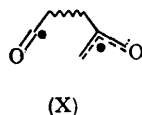
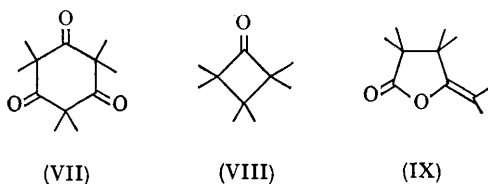
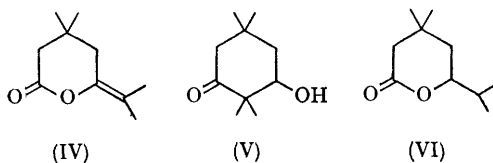
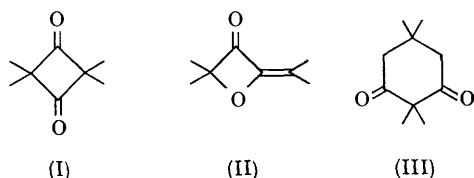


Photochemistry of β -Diketones

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THE equilibration of cyclic non-enolisable β -diketones with the isomeric enol lactones, induced by heat, acid, or base, has long been known.¹



We describe here the conversion of some β -diketones into enol lactones by ultraviolet light filtered through Pyrex glass.

Irradiation of tetramethylcyclobutane-1,3-dione (I) in ether, dioxan, or tetrahydrofuran gave a low yield of the enol lactone (II) in addition to several other products.

On irradiation in ethanol or cyclohexane the dione (III) isomerised to the enol lactone (IV) (35–56% yield) [ν_{\max} . (neat) 1755, 1695, and 1215 cm^{-1} ; p.m.r. (CCl_4) τ 8.98 (intensity 6), 8.36 (3), 8.27 (3), and 7.74 (4)], the structure of which was confirmed by hydrolysis to the same 3,3,6-trimethyl-5-oxoheptanoic acid² as (III). None of the isomeric endocyclic enol lactone was present, although it has recently been mentioned as a product from the unfiltered light of a high-pressure mercury arc.³ The ketol (V) [m.p. 51°, from reduction of (III) with sodium borohydride] rearranged to the saturated lactone (VI) (70% yield) [ν_{\max} . (neat) 1730 and 1250 cm^{-1} ; p.m.r. (CCl_4) isopropyl Me_2 τ 9.05 and 9.01 (two doublets, $J = 6.6$ c./sec.), gem- Me_2 8.96 and 8.93, 4- CH_2 ca. 8.5 (multiplet), isopropyl CH ca. 8.3 (multiplet), OCH 5.98 (octet; $J = 5.1, 5.4,$ and 10.6 c./sec.), 2- CH_2 7.75 and 7.93 (quartet; $J = 16$ c./sec.)], identical with a sample formed by reduction of (IV).

The trione (VII) in methanol or cyclohexane evolved carbon monoxide on irradiation, forming a polyketone, hexamethylcyclobutanone (VIII), [ν_{\max} . (neat) 1765 cm^{-1} ; 2,4-dinitrophenylhydrazones, m.p. 192–193°, λ_{\max} . 361 $\text{m}\mu$, ϵ 22,000], and an enol lactone [m.p. 38–39°; ν_{\max} . 1785, 1695, 1282, 1132, 1095, and 1050 cm^{-1} ; n.m.r. (CCl_4) τ 8.97 (intensity 2), 8.83 (2), 8.68 (1), and 8.27 (1)]. The structure of the enol lactone (IX)

¹ e.g. "Chemistry of Carbon Compounds", Ed. E. H. Rodd, Elsevier, Amsterdam, 1953, Vol. IIA, pp. 106–108

² R. D. Desai, *J.*, 1932, 1079.

³ H. Nozaki, Z. Yamaguti, and R. Noyori, *Tetrahedron Letters*, 1965, 37.

was proved by oxidation with nitric acid to tetramethylsuccinic acid and its anhydride.

The isomerisation of the diketones to the enol lactones is most simply explained by assuming cleavage of the $n \rightarrow \pi^*$ triplet to the diradical (X) which can recyclise on oxygen³ (to II, IV, IX) if it does not first lose carbon monoxide (to tetramethylcyclopropanone,⁴ VIII, IX): although there

is nothing to exclude a concerted rearrangement of the excited singlet state. The rearrangement of the β -ketol (V) to (VI) involving a hydrogen migration is clearly of a different class, perhaps related to the cleavage of saturated ketones to ketens⁵ or the stereospecific rearrangement of α -ketols to lactones.⁶

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⁴ N. J. Turro, G. W. Byers, and P. A. Leermakers, *J. Amer. Chem. Soc.*, 1964, **86**, 955; R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *Proc. Chem. Soc.*, 1964, 144; H. G. Richey, J. M. Richey, and D. C. Clagett, *J. Amer. Chem. Soc.*, 1964, **86**, 3906; P. A. Leermakers, G. F. Vesley, N. J. Turro, and D. C. Neckers, *J. Amer. Chem. Soc.*, 1964, **86**, 4213.

⁵ Reviewed by O. L. Chapman in "Advances in Photochemistry", Interscience, New York, 1963, Vol. 1, p. 366.

⁶ R. C. Cookson and R. P. Gandhi, *Pure Appl. Chem.*, 1965, in press.