

our larger basis set. The corresponding error in P_2 is 3.9 eV. Since these errors appear to be independent of the magnitude of the dissociation energy, we assumed that we could estimate the dissociation energy of Mo_2H_6 by using these errors as additive corrections.

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Michael B. Hall

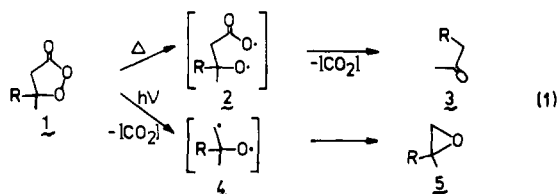
Department of Chemistry, Texas A&M University
 College Station, Texas 77843

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On the Mechanism of β -Peroxylactone Decarboxylation¹

Sir:

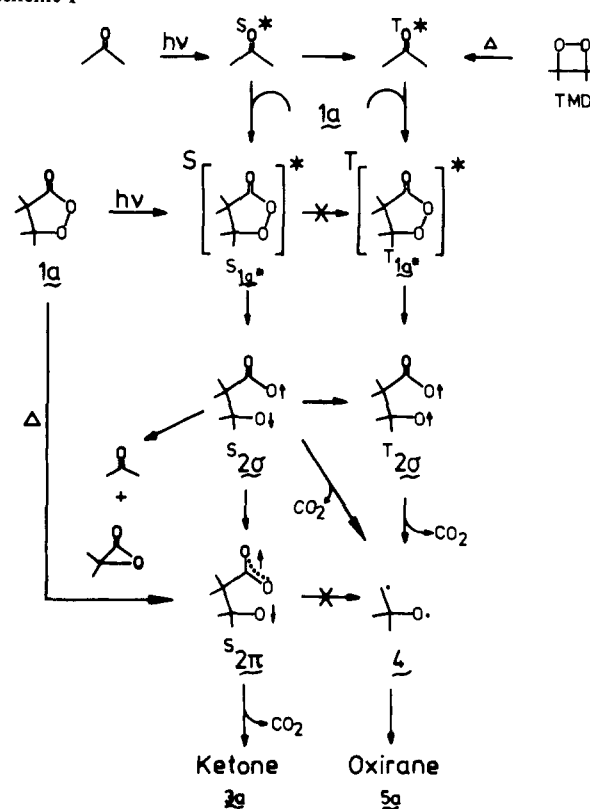
Previous work suggested that the thermolysis² of β -peroxylactones **1** affords the ketone **3** as major product via the 1,5 diradical **2**, while photolysis³ leads predominantly to the epoxide **5** via the 1,3 diradical **4** (eq 1). Herein we present



experimental evidence for the tetramethyl- β -peroxylactone (**1a**), which obliges us to modify this mechanistic interpretation. We postulate that in both decarboxylation modes 1,5 diradicals **2** of different electronic configurations intervene. Our evidence includes the following facts (cf. Table I): (i) thermolysis (125 °C) gives exclusively pinacolone (**3a**); (ii) tetramethyl-1,2-dioxetane (TMD) chemienergization (60 °C) leads exclusively to tetramethyloxirane (**5a**); (iii) direct photolysis (355 nm) affords both pinacolone (**3a**) as major and tetramethyloxirane (**5a**) as minor products; (iv) acetone-sensitized photolysis (313 nm) results predominantly in tetramethyloxirane (**5a**), but the pinacolone product (**3a**) increases with increasing concentration of β -peroxylactone **1a**; (v) photolysis (355 nm) in the presence of piperylene (Pip) causes no alteration of the product composition; (vi) quantum yield of β -peroxylactone disappearance is 100%.

The mechanism which in our opinion accommodates best these unusual results is given in Scheme I. We postulate that the thermolysis gives rise to the singlet state π -type 1,5 diradical $^S2\pi$, the triplet acetone-sensitized process (either via TMD chemienergization⁴ or via photoenergization) leads to the triplet state σ -type 1,5 diradical $^T2\sigma$ via the triplet excited

Scheme I



β -peroxylactone $^T1a^*$, while the direct photolysis affords the singlet state σ -type 1,5 diradical $^S2\sigma$ via the singlet excited β -peroxylactone $^S1a^*$. Intersystem crossing between $^S1a^*$ and $^T1a^*$ appears unlikely because the product compositions of the direct photolysis in the absence and presence of the triplet-state quencher piperylene (facts iii and v, respectively; cf. entries 3 and 5 in Table I) remained constant within experimental error, the TMD chemienergized process gave only oxirane **5a** (fact ii; cf. entry 2 in Table I), and the quantum yield of disappearance of the singlet excited β -peroxylactone is 100% (fact vi), which suggests that the weak peroxide bond in $^S1a^*$ cleaves prior to any spin reorganization.

The fate of the singlet-state π -type 1,5-diradical $^S2\pi$ in the thermolysis is exclusive formation of the rearrangement product pinacolone (fact i; cf. entry 1 in Table I). Although acyloxy radicals decarboxylate considerably more readily than alkoxy radicals undergo β scission,⁵ theoretical considerations⁶ imply that the resonance-stabilized π -type carboxylate radicals should be relatively reluctant in decarboxylating. Since no oxirane **5a** product was formed in the thermolysis, the decarboxylation process $^S2\pi \rightarrow 4$ is not taking place. In fact, the

Table I. Product and Quantum Yields for the Decarboxylation of β -Peroxylactones **1a**

process	conditions	yields, %			total
		ketone 3a	oxirane 5a	acetone	
thermolysis ^a	125 °C, <i>c</i> -C ₆ H ₁₂	100 ± 0.5	0.0	0.0	100 ± 0.5
TMD energized ^{a,b}	60 °C, <i>n</i> -C ₆ H ₁₄	0.9 ± 0.1	97 ± 2	<i>c</i>	98 ± 2
photolysis ^{d,e} (direct)	355 nm, <i>n</i> -C ₆ H ₁₄	49 ± 3	22 ± 1	26 ± 4	97 ± 4
photolysis ^{a,d-f} (sensitized)	313 nm, acetone	32 ± 1	44 ± 1	<i>c</i>	76 ± 2
photolysis ^{d,e} (1.0 M Pip)	355 nm, <i>n</i> -C ₆ H ₁₄	50 ± 2	20 ± 2	25 ± 5	95 ± 5

^a Product yields were determined by GLC. ^b 72 mmol of **1a** and 172 mmol of tetramethyl-1,2-dioxetane in 2 mL of Spectrograde *n*-hexane. ^c In the latter case the acetone product yield could not be determined since acetone was the solvent. Besides, as shown, the acetone yields are essentially constant in those cases in which it could be determined. ^d Quantum yields were determined by GLC for 15–20% consumption of **1a**; remaining **1a** was destroyed by catalytic hydrogenolysis. ^e To minimize product-sensitized decarboxylation of **1a**, we irradiated at as long a wavelength as was feasible. Furthermore, we measured the quantum yields for up to 15–20% β -peroxylactone **1a** consumption. Before GLC quantitation, the excess **1a** was destroyed by catalytic hydrogenolysis. ^f The [3a]/[5a] ratio was 0.08 and 0.70 at 0.01 and 0.10 M [**1a**], respectively.

migratory aptitude of β -alkyl groups in β -peroxylactones follows the ease of alkoxy radical fragmentation, i.e., $i\text{-Pr} > \text{Et} > \text{Me} > \text{Ph}$,^{2b} indicating that the driving force for rearrangement is alkoxy center dominated. These facts corroborate the suggestion that the 1,5 diradical $^S2\pi$ is very selective in its chemical behavior.

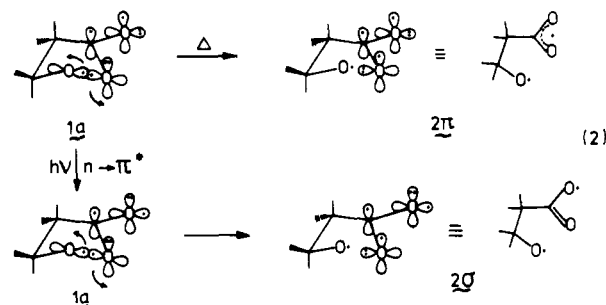
The fate of the triplet state σ -type 1,5 diradical $^T2\sigma$ is also quite well defined since the TMD chemienergized process (fact ii; cf. entry 2 in Table I) affords exclusively oxirane **5a** via triplet acetone sensitization. Whether $^T2\sigma$ relaxes into the more stable $^T2\pi$ 1,5 diradical or whether it directly decarboxylates into the 1,3 diradical **4** cannot be differentiated on the basis of our results. The disadvantage of a π -type 1,5 diradical $^T2\pi$ is that decarboxylation should be more difficult. However, it is clear from previous stereolabeling experiments³ that the 1,3 diradical is the immediate precursor to the oxirane product.

The most complex behavior is exhibited by the singlet-state σ -type 1,5 diradical $^S2\pi$, which is formed in the direct photolysis (fact iii; cf. entry 3 in Table I) and the acetone-sensitized photolysis (fact iv; cf. entry 4 in Table I) via the singlet excited β -peroxylactone $^S1a^*$. Since in the *acetone-sensitized photolysis increasing β -peroxylactone concentration leads to proportionally more pinacolone vs. oxirane product* (cf. footnote f in Table I), it appears that the β -peroxylactone is an effective quencher of singlet excited acetone in order to intervene with the efficient intersystem crossing to triplet excited acetone.

Why do we need to propose a singlet-state σ -type 1,5 diradical $^S2\sigma$ as an intermediate? The direct photolysis and acetone-sensitized photolysis lead to pinacolone, oxirane, and acetone products. Since the pinacolone is $^S2\pi$ derived and the oxirane $^T2\sigma$ derived, for the direct photolysis we need a branching point in our mechanism to interconnect these intermediates. The branching point must come after the intersystem-crossing step $^S1a^* \rightarrow ^T1a^*$ since the direct photolysis in the presence of the triplet-state quencher piperylene did not alter the product composition (facts iii and v; compare entries 3 and 5 in Table I). The new intermediate representing this branching point must be able to relax into the stabilized singlet-state π -type 1,5 diradical $^S2\pi$ to account for pinacolone product, it must either intersystem cross to the triplet-state σ -type 1,5 diradical $^T2\sigma$ or decarboxylate into the 1,3 diradical **4** to account for the oxirane product, and it must be able to fragment into acetone and presumably α -lactone product. The most probable candidate that in our opinion embodies all these requisites is the singlet-state σ -type 1,5-diradical $^S2\sigma$, an electronic isomer of the more stable $^S2\pi$ species.⁷

To suppose that the singlet excited β -peroxylactone $^S1a^*$ in the direct photolysis decarboxylates in part into the 1,3 diradical **4** in order to account for the oxirane product and in part affords a singlet 1,5 diradical **2** (without distinction of σ - and π -type electronic configurations) would require a similar behavior for the triplet excited β -peroxylactone $^T1a^*$ in the TMD chemienergized process. However, only oxirane product is formed in the latter case (fact ii; cf. entry 2 in Table I). It appears to us that the above mechanistic premise, which was the one we originally proposed,^{2,3} should afford pinacolone, oxirane, and acetone products in the TMD chemienergized process.

As to the question of why the thermal and photochemical activation processes of β -peroxylactone **1a** lead to 1,5 diradicals of distinct electronic configurations, i.e., 2π and 2σ , cogent arguments are presented in the orbital diagrams of eq 2. In the thermal mode, the already tense five-membered ring, shown in the conformation with an optimal dihedral angle of the peroxide bond, must shear apart rather than stretch apart the oxygen atoms, as indicated by the arrows. This vibrational motion seems to be quite suitable to overlap the odd-electron orbital with the carbonyl bond in generating a 2π -type 1,5



diradical. On the other hand, the photochemical mode appears to be n,π^* derived.⁸ Consequently, suitable line up of the odd-electron orbital that is developing at the carboxylate oxygen through the twisting mode in the n,π^* excited **1a** leads to the 2σ -type 1,5-dioxy radical.

Although other mechanistic interpretations are possible, our suggestion that a common 1,5 diradical, but of distinct electronic configuration, intervenes in the thermal and photochemical decarboxylation of β -peroxylactones is an attractive and internally consistent rationalization of our unusual results. It would be more reassuring if we could provide direct evidence for the 1,5 diradical in the photochemical process. Such experiments are difficult, but attempts along these lines are being presently pursued.

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- (9) NIH Career Development Awardee, 1975-1980.

Waldemar Adam,⁹ Omar Cueto, Luis N. Guedes
Department of Chemistry, University of Puerto Rico
Rio Piedras, Puerto Rico 00931

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2,3-Benzobicyclo[2.2.2]oct-2-ene-5,7-diyl Diradical as a Common Intermediate in the Di- π -methane Rearrangement of 6,7-Benzobicyclo[3.2.1]octa-2,6-diene and the Denitrogenation of the Corresponding Tricycloazoalkane

Sir:

The ubiquitous di- π -methane reaction has been one of the fascinating photorearrangements, both for mechanistic and synthetic investigations.¹ For example, 6,7-benzobicyclo[3.2.1]octa-2,6-diene (**1**) rearranges into 3,4-benzotricyclo[3.2.1:0.2²]oct-3-ene (**2**) on direct (254 nm) or acetone-sensitized (300 nm) photolysis, presumably via the postulated diradicals **3** and **4** (eq 1).² Recently it has been shown³ that