Tetrahedron Letters No.40, pp. 3479-3482, 1970. Pergamon Press. Printed in Great Britain.

SOME PHOTOCHEMICAL REACTIONS OF α-DIKETONES WITH OLEFINS

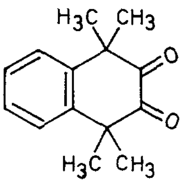
G.E. Gream, M. Mular, and J.C. Paice

Organic Chemistry Department, University of Adelaide
Adelaide, South Australia 5001

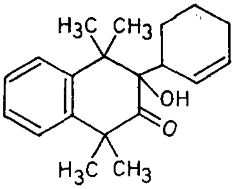
(Received in UK 7 July 1970; accepted for publication 29 July 1970)

The very recent communication by Sakurai and co-workers[1] on the photoreactions of biacetyl with furan, ethyl vinyl ether, indene and 2-methylbut-2-ene prompts us to report some results of our studies on the photochemistry of non-enolisable α-diketones[2] with olefins.

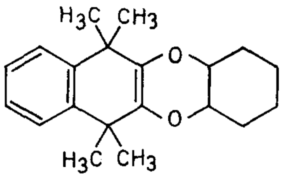
Irradiation[3] (4 hr) of 1,1,4,4-tetramethyl-2,3-dioxotetralin (I) in cyclohexene gave bicyclohexenyl, 2-hydroxy-1,1,4,4-tetramethyl-3-oxotetralin (5%), 2-(cyclohex-3-enyl)-2-hydroxy-1,1,4,4-tetramethyl-3-oxotetralin (II)[4] (70%), m.p. 92-93°, and the dioxene III (6%), m.p. 70.5-72°. Although its n.m.r. spectrum indicated that it was a mixture of the two diastereoisomers, the photo-product II could not be separated into the two components.



I

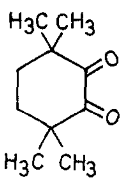


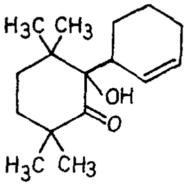
II

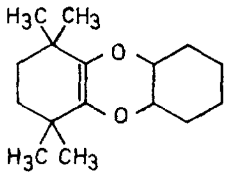


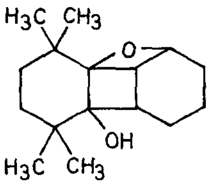
III

When 3,3,6,6-tetramethyl-1,2-dioxocyclohexane (IV) was irradiated (12 hr) in cyclohexene, the products included bicyclohexenyl, 2-hydroxy-3,3,6,6-tetramethylcyclohexanone (7%), a mixture (47%) of the two diastereoisomers (A, m.p. 67-68°, and B, m.p. 71-72°, in the ratio of 3 : 2) of 2-(cyclohex-3-enyl)-2-hydroxy-3,3,6,6-tetramethylcyclohexanone (V), the dioxene VI (7%), b.p. 120° (block temp)/25 mm, and the hydroxyoxetane VII (6%), m.p. 124-126°. That compound VII was a secondary photochemical product was shown when it was formed in good yield on irradiation of the diastereoisomer A in benzene.

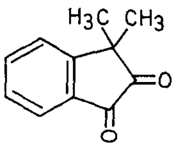

IV

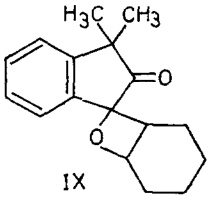

V

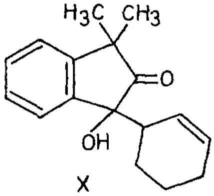

VI


VII

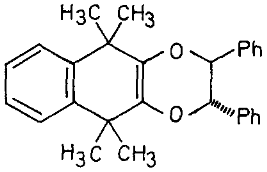
With cyclohexene as solvent, irradiation (4 hr) of 3,3-dimethyl-1,2-dioxoindane (VIII) gave bicyclohexenyl, the keto-oxetane IX (22%), m.p. 78-80°, and 1-(cyclohex-3-enyl)-1-hydroxy-3,3-dimethylindanone (X) (15%), m.p. 91-93°.

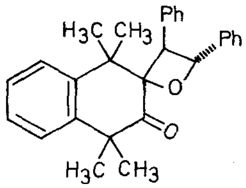

VIII

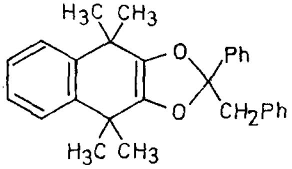

IX


X

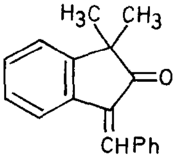
When I was irradiated (42 hr) in the presence of stilbene, the products included the dioxene XI (24%), m.p. 200.5-202, the keto-oxetane XII (25%), m.p. 139-141°, 2-hydroxy-1,1,4,4-tetramethyl-3-oxotetralin (15%) and a compound (3%), m.p. 273.5-275°, tentatively identified as the dioxole derivative XIII on the basis of microanalytical, and infrared and mass spectral data. An n.m.r. spectrum could not be obtained because of the solubility properties of the compound.


XI

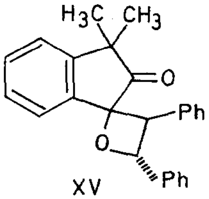

XII


XIII

Irradiation (54 hr) of VIII in the presence of stilbene gave benzaldehyde (3%), 1-benzal-3,3-dimethylindanone (XIV) (10%), b.p. 195° (block temp)/0.5 mm and the keto-oxetane XV (7%), m.p. 174-176°. When XV was itself irradiated in benzene, compound XIV was identified as one of the products.

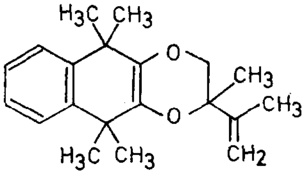


XIV

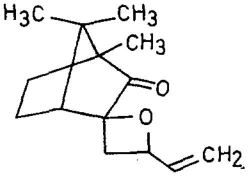


XV

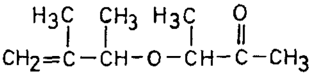
When the α-diketone I was irradiated in the presence of 2,3-dimethylbuta-1,3-diene, the sole product was the dioxene XVI (80%), b.p. 100° (block temp)/0.05 mm. This result contrasts with the recent report[5] that camphorquinone yields the keto-oxetane XVII when irradiated in the presence of buta-1,3-diene. The α-diketone VIII gave only intractable material when irradiated with 2,3-dimethylbuta-1,3-diene.



XVI



XVII



$CH_2{=}C(CH_3)-CH(CH_3)-O-CH(CH_3)-C(=O)-CH_3$

XVIII

In the work described by Sakurai and co-workers[1], biacetyl formed in general only α-keto-oxetanes when irradiated with furan, ethyl vinyl ether, indene and 2-methylbut-2-ene. Only in the case of the last mentioned olefin was an additional type of product formed: it was compound XVIII. de Mayo[6] and Bentrude[7] have reported that biacetyl is photo-reactive in cyclohexene and gives 2-(cyclohex-3-enyl)-2-hydroxybutan-3-one (as a mixture of diastereoisomers) and 3,4-dihydroxy-3,4-dimethylhexane-2,5-dione as the major products. The reactions described by us show that unconjugated non-enolisable α-diketones can form a wider variety of products when irradiated with olefins than has been previously reported.[1,6,7] Many of the reactions are in fact analogous to those undergone by phenanthrene-9,10-quinone.[8]

References

1. H-S Ruang, K. Shima and H. Sakurai, Tetrahedron Letters, 1091 (1970).
2. For previous work from these laboratories, see G.E. Gream and J.C. Paice, Austral.J.Chem., 22, 1249 (1969); G.E. Gream, J.C. Paice and B.S.J. Uszynski, Chem.Comm.; in press.
3. The irradiations reported here were carried out (under N_2) with 1% solutions of the α-diketones in a pyrex reactor equipped with a Philips 125-W mercury quartz high pressure lamp cooled by a water jacket. The olefins were used as follows: cyclohexene as neat solvent; stilbene (1 g) dissolved in benzene (100 ml); 2,3-dimethylbuta-1,3-diene (10 ml) in benzene (90 ml).
4. Satisfactory analyses and spectral data in complete accord with proposed structures have been obtained for all new compounds.
5. W.L. Dilling, R.D. Kroening and J.C. Little, J.Amer.Chem.Soc., 92, 928 (1970).
6. P.W. Jolly and P. de Mayo, Canad.J.Chem., 42, 170, (1964).
7. W.G. Bentrude and K.R. Darnall, Chem.Comm., 810 (1968).
8. M.B. Rubin, Fortschr.chem.Forsch., 13, 251 (1970) and references therein.