A New Photochemical Reaction of βγ-Unsaturated Ketones

By R. C. Cookson* and N. R. Rogers
(*Department of Chemistry, The University, Southampton* SO9 5NH)

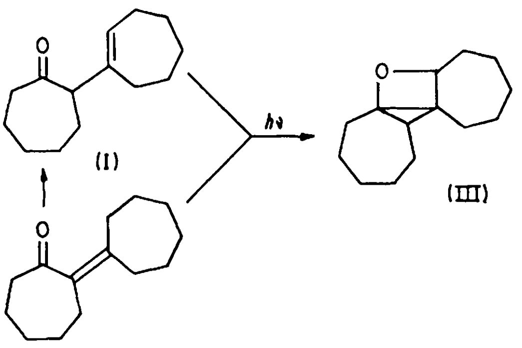
Summary Ultraviolet irradiation of 2-cyclohept-1-enylcycloheptanone (I) and of 2-cyclo-oct-1-enylcyclo-octanone (II) gives the oxetans (III) and (IV), whereas 2-cyclohex-1-enylcyclohexanone (V) forms the cyclobutanol (VII).

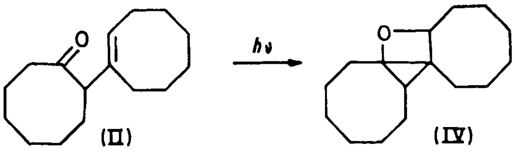
The most frequently reported transformations of βγ-unsaturated ketones on irradiation are 1,3 and 1,2 acyl shifts from, respectively, the excited singlet and excited triplet states.[1] The formation of isomeric cyclobutanols is an important photochemical reaction if there is a γ-hydrogen atom that can be readily abstracted.[2]

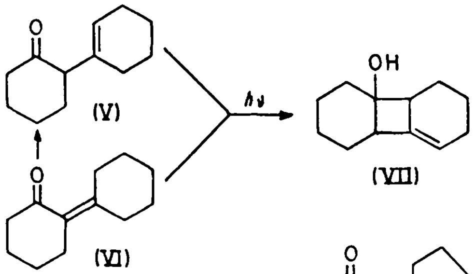
We now report a new photochemical reaction of βγ-unsaturated ketones. The compounds (I) and (II) dissolved in cyclohexane, benzene, or methanol and irradiated with a 450 W Hanovia medium-pressure mercury arc lamp through a Pyrex filter gave the oxetans (III) and (IV) as the major photoproducts as a mixture of stereoisomers.† The 2-oxabicyclo[2,1,0]pentane structures (III) and (IV) rather than the alternative 2-oxabicyclo[1,1,1]pentanes were established by the cyclopropyl proton n.m.r. resonance‡ and by the reversion of the photoisomers into the original ketones on treatment with acid. Oxetans have been reported as photoproducts of γδ-unsaturated ketones[3] but not of βγ-unsaturated ketones.

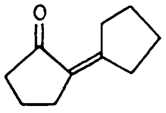
The starting material (I) was a mixture of the αβ- (60%) and βγ- (40%) isomers and (II) contained ⩾ 70% of the βγ-isomer. Our results showed that on direct irradiation the βγ-isomer was responsible for the formation of the oxetans and that deconjugation αβ → βγ also occurred. Irradiation of (I) in acetone resulted in αβ → βγ isomerisation but not in the production of oxetans.

In contrast irradiation of the equilibrium mixture of (V) and (VI) [90% (V), 10% (VI)] or of pure (VI), dissolved in cyclohexane, gave a cyclobutanol (VII) as the major photoproduct. The compound (VII) was easily converted back into the equilibrium mixture of starting materials by acid or heat. Irradiation of (VI) in acetone gave a small amount of the cyclobutanol but the major photoproduct was (V) from αβ → βγ isomerisation. I.r. spectroscopy indicated that the conversion (VI) → (V) occurred on direct irradiation, followed by reaction to (VII); this is also consistent with the faster formation of (VII) from (VI) in methanol than in hydrocarbon solvents.









(VIII)

The ketone (VIII) was inert to direct or sensitised irradiation, presumably owing to the unfavourable conformation for hydrogen transfer, or the rapid thermal reversion of the βγ-isomer to (VIII).

---

† One stereoisomer of (III) was rapidly converted into another at 70°.

‡ At δ 0·5 p.p.m. for both stereoisomers of (III) and at δ 0·39 and 0·65 p.p.m. for the two stereoisomers of (IV).

The variation of behaviour with ring size has a counterpart in the reported reactions of acetone and cyclo-olefins on irradiation.[4] Cyclo-octene combines with acetone to give oxetans whereas cyclohexene reacts to give alcohols. In our system conformational factors may also inhibit oxetan formation from (V).

There was no evidence of products from 1,3- or 1,2-acyl shifts from any of the ketones.

We thank Dr. R. Baker for helpful discussion and advice, and acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(*Received*, *22nd May* 1972; *Com.* 884.)

---

[1] *E.g.* J. Ipaktschi, *Tetrahedron Letters*, 1969, 2153; 1970, 3179; D. I. Schuster and D. H. Sussman, *ibid.*, 1970, 1661; K. G. Hancock and R. O. Grider, *ibid.*, 1971, 4281; 1972, 1367; D. I. Schuster, G. R. Underwood, and T. P. Knudsen, *J. Amer. Chem. Soc.*, 1971, **93**, 4304; L. A. Paquette, R. E. Eizenber, and O. Cox, *ibid.*, 1970, **90**, 5153; J. R. Williams and G. M. Sarkisian, *Chem. Comm.*, 1971, 1564 E. Baggiolini, K. Schaffner, and O. Jeger, *ibid.*, 1969, 1103.

[2] N. C. Yang and D. Thap, *Tetrahedron Letters*, 1966, 3671; E. F. Keifer and D. A. Carlson, *ibid.*, 1967, 1617; R. C. Cookson, J. Hudec, G. E. Usher, and A. Szabo, *Tetrahedron*, 1968, **24**, 4353.

[3] *E.g.* S. R. Kurowsky and H. Morrison, *J. Amer. Chem. Soc.*, 1972, **94**, 507.

[4] K. Shima, Y. Sakai, and H. Sakurai, *Bull. Chem. Soc. Japan*, 1971, **44**, 215.