Photorearrangement of 3-Oxo-1-pyrroline 1-Oxides

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Summary 3-Oxo-1-pyrroline 1-oxides undergo photorearrangement to *N*-acylazetidin-2-ones and/or oxazin-6-ones depending on their substituents.

Photochemical irradiation (254 nm) of the 3-oxo-1-pyrroline 1-oxide (**1a**) in benzene for 18 h afforded a mixture of the *N*-acylazetidinone (**2a**)[1] and the oxazinone (**3a**)[2] (see Table). The related compound (**1b**) was similarly converted in 10 h into a mixture of (**2b**) and (**3b**). In both cases the azetidinones (**2a**) and (**2b**) could be isolated in good yield after preparative t.l.c. or after treatment of the product mixture with dilute hydrochloric acid. Both processes resulted in the hydrolysis of the oxazinones (**3a**) and (**3b**) to the corresponding amidocarboxylic acids, which were readily separated from the azetidinones (**2a**) and (**2b**), respectively. The reaction thus provides a promising synthesis of azetidinones. In contrast to these results, the irradiation of the 2-t-butyloxopyrroline 1-oxide (**1c**) yielded only one product, the oxazinone (**3c**).

Table

Photorearrangement of the 3-oxo-1-pyrroline 1-oxides (**1**)

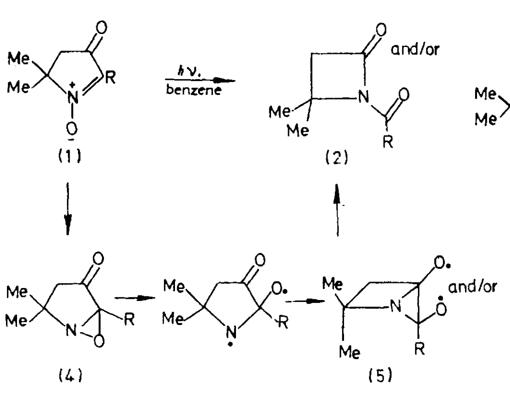
	% Composition estimated by ^{1}H n.m.r.[a]	
	(**2**)	(**3**)
(**1a**)	58 (42)	42
(**1b**)	64 (50)	36
(**1c**)	0	100 (47)

[a] Figures in parentheses indicate % yields of isolated pure products. All new compounds were fully characterised by independent synthesis and comparison of spectral data.

A possible mechanistic pathway for the conversion of compounds (**1**) into (**2**) and (**3**) could involve the oxaziridines (**4**) and the bicyclic radical intermediates (**5**) and (**6**). Consequently, the presence of a bulky R group (such as

Bu^t) could increase the energy of the transition state resembling (**5**) relative to that of one resembling (**6**).

This mechanism is also consistent with the earlier results[3] of the photorearrangement of isatogens to benzoxazinones and in which no products of ring contraction were observed. The intermediacy of the oxaziridine (**4a**) has been established both by ^{1}H n.m.r. spectroscopy and by isolation and characterisation after irradiation of compound (**1a**) for only 5 h. On irradiation, the oxaziridine (**4a**) was further converted into a similar mixture of the azetidinone (**2a**) and the oxazinone (**3a**) as obtained from (**1a**) directly. However the oxaziridines (**4b**) and (**4c**) could not be detected by ^{1}H n.m.r. spectroscopy.



a; R = Ph
b; R = Me
c; R = Bu^t

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