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Rearrangement of an Excited β,γ -Unsaturated Ketone Generated by Dioxetane Thermolysis. On the T₁ (π,π^*) and T₂ (n,π^*) Reactivities

Sir:

Most β,γ -enones undergo two characteristic photoreactions: a triplet sensitized oxadi- π -methane (ODPM) rearrangement which is assumed to occur from the lowest lying $^3\pi,\pi^*$ state, and an allylic 1,3-acyl shift upon direct irradiation which is commonly ascribed to an $^1n,\pi^*$ state.¹⁻³ However, it has recently been pointed out that all available evidence can also be

Table I. Direct and Triplet-Sensitized Photolysis of **1** at 25 °C. Quantum Yields of Conversion and Product Formation^a

excitation	Φ_{-1}	Φ_2	Φ_3	Φ_2/Φ_3
direct ^b	0.65	0.20	0.04	5.0
sensitized ^c	0.70	0.015	0.46 ^d	0.033

^a Conversions $\leq 20\%$. Φ values were measured with argon-degassed solutions in an electronically integrating actinometer: W. Amrein, J. Gloor, and K. Schaffner, *Chimia*, **28**, 185 (1974). Product analysis was by GLC. Overall experimental error was ca. $\pm 7\%$. ^b 0.1 M in cyclohexane, 313 nm. ^c 0.22 M in acetone, 254 nm. ^d Endo-exo isomer ratio 1:30.

Table II. Rearrangement Products of **1** at 80 °C

starting material	excitation	products ^a		ratio of 2/3
		2, %	3, %	
1 ^b	direct, λ 313 nm, in acetonitrile	15.3	5.6	2.73
1 ^b	sensitized, λ 254 nm, in acetone	2.3	74.4	0.031
5a,b ^c	thermal decomposition (20 min) in acetonitrile	(1.9 \pm 0.3)	(2.7 \pm 0.3)	0.70

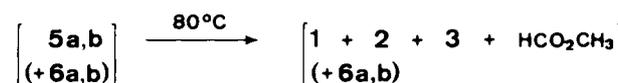
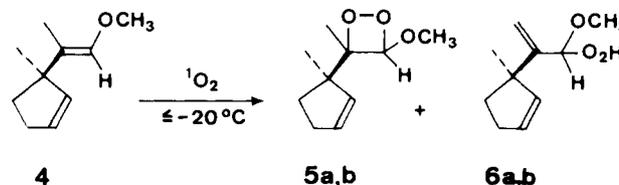
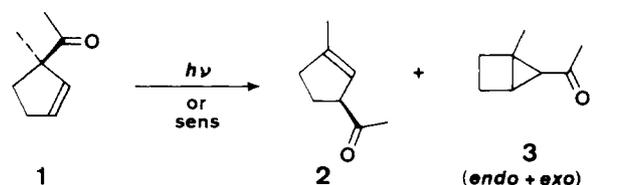
^a Conversions $\leq 25\%$. Yields are based on converted starting material. ^b Average values from two runs. ^c Average values from six runs.

reconciled with a 1,3 shift from a short-lived T₂ state dominantly n,π^* in character.^{2,4-6} As yet, allylic 1,3 shifts from $^3n,\pi^*$ states have only been found with 3-benzoylcyclopentenes which, however, do not undergo the ODPM rearrangement.⁷

We report now on work designed to probe into the reactivity of the $^3n,\pi^*$ state of 3-acetyl-3-methylcyclopentene (**1**), generated by thermal decomposition of the dioxetanes **5a,b**.⁸ The product distribution obtained was compared with that from direct and triplet-sensitized photolyses.⁹

The photochemistry of ketone **1**¹⁰ closely parallels that of other 3-acetylcyclopentenes.^{2,11} At 25 °C, direct irradiation preferentially yielded the 1,3-acetyl shift product **2**, whereas acetone sensitization favored the ODPM rearrangement to **3** (Table I). As with other β,γ -unsaturated ketones,^{4,5} fluorescence of **1** was observed at λ_{\max} 410 nm ($\tau_F = 4.5 \pm 0.5$ ns and $\Phi_F = (9 \pm 3) \times 10^{-4}$ in acetonitrile at 25 °C).

Enol ether **4** (0.2 M) was photooxygenated in deuterioacetonitrile at ≤ -20 °C with polymer-bound rose bengal and light from a sodium vapor lamp. Monitoring by NMR¹² indicated a selective attack of 1O_2 at the enol ether double bond and formation of the two diastereoisomeric dioxetanes **5a** and **5b**¹³ ($\sim 12\%$ each) and the hydroperoxides **6a** and **6b** (75%).



When the crude photooxygenation mixture was heated to 80 °C, chemiluminescence identical with the fluorescence of **1** was recorded. The luminescence decreased exponentially with $\tau_{1/2}$ (80 °C) = 375 ± 15 s. After 20 min, when it had reached $< 10\%$ of its original intensity, $\geq 90\%$ of **5a,b** had decomposed to methyl formate and the isomers **1**, **2**, and **3** (analysis of the thermolyzed solution by NMR, GLC, and GLC/mass spectrometry; ratio of **1**:**2**:**3**, 95.4:1.9:2.7).¹⁴ The concentration of **6a,b** remained unchanged within a 10% margin in this experiment. The formation of rearranged ketones (**2** and **3**) indicates that dioxetane cleavage had in part produced excited states of ketone **1**, and the chemiluminescence in turn identifies a fraction of these as the excited singlet. Using luminol as a chemiluminescence standard,¹⁵ a fluores-

cence efficiency of $\eta_F \leq 6 \times 10^{-6}$ was found for the dioxetane decomposition.¹⁶ This value allows for an upper limit of 15% excited singlet vs. at least 85% triplet ketone formed in the reaction,¹⁷ which thus falls in line with the large majority of thermal dioxetane decompositions known to yield a high triplet:singlet ratio of excited states.^{8,18}

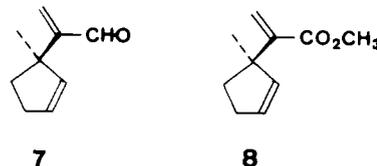
We may therefore assume that the rearranged products from thermolyzed **5a,b** had formed predominantly via the triplet ketone manifold.¹⁹ With this in mind, inspection of the relative yields at 80 °C (Table II) reveals a striking discrepancy in the product distribution (**2** and **3**) obtained from the two triplet reactions. The acetone-sensitized reaction of **1** gave **3** in a much higher proportion than the decomposition of **5a,b**. This result demands the existence of two triplet states of **1** with different reactivities, which are not populated equally by the two modes of generation. This is in accord with a modified²⁰ CNDO/S calculation of **1** indicating two triplets with predominantly $^3n,\pi^*$ and $^3\pi,\pi^*$ character, respectively, and with energies separated by no more than 12 kJ/mol.²¹

Enone **1** and cyclopentene²² quenched acetone phosphorescence with similar rates (2×10^7 and $1.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, respectively), about ten times faster than energy transfer rates between saturated ketones.^{8b} This supports the widely accepted assumption¹⁻³ that triplet acetone preferably sensitizes the $^3\pi,\pi^*$ state of **1** which then undergoes the ODPM rearrangement. Similarly, the π,π^* configuration has also been established for the lowest lying ODPM-reactive triplet of the 1-phenyl analogue of **1**.¹¹ On the other hand, the excited states generated from dioxetanes **5a,b** should be at least predominantly $^3n,\pi^*$.²³ It should therefore be the $^3n,\pi^*$ state from which the triplet-born 1,3-shifted product **2** derives. In fact, the ratio of **2** and **3** obtained on thermal decomposition of **5a,b** clearly indicates that the 1,3 shift from $^3n,\pi^*$ and the internal conversion from $^3n,\pi^*$ to $^3\pi,\pi^*$ occur at comparable rates. Yet, the dioxetane experiment does not exclude the occurrence of this reaction also from the $^1n,\pi^*$ state, and indeed the 2:3 ratio from the direct irradiation of **1** is even higher than from the dioxetane decomposition. Provided that vibrational modes do not control the reaction selectivity, the photochemical result is most adequately explained by 1,3 shifts from both the $^1n,\pi^*$ and $^3n,\pi^*$ states.²⁴

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