vacuum pyrolysis of 5-substituted 3-methyl-1,2-dioxanes and is followed by decarbonylation when the substituent is the vinyl group.

Acyclic 1,6-dioxyl diradicals are accessible by homolysis of 1,2-dioxanes. Interest lies in comparing the behaviour of such diradicals with that of free alkoxyl radicals. Examples derived from 3,3,6,6-tetrasubstituted 1,2-dioxanes have unexceptional chemistry, undergoing β-scission to afford ketones and ethene.[1,2] However, the diradical from 3.6-dimethyl-1,2-dioxane principally undergoes 1,5-hydrogen transfer, and rearrangement to 5-hydroxyhexan-2-one is the main outcome† of the flash vacuum pyrolysis (fvp) of this peroxide.[3] We have

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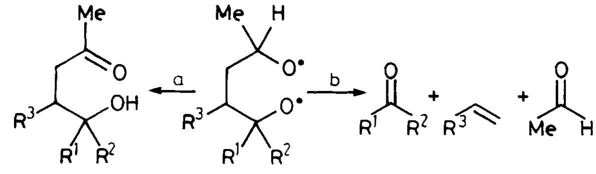
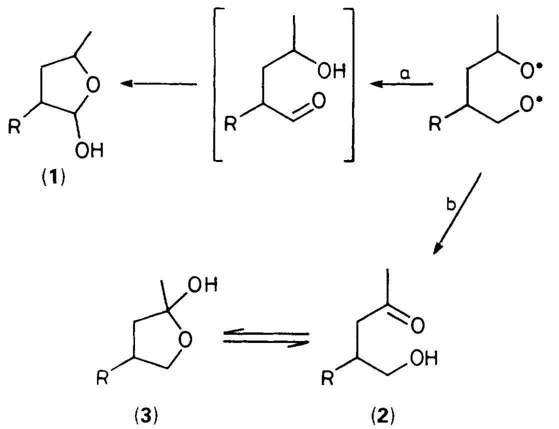
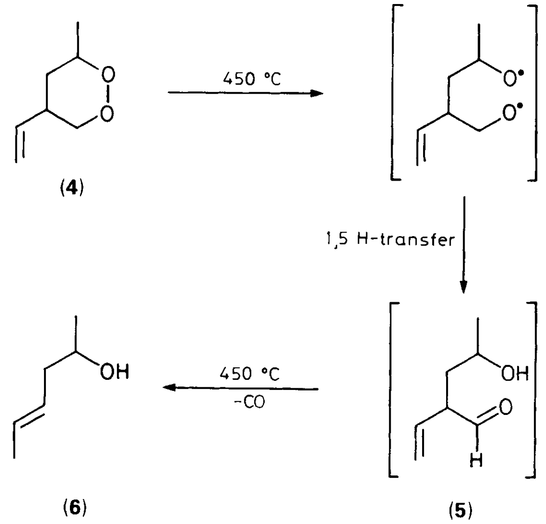
† This has been confirmed in several independent experiments but we have been unable to verify the reported formation of 16% of hexa-2,5-dione; the extent of dehydrogenation appears to be at least an order of magnitude lower.



(1)



(2)



(3)

now carried out the fvp[3] of several secondary 1,2-dioxanes to investigate the influence of the number and position of substituents upon the competition between 1,5-hydrogen transfer to give rearrangement [equation 1(a)] and β-scission to give fragmentation [equation 1(b)]. In the course of this work we have discovered a unique transformation that involves tandem 1,5-hydrogen transfer and decarbonylation.

3,3,6-Trimethyl-1,2-dioxane gave 5-hydroxy-5-methylhexan-2-one and little or no acetone. Thus, the introduction of a methyl group in place of one of the hydrogen atoms capable of undergoing 1,5-transfer does not alter the observed chemistry, and as with 3,6-dimethyl-1,2-dioxane,[3] rearrangement takes place almost exclusively [equation 1(a); $R^1 = R^2 =$ Me, $R^3 =$ H]. With 3,6-dimethyl-3-phenyl-1,2-dioxane, rearrangement was again the major pathway, but some 40% of fragmentation [equation 1(b); $R^1 =$ Me, $R^2 =$ Ph, $R^3 =$ H] occurred as indicated by the molar ratio of acetophenone to 5-hydroxy-5-phenylhexan-2-one in the product. Presumably the energy of the transition state for β-scission is sufficiently lowered by conjugation between the phenyl group and the partially formed carbonyl group for fragmentation now to compete effectively with rearrangement.

By contrast, the introduction of a phenyl group at the 5-position ($R^3 =$ Ph) failed to enhance β-scission. Thus both 3-methyl-1,2-dioxane and 3-methyl-5-phenyl-1,2-dioxane gave only traces of fragmentation products. Interest here centred on the competition between 1,5-transfer of a primary hydrogen atom [equation 2(a)] and that of the secondary hydrogen atom [equation 2(b)]. With both compounds the abstraction of a primary hydrogen atom was preferred, the ratio of product (**1**) to equilibrium mixture (**2**) plus (**3**) being 2 : 1 when R = H and 8 : 1 when R = Ph.

These results helped to provide an interpretation of the novel transformation undergone by 3-methyl-5-vinyl-1,2-dioxane (**4**) upon fvp. The strongly dominant product was identified as *trans*-hex-4-en-2-ol (**6**) by a comparison of its ^1H and ^{13}C NMR spectra with literature data.[4]‡

By analogy with the corresponding 5-phenyl compound, abstraction of a primary hydrogen atom will predominate and lead to formation of the hydroxyaldehyde (**5**). However, instead of hemiacetal formation, a tandem 1,4-hydrogen transfer with decarbonylation takes place [equation (3)], analogous to that previously established[5] for 2,2-dimethylbut-3-enal.

All the 1,2-dioxanes described here are new. Each was prepared by treating an appropriate unsaturated hydroperoxide [$R^1R^2C(OOH)CH(R^3)CH_2CH{=}CH_2$] with mercury(II) nitrate followed by reductive demercuriation of the resultant cycloperoxymercurial with basic sodium borohydride. For the vinyl derivative (**4**), it was necessary to separate the mercuriated precursor from an isomeric 1,2-dioxolane[6] prior to reduction. The flash vacuum pyrolyses were carried out on 50—100 mg of each 1,2-dioxane. The trapped products were allowed to warm to about 0° C, dissolved in $CDCl_3$, and examined by ^1H and ^{13}C NMR spectroscopy. Products were identified by comparison with authentic samples prepared independently or available commercially. The $CDCl_3$ was then removed at a rotary evaporator at 0—10 °C, taking the sample to constant weight. Recoveries of materials were in the range 69—76%. Ratios of identified products are indicated in the text and any unassigned signals in the NMR spectra were very weak by comparison.

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‡ Our data are in very good agreement with those reported except that our alkenic carbon chemical shifts resemble more closely those previously assigned[4] to the *cis*-isomer.