The Synthesis of NH Aldimines and Derivatives by Spontaneous and Base-catalysed Decomposition of Oxaziridines

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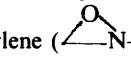
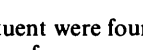
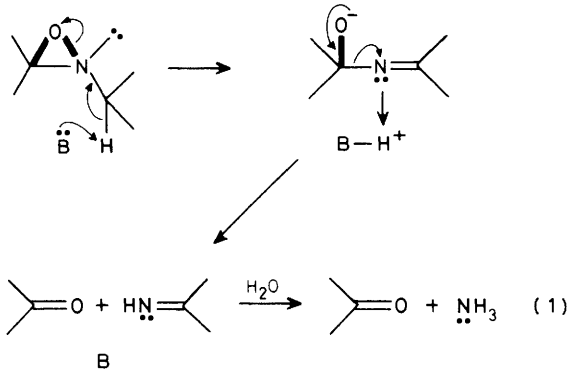
A range of oxaziridines containing *N*-methylene substituents has been synthesized by peracid oxidation of the corresponding fluorenylidene *N*-alkylamines. Spontaneous and tertiary amine base-catalysed decomposition of the oxaziridines into unstable NH aldimines and derivatives was observed. Acrylaldehyde, 2-methylacrylaldehyde, and benzaldehyde NH imines have been identified as initial products from decomposition of the corresponding oxaziridines. 2,4,6-Trialkylhexahydro-1,3,5-triazines, *N,N'*-dialkylidene-1,1-diaminoalkanes, *N,N'*-diarylidene-1,1-diaminoalkanes, and *N*-isobutylidene-2-methylpropenylamine were among the isolated products formed *via* the undetected alkyl aldehyde NH imines resulting from oxaziridine decomposition.

The oxaziridine ring system has been known for more than thirty years,[1,2] but unlike other three-membered heterocyclic rings containing an oxygen (*e.g.*, epoxides) or a nitrogen atom (*e.g.*, aziridines), has not been widely used in synthesis. The ability of oxaziridines to act as relatively weak neutral oxidizing agents was initially recognized by Emmons[2,3] who found that hydrogen iodide and triphenylphosphine in the presence of oxaziridines yielded iodine and triphenylphosphine oxide respectively. Recent results have indicated that some bis(*N*-alkyl)oxaziridines[4] and oxaziridines substituted by electron-withdrawing *N*-sulphonyl[5] and *N*-phosphinoyl groups[6] are stronger oxidants capable of oxidizing sulphides to sulphoxides. Both *N*-sulphonyl-[7] and *N*-phosphinoyl-oxaziridines[6] have also been found to epoxidize olefins. The thermal isomerization of oxaziridines in a range of solvents provides a useful synthetic route to *N*-alkyl nitrones (and thus *N*-alkylhydroxylamines).[2,3,8,9]

The value of oxaziridines in synthesis has in general been limited by their variable stability and their propensity to fragment into two or more products. A t-butyl substituent on the oxaziridine ring nitrogen atom has a stabilizing effect.[2,3] By contrast, oxaziridines having an *N*-methylene () or an *N*-methinyl () substituent were found to be less stable and decomposed in the presence of aqueous alcoholic alkali to yield aldehydes or ketones and ammonia.[3] Liquid-phase thermal decomposition of *N*-methylene- or *N*-methinyl-oxaziridines gave a similar range of products (plus olefinic imines) although the mechanisms proposed were different in the thermal (homolytic) and base-catalysed (heterolytic) reactions.[3]

The proposal that base-catalysed decomposition of oxaziridines may act as a chemical model system for the oxidative deamination reaction of amines by amine oxidase enzymes[10] has been followed by further mechanistic studies of this reaction.[11–13] The formation of an aldehyde as decomposition product from the *N*-alkyl group of *N*-alkyl oxaziridines[3,10–13] (in the presence of base) was assumed to occur *via* an NH aldimine intermediate which hydrolysed rapidly *in situ* [reaction (1)]. No direct evidence for the formation of NH aldimine intermediates had been reported prior to the preliminary results from the present study.[14]

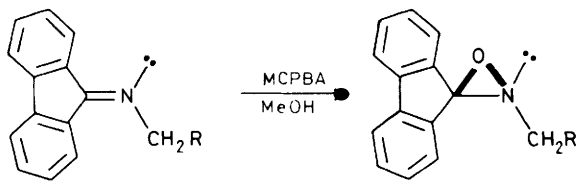
The highly unstable nature of the NH aldimines is well documented[15–18] and to date no generally applicable synthetic route is available to permit the isolation of both volatile and non-volatile NH aldimines. The isolation of NH aldimine



(1)

intermediates and their nitrogenous derivatives resulting from oxaziridine decomposition is discussed herein.

Imines (**1**)—(**8**) were synthesized by $TiCl_4$-catalysed condensation of fluorenone with the appropriate amine. *m*-Chloroperbenzoic acid (MCPBA) oxidation of imines (**1**)—(**8**) in methanol solution (0 °C) yielded the corresponding oxaziridines (**9**)—(**16**) exclusively. Several of the lower molecular weight oxaziridines in the series (**9**)—(**16**) proved to be unstable at ambient temperature and were thus used immediately after



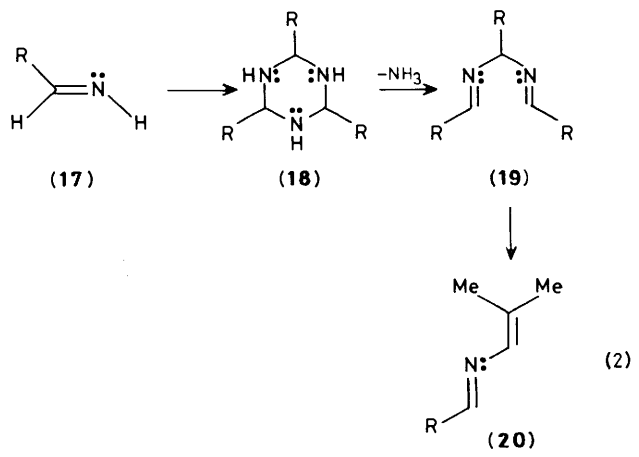
R	Imine	Oxaziridine
H	(**1**)	(**9**)
Me	(**2**)	(**10**)
Et	(**3**)	(**11**)
Pr^i	(**4**)	(**12**)
Bu^t	(**5**)	(**13**)
CH=CH$_2$	(**6**)	(**14**)
C(Me)=CH$_2$	(**7**)	(**15**)
Ph	(**8**)	(**16**)

Table. Relative proportions of nitrogenous decomposition products from oxaziridines (9)—(16)

N-atom substituent (R)	Oxaziridine	Decomposition conditions[a]	Products (%)[b] (17)	(18)	(19)	(20)	RCHO
H	(9)	7 days, r.t.	*c*	*c*	*c*	*c*	*c*
Me	(10)	1—2 days, r.t.	*c*	83	*c*	*c*	17
Me	(10)	DABCO, 1 h, r.t.	*c*	91	*c*	*c*	9
Et	(11)	2—3 days, r.t.	*c*	67	26	*c*	7
Et	(11)	DBN, instantaneous	*c*	100	*c*	*c*	*c*
Et	(11)	DABCO, 12 h, r.t.	*c*	91	9	*c*	*c*
Pr^i	(12)	DBN, instantaneous	*c*	100	*c*	*c*	*c*
Pr^i	(12)	DABCO, 1 h, r.t.	*c*	42	23	23	12
Pr^i	(12)	Et_3N, 2—3 h, r.t.	*c*	58	17	17	8
Bu^t	(13)	2—3 weeks, r.t.	*c*	*c*	>95	*c*	*c*
Bu^t	(13)	DABCO, 1 h, r.t.		*c*	83	*c*	17
$CH{=}CH_2$	(14)	DABCO, instantaneous	*d*	*c*	*c*	*c*	*c*
$CH{=}CH_2$	(14)	DBN, instantaneous	*d*	*c*	*c*	*c*	*c*
$C(Me){=}CH_2$	(15)	DABCO, instantaneous	*d*	*c*	*c*	*c*	*c*
$C(Me){=}CH_2$	(15)	DBN, instantaneous	*d*	*c*	*c*	*c*	*c*
Ph	(16)	12 h, r.t.	*c*	*c*	86	*c*	14
Ph	(16)	DABCO, 0.5 h, r.t.	*c*	*c*	83	*c*	17
Ph	(16)	DBN, instantaneous	*d*	*c*	71	*c*	29

[a] Spontaneous decomposition occurred in the neat liquid or crystalline state. Base-catalysed decomposition occurred in $CDCl_3$ solution. Fluorenone was found to be the major decomposition in all cases (r.t. = room temperature). [b] Relative proportions of decomposition products determined by n.m.r. analysis. [c] Not detected. [d] Isolated by trap-to-trap distillation at 0.001 mmHg.

synthesis. The spontaneous decomposition products of oxaziridines (9)—(16) included compounds of general structures (18), (19), and (20) [reaction (2)] which have all been isolated during previous[15,16,19] attempts to synthesize NH aldimines (17) by alternative routes.



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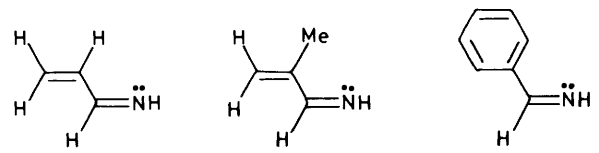
As part of the present study, attempts were made to prepare NH aldimines (17) having a saturated alkyl group R, by either spontaneous or base-catalysed decomposition of the appropriate oxaziridines (9)—(13) (and detection by n.m.r. analytical methods), but have to date been unsuccessful (Table). During these unsuccessful investigations the first unequivocal evidence for the existence of the NH aldimines containing a saturated alkyl group (17; R = Me or Et) was reported.[18] Using a vacuum dynamic gas-phase/solid-phase α-elimination reaction of chloroamines ($KOBu^t$; 50 °C/0.1 mmHg) these NH aldimines (17; R = Me or Et) were detected by low-temperature (−100 °C; CD_2Cl_2) n.m.r. spectroscopy. Spontaneous decomposition occurred at temperatures above −120 °C in the neat state and above −70 °C in solution to yield the corresponding hexahydrotriazines (18; R = Me or Et).

The rate of base-catalysed decomposition of oxaziridines (9)—(13) generally appeared to be slower than that observed for oxaziridines (14)—(16) where the α-hydrogen atom was either allylic or benzylic. Thus, the low temperatures (−70 °C) required for stabilization of the NH aldimines (17; R = Me, Et, Pr^i, Bu^t) in solution prevented base-catalysed decomposition occurring at an acceptable rate. Decomposition of oxaziridine (10) in the crystalline state, however, occurred at ambient temperature under reduced pressure (*ca.* 0.01 mmHg) within a period of 24 h to yield crystals of fluorenone and 2,4,6-trimethylhexahydro-1,3,5-triazine (18; R = Me). Several preliminary attempts to isolate the NH aldimine (17; R = Me) at low temperatures (−196 °C) by trap-to-trap distillation into an n.m.r. tube containing CD_2Cl_2–$CFCl_3$ were unsuccessful. When a crystalline sample of the oxaziridine (10) was heated (*ca.* 70 °C) in order to speed up the spontaneous decomposition to NH aldimines, the corresponding nitrone isomer was obtained in quantitative yield by a competing reaction pathway.

Although the decomposition of oxaziridines (9)—(11), (13), and (16) occurred in the neat state at ambient temperature without addition of base (either at atmospheric or reduced pressure), and has thus been described as a spontaneous decomposition, it is possible that the reaction was catalysed by traces of base resulting from partial decomposition or from the oxaziridine itself (autocatalysis). A mechanism involving spontaneous decomposition of oxaziridines *via* nitrene intermediates cannot at present be excluded (*cf.* reference 20). The differences in rates of decomposition between oxaziridines [*e.g.*, (10) and (13)] are, however, more difficult to accommodate by this pathway.

The observed differences in the relative rates of decomposition of oxaziridines having a saturated alkyl group [*e.g.*, (9)—(13)] and those containing an unsaturated group (14)—(16) are in accord with the currently accepted mechanism for the base-catalysed decomposition of oxaziridines.[3,10,11] The faster rate of base-catalysed decomposition of oxaziridine reactants (14)—(16) having more acidic α-H atoms, allied to the greater stability of conjugated NH aldimines,[15–18] led to the detection of compounds [17; R = $CH_2{=}CH$, $CH_2{=}C(Me)$, Ph] as initial products from the base-catalysed decomposition of



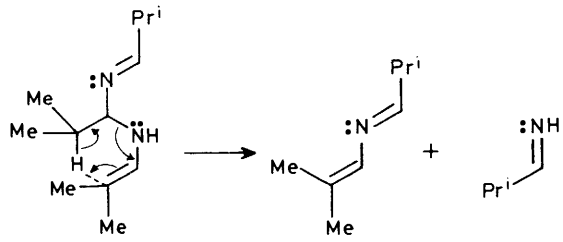
(**17**; R = CH_2=CH) [**17**; R = CH_2=C(Me)] (**17**; R = Ph)

oxaziridines (**14**)—(**16**). Thus, addition of tertiary amines, *e.g.*, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) or 1,4-diazabicyclo-[2.2.0]octane (DABCO) to solutions of oxaziridines (**14**), (**15**), and (**16**) in $C_6D_5CD_3$ at room temperature resulted in the immediate formation of the corresponding NH aldimines [**17**; R = CH_2=CH, CH_2=C(Me), Ph]. Acrylaldehyde (**17**; R = CH_2=CH) and 2-methylacrylaldehyde [**17**; R = CH_2=C(Me)] NH imines were purified by trap-to-trap distillation (0.001 mmHg). Identification of the NH aldimine relied upon n.m.r. analysis ($C_6D_5CD_3$) which was carried out at low temperature (−70 °C) in order to facilitate a direct comparison with the reported δ values and coupling constants. Confirmation of the NH aldimine structures was obtained by extensive decoupling and observation of their decomposition products as the temperature of the n.m.r. tube increased. Since the simple n.m.r. spectrum of benzaldehyde imine (**17**; R = Ph) was of less value as a molecular fingerprint, further structural evidence was provided by the reaction with methylamine to yield *N*-benzylidenemethylamine *via* a transimination step.[21] The latter imine was identified by peracid oxidation to form a mixture of *cis* and *trans* oxaziridines, and an n.m.r. comparison of both imine and oxaziridine products with authentic samples. Benzaldehyde imine (**17**; R = Ph) yielded hydrobenzamide (**19**; R = Ph) as a major decomposition product.

The decomposition of *N*-methyl-substituted oxaziridines either thermally[22] or in the presence of a tertiary amine base[13] was found to yield hexamethylenetetra-amine as a product resulting from reaction between the initially formed product methanimine (**17**; R = H) and its hydrolysis product (formaldehyde). No indication of hexamethylenetetra-amine was observed from either spontaneous or base-catalysed decomposition of oxaziridine (**9**), fluorenone being the only identified product (Table).

The oxaziridine (**10**) decomposed spontaneously in the crystalline state or in solution containing base to yield fluorenone and 2,4,6-trimethylhexahydro-1,3,5-triazine (**18**; R = Me) which was isolated by sublimation from the product mixture. The small proportion of aldehyde detected may have resulted from imine hydrolysis as reported in other oxaziridine decompositions.[2,3,11,12] The hexahydrotriazine product (**18**; R = Me) was stable and did not decompose into further products [*e.g.*, (**19**) or (**20**)].

Decomposition of oxaziridines (**11**) and (**12**) either spontaneously in the neat state or under base catalysis in solution again yielded the corresponding hexahydrotriazines (**18**; R = Et and Pr^i) as the major products. Use of the stronger base DBN gave instantaneous breakdown of the oxaziridines to hexahydrotriazines which were the only detectable initial products. The hexahydrotriazines (**18**; R = Et and Pr^i) were found to decompose to the bis-imines (**19**; R = Et and Pr^i) at ambient temperature and particularly during attempted distillation. The slower rate of decomposition found with weaker bases, *e.g.* DABCO or Et_3N, thus resulted in both hexahydrotriazine (**18**) and bis-imine (**19**) formation. The decrease in hexahydrotriazine stability with increasing size of substituent R is in concurrence with previous reports.[15,16,19] The vinyl imine product (**20**; R = Pr^i) resulted from spontaneous decomposition of the bis-imine (**19**; R = Pr^i) *via* the enamine tautomer.[19] It is noteworthy that *N*-isobutylidene-2-methylprop-1-enylamine (**20**; R = Pr^i) has previously been identified as the major product isolated from liquid-phase pyrolysis of 2-isobutyl-3-isopropyloxaziridine.[2] When the product mixture of (**18**), (**19**), and (**20**), isolated from spontaneous or base-catalysed decomposition of the oxaziridine (**12**), was refluxed in benzene only the vinyl imine (**20**) remained.



(**19**; R = Pr^i) (**20**; R = Pr^i)

The only stable nitrogenous products obtained from either spontaneous or base-catalysed decomposition of oxaziridines (**13**) and (**16**) were the bis-imines (**19**; R = Bu^t and Ph). The isolation of the latter bis-imines resulted from the instability of the NH aldimine (**17**) and hexahydrotriazine (**18**) precursors [previous attempts to isolate compounds (**18**; R = Bu^t or Ph) as stable products at room temperature were unsuccessful[15,16]] and the inability of the bis-imines (**19**; R = Bu^t and Ph) to equilibrate with an enamine tautomer and thus to undergo a cyclic elimination process as found in the formation of the vinyl aldimine (**20**; R = Pr^i).

The present results indicate that a wide range of unstable NH aldimines (**17**) and their derivatives (**18**)—(**20**) are produced both by spontaneous and base-catalysed decomposition of oxaziridines having an *N*-methylene substituent. In the light of these observations it is probable that the previously reported spontaneous,[3] liquid-phase pyrolysis,[3] and base-catalysed[3,10–13] decompositions of *N*-methylene-substituted oxaziridines into carbonyl compounds and ammonia all proceed *via* unstable (and undetected) NH aldimine intermediates. While the present report has been confined to oxaziridines derived from fluorenone, a similar profile of reaction products was observed using oxaziridines derived from other ketones (*e.g.*, benzophenone[14]) and aldehydes (*e.g.*, 4-nitrobenzaldehyde[14]) and this decomposition pathway appears to be general.

The formation of NH aldimine intermediates during monoamine oxidase-catalysed transformation of amines (*e.g.*, 1-aminoheptane or benzylamine) has been established by biosynthetic investigations.[23,24] The present route, allied to the recent flash vacuum pyrolysis method,[18] provides a source of unstable NH aldimines although low thermal stability may exclude their use in biosynthetic studies.

Experimental

^{1}H N.m.r. spectra were obtained using Jeol JNM-PMX60 (60 MHz), Hitachi-Perkin-Elmer R-24B (60 MHz), Bruker WH90 (90 MHz), or Bruker WH250 (250 MHz) instruments. Unless stated otherwise, ^{1}H n.m.r. spectra were obtained in deuteriochloroform solvent with tetramethylsilane as internal reference.

Mass spectra were recorded on an AEI MS-902 instrument, upgraded by V.G. Analytical, operating at 70 eV using a heated inlet system. Accurate mass measurements were obtained on this instrument using the peak-matching method.

M.p.s were obtained using a Reichert-Kofler block and are uncorrected.

The imines (**1**)—(**7**) were synthesized from equimolar quantities of fluorenone and the corresponding primary amines using anhydrous toluene as solvent and titanium tetrachloride catalyst in the presence of a five-fold molar excess of trimethylamine[25] (Method A). An alternative method for the synthesis of imines from fluorenone involved the transimination procedure reported by O'Donnell *et al.*[21] A solution of fluorenone imine (synthesized by the literature method[26]) in methylene dichloride was stirred for *ca.* 12 h at room temperature with an excess of the amine under anhydrous conditions. The product was obtained after drying and removal of solvent (Method B). Yields for methods (A) and (B) were generally in the range 80—90%.

Physical Properties and N.m.r. Spectral Data of Imines (**1**)—(**8**).—*Compound* (**1**), method A, m.p. 36—40 °C (lit.,[27] b.p. 125 °C/0.01 mmMg); δ_H (60 MHz) 3.93 (3 H, s, Me) and 7.17—7.91 (8 H, m, ArH).

Compound (**2**), methods A and B, m.p. 59—63 °C (lit.,[27] b.p. 152 °C/0.01 mmHg); δ_H (60 MHz) 1.54 (3 H, t, *J* 7 Hz, CH_2Me), 4.16 (3 H, q, *J* 7 Hz, CH_2Me), and 7.12—7.92 (8 H, m, ArH).

Compound (**3**), method B, m.p. 57—59 °C (Found: C, 86.3; H, 7.0; N, 6.3. $C_{16}H_{15}N$ requires C, 86.8; H, 6.8; N, 6.3%); δ_H (250 MHz) 1.12 (3 H, t, *J* 7.4 Hz, CH_2Me), 1.96 (2 H, m, CH_2Me), 4.09 (2 H, t, *J* 7.2 Hz, CH_2CH_2Me), and 7.21—7.86 (8 H, m, ArH).

Compound (**4**), method B, m.p. 44—45 °C (Found: C, 86.5; H, 7.2; N, 5.9. $C_{17}H_{17}N$ requires C, 86.8; H, 7.3; N, 6.0%); δ_H (250 MHz) 1.11 (6 H, d, *J* 6.7 Hz, $CHMe_2$), 2.22 (1 H, m, $CHMe_2$), 3.90 (2 H, d, *J* 6.7 Hz, CH_2Pr^i), and 7.18—8.55 (8 H, m, ArH).

Compound (**5**), method A, m.p. 65—66 °C (Found: C, 86.7; H, 7.7; N, 5.6. $C_{18}H_{19}N$ requires C, 86.7; H, 7.7; N, 5.6%); δ_H (60 MHz) 1.11 (9 H, s, Bu^t), 3.80 (2 H, s, CH_2Bu^t), and 7.10—7.88 (8 H, m, ArH).

Compound (**6**), method A, low m.p. solid (Found: C, 87.5; H, 6.0; N, 6.4. $C_{16}H_{13}N$ requires C, 87.6; H, 6.0; N, 6.4%); δ_H (250 MHz) 4.81 (2 H, dt, *J* 5.4 and 1.7 Hz, NCH_2), 5.26 (1 H, m, HCH=CH), 5.41 (1 H, m, HCH=CH), 6.01—6.45 (1 H, m, $CH_2=CH$), and 7.17—7.90 (8 H, m, ArH).

Compound (**7**), method A, m.p. 41—44 °C (Found: C, 87.5; H, 6.4; N, 6.0. $C_{17}H_{15}N$ requires C, 87.5; H, 6.5; N, 6.0%); δ_H (250 MHz) 1.97 (3 H, s, HCH=C*Me*), 4.67 (2 H, s, NCH_2), 4.98 [1 H, m, HCH=C(Me)], 5.12 [1 H, m, HCH=C(Me)], and 7.20—7.91 (8 H, m, ArH).

Compound (**8**), method A, m.p. 76—78 °C (Found: C, 89.3; H, 5.9; N, 4.9. $C_{20}H_{15}N$ requires C, 89.2; H, 5.6; 5.2%); δ_H (250 MHz) 5.40 (2 H, s, NCH_2) and 7.26—7.95 (13 H, m, ArH).

Oxaziridines (**9**)—(**16**) were obtained by MCPBA oxidation of the imine in methanol solvent at *ca.* 0 °C during a period of 1—2 h. Upon completion the reaction mixture was poured into methylene dichloride and worked up as in previous preparations.[2,3,28] Solid oxaziridines were purified by recrystallization. Liquid oxaziridines in the series (**9**)—(**16**) were generally found to have high b.p.s and thus could not be purified by distillation. Purification of liquid oxaziridines was effected by rapid column chromatography on silica-gel using light petroleum (boiling range 40—60 °C) in combination with either distilled diethyl ether or methylene dichloride as eluant. Yields of oxaziridines produced by this method were generally in the range of 70—90%.

Physical Properties and N.m.r. Spectral Data of Oxaziridines (**9**)—(**16**).—*Compound* (**9**), m.p. 39—44 °C (Found: M^+, 209.0841. $C_{14}H_{11}NO$ requires *M*, 209.0841); δ_H (90 MHz) 3.12 (3 H, s, Me) and 7.17—7.80 (8 H, m, ArH).

Compound (**10**), m.p. 76—78 °C (Found: C, 80.5; H, 5.9; N, 6.1. $C_{15}H_{13}NO$ requires C, 80.7; H, 5.9; N, 6.3%); δ_H (250 MHz) 1.23 (3 H, t, *J* 7 Hz, CH_2Me), 3.25 (2 H, m, CH_2Me), 7.13—7.80 (8 H, m, ArH).

Compound (**11**), high b.p. oil (Found: M^+, 237.1152. $C_{16}H_{15}NO$ requires *M*, 237.1154); δ_H (250 MHz) 0.97 (3 H, t, *J* 7.4 Hz, CH_2Me), 1.73 (2 H, m, CH_2Me), 3.00—3.11 (1 H, m, CHHEt), 3.21—3.31 (1 H, m, CHHEt), and 7.12—8.00 (8 H, m, ArH).

Compound (**12**), high b.p. oil (Found: M^+, 251.1307. $C_{17}H_{17}NO$ requires *M*, 251.1310); δ_H (250 MHz) 0.94 (3 H, d, *J* 6.7 Hz, Me), 1.06 (3 H, d, *J* 6.7 Hz, Me), 2.07 (1 H, m, $CHMe_2$), 2.92 (1 H, dd, *J* 13.4 and 6.8 Hz, $CHHPr^i$), 3.11 (1 H, dd, *J* 13.4 and 6.7 Hz, $CHHPr^i$), and 7.26—7.74 (8 H, m, ArH).

Compound (**13**), m.p. 49—51 °C (Found: C, 81.4; H, 7.0; N, 5.0. $C_{18}H_{19}NO$ requires C, 81.5; H, 7.2; N, 5.3%); δ_H (250 MHz) 1.02 (9 H, s, Bu^t), 2.84 (1 H, d, *J* 13.4 Hz, $CHHBu^t$), 3.07 (1 H, d, *J* 13.2 Hz, $CHHBu^t$), and 7.11—7.70 (8 H, m, ArH).

Compound (**14**), low m.p. solid (Found: M^+, 235.0997. $C_{16}H_{13}NO$ requires *M*, 235.0999); δ_H (60 MHz) 3.80 (2 H, br s, NCH_2), 5.03—5.42 (2 H, m, $CH_2=CH$), 5.60—6.42 (1 H, m, $CH_2=CH$), and 7.00—7.75 (8 H, m, ArH).

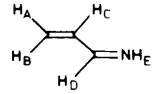
Compound (**15**), low m.p. solid (Found: *M*, 249.1153. $C_{17}H_{15}NO$ requires *M*, 249.1154); δ_H (250 MHz) 1.84 (3 H, s, Me), 3.56 (1 H, d, *J* 14 Hz, NCHH), 3.88 (1 H, d, *J* 14 Hz, NCHH), 4.91 (1 H, m, HCH=C), 4.96 (1 H, m, HCH=C), 7.25—8.00 (8 H, m, ArH).

Compound (**16**), high b.p. oil (Found: C, 84.3; H, 5.5; N, 4.9. $C_{20}H_{15}NO$ requires C, 84.2; H, 5.3; N, 4.9%); δ_H (250 MHz) 4.19 (1 H, d, *J* 14.5 Hz, NCHH), 4.37 (1 H, d, *J* 14.5 Hz, NCHH), and 7.21—7.76 (13 H, m, ArH).

Oxaziridines (**9**)—(**11**), (**13**), and (**16**) in either the neat liquid or crystalline state were found to decompose in sealed sample tubes or flasks at ambient temperature in either the presence or absence of light. Decomposition was also found to occur in the crystalline state when the sample was maintained under high vacuum (<0.01 mmHg) where moisture was excluded from the sample. The decomposition products from spontaneous decomposition [fluorenone, and (**17**)—(**20**)] were in some cases isolated and purified, while in others they were identified by n.m.r. spectral comparison with authentic samples.

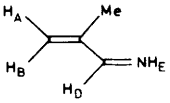
Decomposition of oxaziridines (**9**)—(**16**) in solution required the addition of a tertiary amine base (DBN, DABCO, Et_3N) and was monitored by n.m.r. analysis. NH Aldimines [**17**; R = CH_2=CH, CH_2=C(Me) or Ph] were all detected as transient intermediates in $CDCl_3$ solution. Acrylaldehyde imine (**17**; R = CH_2=CH) and 2-methylacrylaldehyde imine [**17**; R = CH_2=C(Me)] were also synthesized by addition of DBN or DABCO to oxaziridines (**14**) and (**15**) in $C_6D_5CD_3$ and purified by trap-to-trap distillation in $C_6D_5CD_3$ solution (−70 °C; 0.001 mmHg).

Physical Properties and N.m.r. Spectral Data of Oxaziridine Decomposition Products.—*Compound* (**17**; R = CH_2=CH).



Unstable oil, δ_H (90 MHz; −70 °C; $C_6D_5CD_3$) 5.15 (1 H, d, J_{AB} 17 Hz, H_B), 5.25 (1 H, d, J_{AC} 10 Hz, H_A), 6.54 (1 H, ddd, J_{AC} 17, J_{BC} 10, J_{DC} 9 Hz, H_C), 7.50 (1 H, dd, J_{DE} 16, J_{DC} 9 Hz, H_D), and 9.74 (1 H, d, J_{DE} 16 Hz, H_E).

Compound [**17**; R = CH_2=C(Me)].



Unstable oil, δ_H (90 MHz; −70 °C; $C_6D_5CD_3$) 4.95 (1 H, s, H_A), 5.15 (1 H, s, H_B), 7.60 (1 H, d, J_{DE} 16 Hz, H_D), 9.45 (1 H, d, J_{DE} 16 Hz, H_E), and 2.32* (3 H, s, Me).

Compound (**17**; R = Ph) δ_H (90 MHz; −70 °C; $C_6D_5CD_3$) 7.76 (1 H, d, *J* 16 Hz, HC=N), 9.70 (1 H, d, *J* 16 Hz, C=N*H*), and 7.20—7.50† (5 H, m, ArH).

Compound (**18**; R = Me). M.p. 89—93 °C (lit.,[15] m.p. 94—96 °C), isolated by direct sublimation from product mixture; authentic specimen purchased from the Aldrich Chemical Co. δ_H (250 MHz) 1.22 (9 H, d, *J* 6 Hz, Me), 1.80 (3 H, br s, NH), and 3.87 (3 H, q, *J* 6 Hz, Me).

Compound (**18**; R = Et). B.p. 24—28 °C/0.02 mmHg (lit.,[15] m.p. 2—3 °C, b.p. 55—69 °C/10 mmHg). Isolated by trap-to-trap distillation and synthesized from reaction of propionaldehyde with conc. aqueous ammonia solution as previously reported;[15] δ_H (250 MHz) 0.98 (9 H, t, *J* 7.4 Hz, CH_2Me), 1.45—1.69 (6 H, m, CH_2Me), and 3.61 (3 H, t, *J* 6.5 Hz, C*H*Et).

Compound (**18**; R = Pr^i). Low m.p. solid (lit.,[15] m.p. 26—27 °C). Synthesized by the literature route,[15] and identified by n.m.r. analysis of the decomposition mixture from the oxaziridine (**12**); δ_H (250 MHz) 0.96 (18 H, d, *J* 6.8 Hz, $CHMe_2$), 1.58—1.69 (3 H, m, $CHMe_2$), 3.35 (3 H, d, *J* 5.8 Hz, C*H*Pr^i).

Compound (**19**; R = Et). B.p. 24—28 °C/0.02 mmHg (lit.,[15] b.p. 48—50 °C/5 mmHg). Synthesized by the literature route[15] and detected among the decomposition products of the oxaziridine (**11**) by n.m.r. analysis: δ_H (250 MHz) 0.97 (3 H, t, *J* 7.5 Hz, CH_2Me), 1.11 (6 H, t, *J* 7.5 Hz, CH_2Me), 1.38—1.90 (2 H, m, CH_2Me), 2.48 (4 H, q, *J* 7.4 Hz, CH_2Me), 4.27 (1 H, t, *J* 5.7 Hz, CH), and 7.72 (2 H, d, *J* 4.2 Hz, CH=N); $\nu_{max.}$ 1 660 cm^{-1} (C=N).

Compound (**19**; R = Pr^i). Oil (lit.,[15] b.p. 78—80 °C/12 mmHg). Synthesized by the literature method[15] and detected among the decomposition products of the oxaziridine (**12**) by n.m.r. analysis: δ_H (250 MHz) 0.94 (6 H, d, *J* 6.9 Hz, $CHMe_2$), 1.08 (12 H, d, *J* 6.9 Hz, $CHMe_2$), 1.70—1.95 (1 H, m, $CHMe_2$), 2.46—2.91 (2 H, m, $CHMe_2$), 3.89 (1 H, d, *J* 5.9 Hz, C*H*Pr^i), and 7.52 (2 H, d, *J* 4.4 Hz, CH=N); $\nu_{max.}$ 1 655 cm^{-1} (C=N).

Compound (**20**; R = Pr^i). B.p. 56—58 °C/0.02 mmHg (lit.,[19] b.p. 143—144 °C/760 mmHg). Synthesized by refluxing isobutyraldehyde and ammonia in benzene for *ca.* 1 h in the presence of a Dean–Stark trap. Identified by n.m.r. analysis as one of the products obtained by decomposition of the oxaziridine (**12**); δ_H (250 MHz) 1.09 (6 H, d, *J* 6.9 Hz, $CHMe_2$), 1.74 (3 H, s, Me), 1.95 (3 H, s, Me), 2.51 (1 H, m, $CHMe_2$), 6.35 (1 H, br s, C=CHN), and 7.44 (1 H, d, *J* 5.1 Hz, CH=N).

Compound (**19**; R = Bu^t). B.p. 35—40 °C/1.0 mmHg (lit.,[15] b.p. 78 °C/9 mmHg). This compound was synthesized by the literature method;[15] δ_H (60 MHz) 0.88 (9 H, s, Bu^t), 1.08 (18 H, s, Bu^t), 3.80 (1 H, s, CH), and 7.48 (2 H, br s, CH=N).

Compound (**19**; R = Ph). M.p. 100—101 °C (lit.,[29] m.p. 101 °C). This compound was synthesized by the literature method;[29] δ_H (60 MHz) 5.94 (1 H, s, CH), 7.12—7.92 (15 H, m, Ph), and 8.48 (2 H, s, CH=N).

Reaction of Benzaldehyde Imine (**17**; R = Ph) *with Methylamine Hydrochloride* (*Transimination*).—The imine (**17**; R = Ph) was treated with methylamine hydrochlorine (three-fold excess) in $CDCl_3$ solution and the transimination product *N*-benzylidenemethylamine was formed immediately: δ_H (60 MHz) *inter alia* 3.45 (3 H, d, *J* 2 Hz, NMe) and 8.14 (1 H, d, *J* 2 Hz, CH=N).

Oxidation of the *N*-benzylidenemethylamine product was carried out at *ca.* +5 °C in $CDCl_3$ solution *in situ* using an equimolar quantity of MCPBA and gave the previously reported *cis*- and *trans*-2-methyl-3-phenyloxaziridine in the ratio 57:43.

The oxaziridines were found to have identical t.l.c. and n.m.r. characteristics with those of authentic samples which were prepared by the literature method.[30]

* CD_2H Signal from solvent superimposed on this signal.
† Signals superimposed on fluorenone proton signals.

Acknowledgements

We thank Dr. L. Waring for 90 MHz and 250 MHz n.m.r. spectra, and the D.E.N.I. (to P. B. C.) and the S.E.R.C. (to N. D. S.) for financial support.

References

1 H. Krimm and K. Hamann, B.P. 743940/1956 (*Chem. Abstr.*, 1957, **51**, 3656f).
2 W. D. Emmons, *J. Am. Chem. Soc.*, 1956, **78**, 6208.
3 W. D. Emmons, *J. Am. Chem. Soc.*, 1957, **79**, 5739.
4 M. N. Akhtar, D. R. Boyd, J. D. Neill, and D. M. Jerina, *J. Chem. Soc., Perkin Trans. 1*, 1980, **1693**.
5 F. A. Davis, R. Jenkins, and S. G. Yocklovich, *Tetrahedron Lett.*, 1978, 5171.
6 D. R. Boyd, W. B. Jennings, R. M. McGuckin, M. Rutherford, and B. M. Saket, *J. Chem. Soc., Chem. Commun.*, 1985, 582.
7 F. A. Davis, M. E. Harakal, and S. B. Awad, *J. Am. Chem. Soc.*, 1983, **105**, 3123.
8 J. Bjorgo, D. R. Boyd, D. C. Neill, and W. B. Jennings, *J. Chem. Soc., Perkin Trans. 1*, 1977, 254.
9 D. R. Boyd, P. B. Coulter, W. J. Hamilton, W. B. Jennings, and V. E. Wilson, *Tetrahedron Lett.*, 1984, **25**, 2287.
10 S. E. Dinizo and D. S. Watt, *J. Am. Chem. Soc.*, 1975, **97**, 6900.
11 W. H. Rastetter and J. W. Frost, *Tetrahedron Lett.*, 1979, 3353.
12 W. H. Rastetter, W. R. Wagner, and M. A. Findeis, *J. Org. Chem.*, 1982, **47**, 419.
13 Y. Hata and M. Watanabe, *J. Am. Chem. Soc.*, 1979, **101**, 6671.
14 D. R. Boyd, R. Hamilton, N. T. Thompson, and M. E. Stubbs, *Tetrahedron Lett.*, 1979, 3201.
15 A. T. Nielsen, R. L. Atkins, D. W. Moore, R. Scott, D. Mallory, and J. M. La Berge, *J. Org. Chem.*, 1973, **38**, 3288.
16 A. T. Nielson, R. L. Atkins, J. DiPol, and D. W. Moore, *J. Org. Chem.*, 1974, **39**, 1349.
17 B. Bogdanovic and M. Velic, *Angew. Chem., Int. Ed. Engl.*, 1967, **6**, 803.
18 J.-C. Guillemin and J. M. Denis, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 690.
19 R. H. Hasek, E. U. Elam, and J. C. Martin, *J. Org. Chem.*, 1961, **26**, 1822.
20 J. E. Baldwin, D. A. Jackson, R. M. Adlington, and B. J. Rawlings, *J. Chem. Soc., Chem. Commun.*, 1985, 206.
21 M. J. O'Donnell, R. L. Polt, *J. Org. Chem.*, 1982, **47**, 2663.
22 W. B. Jennings and V. E. Wilson, personal communication.
23 A. R. Battersby, D. G. Buckley, J. Staunton, and P. J. Williams, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2550.
24 A. R. Battersby, J. Staunton, and M. C. Summers, *J. Chem. Soc., Perkin Trans. 1*, 1976, 1052.
25 D. R. Boyd, M. E. Stubbs, N. J. Thompson, H. J. C. Yeh, D. M. Jerina, and R. E. Wasylishen, *Org. Magn. Reson.*, 1980, **14**, 528.
26 A. Kliegl, *Chem. Ber.*, 1910, **43**, 2488.
27 D. R. Boyd and D. C. Neill, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1308.
28 R. G. Pews, *J. Org. Chem.*, 1967, **32**, 1628.
29 H. H. Strain, *J. Am. Chem. Soc.*, 1927, **49**, 1558.
30 D. R. Boyd, D. C. Neill, C. G. Watson, and W. B. Jennings, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1813.

Received 26*th February* 1985; *Paper* 5/325