A New Approach to Fused Carbocycles. Intramolecular Photocyclisations of 1,3-Dione Enol Acetates

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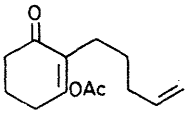
Summary Irradiation of the enol acetate (**1**) gave the tricyclic adduct (**2**) regioselectively and in quantitative yield, whereas (**12**) led (93%) to a mixture (3:2) of adducts (**13**) and (**14**), and the enol acetates (**9**) and (**10**) produced mainly the photo-Fries rearrangement products (**8**) and (**11**), respectively; hydrolytic cleavage of the tricyclic adducts (**2**) and (**14**) gave rise to the bicyclo-[6.3.0]undecane (**3**) and bicyclo[5.3.0]decane (**15**) ring systems.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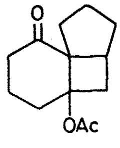
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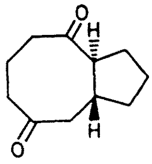
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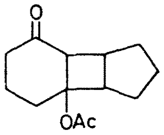
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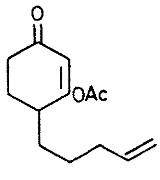
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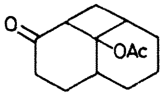
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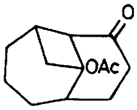
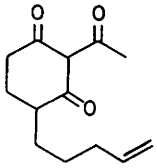
We have recently described a new approach to the bicyclo-[3.2.1.]octane ring system based on intramolecular [2 + 2] photocycloadditions using cyclopentane-1,3-dione enol acetates followed by Grob fragmentation of the resulting tricyclic adducts.[1] In contemporaneous studies Oppolzer and Godel have reported an application of this approach in a synthesis of longifolene.[2] In continuation of our research on the potential for intramolecular photocyclisations of 1,3-dione enol acetates in the elaboration of fused carbocycles, we have now explored a number of related systems. This paper describes some of these possibilities, and in particular the elaboration of the bicyclo[6.3.0]undecane and bicyclo[5.3.0]decane ring systems.

Irradiation of the enol acetate (**1**) in hexane resulted in quantitative conversion into the tricyclic compound (**2**), ν_{max} 1720 and 1690 cm^{-1}, τ 7·2—8·6 m, (15 H) and 7·94 (OAc) which, on treatment with ethanolic potassium hydroxide, (0 °C; 2 h) led (78%) to bicyclo[6.3.0]undecane-2,6-dione (**3**), m.p. 64·5 °C, ν_{max} 1695 cm^{-1}. The dione (**3**) was also obtained by photochemical cycloaddition of the enol acetate of cyclohexane-1,3-dione to cyclopentene followed by retro-aldol cleavage of the resulting adduct (**4**)[3] in the presence of methanol–sulphuric acid;[4] *X*-ray measurements established a *trans*-fusion for the rings.



(**7**)



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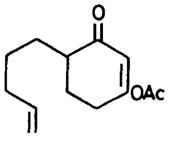

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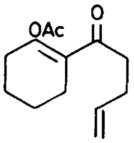

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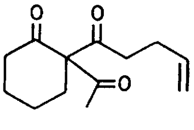
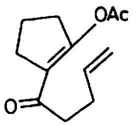
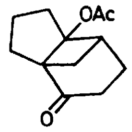


(**11**)

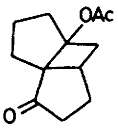
In contrast to the regiospecific behaviour observed with (**1**), irradiation of the isomeric enol acetate (**5**) led to a mixture of tricyclic adducts (**6**) and (**7**) (47%; ratio 2 : 3) whose formation was accompanied by the product (**8**) (28%) ν_{max} 1670 and 1565 cm^{-1}, τ 7·35 (COMe), of photo-Fries rearrangement. Furthermore the photo-Fries rearrangement products (**8**) (40%) and (**11**) (30%) were the single major products obtained from irradiations of (**9**) and (**10**), respectively.



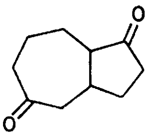
(**12**)



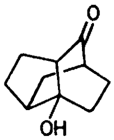
(**13**)



(**14**)



(**15**)



(**16**)

When a hexane solution containing a mixture (*ca.* 2 : 1) of enol acetates of 2-(pent-4-enoyl)cyclopentanone was irradiated through Pyrex for 2·5 h, a mixture of two photoadducts (93%, ratio 2 : 3) was obtained resulting from intramolecular [2 + 2] cycloaddition in only the *endo* enol acetate (**12**). The major product, m.p. 74—75 °C, ν_{max} 1725 and 1705 cm^{-1}, τ 6·83—7·0 (m, 1H), 7·96 (OAc), and 7·2—8·6 (m, 12H) was shown by *X*-ray measurements to have the structure (**13**), and the minor product, m.p. 78—79 °C, ν_{max} 1720 cm^{-1}, τ 7·97 (OAc) and 7·02—8·85 (m, 13H) to have the constitution (**14**).

Hydrolytic cleavage of (**14**) in EtOH–KOH then led to the bicyclo[5.3.0]decanone (**15**), ν_{max} 1725 and 1705 cm^{-1}, whereas similar treatment of (**13**) instead gave directly the aldol (**16**) ν_{max} 3605, 3450, and 1710 cm^{-1}, by way of the transient retro-aldol intermediate.

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[1] M. Mellor, D. A. Otieno, and G. Pattenden, *J.C.S. Chem. Comm.*, **1978**, 138; M. Mellor and G. Pattenden, *Synth. Comm.*, in the press.

[2] W. Oppolzer and T. Godel, *J. Amer. Chem. Soc.*, 1978, **100**, 2583.

[3] T. S. Cantrell, W. S. Haller, and J. C. Williams, *J. Org. Chem.*, **1969**, **34**, 509.

[4] *Cf.* M. Umehara, T. Oda, Y. Ikebe, and S. Hishida, *Bull. Chem. Soc. Japan*, **1976**, **49**, 1075.