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 re-

arrangement 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.
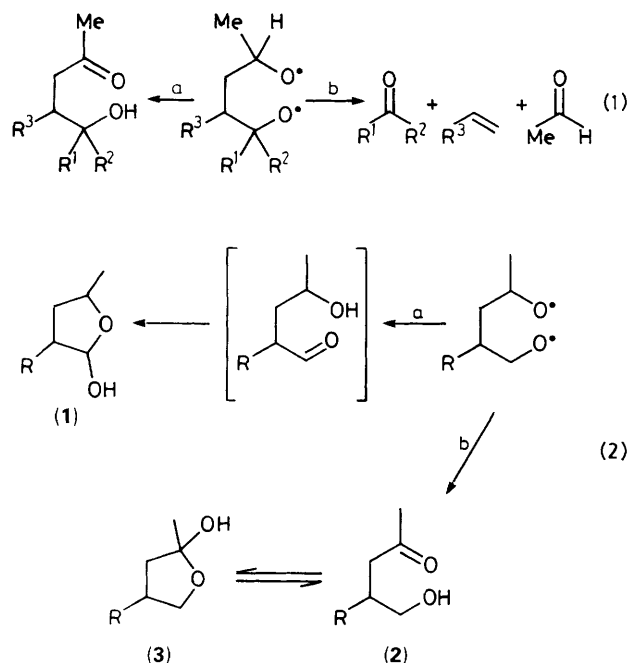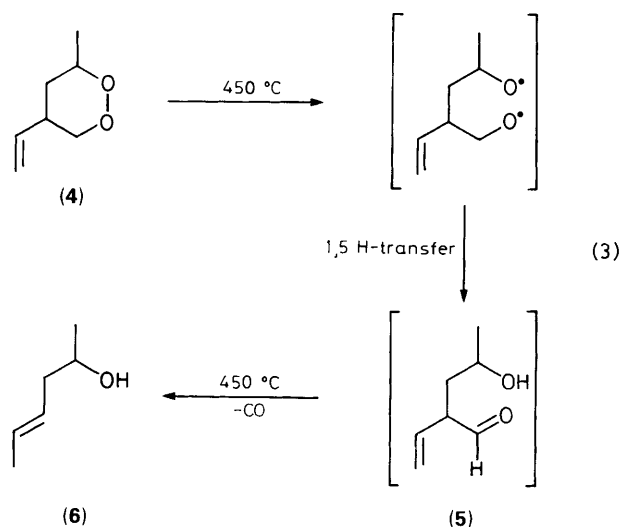
now carried out the fvp[3] of several secondary 1,2-dioxanes to investigate the influence of the number and position of substituents upon the competition between 1,5-hydrogen transfer to give rearrangement [equation 1(a)] and β-scission to give fragmentation [equation 1(b)]. In the course of this work 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-methyl-hexan-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 ^{1}H 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 CDCl₃, and examined by ^{1}H and ^{13}C NMR spectroscopy. Products were identified by comparison with authentic samples prepared independently or available commercially. The CDCl₃ 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.

‡ 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.

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