Photochemical Synthesis of Spiro-β-lactams

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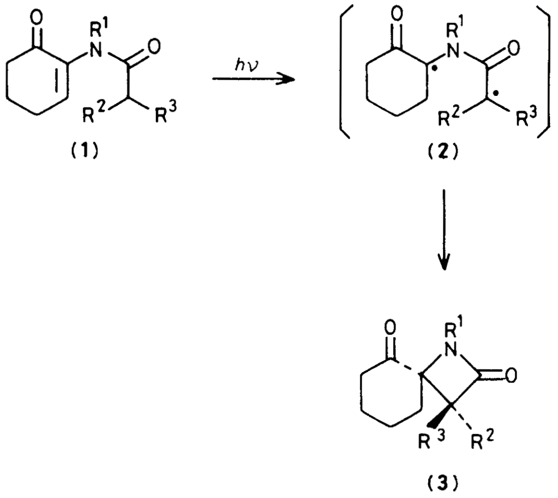
Photoirradiation of 2-(*N*-acyl-*N*-alkylamino)cyclohex-2-enones gave the *N*-alkyl-1-azaspiro[3.5]nonane-2,5-diones in moderate yields; an *X*-ray crystal structure determination was performed on one of the products.

Recently a number of preparative methods for the β-lactams, including photochemical routes, have been reported.[1] Here we describe a new photochemical entry to the spiro-β-lactams.

A solution of a 2-(*N*-acyl-*N*-alkylamino)cyclohex-2-enone (**1**)† in acetone‡ was irradiated with a 300 W high-pressure mercury lamp in a Pyrex vessel under nitrogen. Concentration of the reaction mixture and purification of the residue using column chromatography on silica gel afforded the corresponding spiro-β-lactam (**3**).§ The β-lactam structure was deduced from the spectroscopic data [*e.g.*, the β-lactam carbonyl absorption appeared between 1730 and 1765 cm^{-1} in the i.r. spectra (in CCl_4), depending upon the nature of the substituents R^2 and R^3 (see Table 1)]. The final confirmation of the structure was given by an *X*-ray analysis of (**3f**).



Crystal data for (**3f**): $C_{16}H_{19}NO_2S$, monoclinic, space group $P2_1/c$; $a = 9.066(6)$, $b = 8.720(8)$, $c = 19.318(13)$ Å; $\beta = 101.20(5)°$; $D_c = 1.28$ g cm^{-3}; $Z = 4$. The structure was solved by direct methods (MULTAN[2]) and refined by block-diagonal least squares to $R = 0.079$ using 1523 indepen-

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† The starting materials (**1a—g**) were prepared by refluxing cyclohexane-1,2-dione with an alkylamine in benzene followed by treatment with the corresponding acyl chloride in the presence of pyridine.

‡ Use of diethyl ether or benzene as the solvent gave similar results.

§ All new compounds reported in this paper gave satisfactory elemental analyses, i.r., ^{1}H and ^{13}C n.m.r., and high-resolution mass spectra.

Table 1. *N*-Alkyl-1-azaspiro[3.5]nonane-2,5-diones, (**3**).

	R^1	R^2	R^3	% Yield	M.p. /°C	ν(C=O)[b] /cm^{-1}
(**a**);	Me	Me	Me	28	78—80	1760, 1715
(**b**);	Pr^i	Me	Me	45	69—70	1755, 1715
(**c**);	Pr^i	-[CH$_2$]$_5$-		48	113—114	1735, 1715
(**d**);	Pr^i	SMe	H	45	Oil	1755, 1715
(**e**);	Pr^i	Ph	H[a]	45	149—150	1755, 1715
(**f**);	CH$_2$Ph	SMe	H	57	118—119	1760, 1715
(**g**);	CH$_2$Ph	Ph	H[a]	65	152—153	1765, 1715

[a] The stereochemistry is uncertain. [b] Measured in CCl$_4$.

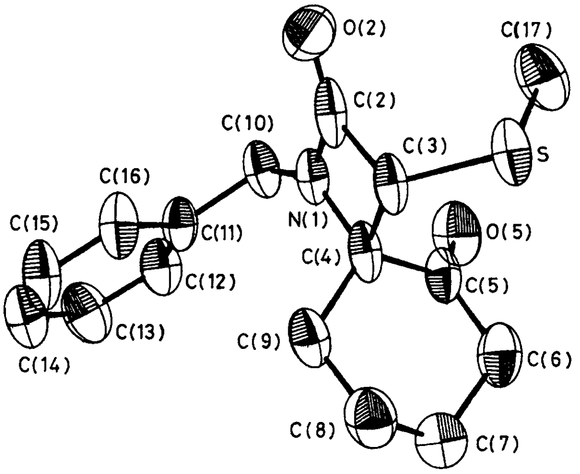

Figure 1. Perspective ORTEP drawing of compound (**3f**).

dent reflections. The molecular structure of (**3f**) is illustrated in Figure 1.¶

Although few mechanistic details for this reaction are available, the results summarized in Table 1 are consistent with the intervention of the 1,4-diradical intermediate (**2**) formed *via* abstraction of a hydrogen on the *N*-acyl group by the β-carbon atom of the α,β-enone system.[3] This behaviour is in sharp contrast to the case of 2-(*N*-alkyl-*N*-sulphonylamino)cyclohex-2-enones in which abstraction of a hydrogen on the *N*-alkyl group by the carbonyl oxygen is predominant, leading to the azetidine derivatives.[4]

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References

1 For a review, see A. K. Mukerjee and A. K. Singh, *Tetrahedron,* 1978, **34**, 1731.

2 G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A,* 1971, **27**, 368.

3 For examples, see B. Byrne, C. A. Wilson, II, S. Wolff, and W. C. Agosta, *J. Chem. Soc., Perkin Trans. 1,* 1978, 1550; H. Aoyama, T. Hasegawa, M. Okazaki, and Y. Omote, *ibid.,* 1979, 263, and references cited therein.

4 J. C. Arnould, J. Cossy, and J. P. Pete, *Tetrahedron,* 1980, **36**, 1585.

¶ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.