

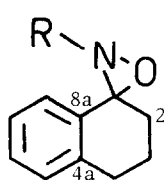
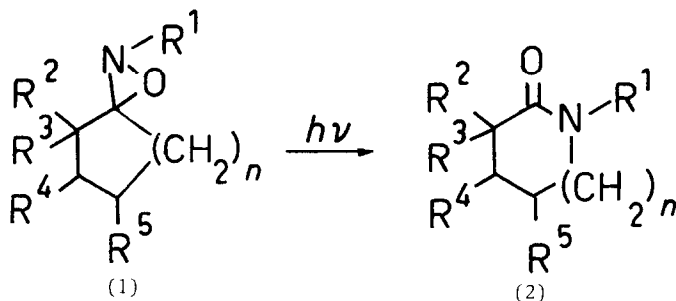
PHOTOCHEMISTRY OF N-SUBSTITUTED SPIROOXAZIRIDINES
 DERIVED FROM TETRALONE-1[†]

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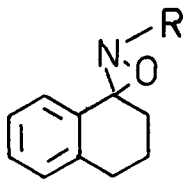
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Summary Photolyses of spirooxaziridines from tetralone-1 in which the N-substituent is syn to the aromatic ring are less regioselective than their anti-isomers suggesting the first formed N-O bond cleaved species has a significant life time.

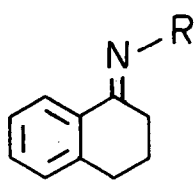
It has been reported^{1,2} that spirooxaziridines (1) photo-rearrange to the lactams (2) under stereoelectronic control and the group anti to the nitrogen lone pair migrates highly regioselectively. In α -alkylated derivatives the less substituted group migrates owing to the N-R¹ group being anti to the α -alkyl substituents. There are no reported examples of photo-isomerisation of spirooxaziridines in which aryl migration may compete with alkyl migration and there are no examples in which the N-substituent suffers any significant steric compression with syn substituents. We report here the photolysis of the syn and anti N-butylspirooxaziridines (3) and (4) and the N-benzyl analogues (5) and (6).



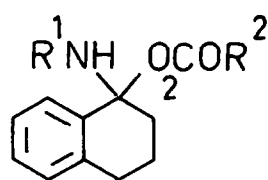
(3) R = Bu
 (5) R = PhCH₂



(4) R = Bu
 (6) R = PhCH₂



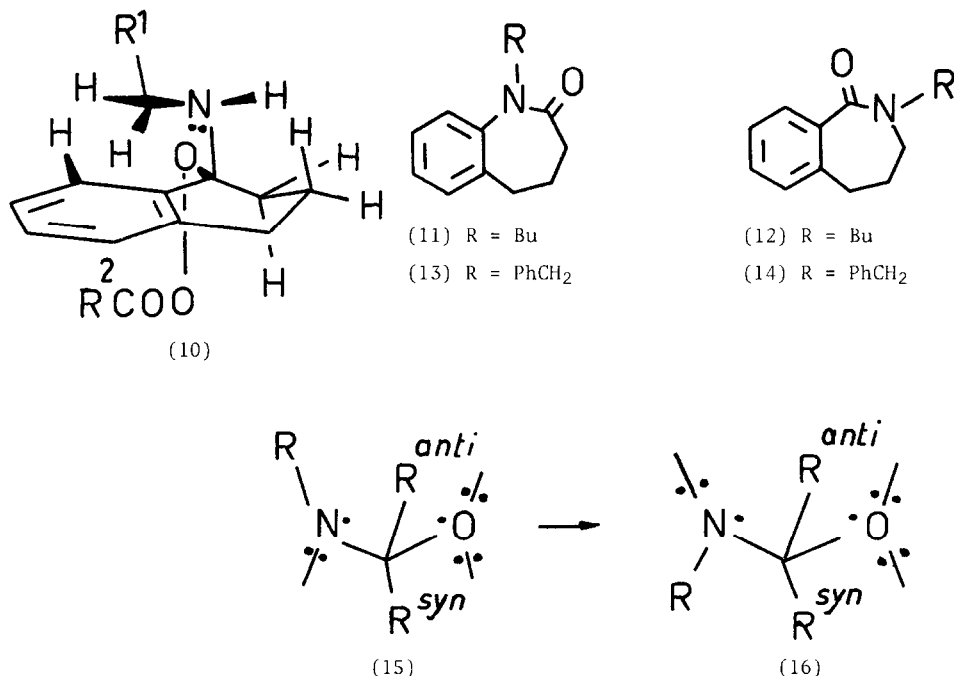
(7) R = Bu
 (8) R = PhCH₂



(9)

[†] Part of this work was presented at the Fifth East Midlands Regional Symposium of the Perkin Division of the Royal Society of Chemistry at Leicester University on the 13th December, 1983.

Tetralone-1 was converted to the imines (7) ($\nu_{\max}$ 1635 (C=N) cm^{-1} , δ 3.40, t J ~ 7 Hz, N-CH₂) and (8)³ by the usual procedure.³ The expected configurations in which R is anti to the aromatic ring were confirmed by their ¹³C nmr spectra (Table 1) in which the chemical shifts of C-2 demonstrated they were considerably shielded relative to that in tetralone-1.^{4,5} The major products of oxidation of the imines (7) and (8) with MCPBA in dichloromethane: ethanol⁶ were, surprisingly, the spirooxaziridines (3) and (5) in which R is syn to the aromatic ring. The syn:anti ratios were respectively 6:1 and 4:1 for (3):(4) and (5):(6). The configurations of (3) and (5) were confirmed by the relatively high field signals in the ¹³C nmr spectra for C-8a (Table 1) and the relatively low field signals for C-2. Further, the syn compounds (3) and (5) were converted to the anti isomers (4) and (6) respectively by heating under reflux in toluene. As expected,⁵ their ¹³C nmr spectra (Table 1) confirmed the shielding effect of the N-substituent on C-2. The formation of largely the syn spirooxaziridines (3) and (5) from the anti imines (7) and (8) respectively demonstrates that the peroxidation involves two steps, possibly through the intermediate (9) by analogy with previous work.⁷ The preferential formation of the syn spirooxaziridines (3) and (5) may be rationalised by the assumption that oxaziridine ring closure takes place through the conformation (10) in which steric compression experienced by the N-R group is minimal.



Photolysis of the spirooxaziridines (3)-(6) in ethanol using a low pressure mercury lamp in a water cooled quartz reactor gave the products in Table 2. The lactams, either mixtures of regioisomers or single substances, were separated from tetralone-1 by preparative tlc and separation of the regioisomeric lactams was achieved by reverse phase HPLC using an ODS hypersil column and methanol:water mixtures. The spectroscopic data for the lactams (11), (12), (13)⁸ and (14)⁹ are satisfactory.

Table 1
SELECTED ^{13}C NMR DATA

COMPOUND	δ ppm									
	1	2	3	4	8a	4a	α	β	γ	δ
3	84.09	33.46	20.94	29.96	130.78	141.22	52.70	28.65	20.39	13.78
4	79.17	26.68	21.81	29.63	134.77	140.40	53.80	30.73	20.67	13.94
5	84.52	33.13	20.72	28.37	130.78	141.66	57.24			
6	79.66	26.95	21.81	29.58	134.30	140.52	57.95			
7	163.74	27.66	20.94	29.96	135.26	140.29	50.79	33.40	22.74	14.05
8	164.89	27.99	22.47	29.63	134.82	140.40	54.34			
TETRALONE-1	197.97	30.09	23.29	29.63	132.74	144.55				

Table 2
PHOTOLYSIS PRODUCTS

STARTING MATERIAL	RELATIVE YIELD OF LACTAMS (TOTAL YIELD %)	% RECOVERED TETRALONE-1
3	(11):(12) = 77.5:22.5 (28)	15
4	(11):(12) = 0:100 (25)	13
5	(13):(14) = 61:39 (27)	20
6	(13):(14) = 0:100 (22)	18

In particular, the infrared spectra allow distinction between the regioisomers (11) ($\nu_{\max}$ 1660 cm^{-1}) and (12) ($\nu_{\max}$ 1640 cm^{-1}) and (13) ($\nu_{\max}$ 1665 cm^{-1}) and (14) ($\nu_{\max}$ 1640 cm^{-1}). The ratios of the regioisomers (Table 2) were determined by glc (5% SE 30 column) of the crude photolysates and of the lactam mixtures obtained from preparative tlc.

In the case of the anti spirooxaziridines (4) and (6) no migration of the aryl group was detected as would be expected from a stereoelectronically controlled rearrangement. However, the lower regioselectivity of the reaction with the syn spirooxaziridines (3) and (5) may suggest that the first formed¹ N-O bond cleaved species (15) has sufficient life time to rotate (invert) to give (16) in which the group originally syn to the nitrogen lone pair may migrate. In the absence of the considerable steric compression experienced by the N-R groups in the syn spirooxaziridines (3) and (5) the rearrangement competes effectively with rotation (inversion). Partial photolysis of the syn spirooxaziridine (3) established that there was no significant pre-equilibration of (3) with (4) in support of this conclusion.

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