Synthesis of γ-Methyl-γ-peroxyvalerolactone, its Thermolysis and Photolysis[1]

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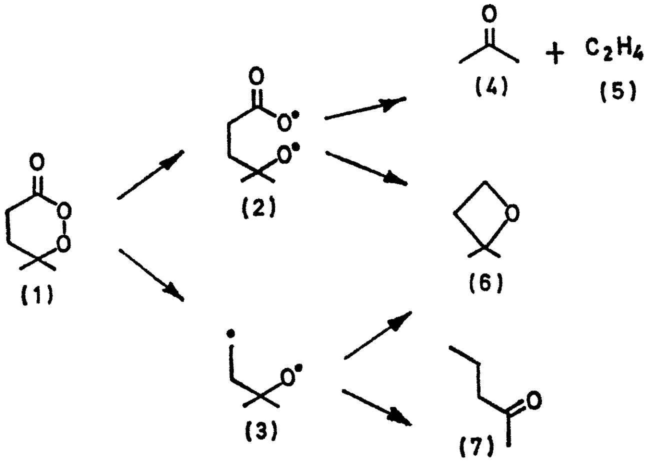
Summary The diradical generated by thermolysis and photolysis of γ-methyl-γ-peroxyvalerolactone is shown to fragment into acetone, ethylene, and 2,2-dimethyloxetan.

THE thermolysis and photolysis of the β-peroxylactones have been studied in detail.[2] We report now on the synthesis and transformations of γ-methyl-γ-peroxyvalerolactone (**1**). Our interest in this cyclic peroxy-ester was to determine the chemical fate of the diradical (**2**), generated thermally or photochemically from (**1**), in order to elucidate the effect of extension of the carbon backbone on the interaction of the two radical sites in such oxygen diradicals. Some of the more obvious modes of energy dissipation of diradical (**2**) are illustrated in the Scheme.



SCHEME

After numerous failures, the synthesis of γ-peroxylactone (**1**) (b.p. 33°/0·05 mm; 99·1 ± 0·2% pure by iodometric titration) was achieved in 63% yield by treating γ-hydroxy-γ-methylvaleramide, prepared from γ-methyl-γ-valerolactone[3] by reaction with aqueous ammonia in 65% yield, with a solution of 98% hydrogen peroxide in methanesulphonic acid for 5 min at 0°. Reaction of (**1**) with a stoicheiometric amount of triphenylphosphine in hexane resulted in quantitative precipitation of triphenylphosphine oxide and 85% of γ-methyl-γ-valerolactone was isolated after fractional distillation. Similarly, the γ-valerolactone was the exclusive product after halogenolysis with acidic sodium iodide in acetone.

The thermolysis of (**1**) in carbon tetrachloride followed clean first-order kinetics out to seven half-lives, with first-order rate constants $k_1 = (0{\cdot}601 \pm 0{\cdot}006) \times 10^{-5}\ \mathrm{s}^{-1}$ at 382·7 K, $(1{\cdot}92 \pm 0{\cdot}01) \times 10^{-5}\ \mathrm{s}^{-1}$ at 391·8 K, and $(5{\cdot}05 \pm 0{\cdot}01) \times 10^{-5}\ \mathrm{s}^{-1}$ at 401·2 K. From these rate data the Eyring activation parameters were calculated as $\Delta H^{\ddagger} = 34{\cdot}1 \pm 0{\cdot}2$ kcal/mol and $\Delta S^{\ddagger} = +6{\cdot}6 \pm 0{\cdot}4$ gibbs/mol. For comparison, the values for the β-peroxylactones are $\Delta H^{\ddagger} = 31{\cdot}7$ kcal/mol and $\Delta S^{\ddagger} = +0{\cdot}1$ gibbs/mol.[2] Thus, we find that for the γ-peroxylactone and β-peroxylactones the free energies of activation are $\Delta G^{\ddagger} = 31{\cdot}5$ and 31·7 kcal/mol, respectively at 400 K. Since we suggested that the thermolysis of β-peroxylactones proceeds *via* the 2-oxo-1,5-dioxapentamethylene diradical,[2] in view of the close correspondence in the activation parameters, we are justified in concluding that the thermolysis of γ-peroxylactone (**1**) affords the 2-oxo-1,6-dioxa-hexamethylene diradical (**2**) as the intermediate from which the thermoproducts are derived.

The products of the thermolysis at 120° for 50 h and photolysis at 310 nm (Rayonet RPR-100) in Pyrex vessels for 65 h of 1·0M-*o*-xylene solutions of (**1**) were identified as acetone, ethylene (trapped in form of ethylene dibromide with molecular bromine), 2,2-dimethyloxetan, and methyl propionate, by g.l.c. collection and comparison of retention times and i.r. spectra with those of the authentic materials. No trace of ethyl methyl ketone could be detected.

The quantitative product compositions in terms of absolute yields for the thermolysis and photolysis of (1) are summarized in the Table. The total product balance in each case is better than 97%. Control experiments showed that the oxetan was thermo- and photo-stable under the reaction conditions. Furthermore, a thermally decomposed reaction mixture was submitted to the photolysis conditions and no enhancement of the oxetan yield was observed. This excludes the possibility that the higher oxetan yield in the photolysis arose from photo-addition of acetone to ethylene.[4]

Absolute thermo- and photo-product yields from (**1**)

Mode of decomposition	Acetone[a]	Oxetan[b]	Methyl propionate[a]	Non volatile residue[c]	Unknown
Thermal	87·7 ± 1·7	5·8 ± 0·7	0·5	*ca.* 2·0	*ca.* 2·0
Photochemical	73·7 ± 0·6	16·0 ± 1·0	0·5	*ca.* 3·5	*ca.* 3·0

[a] Determined by quantitative i.r.
[b] Determined by quantitative g.l.c.
[c] Determined gravimetrically.

From the data on hand we conclude that diradical (**2**), generated thermally or photochemically from (**1**), decarboxylates with preferential fragmentation into acetone and ethylene, although significant amounts of cyclization into oxetan is observed, especially in the photolysis. However, it is quite clear that rearrangement of diradical (**2**) *via* a methyl 1,3-shift into ketone (**7**) does not take place even in trace amounts. This is quite contrary, although not entirely surprising in view of the rarity of 1,3-shifts,[5] to our results on the β-peroxylactones,[2] for which the thermally generated 2-oxo-1,5-dioxapentamethylene diradical rearranges preferentially *via* alkyl 1,2-shift, while the photochemically generated 1-oxatrimethylene diradical preferentially cyclizes. Stereolabelling experiments are in progress to decide whether the thermo- and photo-products are formed directly from diradical (**2**) or whether (**2**) decarboxylates to give diradical (**3**), which then serves as precursor to the products.

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