Structural Requirements for the Photochemical Ring Expansion of Dihydrofuran-3(2*H*)-ones to Cyclic Acetals

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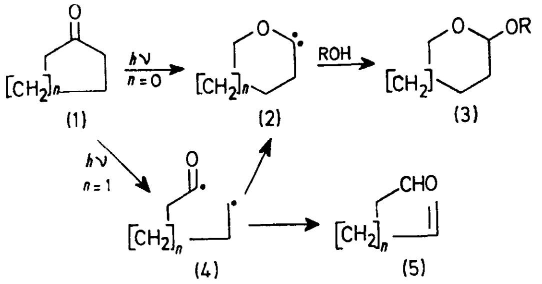
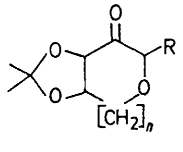
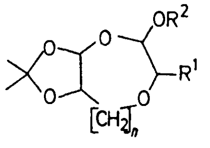
Summary Evidence is presented that photochemical ring expansion of dihydrofuran-3(2*H*)-ones to cyclic acetals takes place when the substitution pattern of the furanones is such that α-cleavage of the C(3)–C(4) bond occurs.

The photochemical ring expansion of cyclic ketones (**1**) in alcoholic solvents to cyclic acetals (**3**) is considered to proceed *via* cyclic oxacarbenes (**2**).[1] Although the reaction is general for cyclobutanones,[2] reports of the ring expansion of other carbocyclic ketones are limited to cyclopentanones incorporated into bridged ring systems and/or having an α carbon atom incorporated into a cyclopropane ring. It has been proposed[1,3] that in the case of these cyclopentanones ring expansion occurs because structural features inhibit the formation of the enal (**5**) from the biradical (**4**) resulting from α-cleavage of (**1**) and/or facilitate the formation of oxacarbene (**2**) from (**4**).† In this context the recent report[4] that the 3-oxacycloalkanones (**6**) and (**7**) undergo efficient photochemical ring expansion to the acetals (**8**) and (**9**) was of considerable interest. We report now on an investigation designed to delineate the structural features that lead to ring expansion of dihydrofuran-3(2*H*)-ones in general.

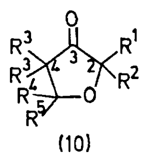




(**6**) *n* = 0, R = Me
(**7**) *n* = 1, R = H

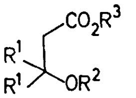


(**8**) *n* = 0, R^1 = R^2 = Me
(**9**) *n* = 1, R^1 = H, R^2 = Et



(**10**)

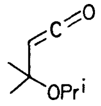
a; R^1=R^2=R^4=R^5=Me, R^3=H
b; R^1=R^2=R^3=H; R^4=R^5=Me
c; R^1=Me, R^2=R^3=R^4=R^5=H
d; R^1=R^2=Me, R^3=R^4=R^5=H
e; R^1=R^2=R^4=R^5=H, R^3=Me
f; R^1=R^2=R^4=H, R^3=R^5=Me



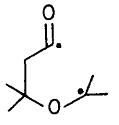
(**11**)

a; R^1=R^3=Me, R^2=Pr^i
b; R^1=R^2=R^3=Me
c; R^1=R^2=H, R^3=Et
d; R^1=H, R^2=Pr^i, R^3=Me

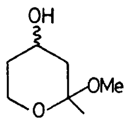
The photochemistry of (**10a**) in methanol has been shown[5] to give (**11a**) and other products derived from the keten (**12**) formed *via* α-cleavage of the C(2)–C(3) bond to the biradical (**13**). Irradiation‡ of (**10b**) in methanol gave (**11b**), the analogue of (**11a**), while photolysis of (**10c**) in ethanol gave (**11c**), a product that must also arise *via* a keten analogous to (**12**). No cyclic acetals could be



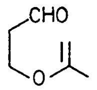
(**12**)



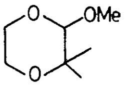
(**13**)



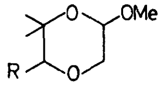
(**14**)



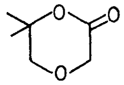
(**15**)



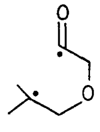
(**16**)



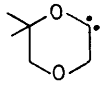
(**17a**) R = H
(**17b**) R = Me



(**18**)



(**19**)



(**20**)

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† In the case of cyclobutanones the formation of (**2**) from (**1**) may occur in a concerted fashion without the intermediacy of (**4**) (see ref. 2).

‡ Irradiations were carried out on 1—5% solutions in the presence of Na_2CO_3 (see ref. 1) in quartz tubes with a 450 W Hanovia medium pressure Hg lamp. New compounds were characterized by elemental analysis and/or high resolution mass spectrometry and by i.r. and ^1H n.m.r. spectroscopy.

detected in the total photolysates obtained from (**10a**), (**10b**), or (**10c**). Irradiation of (**10d**) in methanol gave the keten-derived ester (**11d**) together with (**14**),§ which is considered to be derived from the aldehyde (**15**), and a very small amount (*ca.* 2%) of the oxacarbene-derived product (**16**). It may be noted that, in accord with expectation,[1] the dihydrofuranones (**10a**—**d**) all undergo cleavage of the C(2)–C(3) bond exclusively and give, at most, minor amounts of oxacarbene-derived products.

Irradiation of compounds (**10e**) and (**10f**) in methanol, however, gave the oxacarbene-derived acetals (**17a**) and (**17b**)§ as the only major products; the structure of (**17a**) was confirmed by oxidation with Jones reagent to the lactone (**18**) and comparison of this with an independently synthesized sample. Compounds (**10e**) and (**10f**) resemble (**6**) in undergoing exclusive cleavage of the C(3)–C(4) bond of the dihydrofuranone ring. It may be concluded that the structural requirement for the significant production of oxacarbene-derived products from dihydrofuran-3(2*H*)-ones is a substitution pattern such that cleavage of the C(3)–C(4) rather than the C(2)–C(3) bond occurs. Furthermore the presence of the annular oxygen atom must play a vital role since simple five-membered carbocyclic ketones do not undergo photochemical ring expansion. In the cases of (**6**), (**10e**), and (**10f**) there is no apparent reason why the presence of the annular oxygen atom should lead to inhibition of keten or enal formation from an intermediate biradical, *e.g.*, (**19**), any more than it should in the cases of (**10a**) and (**10d**). Thus, in terms of our earlier proposals,[1,3] we suggest that the function of the dihydrofuranone annular oxygen atom in (**6**), (**10e**), and (**10f**) is to stabilize and thereby facilitate the formation of the oxacarbene, *e.g.*, (**20**).

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§ Obtained as a mixture of anomers.

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[5] G. Hagens, J. P. Wasacz, M. Joullié, and P. Yates, *J. Org. Chem.*, 1970, **35**, 3682.