Photochemical Syntheses of 2,6-Dioxabicyclo[3.2.0]heptanes

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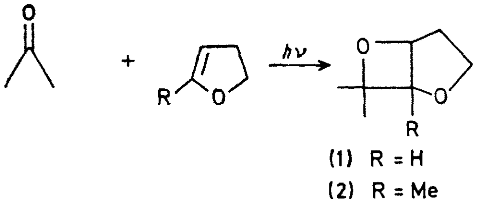
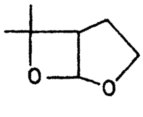
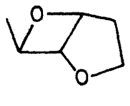
Summary Photocycloaddition of carbonyl compounds to dihydrofurans gives 2,6-dioxabicyclo[3.2.0]heptanes with high orientational selectivity; other examples of the same ring system can be produced by u.v. irradiation of β-vinyloxy-ketones.

There is current interest in the synthesis of dioxabicycloheptanes, partly because of their involvement in biological processes; the best known examples are prostaglandin *endo*-peroxides (2,3-dioxabicyclo[2.2.1]heptanes)[1] and thromboxane A_2 (2,6-dioxabicyclo[3.1.1]heptane ring system).[2] In contrast, simply substituted 2,6-dioxabicyclo[3.2.0]heptanes have not been prepared, the only derivatives which are known being based on sugars and nucleosides. We now describe two photochemical routes, depending upon intermolecular and intramolecular [2 + 2] cycloaddition, which yield simply substituted 2,6-dioxabicyclo[3.2.0]heptanes.



(1) R = H
(2) R = Me


(3)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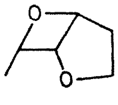
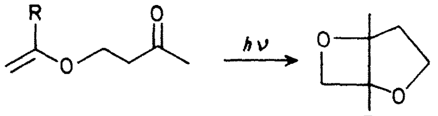
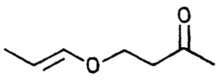

(5)

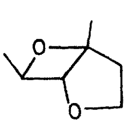
U.v. irradiation of a solution of acetone in the presence of 2,3-dihydrofuran gave the adduct (**1**) in 52% yield, and some polymeric material.† The photochemical reaction shows remarkedly high selectivity in the orientation of addition, which is quite unexpected on the basis of photocycloaddition of acetone to acyclic vinyl ethers.[3] To prove this selectivity, we have synthesised the alternative isomer (**3**) by photocycloaddition of acetone to furan,[4] followed by hydrogenation (rhodium on alumina). The ratio of (**1**) to (**3**) in the crude reaction product from acetone–dihydrofuran irradiation is at least 200 : 1. It is worth noting that the orientation of addition of acetone to furan is also highly selective, *but in the opposite sense,* so that this sequence of photocycloaddition to furans and subsequent hydrogenation provides an entirely complementary synthesis of the 2,7-dioxabicyclo[3.2.0]heptane system. The cycloaddition to give (**1**) would appear to be a reasonably general reaction: irradiation of acetone and 5-methyl-2,3-dihydrofuran led to the adduct (**2**) (30%), whilst irradiation of acetaldehyde and 2,3-dihydrofuran led to a mixture of the two stereoisomeric adducts (**4**) and (**5**) (63%), in the ratio 4 : 3.‡



(6) R = H
(7) R = Me

(8) R = H
(9) R = Me


(10)


(11)


(12)

There are no reports of the successful use of formaldehyde as a carbonyl component in [2 + 2] photocycloadditions to yield oxetans,[5] so that a different route must be used to provide 7-unsubstituted 2,6-dioxabicyclo[3.2.0]heptanes. We have therefore investigated intramolecular photoaddition of vinyloxycarbonyl compounds such as (**6**), (**7**), and (**10**).[6]§ Irradiation of (**6**) in benzene solution gave the required bicyclic product (**8**) (63%); similarly, irradiation of (**7**) in pentane solution gave compound (**9**) (72%). Interestingly, irradiation of the *trans*-propenyloxy-ketone (**10**) in various solvents led to *trans–cis* isomerisation, and formation of a single adduct (64%), assigned the *exo*-configuration (**11**). Irradiation of the *cis*-isomer of (**10**) gave only *cis–trans* isomerisation, with subsequent formation of the adduct (**11**); no evidence was found for an adduct arising directly from the *cis*-isomer of (**10**). This lack of reactivity of the *cis*-isomer towards oxetan formation has a parallel in the photochemical behaviour of hept-5-en-2-one,[7] and may indicate efficient formation of an intramolecular exciplex.¶ We have also synthesised the corresponding 2-methylprop-1-enyloxy-ketone, but find that its irradiation leads

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† A mixture of acetone (12 g) and 2,3-dihydrofuran (2 g) was irradiated, using a medium-pressure mercury arc lamp and quartz apparatus. Apart from polymer, the reaction was quite specific; adduct (**1**) formed >95% of the volatile products detected by g.l.c. analysis.

‡ Adducts were purified by preparative g.l.c., and characterised by methods including ^{1}H and ^{13}C n.m.r. spectroscopy.

§ Compounds (**6**) and (**7**) were prepared by transetherification of the corresponding hydroxy-ketones; compound (**10**) by palladium-catalysed isomerisation of the corresponding allyloxy-ketone (H. A. J. Carless and D. J. Haywood, *J. Chem. Soc., Chem. Commun.*, 1980, 980.

¶ We have been unable to detect any separate exciplex emission in the fluorescence spectrum from the *cis*-isomer of (**10**), although the quantum yield of fluorescence is reduced below that of a comparable saturated alkoxy-ketone, and below that of (**6**).

to no detectable photoproducts The importance of deactivation for this latter ketone *via* an *intramolecular* exciplex is indicated by the fact that acetone can nevertheless add photochemically to the vinyl ether functional group of the ketone to give 2-alkoxy- and 3-alkoxy-oxetans in the ratio 3 1

In the present intramolecular [2 + 2] photoreactions, there was no evidence for the formation of a product arising from the alternative orientation of addition, *i e* the elusive thromboxane A_2 ring system [*e g* (**12**), produced from (**6**)] [8]

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[1] For recent examples, see N A Porter, J D Byers, K M Holden, and D B Menzel, *J Am Chem Soc* , 1979, **101**, 4319, N A Porter, J D Byers, A E Ali, and T E Eling, *ibid* , 1980, **102**, 1183

[2] M Hamberg, J Svensson, and B Samuelsson, *Proc Natl Acad Sci USA*, 1975, **72**, 2994

[3] Acetone adds to propenyl propyl ether to give 2- and 3-alkoxyoxetans in the ratio 43 57, S H Schroeter, *Chem Commun* , 1969, 12, see also N J Turro and P A Wriede, *J Am Chem Soc* , 1968, **90**, 6863

[4] K Shima and H Sakurai, *Bull Chem Soc Jpn* , 1966, **39**, 1806

[5] D R Arnold, *Adv Photochem* , 1968, **6**, 301

[6] For a related route to 2,5-dioxabicyclo[2 2 0]hexanes, see J C Dalton and S J Tremont, *J Am Chem Soc* , 1975, **97**, 6916, J Mattay, *Tetrahedron Lett* , 1980, **21**, 2309

[7] S R Kurowsky and H Morrison, *J Am Chem Soc* , 1972, **94**, 507

[8] No examples containing this ring system appear to have been synthesised yet, for recent oxacarbocyclic analogues of the thromboxane A_2 ring, see E J Corey, J W Ponder, and P Ulrich, *Tetrahedron Lett* , 1980, **21**, 137, K M Maxey and G L Bundy, *ibid* , p 445 and references therein