Oxidation of Some Dibenz[*b,f*][1,4]oxazepines by Peracetic Acid

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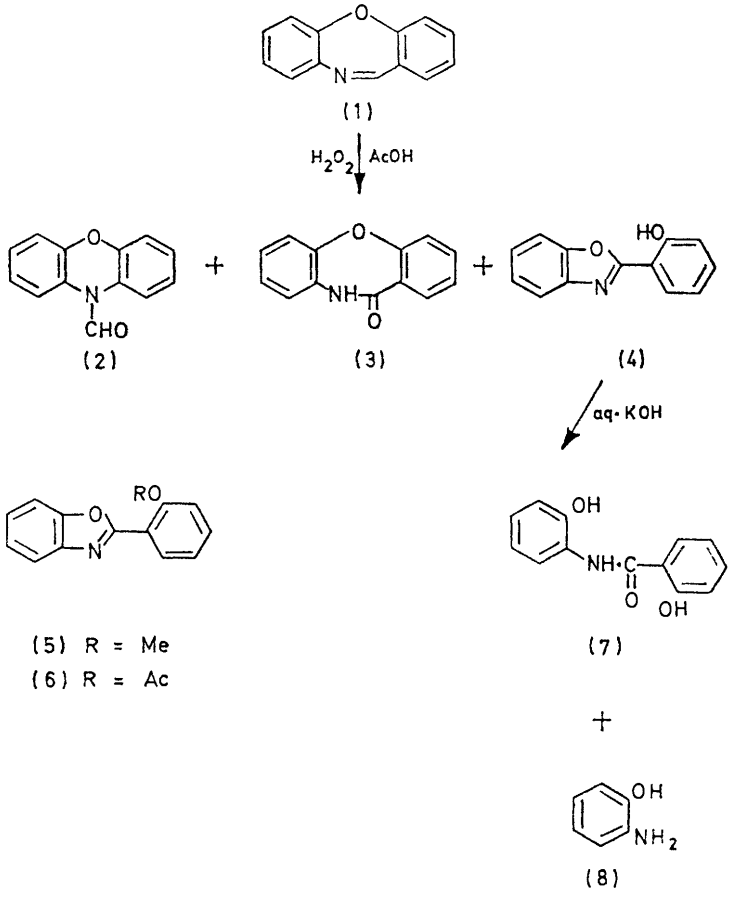
A series of variously substituted dibenz[*b,f*][1,4]oxazepines on treatment with hydrogen peroxide in glacial acetic acid affords the correspondingly substituted 2-(2-hydroxyphenyl)benzoxazole, 10-formylphenoxazine, and dibenz[*b,f*][1,4]oxazepin-11(10*H*)-one. An oxaziridine intermediate is implicated as the common precursor of the observed products.

THE syntheses of a series of dibenz[*b,f*][1,4]oxazepines and dibenz[*b,f*][1,4]oxazepin-11(10*H*)-ones have been described.[1,2] Many other reports[3] (and numerous patents) have appeared on the synthesis and chemistry of these ring systems in which the azomethine carbon and nitrogen atoms (positions 10 and 11) are substituted. However, little of the chemistry associated with the azomethine link has been described, especially where pertinent to its reactions with electrophilic reagents. In this paper, the products afforded by variously substituted dibenz[*b,f*][1,4]oxazepines on treatment with peracetic acid (generated *in situ*) are compared with those products derived from several related Schiff's bases under similar conditions.

Dibenz[*b,f*][1,4]oxazepine (1) on treatment with hydrogen peroxide in glacial acetic acid overnight at room temperature gave essentially a mixture of three major products, together with some polymeric material and many trace components (the latter were not investigated further). The three major products were isolated by chromatography over silica. The major product (R_F 0.51) was identified as *N*-formylphenoxazine (2) on the basis of elemental analysis and spectroscopic data, and the identification was confirmed by synthesis. The lactam (3) (R_F 0.33) was identified similarly. The third, unexpected product (R_F 0.75) was identified on the basis of chemical and spectroscopic (i.r. and n.m.r.)



SCHEME 1

[1] A. W. H Wardrop G L. Sainsbury, J. M. Harrison, and T. D. Inch, *J.C.S. Perkin I*, 1976, 1279.

[2] K. Brewster, R. J. Clarke, J. M. Harrison, T. D. Inch, and D. Utley, preceding paper.

[3] Refs. 1 and 2 and references therein.

TABLE 1

Product yields from dibenz[*b*,*f*][1,4]oxazepine–peracetic acid reactions

Dibenzoxazepine		Benzoxazole	%		Phenoxazine		%	Lactam		%	Chromatography solvent for separation of the reaction mixture *
Unsubst.	(1)	Unsubst.	(4)	12	Unsubst.	(2)	48	Unsubst.	(3)	7	CH–EtOAc (3 : 1)
2-Cl	(9)	5′-Cl	(46)	57	2-Cl	(26)	Trace	2-Cl [a]	(36)	Trace	CH–EtOAc (3 : 1)
7-Cl	(10)	6-Cl	(47)	43	3-Cl	(27)	Trace	7-Cl [a]	(37)	21	CH–EtOAc (4 : 1)
8-Cl	(11)	5-Cl	(48)	49	2-Cl	(26)	12	8-Cl [a]	(38)	16	CH–EtOAc (4 : 1)
2-Me	(12)	5′-Me	(49)	26	2-Me	(28)	15	2-Me			CH–EtOAc (4 : 1)
3-Me	(13)	4′-Me	(50)	19	3-Me	(29)	46	3-Me [a]	(39)	9	CH–EtOAc (4 : 1)
4-Me	(14)	3′-Me	(51)	36	4-Me	(30)	20	4-Me			CH–EtOAc (9 : 1)
6-Me	(15)	7-Me	(52)	39	4-Me	(30)	23	6-Me	(40)	7	CH–EtOAc (4 : 1)
7-Me	(16)	6-Me	(53)	51	3-Me	(29)		7-Me	(41)	3	CH–EtOAc (9 : 1)
8-Me	(17)	5-Me	(54)	43	2-Me	(28)	Trace	8-Me			CH–EtOAc (4 : 1)
9-Me	(18)	4-Me	(55)	59	1-Me	(31)	12	9-Me	(42)	Trace	CH–EtOAc (9 : 1)
1,3-Me_2	(19)	4′,6′-Me_2	(56)	18	1,3-Me_2	(32)	23	1,3-Me_2			CH–MeOH (19 : 1)
1,4-Me_2	(20)	3′,6′-Me_2	(57)	16	1,4-Me_2	(33)	43	1,4-Me_2			CH–EtOAc (9 : 1)
2,4-Me_2	(21)	3′,5′-Me_2	(58)	30	2,4-Me_2	(34)	12	2,4-Me_2	(43)	5	CH–$CHCl_3$ (8 : 2)
6,9-Me_2	(22)	4,7-Me_2	(59)	73	1,4-Me_2	(33)	Trace	6,9-Me_2			CH–EtOAc (9 : 1)
2-NO_2	(23)	5′-NO_2	(60)	68	2-NO_2			2-NO_2 [b]	(44)	17	EtOAc
3-OMe	(24)	4′-OMe	(61)	12	3-OMe	(35)	44	3-OMe			CH–EtOAc (9 : 2)
7-OMe	(25)	6-OMe	(62)	47	3-OMe	(35)		7-OMe [c]	(45)	41	CH–EtOAc (9 : 2)

* CH = cyclohexane.

[a] Ref. 21. [b] K. Nagarajan, C. L. Kulkarni, and A. Venkateswarlu, *Indian J. Chem.*, 1974, **12**, 247. [c] Ref. 2.

TABLE 2

Analytical data for new compounds

Compd.	M.p. (°C)	Cryst. solvent *	Analysis (%) (Reqd./Found) C	H	N
(2)	144	MeOH	73.6/73.9	4.45/4.3	6.55/6.65
(26)	95	EtOH	63.55/63.3	3.3/3.4	5.7/5.6
(28)	98	CH	74.65/74.2	4.9/4.8	6.2/6.0
(29)	101	LP	74.65/74.7	4.9/48.85	6.2/6.2
(30)	84	LP	74.65/74.75	4.9/4.85	6.2/6.2
(31)	89—90	CH	74.65/74.25	4.9/4.8	6.2/6.1
(32)	88	LP	75.3/75.1	5.5/5.45	5.85/5.8
(33)	86	EtOH	75.3/75.65	5.5/5.7	5.85/6.0
(34)	104	CH	75.3/75.3	5.5/5.6	5.85/6.1
(40)	192		74.65/74.0	4.9/4.8	6.2/6.0
(41)	198		74.65/74.5	4.9/4.9	6.2/6.15
(43)	172		75.30/75.05	5.5/5.6	5.85/5.6
(46)	144		63.55/63.5	3.3/3.3	5.7/5.85
(47)	135		63.55/63.55	3.3/3.35	5.7/5.9
(48)	140		63.55/63.2	3.3/3.35	5.7/5.55
(49)	126—128		74.65/74.5	4.9/5.05	6.2/6.25
(50)	146		74.65/73.95	4.9/5.05	6.2/6.0
(51)	118	EtOH	74.65/74.0	4.9/5.25	6.2/6.2
(52)	106—108		74.65/74.4	4.9/5.1	6.2/6.05
(53)	118		74.65/74.35	4.9/5.05	6.2/6.35
(54)	128		74.65/74.35	4.9/5.0	6.2/6.15
(55)	102		74.65/74.3	4.9/4.95	6.2/6.1
(56)	152		75.3/72.25	5.5/5.65	5.85/5.8
(57)	122		75.3/75.25	5.5/5.55	5.85/5.85
(58)	168		75.3/74.9	5.5/5.2	5.85/5.8
(59)	108		75.3/74.9	5.6/5.45	5.85/5.75
(60)	188	AcOH	60.95/60.95	3.15/3.25	10.45/10.9

* CH = cyclohexane; LP = light petroleum (b.p. 60—80°).

properties as 2-(2-hydroxyphenyl)benzoxazole (4), which was synthesised from 2-aminophenol and salicylaldehyde in nitrobenzene.[4] In spite of the strong intramolecular hydrogen bond [5] in (4), the *O*-methyl derivative (5) and the acetate (6) were formed under relatively mild conditions. Basic hydrolysis of (4) gave mainly the amide (7), together with a small amount of 2-aminophenol (8), but the benzoxazole was stable under forcing acidic conditions. The noise-decoupled ^{13}C n.m.r. spectrum of compound (4) showed thirteen lines. Estimation of the ^{13}C shifts initially on the assumption of simple additivity of substituent effects, by use of

[4] V. V. Somayajulu and N. V. Subba Rao, *Proc. Indian Acad. Sci.* 1964, **59***A*, 396 (*Chem. Abs.*, 1965, **62**, 1639g).

[5] J. Durmis, M. Karvas, and Z. Manasek, *Coll. Czech. Chem. Comm.*, 1973, **38**, 243; V. I. Minkin, Yu. A. Zhdanov, I. D. Sadekov, Yu. A. Ostroumov, N. E. Shelepin, and O. A. Raevskii, *Doklady Akad. Nauk. S.S.S.R.*, 1966, **169**, 1095 (*Chem. Abs.*, 1966, **65**, 1457c).

published [6-8] and unpublished data [9] in conjunction with the coupling constants and multiplicity of the lines exhibited in the undecoupled spectrum, allowed the assignment of structure (4).

In an attempt to assess the scope and mechanism of the reaction, a series of substituted dibenz[*b*,*f*][1,4]-oxazepines (9)—(25) and related diaryl Schiff's bases (63), (66), (69), and (72) were examined under similar reaction conditions. Substituted dibenzoxazepines in the majority of cases gave mixtures of the correspondingly substituted *N*-formylphenoxazine, lactam, and benzoxazole, showing the reaction to be of general applicability (see Tables 1—4). The patterns of aromatic substitution could not be determined from individual ^{1}H n.m.r. spectra, but could be inferred from the structure of the parent dibenzoxazepine. The overall yields and relative proportions of the three products varied, but the benzoxazole was always present and was frequently the major product. The ^{13}C n.m.r. spectra of many of the benzoxazoles will be discussed elsewhere.[10]

On treatment with hydrogen peroxide–acetic acid, the 11-methyl derivative (63) afforded the anticipated 10-acetylphenoxazine (64), together with, as major product, 2′-hydroxyacetophenone (65) and a small amount of an anomalous product, the unsubstituted lactam (3) (Scheme 2). Predictably, no benzoxazole derivative was isolated. Dibenz[*b*,*e*]azepine (66) gave *N*-formylacridan (67) and the lactam (68) as major products, together with small amounts (>4%) of the

TABLE 3

I.r.[a] and ^{1}H n.m.r.[b] data for benzoxazoles

Compd.	$\nu_{C=N}$/cm^{-1}	δ (subst.)	δ (ArH)
(4)	1 640		6.9—7.8 (7 H), 8.02 (1 H, dd, *J* 8 and 2 Hz)
(46)	1 634		7.0—7.8 including 7.1 (d, *J* 9.0 Hz) (6 H), 8.0 (1 H, d, *J* 2.5 Hz)
(47)	1 637		6.9—8.03 including 8.03 (dd, *J* 2.5 and 9.0 Hz) (7 H)
(48)	1 626		6.92—7.85 including 7.7 (d, *J* 2.0 Hz) (6 H), 7.97 (1 H, dd, *J* 2 and 9 Hz)
(49)	1 639	2.37 (3 H, Me)	6.95—7.85 including 7.02 and 7.30 (ABq J_{AB} 9.0 Hz) (7 H)
(50)	1 639	2.30 (3 H, Me)	6.6—7.8 (7 H)
(51)	1 637	2.38 (3 H, Me)	6.78—8.1 (7 H)
(52)	1 639	2.57 (3 H, Me)	6.89—7.6 (6 H), 8.0 (1 H, dd, *J* 2.0 and 8.0 Hz)
(53)	1 637	2.48 (3 H, Me)	6.8—7.65 (6 H), 8.0 (1 H, dd, *J* 2.0 and 8.0 Hz)
(54)	1 636	2.50 (3 H, Me)	6.9—7.6 (6 H), 7.95 (1 H, dd, *J* 2.0 and 8.0 Hz)
(55)	1 634	2.60 (3 H, Me)	6.87—7.47 (6 H), 7.95 (1 H, dd, *J* 2.0 and 8.0 Hz)
(56)	1 638	2.32 (4′-Me) and 2.77 (6′-Me)	6.6—6.9 (2 H) and 7.2—7.8 (4 H)
(57)	1 634	2.32 (3′-Me) and 2.80 (6′-Me)	6.65—7.9 including 6.62 and 7.18 (ABq, J_{AB} 8.0 Hz) (6 H)
(58)	1 638	2.32 (6 H, 3′- and 5′-Me)	7.1—7.85 (6 H)
(59)	1 634	2.56 (3 H, Me) and 2.58 (3 H, Me)	6.8—7.55 (5 H), 2.02 (1H, dd, *J* 2.0 and 8 Hz)
(60)	1 642		7.15—8.0 (5 H), 8.26 (1 H, dd, *J* 2.0 and 9.0 Hz), 8.90 (1 H, d, *J* 2.0 Hz)
(61)	1 642	3.78 (3 H, OMe)	6.64 (1 H, s) overlapping *ca.* 6.6 (1 H, dd), 7.2—7.8 (4 H), 7.91 (1 H, d, *J* 7.5 Hz)
(62)	1 639	3.81 (3 H, OMe)	6.93—7.67 including 7.63 (d, *J* 8 Hz) (6 H), 7.98 (1 H, dd, *J* 2 and 8 Hz)

[a] KBr disc; in all cases, the hydroxy-group gave a broad band centred at 3 030 cm^{-1}. [b] Solvent $CDCl_3$; The OH resonance occurred in the range δ 11—12, but in some cases was too broad for observation.

TABLE 4

I.r.[a] and ^{1}H n.m.r.[b] data for phenoxazines

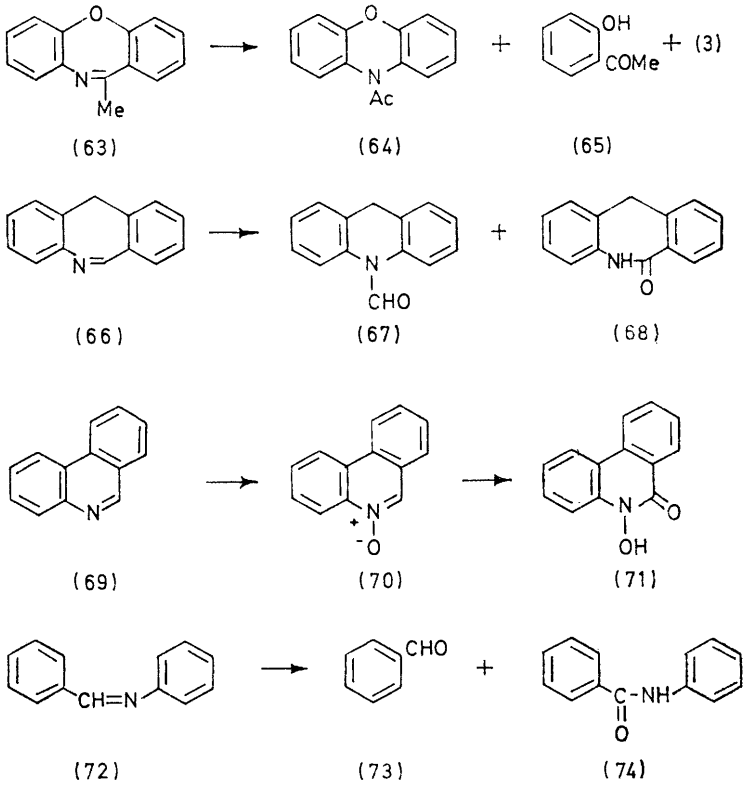
Compd.	$\nu_{C=O}$/cm^{-1}	δ (subst.)	δ(CHO)	δ(ArH)
(2)	1 689		8.68	6.9—7.2 (7 H) and 2.1 (1 H)
(26)	1 689		8.65	6.92—7.4 (7 H)
(27)	1 695		8.70	6.90—7.7 (7 H)
(28)	1 681	2.35 (3 H, Me)	8.65	6.90—7.25 (7 H)
(29)	1 695	2.39 (3 H, Me)	8.60	6.80—7.3 (7 H)
(30)	1 689	2.34 (3 H, Me)	8.65	6.7—7.4 (7 H)
(31)	1 689	2.36 (3 H, Me)	8.39	6.85—7.35 (7 H)
(32)	1 696	2.28 (6 H, 1,3-Me_2)	8.38	6.8 (2 H), 7.15 (4 H)
(33)	1 686	2.31 (6 H, 1- and 4-Me)	8.37	6.83—7.45 (6 H) including 6.87 and 6.97 (ABq, *J* 8 Hz)
(34)	1 695	2.3 (6 H, 2- and 4- Me)	8.66	6.85br (2 H, s), 7.13br (4 H, s)
(35)	1 695	3.8 (3 H, OMe)	11.38	6.6—6.75 (2 H), 7.0—7.6 (4 H)
(40)	1 675	2.51 (3 H, Me)		6.85—7.60 (6 H), 7.9 (1 H, dd, *J* 2 and 8 Hz)
(41)	1 672	2.32 (3 H, Me)		6.9—7.55 (6 H), 7.9 (1 H, dd, *J* 2 and 8 Hz)
(43)	1 681	2.38 (3 H, Me) and 2.47 (3 H, Me)		7.0—7.4 (5 H), 7.52 (1 H, d, *J* 2 Hz)
(64)	1 672		NH*Ac*, 2.32	7.0—7.35 (6 H), 7.45—7.57 (2 H)

[a] KBr disc; $\nu_{C=O}$ refers to N·CHO or NH·CO as appropriate. [b] Solvent $CDCl_3$; for lactams [(40), (41), and (43)] the NH resonance appeared as broadened low field signal.

[6] L. F. Johnson and W. C. Jankowski, 'Carbon-13 N.m.r. Spectra,' Wiley–Interscience, New York, 1972.
[7] J. B. Stothers, 'Carbon-13 N.m.r. Spectroscopy,' New York, 1972.
[8] G. C. Levy and G. L. Nelson, 'Carbon-13 N.m.r. for Organic Chemists,' Wiley–Interscience, New York, 1972.
[9] C. Brown and R. S. Oliver, unpublished observations.
[10] C. Brown, in preparation.

corresponding products in which the methylene bridge had been oxidised to the carbonyl entity. The latter were not fully characterised, however. Phenanthridine (69) gave initially in good yield the *N*-oxide (70), which was converted into the *N*-hydroxyphenanthridone (71) after longer reaction times or on warming as previously reported.[11] Benzylideneaniline (72), the simplest example of a 1,2-diaryl Schiff's base, afforded benzaldehyde (73) (presumably by acidic hydrolysis) and some benzanilide (74).

of (75) yields the nitrogen cation (76). Migration of the aryl group from carbon to the electron deficient nitrogen atom results in ring contraction and phenoxazine formation, whereas hydride ion migration leads to lactam formation with retention of the seven-membered ring. Although Scheme 3 shows a purely ionic process, some degree of participation by the aryl or hydride groups in N–O fission is a possibility. It is however, a matter for speculation, and the extent of participation should show a dependency on the stabilisation afforded to the



SCHEME 2

Treatment of imines with peroxy-acids constitutes the recognised method of laboratory preparation of a wide range of acid-stable oxaziridines.[12-14] We suggest that the observed products from (1) (which will be used as an example) and its derivatives (Table 1) with peracetic acid are consistent with the formation of the oxaziridine (75) as intermediate.* The rearrangement of (75) to phenoxazine and lactam is outlined in Scheme 3 and to benzoxazole in Scheme 4. Scheme 3 shows a recognised mode of oxaziridine rearrangement in a highly ionising acidic solvent medium.[16] Acid-promoted N–O fission

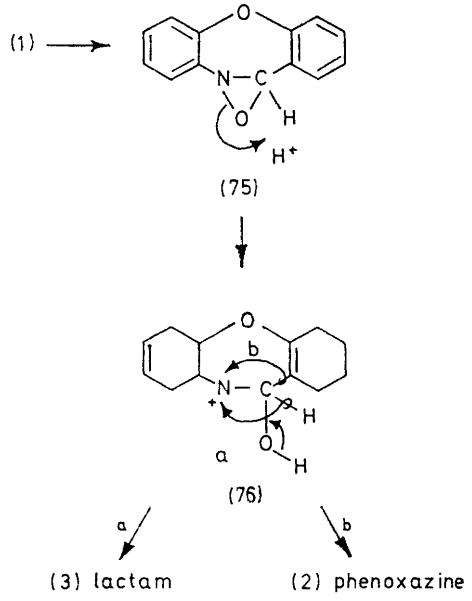
* The instability of such 2,3-diaryloxaziridines is well recognised [15] and is a result of ready heterolytic N–O or C–O fission of the three-membered ring in the presence of substituents which are capable of stabilising the positive charge formed on the nitrogen or carbon atoms during such a process. Highly ionising solvent media further facilitate the process. With simple 2,3-diaryloxaziridines, N–O cleavage predominates, whereas ionic C–O cleavage is preferred only when charge stabilisation factors available to the carbon atom outweigh those available to nitrogen, *e.g.* in 2-alkyl-3-aryloxaziridines,[12,15] and leads to *N*-oxides and hydrolysis products.

incipient charge developing on nitrogen as bond fission occurs and on the migratory aptitudes of the groups involved for each individual dibenzoxazepine. A strictly concerted mechanism may be ruled out as a consequence of the nature of the reactants, the polar reaction medium, and the high energy transition state resulting from the bond deformations necessary for the back-side displacement of oxygen by the migrating group during bond fission.

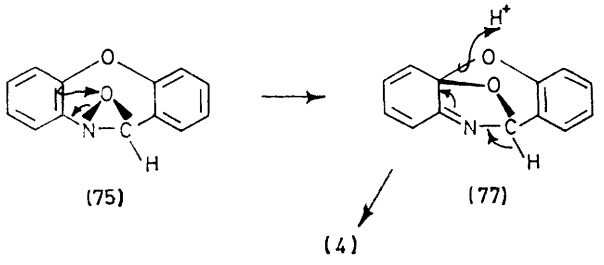
Scheme 4 shows the proposed mechanism for benzoxazole formation and requires that the oxaziridine

[11] E. Hayashi and Y. Hotta, *J. Pharm. Soc. Japan*, 1960, **80**, 834.
[12] W. D. Emmons, *J. Amer. Chem. Soc.*, 1957, **79**, 5739.
[13] W. D. Emmons in 'The Chemistry of Heterocyclic Compounds,' ed. A. Weissberger, vol. 19, Interscience, New York, 1964, p. 624.
[14] E. Schmitz, *Adv. Heterocyclic Chem.*, 1963, **2**, 83.
[15] C. J. O'Connor, E. J. Fendler, and J. H. Fendler, *J.C.S. Perkin II*, 1973, 1744.
[16] J. S. Splitter and M. Calvin, *J. Org. Chem.*, 1965, **30**, 3427, and references therein.

should act as an electrophile. Intramolecular electrophilic attack by the oxygen atom of the oxaziridine ring at the ether linkage carbon atom adjacent to C-6 gives (77) (models show this step to be feasible), which



SCHEME 3

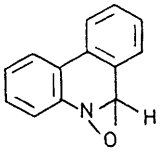


SCHEME 4

yields (4) after rearomatisation by fission of the ether linkage and elimination of (what was) the azomethine proton. Electrophilic properties of oxaziridines have been noted previously. Emmons [12] observed that oxaziridines liberated iodine when treated with potassium iodide. More recently, an oxaziridine [17] has been proposed as the active oxygenating agent in the enzymic hydroxylation reaction of flavin mono-oxygenases in biological systems, a process involving intermolecular electrophilic attack on an aromatic substrate.

Rationalisation of product ratios in terms of steric and electronic effects of the substituents is difficult especially, as in several cases, overall product yields were low. The effect of a given substituent on any of the pathways outlined above may be of different importance to each, and may be considerably distorted where it serves to enhance those processes leading to alternative unidentified by-products. Several trends are apparent, however. Methyl groups at C-6, -7, -8, and -9 [(15)—(18) and (22)] all gave high proportions of benzoxazole, supporting the contention that the oxaziridine acts as an electrophile. These observations seem to rule out an intramolecular nucleophilic process involving the substituted analogue of (75) or (76) with the electron shifts simply reversed in direction. Dibenzoxazepines with electron-releasing groups at C-2, -3, and -4 gave significant proportions of the appropriate phenoxazine as a result of the increased migratory aptitude of that ring. Conversely, the 2-nitro-substituent in (23), by virtue of its powerful electron-withdrawing properties, suppressed phenoxazine formation to the extent that none could be isolated. Similarly low [or zero, *e.g.* from (16) and (25)] yields of phenoxazine were returned from dibenzoxazepines with electron-releasing groups at C-6, -7, -8, and -9 as a consequence of the increased electron density on that ring and hence at the nitrogen atom, the migration terminus. Yields of lactam were generally low (or zero) and no trend was apparent, presumably reflecting the less well-defined interactions experienced by the methine proton when not directly bonded to an aromatic nucleus.

Dibenz[*b*,*e*]azepine (66) gave the products (67) and (68) presumably by a mechanism similar to that outlined in Scheme 3. Phenanthridine gave the *N*-oxide (70) as the primary product which, again on the assumption of an oxaziridine intermediate (78), is the result of C–O fission. This is in marked contrast to the dibenzoxazepine series where no *N*-oxides were isolated. 11-Methyldibenzoxazepine (63) gave 2′-hydroxyacetophenone (65) as the major product, together with lesser amounts of *N*-acetylphenoxazine (64) and the lactam (3). In comparison with dibenzoxazepines unsubstituted at C-11, the oxaziridine from (63) would be more likely to undergo C–O fission by virtue of the additional stabilisation afforded to the resulting carbocation by the methyl group. However, no *N*-oxide was



isolated from (63) on treatment with peroxy-acid. This creates the possibility that, in these systems, C–O fission of the oxaziridine does not give *N*-oxide but results in hydrolysis and total fission of the oxazepine ring, giving (unidentified) minor products.* Thus, although this argument gives no insight into the exclusive *N*-oxide formation observed with phenanthridine, it offers an

* Current work [18] provides some basis in fact for this hypothesis. Reduction of 2-(2-nitrophenoxy)benzaldehyde with zinc dust in methanol gave dibenz[*b*,*f*][1,4]oxazepine 10-oxide, which decomposed on treatment with hydrogen peroxide in glacial acetic acid under the standard conditions (see Experimental section).

[17] H. W. Orf and D. Dolphin, *Proc. Nat. Acad. Sci. U.S.A.*, 1974, **71**, 2646.

[18] J. M. Harrison and T. D. Inch, unpublished results.

explanation for the apparent absence of *N*-oxide formation in the dibenzoxazepine series and at the same time presents a more realistic view of the fate of the oxaziridine, with fission of both the N–O and C–O bonds being implicated.

In conclusion and summary, for all isolated products, an oxaziridine is believed to be the common intermediate. However its decomposition under polar acidic conditions is clearly complex, with small energy differences separating the competing pathways. It is not possible to describe the precise course of the reaction on the basis of product analysis, but in the light of known oxaziridine chemistry,[12-15,19] it is possible to propose reasonable mechanisms to accommodate the observed facts.

EXPERIMENTAL

Routine experimental and spectroscopic procedures are described elsewhere,[2] as are the syntheses of all the dibenzoxazepine derivative utilised. The hydrogen peroxide used throughout was a 30% solution (100 vol.).

General Procedure for Oxidation of Dibenzoxazepines (1), *and* (9)—(25) *with Peracetic Acid*.—The dibenzoxazepine (*ca.* 5 mmol) was stored overnight at room temperature with a mixture of acetic acid (9 ml) and hydrogen peroxide (3 ml). The mixture was poured into brine and extracted with several portions of chloroform, which were combined, dried, and concentrated. The products were separated by column chromatography. In each instance, the order of elution was benzoxazole, phenoxazine, and lactam. Where necessary, further purification was achieved by crystallisation. Each product was characterised by n.m.r. and i.r. (Tables 3 and 4), u.v., and mass spectroscopy. Yields and chromatography solvents are shown in Table 1. Microanalyses, m.p.s, and recrystallisation solvents for new compounds are reported in Table 2.

Oxidation of 11-*Methyldibenz*[b,f][1,4]*oxazepine* (63).—Compound (63) (250 mg) was stored with hydrogen peroxide (2 ml) and glacial acetic acid (6 ml) at room temperature for 3 days; t.l.c. (chloroform) then showed no starting material. The usual work-up and subsequent chromatography (benzene as eluant) gave, in order of elution, 2′-hydroxyacetophenone (65) as a yellow oil (80 mg, 48%), indistinguishable spectroscopically from an authentic sample, 10-acetylphenoxazine (64) as a crystalline solid (65 mg, 24%), m.p. 140—141° (from benzene) [lit.,[20] 146° (from ethanol)], and the unsubstituted lactam (3) (identical with an authentic specimen).

Oxidation of Dibenz[b,e]*azepine* (66).—Compound (66) (1 g) was stored at room temperature with hydrogen peroxide (3 ml) and acetic acid (7 ml) for 3 days. Conventional processing and chromatography (cyclohexane–ethyl acetate, 8 : 2) gave, in order of elution, N-*formylacridan* (67) (0.64 g, 57%), m.p. 110° (from cyclohexane) (Found: C, 80.2; H, 5.35; N, 6.65. $C_{14}H_{11}NO$ requires C, 80.35; H, 5.3; N, 6.7%) and 5,6-dihydro-6-oxodibenz-[*b*,*e*]azepin-6(5*H*)-one (68) (0.20 g, 18%), m.p. 198° (from ethanol) (lit.,[21] 201—203°).

Oxidation of Benzylideneaniline (72).—Benzylideneaniline (72) (0.7 g) was treated with hydrogen peroxide (2 ml) in glacial acetic acid (8 ml) for 8 h. Usual work-up and chromatography over silica (chloroform) gave benzaldehyde (0.22 g, 50%) and benzanilide (0.07 g, 11%), both identical with authentic samples.

Basic Hydrolysis of 2-(2-*Hydroxyphenyl*)*benzoxazole* (4).—The benzoxazole (4) (1.0 g) in aqueous 30% potassium hydroxide was stirred and heated at *ca.* 70 °C for 4 h. The solution was cooled, neutralised to *ca.* pH 7 with hydrochloric acid, and extracted with chloroform. The extracts were combined, dried, concentrated, and chromatographed [chloroform–methanol (38 : 1) as eluant]. The first-eluted compound was 2-aminophenol (0.06 g, 11%), identical with an authentic specimen. The second, major product (0.57 g, 65%) was N-(2-*hydroxyphenyl*)-2-*hydroxybenzamide* (7), m.p. 156—158° (from toluene–cyclohexane) (Found: C, 67.95; H, 4.9; N, 5.85. $C_{13}H_{11}NO_3$ requires C, 68.1; H, 4.85; N, 6.1%).

2-(2-*Methoxyphenyl*)*benzoxazole* (5).—A solution of 2-(2-hydroxyphenyl)benzoxazole (4) (100 mg) and sodium hydride (0.3 g of an 80% dispersion in mineral oil) in dry dimethylformamide (5 ml) was stirred for 1 h at 60 °C. Methyl iodide (2 g) was added and heating and stirring were continued for 3 h. The mixture was then set aside overnight at room temperature. Work-up in the usual way and chromatography (chloroform) gave (5) as a white crystalline solid (85 mg, 81%), m.p. 66° [from petroleum (b.p. 40—60°)].

2-(2-*Acetoxyphenyl*)*benzoxazole* (6).—A solution of compound (4) (0.4 g) and acetic anhydride (2 ml) in pyridine was stored overnight at room temperature, then poured into water, and the resulting crystalline solid was filtered off and dried. Recrystallisation gave 2-(2-*acetoxyphenyl*)-*benzoxazole* as white crystals (288 mg, 54%), m.p. 72° [from petroleum (b.p. 60—80°)] (Found: C, 71.15; H, 4.5; N, 5.7. $C_{15}H_{11}NO_3$ requires C, 71.15; H, 4.4; N, 5.55%).

10-*Formylphenoxazine* (2).—Phenoxazine (1 g) with formic acid (10 ml) and acetic anhydride (1 ml) was heated under reflux for 2 h. The mixture was poured onto ice and the resulting crystals filtered off, dried, and recrystallised from methanol [m.p. 144° (0.7 g, 60%)]; see Tables 2 and 4 for analytical and spectroscopic data.

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