Photochemical Ring Expansion of Dispiro Substituted Cyclobutane-1,3-diones

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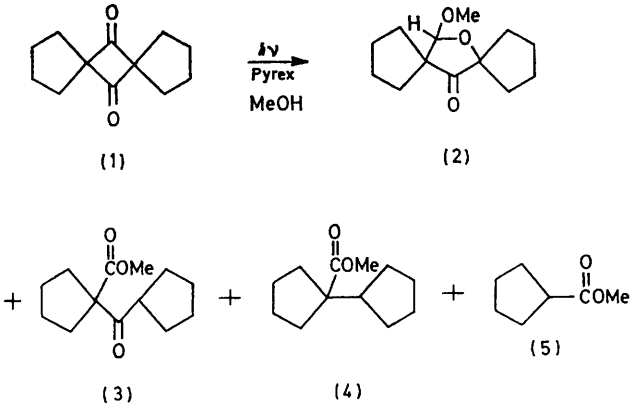
Summary A ring-expanded acetal has been obtained from the photolysis of dispiro[4,1,4,1]dodecane-6,12-dione in methanol, *via* an oxacarbene intermediate.

In the study of electronically excited alicyclic ketones, increasing interest has been shown in photochemical ring expansion *via* an oxacarbene intermediate. Recently, it has been shown by Conia[1] that some cyclobutane-1,2-diones as well as cyclobutanones[2,3] and cyclopentanones undergo photochemical ring expansion. The photochemical reactions of various cyclobutane-1,3-diones have also been extensively studied,[4] but ring expansion has not been reported.

We now report the ring expansion of dispiro substituted cyclobutane-1,3-diones. When dispiro[4,1,4,1]dodecane-6,12-dione (**1**) (18 mmol) was irradiated in methanol (200 ml) using Pyrex filter at −70° for 2 h, the ring expanded acetal (**2**),† arising from the trapping of an oxacarbene intermediate with methanol, was obtained in 6·1% yield.

Besides (**2**), methyl 1-(cyclopentylcarbonyl)cyclopentanecarboxylate (**3**) was also obtained in 55·5% yield, together with small amounts of methyl 1-(cyclopentyl)cyclopentanecarboxylate (**4**)‡ and methyl cyclopentanecarboxylate (**5**). The ring expansion can be explained by a mechanism similar to that suggested by Quinkert *et al.*[3] for light-induced ring expansion of 3-methylenecyclobutanone derivatives.



The ring size of substituted cyclobutane-1,3-diones has a significant effect on the photolysis products. In a similar irradiation of dispiro[3,1,3,1]decane-5,10-dione and dispiro-[5,1,5,1]tetradecane-7,14-dione, no ring-expansion product was detected at all but methyl 1-(cyclobutylcarbonyl)cyclobutanecarboxylate and methyl cyclohexanecarboxylate,§ as the major products, were obtained in 54·9% and 41·7% yields, respectively.

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† All new compounds were characterised by their spectral properties (n.m.r., i.r. and mass) and elemental analyses.

‡ Compound (**4**) was determined to be the secondary photoproduct by the further irradiation of isolated compound (**3**) in methanol.

§ This compound was produced presumably *via* a keten intermediate.

[1] J. M. Conia and J. M. Denis, *Tetrahedron Letters*, 1973, **461**.

[2] D. R. Morton and N. J. Turro, *J. Amer. Chem. Soc.*, 1973, **95**, 3947 and references therein.

[3] G. Quinkert, P. Jacobs, K. H. Kaiser, G. Wiech, and W.-D. Stohrer, *Angew. Chem. Internat. Edn.*, 1974, **13**, 197, 198, 199, 200.

[4] N. J. Turro, P. A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers, and G. F. Vesley, *J. Amer. Chem. Soc.*, 1965, **87**, 2613; A. P. Krapcho and F. J. Waller, *J. Org. Chem.*, 1972, **37**, 1079.