

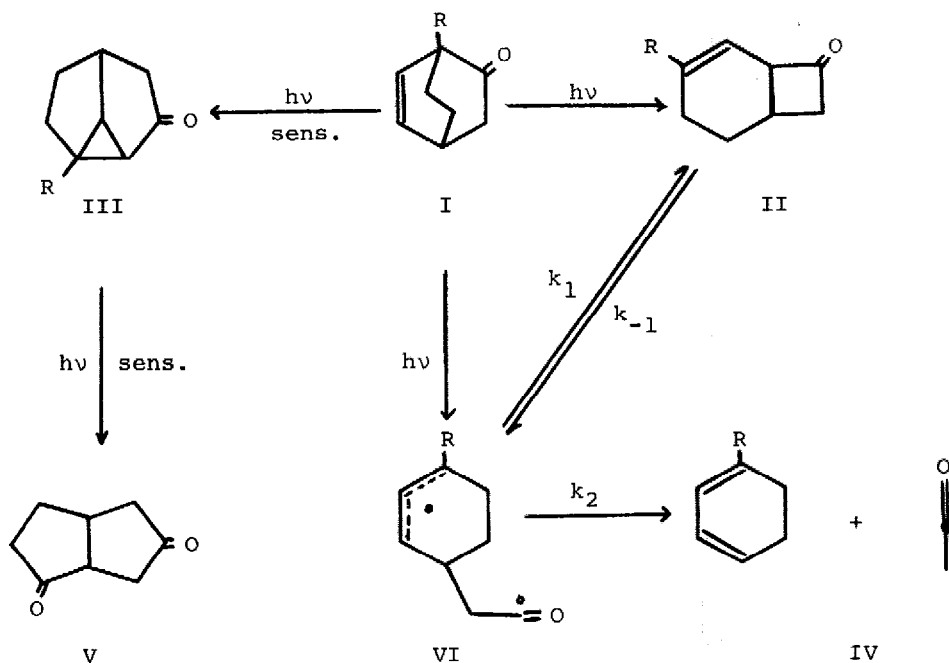
PHOTOCHEMISTRY OF $\beta\gamma$ -ENONES: 1-METHOXYBICYCLO (2.2.2) OCT-5-EN-2-ONE

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The diverse photochemistry of $\beta\gamma$ -enones has attracted much attention and is the subject of two recent reviews¹. In the course of a study of the effects of structure, and in particular, of substituent groups on such photochemistry^{cf. 2}, we have investigated the title compound and its 3-ketoisomer. Some of our results are presented here and in the accompanying communication.

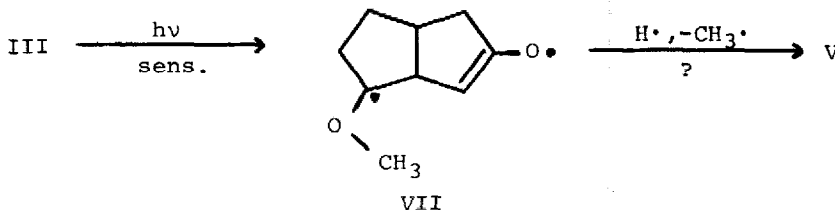


a). R=H; b). R= -OMe

Irradiation³ of Ib⁴ in benzene, ether, heptane or methanol gave the 1,3-acyl shift product (IIb) (see Table)⁵. The chemical yield of IIb was low, because of its photochemical decay to 1-methoxycyclohexa-1,3-diene and ketene (IVb).

In their study of the parent ketone (Ia), Givens *et al.*⁷ concluded that the 1,3-acyl shift was a concerted process from the (n,π*) singlet state, ketene being subsequently formed via the diradical VIa. Houk^{1a} has suggested that their results might also be accommodated by a mechanism involving α-cleavage to VIa as the primary photochemical step, followed by fast and reversible ring closure to IIa and only slow cleavage to ketene ($k_1 \gg k_2$). We have measured the relative yield of IVb (and derived photoproducts) and IIb as a function of time. Extrapolation to zero time shows clearly that ketene formation is competitive with 1,3-acyl shift in the initial stages of the reaction. We conclude that the primary photochemical process is α-cleavage of the (n,π*) singlet state¹⁴ of Ib to the diradical VIb, followed by nearly equal partitioning between ring closure to IIb and cleavage to IVb ($k_2 \approx 0.8k_1$)⁸. It seems reasonable to attribute the difference in behaviour between Ia and Ib to the stabilising effect of the 1-methoxy group on the diradical VIb⁹. A similar enhancement of an α-cleavage associated with radical-stabilising α-substituents has recently been observed¹⁰.

The triplet photochemistry of Ib is also of interest. Irradiation³ in acetone or in benzene solution with acetophenone as sensitiser¹¹ yielded only very small amounts of the expected oxa-di-π-methane product (IIIb), the main product being the diketone (V) (see Table). The detailed mechanism of the conversion of IIIb to V has not yet been studied, but presumably involves β-cleavage followed by the (formal) loss of methyl and capture of a hydrogen atom.



The β-cleavage reactions of cyclopropyl ketones are well known¹² but do not normally appear to intervene in oxa-di-π-methane reactions. The stabilising effect of the methoxy group on the diradical VII⁹ may be held responsible for the anomalous behaviour of IIIb.

Table: quantum yields for photochemistry of Ib.

Reaction	Solvent	Φ_{-I}	Φ_{II}	Φ_{III}	Φ_V
Direct irradiation of Ib	benzene ^a	0.8	0.5		
	heptane ^a	0.8	0.5		
	methanol ^a	0.5 ⁶			
Acetone sensitization	acetone ^b	0.26	0.06	0.02	0.05
Acetophenone sensitization	benzene ^c	0.034	<0.005		0.016

(a) 0.06M; 10% reaction; 300 nm lamps.

(b) 0.065M; 30% reaction; 300 nm lamps.

(c) 0.068M in Ib; 0.057M in acetophenone; 350 nm lamps.

The formation of IIb in the acetone or acetophenone sensitised reaction of Ib suggests the occurrence of a triplet 1,3-acyl shift¹³. However, the formation of IIb is unaffected by the presence of piperylene or cyclohexadiene, while that of IIIb and V is efficiently quenched. It seems that in this case, IIb must arise from the (n, π^*) singlet state¹⁴, and further, the magnitude of Φ_{IIb} suggests that singlet energy transfer from acetone is involved, in addition to residual direct irradiation¹⁵.

These results led us to re-examine the sensitised reactions of bicyclo (2.2.2)oct-5-en-2-one (Ia)⁷ and norbornenone^{13a}. As expected, we found that IIa is formed in addition to IIIa (10% in acetone; trace in presence of acetophenone), and is unaffected by concentrations of piperylene which completely quench the production of IIIa. Exactly similar results in the case of norbornenone lead us to conclude that the recently described triplet 1,3-acyl shift reaction of this ketone is extremely inefficient and quite possibly illusory¹⁶. It would appear that the enhanced extinction coefficients of β -enones, coupled with residual direct irradiation which is unavoidable in acetone, and difficult to eradicate completely in acetophenone sensitisation, makes the identification of processes which are efficient from the singlet but inefficient from the triplet state, particularly difficult. We suggest that triplet 1,3-acyl shifts may be even rarer than has been supposed.

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Note: benzophenone is not a sensitizer for this reaction.
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14. Or from a very short-lived, unquenchable triplet state.
15. The inefficient production of I Ib ($\phi < 0.01$) on irradiation at 350 nm with acetophenone as sensitizer, must be attributed to incomplete filtering.
16. Energy transfer from acetone triplets generated by the thermolysis of tetramethyldioxetane¹⁷ leads, in the cases of Ia, Ib and norbornenone to no significant quantity of 1,3-acyl shift products, in support of these conclusions.
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