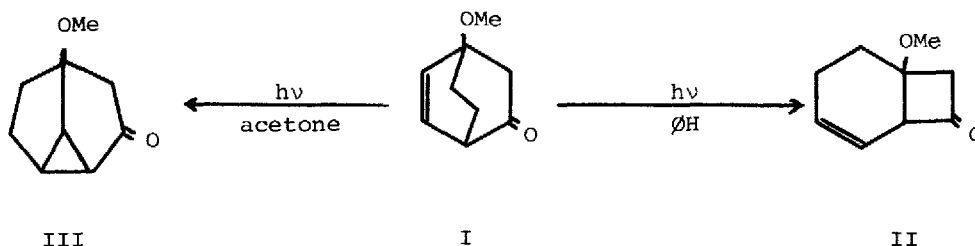


PHOTOCHEMISTRY OF 1-METHOXYBICYCLO (2.2.2) OCT-5-EN-3-ONE:
A SINGLET OXA-DI- π -METHANE REARRANGEMENT

T. Eckersley¹, S.D.Parker and N. A. J. Rogers*,
Chemistry Department, Lancaster University.

(Received in UK 6 October 1976; accepted for publication 18 October 1976)



As part of a study on the effect of structure, and in particular of substituent groups on the photochemistry of $\beta\gamma$ -enones², we have studied the photochemical transformations of the title compound (I). Superficially, the familiar dichotomy³ between singlet 1,3-acyl shift (300 nm in benzene, ether, methanol or pentane solution: product II) and triplet oxa-di- π -methane rearrangement (300 nm in acetone solution: product III) was observed. Closer examination revealed that in acetone, III was accompanied by a small percentage of the 1,3-acyl shift product (II). The efficiency of this process suggested that it might be associated with light absorption by the ketone (I) (see Table and preceding paper).

More significantly, direct irradiation in a variety of solvents gave a low but reproducible yield of the oxa-di- π -methane product (III) in addition to the expected cyclobutanone (II) (see Table). Addition of piperylene or cyclohexadiene failed to quench the production of III although at very high piperylene concentrations the yields of both II and III were reduced by the same proportion, suggesting that they originate from the same excited singlet state⁴.

Although several cases of oxa-di- π -methane reactions resulting from direct irradiation are known^{cf. 5,3b}, this would appear to be the first observation of such a reaction occurring from a singlet state of a structurally simple $\beta\gamma$ -enone.

We are continuing investigations in an effort to elucidate the factors governing the partition between 1,3-acyl shift, α -cleavage (with concomitant ketene loss, or hydrogen abstraction) and oxa-di- π -methane rearrangement from the singlet and triplet states of $\beta\gamma$ -enones. A careful re-examination has revealed no oxadi- π -methane product accompanying direct irradiation at 300 nm of norbornenone^{cf. 6}, 1-methoxybicyclo (2.2.2) oct-5-en-2-one² or bicyclo (2.2.2) oct-5-en-2-one⁷. The latter ketone did give a low yield of the corresponding oxa-di- π -methane product on irradiation in benzene at 254 nm (excitation principally by singlet energy transfer), but this product is quenched by piperylene. Its formation must therefore be associated with intersystem crossing of benzene, and subsequent triplet energy transfer.

Table

Solvent	(I)	(ϕ_{-I})	(ϕ_{II})	(ϕ_{III})	% reaction (reaction time)
Benzene	0.066M	0.78	0.54	0.024	14 (6 minutes)
Benzene (a)	0.065M		0.21	0.01	(30 minutes)
Benzene (b)	0.065M		0.14	0.008	(30 minutes)
Acetone	0.063M	0.64	0.036 (c)	0.46	72 (30 minutes)

(a) 0.28M piperylene (b) 1.47M piperylene

(c) $E_{max} = 140$; corresponding to $\sim 4\%$ of incident light absorbed by I.

REFERENCES

1. Work performed during final year undergraduate research project.
2. See previous paper.
3. (a) K. N. Houk, Chem. Rev., **76**, 1 (1976):
(b) W. G. Dauben, G. Lodder and J. Ipaktschi, Fortschr. Chem. Forsch., **54**, 73 (1975).
4. Or very short-lived triplet state.
5. J. R. Williams and H. Ziffer Chem. Comm., **194**, 468 (1967).
6. M. A. Schexnayder and P. S. Engel, Tet. Letters, 1153 (1975).
7. R. S. Givens and W. F. Oettle, J. Amer. Chem. Soc., **93**, 3963 (1971).