# Intramolecular Photochemical Cycloadditions Involving Enolised Cyclopentane-1,3-diones. A New Approach to the Bicyclo[3.2.1]octane Ring System

By Michael Mellor, Dismas A. Otieno, and Gerald Pattenden*
(*Department of Chemistry, The University, Nottingham* NG7 2RD)

*Summary* Irradiation of the enol acetates derived from several substituted 4-(prop-2-enyl)cyclopentane-1,3-diones leads to photoproducts resulting from intramolecular [2+2] cycloaddition, which can then be elaborated to the bicyclo[3.2.1]octane ring system.

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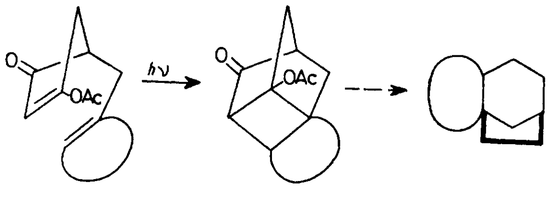
The synthetic utility of photochemical cycloadditions between enolised $\beta$-diketones and alkenes, leading to 2-acylcyclobutanols which then undergo reverse aldol reactions to 1,5-diones, is well documented.[1,2] We now describe an intramolecular variant of the photochemical cycloaddition, using cyclopentane-1,3-dione enol acetates, which leads to the tricyclic system (**1**), suitably functionalised for elaboration to the bicyclo[3.2.1]octane ring system found in gibberellins and several other important natural terpenoids.[3]

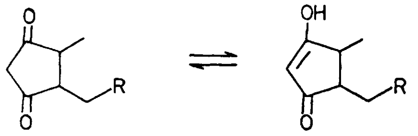
The cyclopentanedione (**2a**) was prepared by reduction of the corresponding cyclopentenedione with zinc amalgam in hydrochloric acid,[4] or by rearrangement of the corresponding hydroxy-cyclopentenone with sodium methoxide in methanol; both chemical and spectral data indicate that formulation (**3a**) best represents the structure of the enol.[4]

Irradiation of the enol acetate derived from (**3a**), in hexane, with Pyrex-filtered light from a 450 W medium-pressure mercury lamp, led to the formation of two photoproducts (ratio 4:1, 82%), resulting from regioselective intramolecular [2+2] cycloaddition in the sense indicated in the Scheme. The major product separated as colourless crystals, m.p. 75—76 °C, in 62% isolated yield, and displayed spectral data, $\nu_{max}$ 1740—1720 cm$^{-1}$, $\tau$ 7·86 (OAc) and 9·19 (d, *J* 7 Hz, CH*Me*), consonant with the tricyclo-[3.2.1.0$^{3,6}$]octanone structure (**4a**); the assignment was confirmed by *X*-ray measurements which also established a *syn*-orientation for the 2-methyl substituent.† The minor photoproduct, an oil, exhibited closely comparable spectral data [*e.g.* $\tau$ 7·88 (OAc), 9·11 (d, *J* 7 Hz, CH*Me*)] thereby supporting the *anti*-epimeric structure (**5**). In a similar manner, photolysis of the enol acetate derived from the *gem*-dimethyl substituted enol (**3b**), led to one major photoproduct (*ca.* 70%) showing $^1$H n.m.r. data {$\tau$ 7·86 (OAc), 8·61 [*exo*-C(Me)Me], 9·16 [*endo*-C(Me)Me], and 9·2 (d, *J* 7 Hz, CH*Me*)}, consistent with the tricyclic ketone (**4b**).



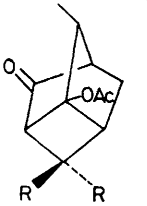
(1)

SCHEME



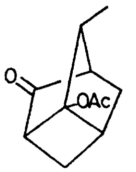
(2) (3)

a; R = CH=CH$_2$
b; R = CH=CMe$_2$

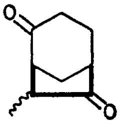


(4)

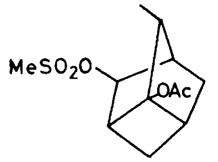
a; R = H
b; R = Me



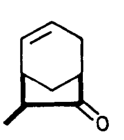
(5)



(6)



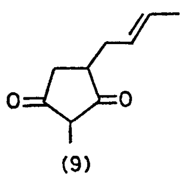
(7)



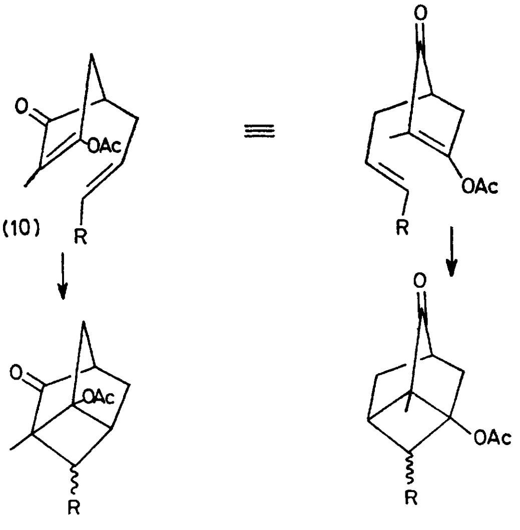
(8)

Treatment of the aldol-acetate (**4a**) with ethanolic potassium hydroxide produced a mixture of epimers of the bicyclo[3.2.1]octane-dione (**6**), $\nu_{max}$ 1735 and 1705 cm$^{-1}$, $\tau$ 7·2—8·16 (9H, m), 8·76 (d, *J* 7 Hz, CH*Me*), and 8·92 (d, *J* 7 Hz, CH*Me*), whereas reduction with sodium borohydride led to the corresponding carbinol which was converted into the mesylate (**7**). Saponification of (**7**) and fragmentation of the resulting carbinol in the presence of sodium hydroxide[5] then gave (58%) the olefinic ketone (**8**), $\nu_{max}$ 1730 and 1640 cm$^{-1}$, $\tau$ 4·04 (m, :C*H*), 4·42 (m, :C*H*), 7·36—7·96 (7H, m), and 8·92 (d, *J* 7 Hz, CH*Me*).

In a separate series of experiments, the cyclopentane-1,3-dione (**9a**) was synthesised from 2-methylcyclopentane-1,3-dione by generation of the corresponding di-enolate,[6] followed by alkylation with allyl bromide. Acetylation of (**9a**), and photolysis of the enol acetate led (90%) to two photoproducts (ratio 7:3) resulting from intramolecular [2+2] cycloaddition. By analogy with the aforementioned results, and from comparative spectral data, structures (**11a**) [$\tau$ 6·96—7·32 (1H, m), 7·5—7·89 (6H, m), 7·94 (OAc), 8·25—8·5 (1H, m), and 8·82 (Me)], and (**12a**) [$\tau$ 7·02—7·29 (1H, m), 7·3—7·9 (6H, m), 7·83 (OAc), 7·98—8·4 (1H, m), and 8·94 (Me)], resulting from alternative modes of cycloaddition to the enol acetate (**10**) are suggested for the major and minor photoproducts respectively. The but-2-enyl substituted enol acetate (**10b**) was prepared in a similar manner, and on photolysis led to a comparable ratio of photoproducts (**11b**) and (**12b**). Experiments are now in progress to establish more fully the specificities of these intramolecular cycloadditions, and to investigate the



(9)



(10) (11) (12)

a; R = H
b; R = Me

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application of the tricyclic adducts in natural product synthesis.

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[3] For recent approaches to the bicyclo[3.2.1]octane ring system see: E. J. Corey, R. L. Danheiser, and S. Chandrasekaran, *J. Org. Chem.*, 1976, **41**, 260; Y. Yamada, H. Nagaoka, and M. Kimura, *Synthesis*, 1977, 581.

[4] *Cf.* G. Pattenden and R. Storer, *J.C.S. Perkin I*, 1974, 1606.

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[6] *Cf.* S. N. Huckin and L. Weiler, *J. Amer. Chem. Soc.*, 1974, **96**, 1082; G. Stork and R. L. Danheiser, *J. Org. Chem.*, 1973, **38**, 1775.