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Photochemistry of 4-Hydroxy-6-methyl-(2*H*)-pyran-2-one (Triacetic Acid Lactone)

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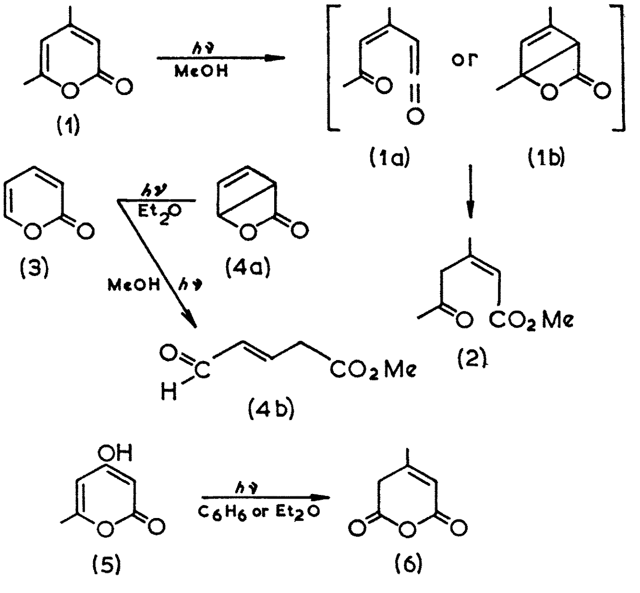
Summary The irradiation of triacetic acid lactone in various solvents results in novel rearrangement to β-methylglutaconic acid derivatives.

de Mayo and his colleagues[1] have shown that irradiation of 4,6-dimethyl-2-pyrone (1) in methanol solution affords methyl β-acetonylcrotonate (2). A keten intermediate (1a) was invoked to explain the formation of this ester, although an alternative explanation involving the bicyclic β-lactone (1b) as intermediate has been suggested by Corey and Streith.[2] The latter workers have shown that low-temperature (−10°) u.v. irradiation of 2-pyrone (3) in ether yields a bicyclic β-lactone (4a). A recent study by Pirkle and McKendry[3] has shown that irradiation of (3) in methanol affords methyl *trans*-4-formylbut-3-enoate (4b).†

Our studies have been concerned with the photochemical behaviour of triacetic acid lactone (5) in benzene, ether, and methanol. Anhydrous solvents were used and all experiments were conducted at room temperature under nitrogen at low concentration (0·05—0·2%) using an internal water-cooled mercury arc lamp (Hanovia, 450 w) and a Pyrex filter.

Since triacetic acid lactone (5) is sparingly soluble in benzene a suspension was used (1 g./l.) and irradiated for 24 hr. at room temperature. Spectroscopic (u.v. and n.m.r.) and t.l.c. (silica gel–chloroform : acetic acid, 9 : 1) examination of the solution indicated that most of the dissolved starting material had been converted‡ into one compound, although a minor product was detectable. Removal of solvent gave a white solid which crystallised from ether or petroleum (80—100°)-benzene to yield β-methylglutaconic anhydride (6),§ m.p. 89—90°; (lit.[4] m.p. 90°); $\lambda_{\max}$ 222 nm. (ϵ 10,700) in MeOH, $\lambda_{\max}$ 236 (ϵ 7500) and 342 (15,600) in MeOH–NaOH; $\nu_{\max}$ ($CHCl_3$) 1800, 1740, and 1660 cm.$^{-1}$; τ ($CDCl_3$) 7·93 (3H, double triplet, *J* 1·5, 1·0 Hz.), 6·57 (2H, double quartet *J* 1·5, 1·0 Hz.), 3·97 (1H, sextet, *J* 1·5 Hz.). Yield of anhydride, based on u.v. and n.m.r. spectra of reaction solution was 85—90%.

At first glance, the smooth conversion of triacetic acid lactone (5) into β-methylglutaconic anhydride (6) is quite remarkable. However, it may be rationalised in the following way. Initial photoisomerisation to the bicyclic β-lactone (5a) could occur, followed by rearrangement to the cyclobutenone (5c). Photoisomerisation of (5c) to the



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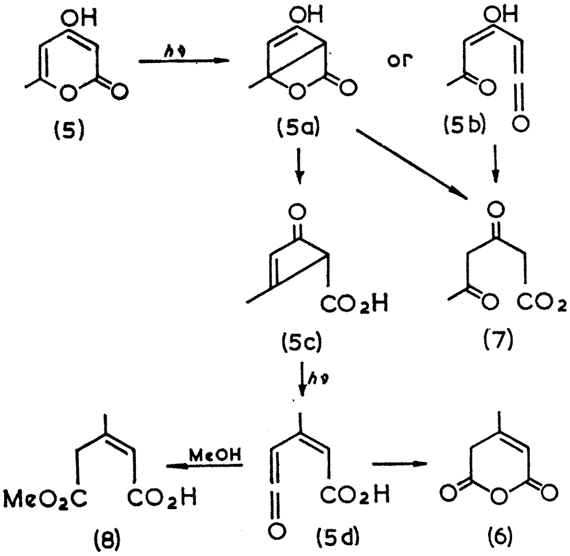
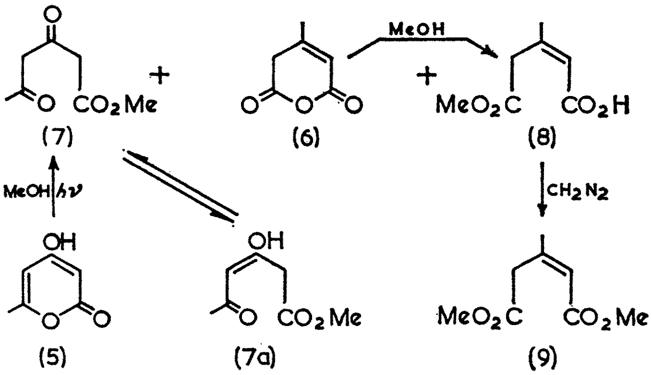
† Evidence for the formation of a keten intermediate during photolysis of 2-pyrone (3) is provided in a recent paper: W. H. Pirkle and L. H. McKendry, *J. Amer. Chem. Soc.*, 1969, **91**, 1179.

‡ Similar treatment of triacetic acid lactone in the dark gave a quantitative recovery of starting material.

§ Satisfactory analyses were obtained for the photo-products described.

keten (5d) (*cf.* ref. 5), which is trapped intramolecularly by the carboxylate group, would complete the sequence. Essentially identical results were obtained when anhydrous ether was used as solvent.





In methanol solution (0·1%) virtually no triacetic acid lactone (5) remained after 3 hr. irradiation, and t.l.c. examination revealed that several new compounds had been formed.‡ Careful removal of the solvent and steam distillation of an aqueous solution (pH 6·3) of the residue yielded a distillate from which methyl 3,5-dioxohexanoate (7)§ could be isolated as a colourless oil, b.p. 65°/11 mm. λ_{max} 276 nm. (ϵ 7650) in MeOH, λ_{max} 296 (ϵ 19,700) in 0·1N-NaOMe–MeOH; ν_{max} (film) 1740, 1621, and 1610 cm^{-1}. The n.m.r. spectrum (12% in CCl_4) showed that the compound existed as a tautomeric mixture of enol (7a) [τ 7·97 (3H, singlet), 6·79 (2H, singlet), 6·35 (3H, singlet), 4·48 (1H, singlet), $-4{\cdot}70$ (1H, broad singlet)] and keto- (7) [τ 7·83 (3H, singlet), 6·57 (2H, singlet), 6·36 (2H, singlet), 6·35 (3H, singlet)] forms. In an alternative work-up of the evaporated reaction mixture, crystallisation from ether–petroleum yielded β-methoxycarbonylmethylcrotonic acid (8),§ m.p. 77—78° (from petroleum); λ_{max} 213 nm. (ϵ 11,840) in MeOH; λ_{max} 204 nm. (ϵ 11,500) in NaOH–MeOH; ν_{max} (CCl_4) 1732, 1690, 1643, 1268, and 1169 cm.$^{-1}$, n.m.r. band (τ CCl_4) at 8·00 (3H, doublet, J 1·4 Hz.), 6·34 (3H, singlet), 6·30 (2H, broad doublet), 4·16 (1H, multiplet), $-2{\cdot}00$ (1H, singlet). This compound could also be obtained by methanolysis of β-methylglutaconic anhydride (6) and further confirmation of its structure was obtained by conversion to dimethyl cis-β-methylglutaconate (9).[6] A third compound present in the crude reaction product was identified as β-methylglutaconic anhydride (6). The formation of this compound during photolysis in methanol solution is somewhat surprising if we invoke the intermediacy of the keten (5d) as described above. It seems evident that cyclisation of the keten (5d) to the anhydride (6) competes favourably with methanol addition to yield (8). Other examples of competition between intramolecular cyclisation of ketens and nucleophilic addition of alcohols have been reported.[7] The yields of compounds (6), (7), and (8) based on u.v. and n.m.r. spectroscopic analysis, were 27, 13, and 42%, respectively. The possibility that anhydride was acting as the precursor of the unsaturated acid (8) was investigated by a series of blank experiments. The anhydride was photochemically inert in ether or benzene. In methanol a 15% conversion of the anhydride into (8) was noted after 3 hr. However, the same conversion into (8) was obtained in the dark, and total conversion was accomplished in 48 hr. While methanolysis of anhydride can thus account for some of (8), the high yield of the latter compound indicates that it is also formed directly from keten (5d). The formation of methyl 3,5-dioxohexanoate (7) is analogous to other results[1,3] noted above and presumably involves the keten (5b) or bicyclic β-lactone (5a) as intermediate.

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