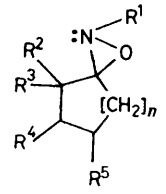
Photochemistry of 2'-Substituted 1,2,3,4-Tetrahydronaphthalene-1-spiro-3'-oxaziridines. Variable-temperature ^{1}H Nuclear Magnetic Resonance Spectroscopy of 1-Substituted 1,3,4,5-Tetrahydro-2*H*-1-benzazepin-2-ones

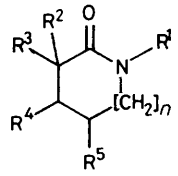
Graham P. Johnson and Brian A. Marples *
Department of Chemistry, University of Technology, Loughborough, Leics. LE11 3TU

The lack of regioselectivity of photorearrangement of the title spiro-oxaziridines in which the *N*-substituent is *syn* to the aromatic ring suggests that the first formed N–O-bond-cleaved species has a significant lifetime allowing rotation (inversion) to compete with rearrangement. The energy barrier to ring inversion of the title tetrahydro-1-benzazepin-2-ones is significantly influenced by the steric interaction between the *N*-substitutent and the *peri* hydrogen atom.

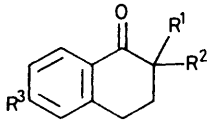
Spiro-oxaziridines (**1**) have been reported [1,2] to photorearrange to the lactams (**2**) under stereoelectronic control and the group *anti* to the nitrogen lone pair migrates highly regioselectively. In all the cases examined the *N*-substituent had the *anti* configuration to the more substituted α-carbon atom and in general the possibility of aryl *versus* alkyl group migrations had not been studied. We report here a study [3] of the regioselectivity of the photorearrangements of the title compounds which allows an evaluation of the influence of the stereochemistry of the oxaziridines and the presence of the aromatic substituent.



(**1**)



(**2**)

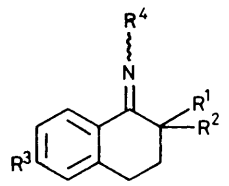


(**3a–d**)

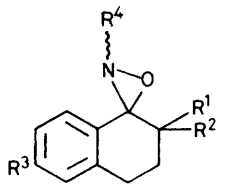
a; $R^1 = R^2 = R^3 = H$
b; $R^1 = R^2 = H$, $R^3 = OMe$
c; $R^1 = Me$, $R^2 = R^3 = H$
d; $R^1 = R^2 = Me$, $R^3 = H$

The spiro-oxaziridines (**6**) were obtained by *m*-chloroperbenzoic acid (MCPBA) oxidation of the corresponding imines (**4**) in dichloromethane containing sodium hydrogencarbonate.[4] The imines (**4b**)—(**4d**) were prepared by toluene-*p*-sulphonic acid (PTSA)-catalysed reaction of the appropriate α-tetralone (**3**) with butylamine or benzylamine. This procedure was unsuccessful for the rather more sterically hindered 2-methyl-α-tetralone (**3c**) [5a] and the 2,2-dimethyl derivative (**3d**) [5b] which were available from α-tetralone (**3a**) by reaction with CH_2O–KOH–$Fe(CO)_5$ and MeI–KOBu^t respectively. Accordingly, it was necessary to employ $TiCl_4$ for catalysis [6] in their reactions with butylamine. The imine (**4a**) was prepared by reaction of α-tetralone with heptamethyldisilazane in the presence of Zn–Cd.[7] The imines (**4**) displayed a characteristic C=N absorption in the i.r. spectra at *ca.* 1 630 cm^{-1} and the ^{13}C n.m.r. spectra allowed the assignment of the configuration in which the *N*-substituent was *anti* to the aromatic ring in all except the dimethyl derivative (**4f**).

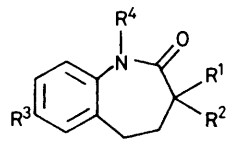
Table 1 shows the expected shielding effect of the *N*-substituent on the chemical shift of C-2 of the imines except for the imine (**4f**). The configuration in which the *N*-substituent is



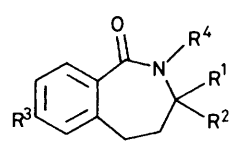
(**4**)



(**6**)

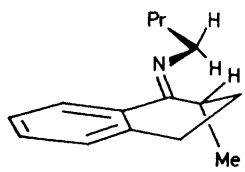


(**9**)

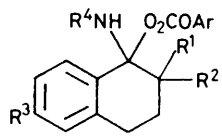


(**10**)

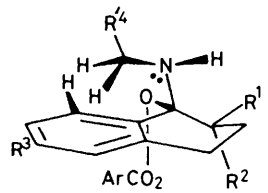
a; $R^1 = R^2 = R^3 = H$, $R^4 = Me$
b; $R^1 = R^2 = R^3 = H$, $R^4 = Bu$
c; $R^1 = R^2 = R^3 = H$, $R^4 = PhCH_2$
d; $R^1 = R^2 = H$, $R^3 = OMe$, $R^4 = Bu$
e; $R^1 = Me$, $R^2 = R^3 = H$, $R^4 = Bu$
f; $R^1 = R^2 = Me$, $R^3 = H$, $R^4 = Bu$
g; $R^1 = R^2 = R^3 = H$, $R^4 = Et$ (**9**) only
h; $R^1 = R^2 = R^3 = H$, $R^4 = Pr^i$ (**9**) only



(**5**)



(**7**)



(**8**)

anti to the aromatic ring would be expected to be more stable than the *syn* owing to steric interaction between the substituent and the hydrogen atom at position 8 in the latter. However, in the imine (**4f**) the interaction between the *N*-substituent and the 2-methyl groups appears to be more significant. In the

Table 1. ^{13}C N.m.r. data (δ_C) for α-tetralones and derived imines

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-4a	C-8a	R^4 α	R^4 β	R^4 γ	R^4 δ	R^1	R^2	R^3
(3a)[a]	197.90	39.07	23.29	29.60	126.98	133.29	126.49	128.74	144.39	132.56							
(3b)	196.93	38.93	23.40	30.18	113.17	163.74	112.73	129.57	147.07	126.46							55.38
(3c)	200.70	42.64	31.44	28.81	127.44	133.18	126.62	128.86	144.23	132.47					15.42		
(3d)	202.73	41.44	36.47	25.53	127.88	132.86	126.51	128.59	143.20	131.38					24.17	24.17	
(4a)	165.71	27.12	22.31	29.63	126.35	129.52	125.47	128.31	140.13	134.77	38.11						
(4b)[b]	163.74	27.66	22.74	29.96	126.34	129.46	125.86	128.32	140.29	135.26	50.79	33.40	20.94	14.05			
(4c)	164.89	27.99	22.47	29.63	126.40	129.63	125.96	128.26	140.40	134.82	54.34						
(4d)	163.25	27.50	22.80	30.23	112.84	160.85	112.46	127.66	141.98	128.43	50.57	33.51	20.94	14.11			55.11
(4e)	167.35	28.92	24.44	29.09	126.46	129.46	126.24	128.54	139.03	133.95	50.03	33.73	20.88	14.10	15.20		
(4f)	170.58	39.48	37.84	26.52	128.65	128.15	128.65	124.38	141.11	130.56	52.65	34.17	20.12	13.62	26.35	26.35	

[a] Chemical shifts assigned by Senda *et al.* (Y. Senda, A. Kasahara, T. Izumi, and T. Takeda, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 2789). [b] Corrected from assignments in previously published work.[3]

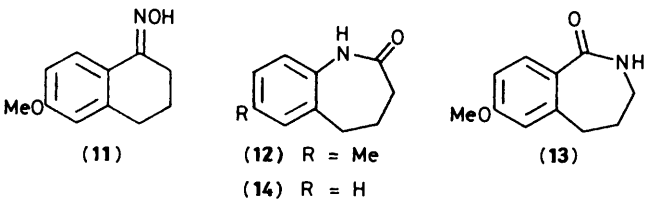
Table 2. Stereoselectivity of spiro-oxaziridine formation

Compound	*syn*:*anti*	Yield (%)
(**6a**)	85:15	46
(**6b**)	80:20	54
(**6c**)	70:30	44
(**6d**)	100:0	42
(**6e**)	100:0	53
(**6f**)	100:0	58

monomethyl derivative (**4e**) significant interaction between the 2-methyl group and the *N*-substituent can be avoided in conformation (**5**).

The oxidation of imines (**4**) with MCPBA afforded mainly or exclusively the spiro-oxaziridines (**6**) in which the *N*-substituents were *syn* to the aromatic ring (Table 2). The spiro-oxaziridines (**6**) were purified by preparative thin-layer chromatography (p.l.c.) and the configurations were assigned principally from their ^{13}C n.m.r. spectra (Table 3). In particular, the signals for C-8a and C-2 were respectively at higher and lower field in the spectra of *syn*-isomers than the corresponding signals for the *anti*-isomers owing to the shielding influence of the *N*-substituent.[8] Also, the signals for C-1 in the spectra of the *syn*-isomers were consistently at lower field (ca. 5 p.p.m.) than for the *anti*-isomers. The *syn*-selectivity in the oxidations is most easily rationalised assuming a two-step mechanism[9] involving oxaziridine formation through the intermediates (**7**) in conformations (**8**) in which the *N*-substituent suffers minimal steric interactions. In the spiro-oxaziridines (**6a**—**d**), the *syn*-isomers would be expected to be less stable than the *anti*-isomers as in the related imines. Support for this view was obtained from the observation that (**6b**) and (**6c**) were converted from the *syn*- into the *anti*-isomers by heating under reflux in toluene. Heating of the *anti*-isomer (**6b**) under similar conditions did not afford any *syn*-isomer. Also, the *syn*-isomer of (**6e**) was not converted into the *anti*-isomer but merely decomposed and demonstrated the importance of the 2-substituent in determining stability. The complete *syn*-selectivity of oxidation of (**4d**) to (**6d**) is not explicable only in terms of steric hindrance, suggesting that electronic factors may have some effect.

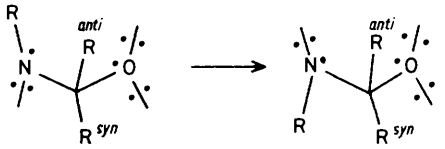
Photorearrangement of Spiro-oxaziridines.—Photolysis of the *syn*- and/or *anti*-spiro-oxaziridines (**6**) in ethanolic solution using a low-pressure mercury lamp afforded the lactams (**9**) and (**10**) which were purified by p.l.c. The isolated yields of the lactams (**9**) and (**10**) and the ratios of (**9**):(**10**) which were determined by gas–liquid chromatography (g.l.c.) are shown in Table 4. It was demonstrated for the lactams (**9b**) and (**10b**) and for the lactams (**9d**) and (**10d**) that the g.l.c. detector (F.I.D.) responded equally for the regioisomers and it is assumed that equally similar sensitivity is likely for all pairs of regioisomers. The Beckmann rearrangement[10] of the oxime (**11**) which affords a readily separable 3:2 mixture of the lactams (**12**) and (**13**) provided a useful approach to (**9d**) and (**10d**) since compounds (**12**) and (**13**) were readily butylated using NaH/BuI–dimethylformamide (DMF).[11] Beckmann rearrangement of the oxime of α-tetralone (**3a**) afforded[12] very largely the lactam (**14**) which on similar alkylation gave compounds (**9a**), (**9b**), and (**9c**) [also (**9g**) and (**9h**), see below]. Separation of (**9b**) from (**10b**) and (**9c**) from (**10c**) was achieved using high-performance liquid chromatography (h.p.l.c.), and pure lactams (**10a**), (**9e**), (**10e**), and (**9f**) were obtained by p.l.c. The i.r. spectra distinguished between the lactams (**9**) ($\nu_{max.}$ *ca.* 1 660 cm^{-1}) and (**10**) ($\nu_{max.}$ *ca.* 1 640 cm^{-1}) owing to the effect of carbonyl group conjugation with the aromatic ring. The ^1H n.m.r. spectrum of the lactam (**9b**) was interesting in that at 35 °C the NCH_2 (δ 3.9) appeared as a poorly resolved multiplet rather than a triplet. This led us to investigate the effect of variation of temperature on the ^1H n.m.r. spectrum of lactam (**9b**) and related derivatives (**9a**), (**9c**), (**9g**), and (**9h**) (see below).



(**11**) (**12**) R = Me (**13**)

(**14**) R = H

It is clear from the photolysis experiments (Table 4) that the *anti*-spiro-oxiridines rearrange almost completely regioselectively. The aryl-group migration does not compete effectively with that of the alkyl group which is *anti* to the nitrogen lone pair.[1,2] However, the *syn*-spiro-oxiziridines do not show the same degree of regioselectivity with the exception of the 2,2-dimethylderivative (**6f**). Since partial photolysis of the *syn*-isomer of (**6b**) does not show any evidence of *syn*- to *anti*-isomerisation, we conclude that the photorearrangements are not synchronous but do require the migrating group to be *anti* to the nitrogen lone pair. It appears that the N–O-bond-cleaved species (**15**)[1] has sufficient lifetime to rotate (invert) to afford (**16**) when there is sufficient steric compression to make this



(**15**) (**16**)

energetically favourable. This rotation then brings the original groups *syn* to the nitrogen lone pair into the *anti* conformation thus allowing them to migrate. The observed highly regioselective rearrangement of the *syn*-spiro-oxaziridine (**6f**) is consistent with this view since there would be no obvious energy gain in the transformation (**15f**) ⟶ (**16f**).

Variable-temperature ^1H *N.m.r. Spectroscopy of* 1-*Substituted* 1,3,4,5-*Tetrahydro*-2*H*-1-*benzazepin*-2-*ones* (**9a**), (**9b**), (**9c**), (**9g**), and (**9h**).—At 60 °C the signal for the NCH_2 (δ 3.9) in the ^1H n.m.r. spectrum of (**9b**) is a clearly resolved triplet whilst at −30 °C the non-equivalence of the methylene protons is evident since they appear as well separated multiplets (Figure). Significantly, the signal assigned to the C-5 methylene group (δ 2.75) shows some variation with temperature, being a triplet at $> \sim 30$ ° but becoming a complex multiplet at below −20 °C (Figure). On the assumption (see below) that the RNCO group is planar the boat conformation (**17**) is most likely. In this chiral conformation it would be expected that the NCH_2 group would exhibit diastereotopicity[13] and that the protons of the ring methylene groups would be non-equivalent.[14] Rapid ring inversion with no significant rotation about the CO–N bond would bring about the observed averaging of the signals. The observed coalescence (Figure) of the NCH_2 signals allows the calculation of the barrier to ring inversion (13.6 kcal mol^{-1}, Table 5). Similar calculations can be made from the coalescence of the NCH_2 signals for the *N*-ethyl and the *N*-benzyl derivatives (**9g**) and (**9c**) respectively and the $NCMe_2$ signals of the isopropyl derivative (**9h**). In achieving the transition state (**18**) involved in the proposed boat ⇌ boat inversion the

Table 3. ^{13}C N.m.r. data (δ_C) of the spiro-oxaziridines (**6**)

											R^4						
Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-4a	C-8a	α	β	γ	δ	R^1	R^2	R^3
(6a) (*syn*)	84.47	33.40	21.10	28.70	129.19	127.50	128.91	124.87	141.49	130.17	40.79						
(6b) (*anti*)	79.44	26.57	21.65	29.58	128.91	126.84	128.21	126.51	140.51	134.38	41.00						
(6b) (*syn*)	84.09	33.46	20.94	28.65[a]	129.08	127.22	128.81	124.82	141.22	130.78	52.70	29.96[a]	20.39	13.78			
(6b) (*anti*)	79.17	26.68	21.81	29.63	128.86	127.17	128.15	126.51	140.40	134.77	53.80	30.73	20.67	13.94			
(6c) (*syn*)	84.52	33.13	20.72	28.37	129.25	127.17	128.86	124.90	141.66	130.78	57.24						
(6c) (*anti*)	79.66	26.95	21.81	29.58	129.03	127.33	128.21	126.57	140.52	134.30	57.95						
(6d) (*syn*)	84.10	33.80	21.10	29.10	113.78	160.35	110.82	128.81	142.91	122.79	52.60	29.50	20.50	13.80			55.20
(6e) (*syn*)	85.78	34.72	29.41	28.54	128.92	127.28	128.92	124.54	140.84	131.71	52.21	29.74	20.39	13.78	13.39		
(6f) (*syn*)	87.85	34.62	34.69	25.62	128.68	128.06	128.57	124.63	140.49	130.37	52.31	29.76	20.40	13.78	21.61	23.36	

[a] The assignments are corrected from the values reported in the literature.[3]

Table 4. Lactams from spiro-oxaziridine photolysis

Spiro-oxaziridine	Total yield of lactam mixture (%)	Relative yield of lactams (**9**):(**10**)
(**6a**) (*syn*)	11	50:50
(**6a**) (*anti*)	13	4:96
(**6b**) (*syn*)	28	77.5:22.5
(**6b**) (*anti*)	25	0:100
(**6c**) (*syn*)	27	61:39
(**6c**) (*anti*)	22	0:100
(**6d**) (*syn*)	20	70:30
(**6e**) (*syn*)	31	52:48
(**6f**) (*syn*)	10	100:0

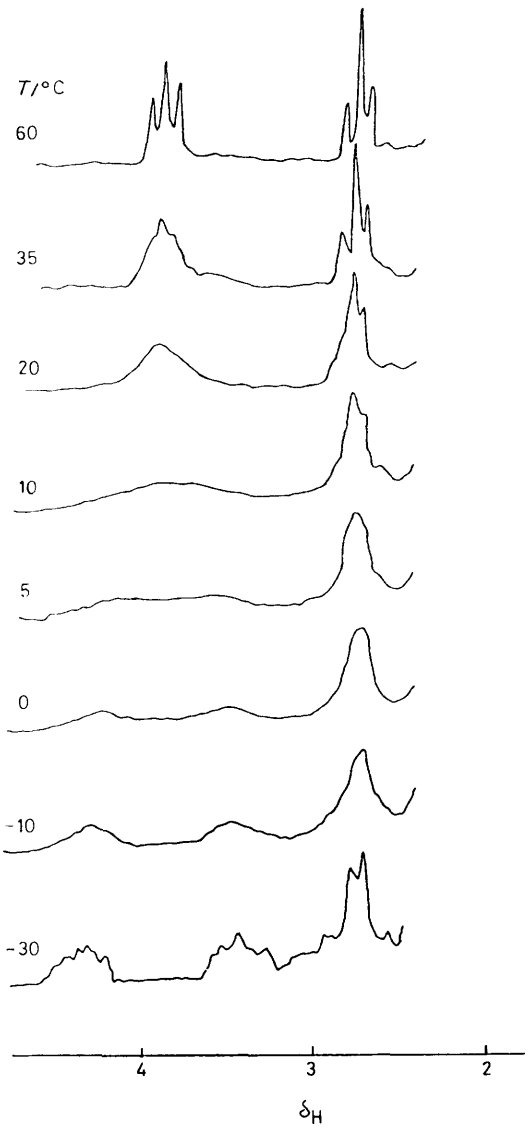


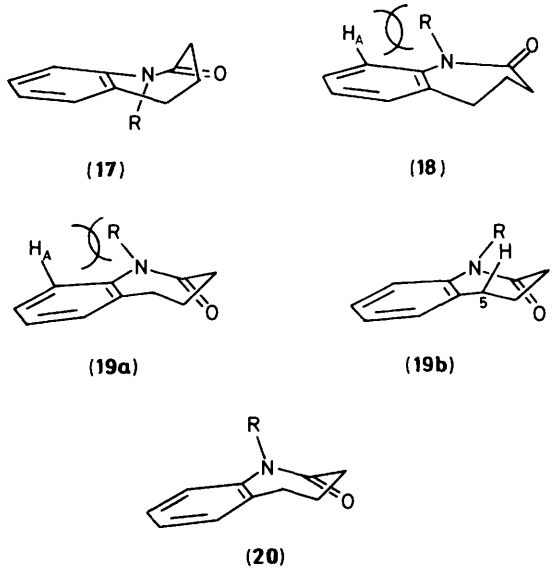
Figure. Variable-temperature ^{1}H n.m.r. spectrum of lactam (**9b**)

N-substituent moves towards the *peri* hydrogen atom (H_A) and it would be expected that the size of the *N*-substituent would be significant in determining $\Delta G^{\ddagger}$. In confirmation of this, there is no significant separation of the signals for the protons of the ring methylene groups of the lactam (**14**) down to −95 °C whereas such low-temperature separation (see above) is observed, though not analysed, for all the *N*-substituted derivatives. The similarity of the $\Delta G^{\ddagger}$ values for (**9b**), (**9c**), and (**9g**) is expected since the R group of NCH_2R would be able to rotate away from the *peri* hydrogen atom. It is interesting that in a study[4] of 1-substituted 5-phenyl-1,3-dihydro-2*H*-1,4-benzodiazepin-2-ones there is little difference (< 1 kcal mol^{-1}) in $\Delta G^{\ddagger}$ for the ethyl and isopropyl derivatives.

Table 5. Variable-temperature 90 MHz ^{1}H n.m.r. spectroscopy of 1-substituted 1,3,4,5-tetrahydro-2*H*-1-benzazepin-2-ones (**9**)

Compound	$NCR^1_2R^2$ R^1	R^2	$\Delta\nu^a$ (Hz)	Coalescence temp. (°C)	$\Delta G^{\ddagger}$ (kcal) mol^{-1})
(**9b**)	H	Pr	87.5	+10	13.6
(**9c**)	H	Ph	23.2	−5	13.5
(**9g**)	H	Me	73.3	+5	13.2
(**9h**)	Me	H	32.2	+55	16.4

^{a} $\Delta\nu = \nu_{R_A} - \nu_{R_B}$



The observed barriers to ring inversion are rather lower than observed[14,15] in some 1-benzazepines as perhaps expected[16] and are too low to be associated with rotation around the N–CO bond[17,18] not withstanding the possible delocalisation of the amidic nitrogen lone pair with the benzenoid ring. Chair conformations (**19**) of the lactams (**9**) in which the RNCO group is non-planar and contain a pyramidal nitrogen seem less attractive than the proposed boat conformations (**17**) because the steric interaction between the *N*-substituent and either the *peri* hydrogen atom or the *syn* 5-hydrogen atom would be significant. Similar conformations (**20**) in which the nitrogen is more nearly planar would experience no such steric constraints. Although conformations similar to (**19**) and (**20**) have been suggested as favoured for 1,3,4,5-tetrahydro-2*H*-1,5-benzodiazepin-2-ones,[19] we favour the boat conformation (**17**) for the lactams (**9**) particularly since chair-to-chair, and chair-to-boat, inversion for (**19**) and (**20**) would involve effective rotation around the CO–N bond.

Experimental

Extracts were dried ($MgSO_4$) and solvents were removed under reduced pressure on a rotatory evaporator. I.r. spectra were

determined using a Perkin-Elmer 177 spectrophotometer and ^{1}H n.m.r. spectra were recorded for deuteriochloroform solutions at 60 MHz and 90 MHz using Varian EM 360A and Perkin-Elmer R32 spectrometers. ^{13}C N.m.r. spectra were determined for deuteriochloroform solutions using a Bruker WP-80 spectrometer. Mass spectra were determined with a Kratos MS80 spectrometer and DS 55 data system and m.p.s. were recorded on a Kofler hot-stage apparatus. Merck silica gels 60 $PF_{254+366}$ and 230—400 mesh were employed for t.l.c. and flash chromatography respectively and gas–liquid chromatography was carried out with Pye Series 104 chromatograph with a 10% SE-30 on Chromasorb W column. Reverse-phase high-performance liquid chromatography was carried out using an ODS Hypersil column with methanol–water as eluant. Photolyses were carried out in a water-cooled Hanovia quartz photoreactor using a low-pressure mercury lamp (3 W). Bulb-to-bulb distillations were performed using a Büchi GKR-50 Kugelrohr oven.

2-*Methyl*-3,4-*dihydronaphthalen*-1(2H)-*one* (**3c**).—A solution of iron pentacarbonyl (18.0 g) and potassium hydroxide (14.8 g) in ethanol (400 ml) was heated under reflux and stirred for 3 h. Formaldehyde (7 ml; 40% aqueous solution) and α-tetralone (**3a**) (12.8 g) were added dropwise and the mixture was heated under reflux for a further 3 h. The mixture was poured into water (1 l), acidified with 2M-hydrochloric acid, and extracted (3 × 100 ml) with ether. The combined extracts were dried, and evaporated under reduced pressure to give 2-methyl-α-tetralone (**3c**)[5a] (10.2 g, 73%), b.p. 75 °C at 0.25 mmHg; $\nu_{max.}$(film) 1 685 cm^{-1} (C=O); δ_H 1.20 (d, *J* 8 Hz, Me), 1.5—2.7 (m, 2-H and 3-H_2), 2.9 (m, 4-H_2), 7.1—7.5 (m, 5-, 6-, and 7-H), and 8.0 (dd, *J* 9 and 2 Hz, 8-H); δ_C (see Table 1).

1-*Methylimino*-1,2,3,4-*tetrahydronaphthalene* (**4a**).—A mixture of α-tetralone (**3a**) (14.6 g), heptamethyldisilazane (17.5 g) and catalytic quantities of cadmium and zinc was heated to 170 °C in a bomb (5 000 psi) for 40 h to afford the *imine* (**4a**) (12.0 g, 75%), m.p. 37—39 °C (from light petroleum, b.p. 40—60 °C), $\nu_{max.}$(film) 1 640 cm^{-1} (C=N); δ_H 1.9 (quintet, *J* 6 Hz, 3-H_2), 2.45 (t, *J* 6 Hz, 2-H_2), 2.73 (t, *J* 6 Hz, 4-H_2), 3.3 (s, NMe), 7.0—7.35 (m, 5-, 6-, and 7-H), and 8.1—8.2 (m, 8-H); δ_C (see Table 1) (Found: M^+, 159.1055. $C_{11}H_{13}N$ requires *M*, 159.1048).

1-*Butylimino*-1,2,3,4-*tetrahydronaphthalene* (**4b**).—A solution of α-tetralone (**3a**) (1 g), butylamine (2.6 g), and PTSA (0.02 g) in benzene (75 ml) was heated under reflux for 2 h with a Dean and Stark water separator. The solution was washed with aq. sodium hydrogen carbonate (2 × 50 ml; 5%), dried, and evaporated to afford the *imine* (**4b**) (1.3 g, 94%) as an oil, $\nu_{max.}$(film) 1 635 cm^{-1} (C=N); δ_H 1.0 (t, *J* 6 Hz, Me), 1.3—1.7 (m, $NCH_2CH_2CH_2$), 1.85 (quintet, *J* 6 Hz, 3-H_2), 2.5 (t, *J* 6 Hz, 2-H_2), 2.75 (t, *J* 6 Hz, 4-H_2), 3.4 (t, *J* 7 Hz, NCH_2), 7.0—7.3 (m, 5-, 6-, and 7-H), and 8.05—8.25 (m, 8-H); δ_C (see Table 1) (Found: M^+, 201.1519. $C_{14}H_{19}N$ requires *M*, 201.1517).

1-*Benzylamino*-1,2,3,4-*tetrahydronaphthalene* (**4c**).—A similar procedure to that used for compound (**4b**) gave, from ketone (**3a**) (1 g) and benzylamine (4.3 g), the imine (**4c**)[20] (1.4 g, 90%) as an oil, $\nu_{max.}$(film) 1 625 cm^{-1} (C=N); δ_H 1.75 (quintet, *J* 5 Hz, 3-H_2), 2.4 (t, *J* 7 Hz, 2-H_2), 2.65 (t, *J* 6 Hz, 4-H_2), 4.5 (s, NCH_2), 6.90—7.5 (m, 5-, 6-, and 7-H, and Ph), and 8.1—8.3 (m, 8-H); δ_C (see Table 1).

1-*Butylimino*-6-*methoxy*-1,2,3,4-*tetrahydronaphthalene* (**4d**).—As above, 6-methoxy-α-tetralone (**3b**) (1 g) and butylamine (2.5 g) gave the *imine* (**4d**) (1.2 g, 91%) as an oil, purified by bulb-to-bulb distillation; $\nu_{max.}$(film) 1 625 cm^{-1} (C=N); δ_H 1.0 (t, *J* 6 Hz, CH_2Me), 1.3—1.8 (m, $NCH_2CH_2CH_2$), 1.9 (quintet, *J* 6 Hz, 3-H_2), 2.55 (t, *J* 6 Hz, 2-H_2), 2.75 (t, *J* 6 Hz, 4-H_2), 3.45 (t, *J* 7 Hz, NCH_2), 3.8 (s, OMe), 6.6 (d, *J* 2 Hz, 5-H), 6.8 (dd, *J* 11 and 2 Hz, 7-H), and 8.15 (d, *J* 11 Hz, 8-H); δ_C (see Table 1) (Found: M^+, 231.1616. $C_{15}H_{21}NO$ requires *M*, 231.1623).

1-*Butylimino*-2-*methyl*-1,2,3,4-*tetrahydronaphthalene* (**4e**).—To a solution of 2-methyl-α-tetralone (**3c**) (5 g) and butylamine (22 g) in dry benzene (100 ml) at 0—5 °C was added titanium tetrachloride (1 g) dropwise under nitrogen. After the mixture had been stirred for 1 h, benzene (50 ml) and water (5 ml) were added and the resultant mixture was filtered through Celite. The filtrate was dried and evaporated to give the *imine* (**4e**) (4.9 g, 76%) as a pale yellow oil, $\nu_{max.}$(film) 1 630 cm^{-1} (C=N); δ_H 1.0 (t, *J* 6 Hz, CH_2Me), 1.1 (d, *J* 7 Hz, 2-Me), 1.3—2.2 (m, 3-H_2 and $NCH_2CH_2CH_2$), 2.5—3.4 (m, 2-H and 4-H_2), 3.6 (t, *J* 6 Hz, NCH_2), 7.1—7.35 (m, 5-, 6-, 7-H), and 8.2—8.35 (m, 8-H); δ_C (see Table 1) (Found: M^+, 215.1673. $C_{15}H_{21}N$ requires *M*, 215.1674).

1-*Butylimino*-2,2-*dimethyl*-1,2,3,4-*tetrahydronaphthalene* (**4f**).—A similar procedure to that used for compound (**4e**) gave, from 2,2-dimethyl-α-tetralone (**3d**) (5 g) and butylamine (12.6 g), the *imine* (**4f**) (3.9 g, 60%) as an oil, purified by bulb-to-bulb distillation, $\nu_{max.}$(film) 1 630 cm^{-1} (C=N); δ_H 0.85 (t, *J* 6 Hz, CH_2Me), 1.15 (s, 2-Me_2), 1.15—2.0 (m, $NCH_2CH_2CH_2$), 1.8 (t, *J* 6 Hz 3-H_2), 2.8 (t, *J* 6 Hz, 4-H_2), 3.7 (t, NCH_2), and 7.25 (m, 5-, 6-, 7-, and 8-H); δ_C (see Table 1) (Found: M^+, 229.1828. $C_{16}H_{23}N$ requires *M*, 229.1830).

Oxidation of Imines to Spiro-oxaziridines.—The imines were allowed to react, without special purification, under nitrogen and at 0 °C with MCPBA (1.1 mol equiv.) for 2 h in a stirred solution in dichloromethane containing sodium hydrogen carbonate in suspension. The reaction mixture was washed with aq. sodium sulphite (2 × ; 5%), dried, and evaporated after which the crude product was purified by p.l.c. with light petroleum (b.p. 40—60 °C)–ether (6:1).

The imine (**4a**) (2 g) gave syn-2′-*methyl*-^{1},2,3,4-*tetrahydronaphthalene*-1-*spiro*-3′-*oxaziridine* (**6a**) (0.85 g, 39%) as a yellow oil, $\nu_{max.}$(film) 1 450 cm^{-1}; δ_H 1.9—2.3 (m, 2- and 3-H_2), 2.5 (s, NMe), 2.9 (t, *J* 6 Hz, 4-H_2), and 7.1—7.5 (m, 5-, 6-, 7-, and 8-H); δ_C (see Table 3) (Found: M^+, 175.0992. $C_{11}H_{13}NO$ requires *M*, 175.0997) and the anti-*isomer* (**6a**) (0.16 g, 7%) as a yellow oil, $\nu_{max.}$ 1 450 cm^{-1}; δ_H 1.9—2.4 (m, 2- and 3-H_2), 2.9 (s, NMe), 2.9 (t, *J* 6 Hz, 4-H_2) and 7.05—7.5 (m, 5-, 6-, 7-, and 8-H); δ_C (see Table 3) (Found: M^+, 175.0990).

The imine (**4b**) (1 g) gave syn-2′-*butyl*-1,2,3,4-*tetrahydronaphthalene*-1-*spiro*-3′-*oxaziridine* (**6b**) (0.46 g, 43%) as an oil, $\nu_{max.}$(neat) 1 450 cm^{-1}; δ_H 0.8 (t, *J* 6 Hz, Me), 1.1—1.6 (m, 2 × CH_2), 1.6—2.8 (m, 3 × CH_2) 2.9 (t, *J* 6 Hz, 4-H_2), and 7.1—7.4 (m, 5-, 6-, 7-, and 8-H); δ_C (see Table 3) (Found: M^+, 217.1471. $C_{14}H_{19}NO$ requires *M*, 217.1467) and the anti-*isomer* (**6b**) (0.12 g, 11%) as an oil, $\nu_{max.}$(film) 1 450 cm^{-1}; δ_H 0.95 (t, *J* 6 Hz, Me), 1.2—1.85 (m, 3 × CH_2), 1.9—3.1 (m, 3 × CH_2), 7.1—7.3 (m, 5-, 6-, and 7-H), and 7.4—7.5 (m, 8-H); δ_C (see Table 3) (Found: M^+, 217.1471).

The imine (**4c**) (1 g) gave syn-2′-*benzyl*-1,2,3,4-*tetrahydronaphthalene*-1-*spiro*-3′-*oxaziridine* (**6c**) (0.33 g, 31%) as an oil, $\nu_{max.}$ 1 450 cm^{-1}; δ_H 1.6—2.2 (m, 2 × CH_2), 2.6—2.9 (m, 4-H_2), 3.6 (d, *J* 14 Hz, NCH), 4.05 (d, *J* 14 Hz, NCH), and 6.9—7.6 (m, 5-, 6-, 7-, and 8-H, and Ph); δ_C (see Table 3) (Found: M^+, 251.1326. $C_{17}H_{17}NO$ requires *M*, 251.1310) and the anti-*isomer* (**6c**) (0.14 g, 13%) as an oil, $\nu_{max.}$(film) 1 450 cm^{-1}; δ_H 1.9—2.5 (m, 2 × CH_2), 2.9 (t, *J* 6 Hz, 4-H_2), 4.26 (s, NCH_2), and 7.0—7.6 (m, 5-, 6-, 7-, and 8-H, and Ph); δ_C (see Table 3) (Found: M^+, 251.1316).

The imine (**4d**) (1 g) gave syn-2′-*butyl*-6-*methoxy*-1,2,3,4-*tetrahydronaphthalene*-1-*spiro*-3′-*oxaziridine* (**6d**) (0.44 g, 42%) as a yellow oil, $\nu_{max.}$(film) 1 450 cm^{-1}; δ_H 0.8 (t, *J* 6 Hz CH_2Me),

1.2—1.6 (m, 3 × CH_2), 2.45—2.6 (m, 2-H_2), 2.6—2.8 (m, NCH_2), 2.9 (t, *J* 6 Hz, 4-H_2), 3.8 (s, OMe), 6.7—6.85 (m, 5- and 7-H), and 7.25 (d, *J* 10 Hz, 8-H); δ_C (see Table 3) (Found: M^+, 247.1568. $C_{15}H_{21}NO_2$ requires *M*, 247.1572).

The imine (**4e**) (1 g) gave syn-2′-*butyl*-2-*methyl*-1,2,3,4-*tetrahydronaphthalene*-1-*spiro*-3′-*oxaziridine* (**6e**) (0.57 g, 53%) as an oil, $\nu_{max.}$(film) 1 465 cm^{-1}; δ_H 0.75 (t, *J* 6 Hz, CH_2Me), 0.9 (d, *J* 7 Hz, 2-Me), 1.1—1.5 (m, 2 × CH_2), 1.7—3.1 (m, 3 × CH_2 and 2-H), and 7.0—7.4 (m, 5-, 6-, 7-, and 8-H); δ_C (see Table 3) (Found: M^+, 231.1616. $C_{15}H_{21}NO$ requires *M*, 231.1623).

The imine (**4f**) (1 g) gave syn-2′-*butyl*-2,2-*dimethyl*-1,2,3,4-*tetrahydronaphthalene*-1-*spiro*-3′-*oxaziridine* (**6f**) (0.62 g, 58%) as an oil, $\nu_{max.}$(film) 1 455 cm^{-1}; δ_H 0.75 (t, *J* 6 Hz, CH_2Me), 0.9 and 1.0 (s, 2-Me_2), 1.1—1.5 (m, 2 × CH_2), 1.6—2.8 (m, NCH_2 and 3-H_2), 2.85—3.05 (m, 4-H_2), and 7.05—7.45 (m, 5-, 6-H, 7-, and 8-H); δ_C (see Table 3) (Found: M^+, 245.1781. $C_{16}H_{23}NO$ requires *M*, 245.1780).

Thermal Isomerisation of the Spiro-oxaziridines.—A solution of the spiro-oxaziridine (50 mg) in toluene (25 ml) was heated under reflux for 1 h and the solvent was evaporated off. P.l.c. afforded the *syn*- and *anti*-isomers.

The *syn*-spiro-oxaziridine (**6b**) gave the *anti*-isomer (**6b**) (25 mg, 50%) and unchanged *syn*-isomer (**6b**) (15 mg, 30% recovery).

The *syn*-spiro-ozaziridine (**6c**) gave the *anti*-isomer (**6c**) (17 mg, 30%) and the unchanged *syn*-isomer (**6c**) (35 mg, 70% recovery).

The *syn*-spiro-oxaziridine (**6e**) gave no significant quantity of *anti*-isomer (**6e**) and unchanged *syn*-isomer (**6e**) (25 mg, 50% recovery).

The *anti*-spiro-oxaziridine (**6b**) gave no significant quantity of *syn*-isomer (**6b**) and unchanged *anti*-isomer (**6b**) (25 mg, 50% recovery).

Photorearrangement of the Spiro-oxaziridines.—A solution of the spiro-oxaziridine (0.2 g) in degassed ethanol (100 ml) was irradiated for 24 h. The solvent was evaporated off and p.l.c. in light petroleum (b.p. 40—60 °C)–ether afforded the lactams (**9**) and (**10**). G.l.c. gave the compositions of the lactam mixtures (Table 4). Samples of pure lactams were obtained by p.l.c. [(**10a**), (**9e**), (**10e**), (**9f**)] or h.p.l.c. [(**9b**), (**10b**), (**9c**), (**10c**)] or by alkylation of the 1,3,4,5-tetrahydro-2*H*-1-benzazepin-2-one (see below) and subsequent p.l.c.

The *syn*-spiro-oxaziridine (**6a**) gave 1-methyl-1,3,4,5-tetrahydro-2*H*-1-benzazepin-2-one (**9a**)[11] as an oil, $\nu_{max.}$(film) 1 655 cm^{-1} (C=O); δ_H 2.15—2.45 (m, 3- and 4-H_2), 2.75 (t, *J* 6 Hz, 5-H_2), 3.4 (s, NMe), and 6.9—7.2 (m, 6-, 7-, 8-, and 9-H); and 2-*methyl*-2,3,4,5-*tetrahydro*-1*H*-2-*benzazepin*-1-*one* (**10a**) as an oil, $\nu_{max.}$(film) 1 625 cm^{-1} (C=O); δ_H 1.8—2.2 (m, 4-H_2), 2.5—2.8 (m, 5-H_2), 3.0 (s, NMe), 3.05 (t, *J* 6 Hz, 3-H_2), 6.8—7.2 (m, 6-, 7-, and 8-H), and 7.3—7.5 (m, 9-H) (Found: M^+, 175.0995. $C_{11}H_{13}NO$ requires *M*, 175.0997). The *anti*-spiro-oxaziridine (**6a**) also gave lactams (**9a**) and (**10a**).

The *syn*-spiro-oxaziridine (**6b**) gave 1-*butyl*-1,3,4,5-*tetrahydro*-2H-1-*benzazepin*-2-*one* (**9b**) as an oil, $\nu_{max.}$(film) 1 640 cm^{-1} (C=O); δ_H 0.9 (t, *J* 6 Hz, Me), 1.1—1.8 (m, $NCH_2CH_2CH_2$), 2.0—2.4 (m, 3- and 4-H_2), 2.6—2.9 (m, 5-H_2), 3.7—4.0 (m, NCH_2), and 7.0—7.4 (m, 6-, 7-, 8-, and 9-H) (Found: M^+, 217.1464. $C_{14}H_{19}NO$ requires *M*, 217.1467); and 2-*butyl*-2,3,4,5-*tetrahydro*-1H-2-*benzazepin*-1-*one* (**10b**) as an oil, $\nu_{max.}$ 1 620 cm^{-1} (C=O); δ_H 1.0 (t, *J* 6 Hz, Me), 1.2—1.8 (m, $NCH_2CH_2CH_2$), 2.05 (quintet, *J* 6 Hz, 4-H_2), 2.8 (t, *J* 6 Hz, 5-H_2), 3.2 (t, *J* 6 Hz, 3-H_2), 3.6 (t, *J* 6 Hz, NCH_2), 7.0—7.45 (m, 6-, 7-, and 8-H), and 7.65—7.75 (m, 9-H) (Found: M^+, 217.1471).

The *anti*-spiro-oxaziridine (**6b**) gave only lactam (**10b**).

The *syn*-spiro-oxaziridine (**6c**) gave 1-benzyl-1,3,4,5-tetrahydro-2*H*-1-benzazepin-2-one (**9c**)[21] as an oil, $\nu_{max.}$(film) 1 665 cm^{-1} (C=O); δ_H 2.2 (quintet, *J* 6 Hz, 4-H_2), 2.35 (t, *J* 6 Hz, 3-H_2), 2.55 (t, *J* 6 Hz, 5-H_2), 5.05 (s, NCH_2), and 7.1—7.4 (m, 6-, 7-, 8-, and 9-H, and Ph) (Found: M^+, 251.1327. Calc. for $C_{17}H_{17}NO$: *M*, 251.1310); and 2-benzyl-2,3,4,5-tetrahydro-1*H*-2-benzazepin-1-one (**10c**)[22] as an oil, $\nu_{max.}$ 1 640 cm^{-1} (C=O); δ_H 1.8 (quintet, *J* 6 Hz, 4-H_2), 2.75 (t, *J* 6 Hz, 5-H_2), 3.2 (t, *J* 6 Hz, 3-H_2), 4.8 (s, NCH_2), 7.3—7.5 (m, 6-, 7-, and 8-H, and Ph), and 7.7—7.85 (m, 9-H) (Found: M^+, 251.1301).

The *anti*-spiro-oxaziridine (**6c**) gave only lactam (**10c**).

The *syn*-spiro-oxiziridine (**6d**) gave 1-*butyl*-7-*methoxy*-1,3,4,5-*tetrahydro*-2H-1-*benzazepin*-2-*one* (**9d**) as a yellow oil, $\nu_{max.}$(film) 1 640 cm^{-1} (C=O); δ_H 0.85 (t, *J* 6 Hz, CH_2Me), 1.1—1.7 (m, $NCH_2CH_2CH_2$), 2.1—2.35 (m, 3-H_2 and 4-H_2), 2.7 (br t, *J* 6 Hz, 5-H_2), 3.8 (s, OMe), 3.8 (t, *J* 6 Hz, NCH_2), 6.8 (d, *J* 2 Hz, 6-H), 6.85 (dd, *J* 9 Hz and 2 Hz, 8-H), and 7.15 (d, *J* 9 Hz, 9-H) (Found: M^+, 247.1571. $C_{15}H_{21}NO_2$ requires *M*, 247.1572); and 2-*butyl*-7-*methoxy*-2,3,4,5-*tetrahydro*-1H-2-*benzazepin*-1-*one* (**10d**) as a yellow oil, $\nu_{max.}$(film) 1 625 cm^{-1} (C=O); δ_H 1.0 (t, *J* 6 Hz, CH_2Me), 1.2—1.8 (m, $NCH_2CH_2CH_2$), 2.05 (quintet, *J* 6 Hz, 4-H_2), 2.8 (t, *J* 6 Hz, 5-H_2), 3.25 (t, *J* 6 Hz, 3-H_2), 3.6 (t, *J* 6 Hz, NCH_2), 3.85 (s, OMe), 6.7 (d, *J* 3 Hz, 6-H), 6.85 (dd, *J* 8 Hz and 3 Hz, 8-H), and 7.7 (d, *J* 8 Hz, 9-H) (Found: M^+ 247.1569).

The *syn*-spiro-oxaziridine (**6e**) gave 1-*butyl*-3-*methyl*-1,3,4,5-*tetrahydro*-2H-1-*benzazepin*-2-*one* (**9e**) as a yellow oil, $\nu_{max.}$(film) 1 655 cm^{-1} (C=O); δ_H 0.9 (t, *J* 6 Hz, CH_2Me), 1.05 (d, *J* 6 Hz, 3-Me), 1.1—1.7 (m, $NCH_2CH_2CH_2$), 1.9—3.1 (m, 3-H, and 4- and 5-H_2), 3.3—3.65 and 4.15—4.45 (m, NCH_2), and 7.05—7.45 (m, 6-, 7-, 8-, and 9-H) (Found: M^+, 231.1625. $C_{15}H_{21}NO$ requires *M*, 231.1623); and 2-*butyl*-3-*methyl*-2,3,4,5-*tetrahydro*-1H-2-*benzazepin*-1-*one* (**10e**) as a yellow oil, $\nu_{max.}$(film) 1 620 cm^{-1} (C=O); δ_H 1.0 (t, *J* 6 Hz, CH_2Me), 1.25 (d, *J* 6 Hz, 3-Me), 1.2—1.8 (m, $NCH_2CH_2CH_2$), 1.85—2.1 (m, 4-H_2), 2.65—2.95 (m, 5-H_2), 3.65—4.3 (m, NCH_2 and 3-H), 7.05—7.45 (m, 6-, 7-, 8-H), and 7.6—7.75 (m, 9-H) (Found: M^+ 231.1624).

The *syn*-spiro-oxaziridine (**6f**) gave 1-*butyl*-3,3-*dimethyl*-1,3,4,5-*tetrahydro*-2H-1-*benzazepin*-2-*one* (**9f**) as a yellow oil, $\nu_{max.}$ 1 645 cm^{-1} (C=O); δ_H 0.95 (t, *J* 6 Hz, CH_2Me), 0.95 (s, 3-Me_2), 1.2—1.8 (m, $NCH_2CH_2CH_2$), 2.05 (t, *J* 6 Hz, 4-H_2), 2.75 (t, *J* 6 Hz, 5-H_2), 3.95 (t, *J* 6 Hz, NCH_2), and 7.2—7.4 (m, 6-, 7-, 8-, and 9-H) (Found: M^+, 245.1778. $C_{16}H_{23}NO$ requires *M*, 245.1780).

Alkylation of 1,3,4,5-*Tetrahydro*-2H-1-*benzazepin*-2-*ones.*—A solution of the lactam (0.5 g) in DMF (50 ml) containing sodium hydride (0.4 g) was stirred under nitrogen for 1 h. A slight excess of alkyl iodide in DMF (10 ml) was added dropwise and the mixture was stirred for a further 2 h before being poured into water (50 ml) and extracted with ether (3 × 30 ml); the extract was dried and evaporated. Purification by p.l.c. gave the pure 1-alkyl derivatives.

The lactam (**14**) gave the 1-methyl derivative (**9a**),[11] the 1-ethyl derivative (**9g**),[23] the 1-benzyl derivative (**9c**),[21] the 1-butyl derivative (**9b**) (see above), and 1-*isopropyl*-1,3,4,5-*tetrahydro*-2H-1-*benzazepin*-2-*one* (**9h**) as an oil, $\nu_{max.}$ 1 660 cm^{-1} (C=O); δ_H 1.1 (d, *J* 6 Hz, *Me*CHMe) and 1.5 (d, *J* 6 Hz, MeCH*Me*), 2.0—2.3 (m, 3 × CH_2), 4.85 (septet, *J* 6 Hz, NCH), and 7.15—7.4 (m, 6-, 7-, 8-, and 9-H) (Found: M^+, 203.1308. $C_{13}H_{17}NO$ requires *M*, 203.1310).

Acknowledgements

We thank the S.E.R.C. for a research studentship (to G. P. J.).

References

1 A. Lattes, E. Olivers, M. Rivière, C. Belzecki, D. Mostowicz, W. Abramskj, C. Piccini-Leopardi, G. Germain, and M. Van Meerssche, *J. Am. Chem. Soc.*, 1982, **104**, 3929.

2 G. J. Edge, S. H. Imam, and B. A. Marples, *J. Chem. Soc., Perkin. Trans.*, **1**, 1984, 2319.
3 Preliminary communication: G. P. Johnson and B. A. Marples, *Tetrahedron Lett.*, 1984, **25**, 3359.
4 W. E. Fristad, T. R. Bailey, and L. A. Paquette, *J. Org. Chem.*, 1980, **45**, 3028.
5 (*a*) I. D. Rae and B. N. Umbrasas, *Aust. J. Chem.*, 1975, **28**, 2669; (*b*) M. Mousseron, R. Jacquier, and H. Cristol, *Bull. Soc. Chim. Fr.*, 1957, 346.
6 H. Weingarten and W. A. White, *J. Org. Chem.*, 1967, **32**, 213.
7 N. Duffaut and J. P. Dupin, *Bull. Soc. Chim. Fr.*, 1966, 3205.
8 E. Oliveros, M. Rivière, and A. Lattes, *J. Heterocycl. Chem.*, 1980, **17**, 107.
9 E. Schmitz, *Adv. Heterocycl. Chem.*, 1979, **24**, 65.
10 Y. Sawa, T. Kato, T. Masuda, M. Hori, and H. Fujimura, *Chem. Pharm. Bull.*, 1975, **23**, 1917.
11 J. H. Barrett, D. E. Kuhla, and L. A. Paquette, *J. Org. Chem.*, 1969, **34**, 2879.
12 P. T. Lansbury and N. R. Mancuso, *Tetrahedron Lett.*, 1965, 2445.
13 P. Linscheid and J.-M. Lehn, *Bull. Soc. Chim. Fr.*, 1967, 992.
14 A. Cromarty, K. E. Haque, and G. R. Proctor, *J. Chem. Soc. C*, 1971, 3536.
15 A. Mamschrenk, G. Rissman, F. Vogtle, and D. Wild, *Chem. Ber.*, 1967, **100**, 335.
16 W. L. F. Armarego, 'Stereochemistry of Heterocyclic Compounds,' Wiley, New York, 1977, Part 1, p. 306.
17 W. E. Stewart and T. H. Siddall, *Chem. Rev.*, 1970, **70**, 517.
18 M. W. Majchrzak, A. Kotełło, R. Guryn, J. B. Lambert, and S. M. Wharry, *Tetrahedron*, 1981, **37**, 1075.
19 M. C. Aversa, P. Giannetto, G. Romeo, P. Ficarra, and M. G. Vigorita, *Org. Magn. Reson.*, 1981, **15**, 394.
20 I. Ninomya, T. Naito, S. Higuchi, and T. Mori, *Chem. Commun.*, 1971, 457.
21 B. S. Pedersen and S. O. Lawesson, *Bull. Soc. Chim. Belg.*, 1977, **86**, 693.
22 M. Mori, K. Chiba, and Y. Ban, *J. Org. Chem.*, 1978, **43**, 1684.
23 D. Evans and I. M. Lockhart, *J. Chem. Soc.*, 1965, 4806.

Received 20*th May* 1988; *Paper* 8/02015I