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PHOTOREARRANGEMENT OF SPIRO-OXAZIRIDINES - APPLICATIONS IN THE SYNTHESES OF HEXAHYDRO-5*H*-PYRROLO-[2]BENZAZEPIN-5-ONES AND A TETRAHYDRO-1*H*,5*H*-PYRROLOISOQUINOLIN-5-ONE

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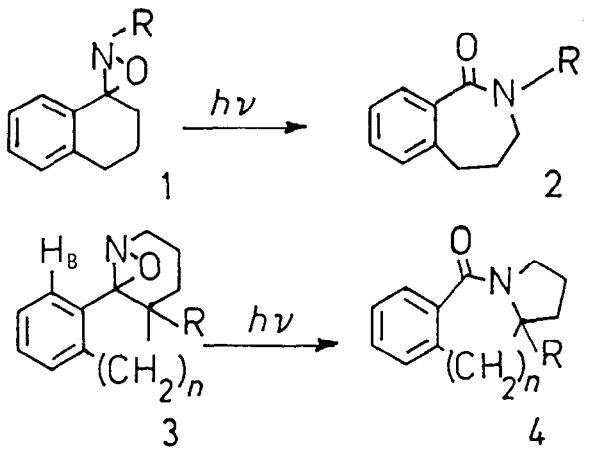
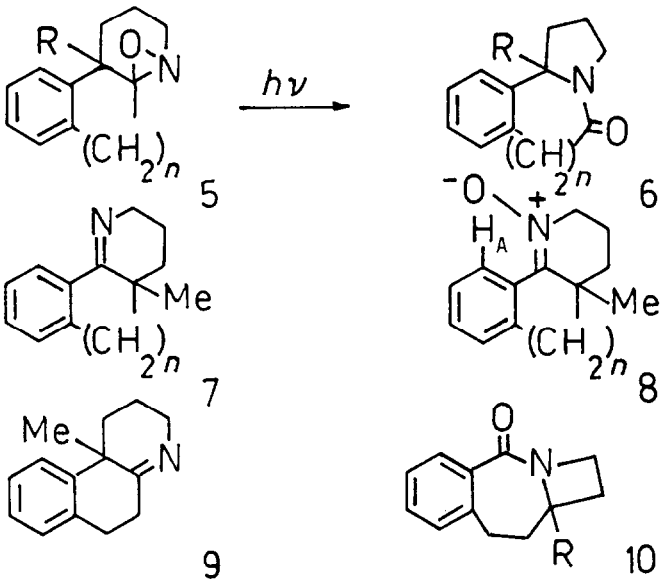
Summary Regiospecific photorearrangements of spiro-oxaziridines derived from 2-methylindan-1-one, 2-methyltetral-1-one and 1-methyltetral-2-one afforded the title compounds.

We have recently established[1] that spiro-oxaziridines (1), in which the N-alkyl group is anti to the aromatic ring, photorearrange regiospecifically to the benzazepinones (2). The migration of the saturated ring carbon atom, which is anti to the nitrogen lone pair, is



in accordance with observations made in the photolysis of related non-aromatic compounds.[2] We anticipated that spiro-oxaziridines of the type (3) should therefore regiospecifically photorearrange to the tricyclic lactams (4). Additionally, the regioisomers (5) would be expected to give the isomeric lactams (6). We report here the synthesis of pyrrolobenzazepinones (4, R=Me, n=2) and (6, R=Me, n=2) and the pyrroloisoquinolone (4, R=Me, n=1) using this strategy.



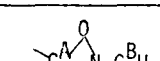
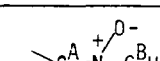
Methylation of tetral-1-one with $Fe(CO)_5$-KOH-CH_2O in ethanol[3] afforded 2-methyltetral-1-one[4] which on reaction in DMF with 3-bromopropylamine hydrobromide in the presence of NaH gave the imine (7, n=2)[5] (64%). This procedure represents a modification of that reported for the preparation of tetrahydropyridines[6] and is an improved preparative procedure for the imine (7, n=2). The demethyl analogue of (7, n=2) was difficult to handle as expected owing to autoxidation.[7]

Oxidation of the imine (7, n=2) at 0^oC with MCPBA in dichloromethane-sodium hydrogen carbonate solution[8] afforded the trans-spiro-oxaziridine (3, R=Me, n=2) (26%), an oil, and the nitrone (8, n=2) (40%), mp 119-121^oC. Selected ^1H and ^{13}C nmr data for compounds (3, R=Me, n=2) and (8, n=2) are recorded in Table 1 and are consistent with the assigned structures. The trans-disposition of the methyl group and the oxygen of the spiro-oxaziridine (3, R=Me, n=2) is inferred since the MCPBA would be expected to attack on the less sterically hindered face of the imine. The imine (7, n=1) (55%)[9] was similarly prepared from 2-methylindan-1-one[10] which was prepared from indan-1-one using the same methylation procedure as described above. Oxidation of the imine (7, n=1) with MCPBA[8] gave only the nitrone (8, n=1) (50%), mp 85-87^oC (Table 1). The nitrones (8, n=1) and (8, n=2) were further characterised by their uv spectra [λ_{max} 292 nm (ε 12730), 304 (ε 13690) and 290 (ε 11210) respectively] and low-field multiplets in the ^1H nmr spectra at δ8.60 and 9.4 respectively assigned to the peri-H_A. The imine (9) (36%)[9] was prepared from 1-methyltetral-2-one[11] by the procedure described for (7) and MCPBA oxidation[8] afforded the trans-spiro-oxaziridine (5, R=Me, n=2) (66%), an oil (Table 1).

Photolysis of ethanolic solutions of the trans-spiro-oxaziridines (3, R=Me, n=2) and (5, R=Me, n=2) using a water cooled quartz apparatus and a low pressure Hg lamp[1] gave respectively the pyrrolo-[1,2-b][2]benzazepin-5-one (4, R=Me, n=2) (38%), mp 103-105°C, ν_{max} 1620 cm^{-1}, and the pyrrolo-[2,1-a][2]benzazepin-5-one (6, R=Me, n=2) (49%), mp 99-101°C, ν_{max} 1615 cm^{-1}. Selected ^{13}C nmr spectral data are shown in Table 2. Photolysis of the nitrone (8, n=1) using a medium pressure Hg lamp led directly to the pyrrolo-[1,2-b]isoquinolin-5-one (4, R=Me, n=1) (36%), mp 128-130°C, ν_{max} 1645 cm^{-1} (Table 2) whereas similar photolysis of the nitrone (8, n=2) gave the cis-spiro-oxaziridine (3, R=Me, n=2) (76%), mp 54-56°C (Table 1). The cis-disposition of the methyl group and the oxygen atom is suggested by the ^1H nmr spectrum in which a multiplet at δ7.65 is assigned to the peri-H_B; models show that in the cis-(3, R=Me, n=2) the H_B is likely to be more deshielded by the N or O atoms of the oxaziridine ring than in the trans-isomer. It is assumed that the nitrone (8, n=1) is initially photorearranged to the spiro-oxaziridine (3, R=Me, n=1) which may thermally or photochemically rearrange to (4, R=Me, n=1).[12] Photolysis of the cis-spiro-oxaziridine (3, R=Me, n=2) using a low pressure Hg lamp gave, as expected, the pyrrolo-[1,2-b][2]benzazepin-5-one (4, R=Me, n=2) (50%).

In the foregoing, the spiro-oxaziridines, nitrones, and photolysis products were purified by preparative tlc on silica gel. All spectroscopic data, in addition to those given were satisfactory.

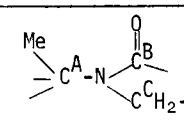
Table 1 : Nmr Data for Oxaziridines and Nitrones

COMPOUND						
	$\delta_C{}^A$	$\delta_C{}^B$	δ_H	$\delta_C{}^A$	$\delta_C{}^B$	δ_H
trans- (3, R=Me, n=2)	80.75	51.88	3.45	-	-	-
(8, n=1)	-	-	-	153.41	57.52	4.0
(8, n=2)	-	-	-	146.58	61.51	4.1
trans- (5, R=Me, n=2)	85.89	51.61	3.5	-	-	-
cis- (3, R=Me, n=2)	81.55	47.18	3.6	-	-	-

The ring systems of compounds (4, R=Me, n=2) and (4, R=Me, n=1) are contained in a number of biologically interesting molecules[13,14,15] and that of the compound (6, R=Me, n=2) is novel.

The preparation of the azeto [1,2-b][2]benzazepin-4-one (10) reported[16] during the course of this study and independently observed in these laboratories, further demonstrates the versatility of this photo-synthetic method.

Table 2 : ^{13}C Nmr Data for Lactams

COMPOUND			
	$\delta_C A$	$\delta_C B$	$\delta_C C$
(4, R=Me, n=1)	61.18	162.70	44.45
(4, R=Me, n=2)	61.35	168.94	48.44
(6, R=Me, n=2)	66.48	173.34	48.22

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