

Azetidine-2,4-diones *via* Photocyclisation of Bis(phenylglyoxylolyl)-alkylamines. A Novel Photochemical Reaction involving a 1,5-Benzoyl Shift

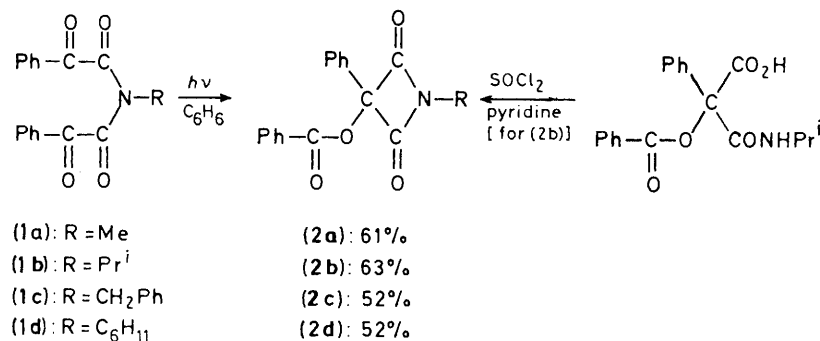
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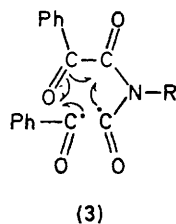
Irradiation of bis(phenylglyoxylolyl)alkylamines leads to cyclisation involving a 1,5-benzoyl shift and the formation of the corresponding 1-alkyl-3-benzoyloxy-3-phenylazetidine-2,4-diones.

The photochemistry of α -dicarbonyl compounds such as α -diketones,¹ α -oxoesters,² and α -oxoacids³ has received much attention because these compounds show considerably different photochemical behaviour from that of monoketones.

In relation to our previous studies on photochemical reactions of α -oxoamides,⁴ we now report reactions of the corresponding imides, the bis(phenylglyoxylolyl)amines which involve an unprecedented photocyclisation *via* a 1,5-benzoyl shift.



Scheme 1



The imides (**1a–d**) were obtained quantitatively by the reduction of the corresponding ozonides⁵ of diphenylmaleimides with dimethyl sulphide. The structure of (**1d**) was determined by an unequivocal synthesis from phenylglyoxyloxy chloride and (phenylglyoxyloxy)cyclohexylamine.

Irradiation of the imide (**1a**) in benzene with a high-pressure mercury lamp under argon gave 3-benzoyloxy-1-methyl-3-phenylazetidione-2,4-dione (**2a**) in 61% yield. Photolysis of the other imides (**1b–d**) under the same conditions also gave the corresponding azetidione-2,4-diones (**2b–d**) in good yields. The structure of (**2b**) was confirmed by the independent synthesis shown in Scheme 1, while those of the other photoproducts were determined on the basis of elemental analyses[†] and spectral data.

The mechanism for the formation of (**2**) may involve α -cleavage *via* (**3**).[‡] The quantum yield for the reaction of (**1a**) was 0.53 [formation of (**2a**)].⁶ The imides (**1a–d**) showed $n\pi^*$ bands in the long wavelength region [(**1a**), λ_{\max} (C₆H₆) 373 nm] as in the case of phenylglyoxylic acid [λ_{\max} (C₆H₆) 376 nm, $E_T = 63$ kcal mol⁻¹ (ref. 7)]. When the imides were irradiated selectively at their $n\pi^*$ bands,[§] the photoreactions also proceeded efficiently. The cyclisations were sensitized by 4-methoxyacetophenone [$E_T = 72$ kcal mol⁻¹ (ref. 8)], but not by Michler's ketone [$E_T = 62$ kcal mol⁻¹ (ref. 8)]. Quenching of the reactions by penta-1,3-diene or stilbene was quite inefficient. These results indicate that the photoreactions proceed from the $n\pi^*$ states though the multiplicity of the

excited state in the direct photolysis cannot be determined from the available data.

It is known that azetidione-2,4-diones are pharmacologically highly active.^{9a} The present reaction provides a useful synthesis of azetidione-2,4-diones bearing an oxygen atom at the 3-position; the yields of the previously reported syntheses are generally low.⁹ Although photocyclisation *via* a 1,2-acyl shift (oxy-di- π -methane rearrangement) is well known, that *via* a 1,5-benzoyl shift was hitherto unknown.

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- S. L. Murov, 'Handbook of Photochemistry,' Marcel Dekker, New York, 1973. Concentrations of the sensitizers were adjusted so that 95% or more of the incident light was absorbed by the sensitizers.
- (a) K. Maruyama, T. Ishitoku, and Y. Kubo, *J. Am. Chem. Soc.*, 1979, **101**, 3670; *J. Org. Chem.*, 1981, **46**, 27, and references cited therein; (b) Y. Kanaoka, H. Okajima, and Y. Hatanaka, *ibid.*, 1979, **44**, 1749. These papers describe a facile synthesis of 3,3-dialkylazetidione-2,4-diones by photoinduced ring contraction of succinimides.

[†] The imides (**1a–d**) and the photoproducts (**2a–d**) gave satisfactory analytical and spectral data.

[‡] A concerted shift or a mechanism with zwitterionic intermediates is also possible.

[§] A filter solution of naphthalene in methanol was used to isolate primarily the 366 nm Hg line.