Photooxidation of Some 1,5-Benzodiazepines

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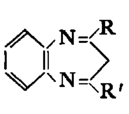
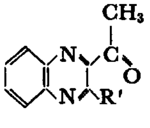
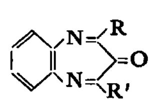
It has been reported that 1,5-benzodiazepines (I) are oxidized to 3-acylquinoxalines (II) with monopersulfuric acid or with peracetic acid, but do not give 3,6-diaza-4,5-benzotropones (III). Syntheses of the ketones (III) have been attempted by several workers, but no attempts have been successful.[1,2]


(I)


(II)


(III)

(I)	(II)	(III)
a : R, R′=CH_3	a : R′=CH_3	a : R, R′=CH_3
b : R=CH_3, R′=C_6H_5	b : R′=C_6H_5	b : R=CH_3, R′=C_6H_5
c : R, R′=C_6H_5		c : R, R′=C_6H_5

This communication will report that 3,6-diaza-4,5-benzotropones (III) can be prepared by the photooxidation of 1,5-benzodiazepines (I) in a non-aqueous medium.

The compound (I-c) in a 4% benzene solution was irradiated with a low-pressure mercury arc under an oxygen atmosphere for 20 hr. After this irradiation, the reaction mixture was chromatographed on silica gel in benzene. Thus a ketone (IV) and an amide (V) were obtained in yields of 1.4% and 2.0%, respectively.

The ketone (IV) consisted of pale yellow needles melting at 120—121°C. The infrared spectrum in KBr showed the absorption of the carbonyl group at 1680 cm^{-1}. The NMR spectrum in $CDCl_3$ simply showed two multiplets centered at τ= 2.0 and 2.6. The ultraviolet spectrum in ethanol showed λ_{max} at 264 mμ (ε=19200), 297 (11300), and 333 (8910). The mass spectrum[3] showed a parent peak at *m/e* 310 and a fragment peak at *m/e* 282 which was probably produced through the elimination of the carbonyl group of the parent ion. On the basis of these results, the ketone (IV) was identified as 2,7-diphenyl-3,6-diaza-4,5-benzotropone (III-c). This compound was very unstable and easily formed 2,3-diphenylquinoxaline by decarbonylation in warm concentrated sulfuric acid or in warm acetic acid.[4]

The amide (V) consisted of colorless needles which melted at 301°C; it was identified as dibenzoyl-*o*-phenylenediamine. The infrared spectrum in KBr showed $\nu_{C=O}$ at 1649 cm^{-1}.

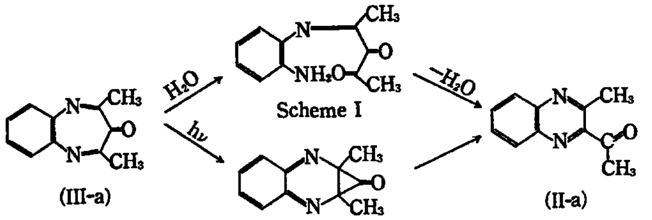
In the case of the photooxidation of 2,4-dimethyl-1,5-benzodiazepine(I-a) in benzene, the corresponding benzotropone (III-a) was not obtained; the ring contraction products, 2-acetyl-3-methylquinoxaline (II-a) and 2-hydroxy-3-methylquinoxaline (VI), were obtained in yields of 29% and 4%, respectively.

2-acetyl-3-methylquinoxaline (II-a) consisted of colorless needles which melted at 87°C after crystallization from aqueous ethanol. The infrared spectrum showed $\nu_{C=O}$ 1668 cm^{-1} in KBr.

As in the oxidation of (I-a) with peracids, in the photooxidation of (I-a) the quinoxaline (II-a) might be produced through the 6-oxo intermediate (III-a). We presumed that the quinoxaline (II-a) might be produced *via* either Scheme I or II;

In Scheme I, as has been described in the work of Barltrop *et al.*,[1] the 6-oxo intermediate (III-a) is hydrolyzed in the first step.

In Scheme II, the benzotropone (III-a) formed under the action of ultraviolet light is subjected to the second photochemical reaction.



Scheme II

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[1] J. A. Barltrop, C. G. Richards, D. M. Russell, and G. Ryback, *J. Chem. Soc.*, **1959**, 1132.

[2] W. Paterson and G. R. Proctor, *ibid.*, **1965**, 485.

[3] Thanks are due to Professor Y. Takegami and Dr. T. Ueno for the mass spectrum.

[4] The mechanism of the decarbonylation reaction may be considered to be as follows, with reference to the decomposition of diphenyltriketone suggested. J. D. Roberts, D. R. Smith and C. C. Lee, *J. Am. Chem. Soc.*, **73**, 618 (1951):