Dibenz[*b,f*][1,4]oxazepine: Homogeneous and Heterogeneous Reactions with Sodium Dichloroisocyanurate (FiClor)

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Dibenz[*b,f*][1,4]oxazepine (1) reacts with sodium dichloroisocyanurate (FiClor) under homogeneous conditions in aqueous ethanol to afford salicylaldehyde as the preponderant primary product, together with smaller amounts of *N*-formylphenoxazine and 2-(2-hydroxyphenyl)benzoxazole. All the products result from oxidation of the azomethine group in (1). Dibenz[*b,f*][1,4]oxazepine reacts with FiClor under heterogeneous conditions in chloroform–water mixtures to give preponderantly the nuclear chlorinated derivatives 7-chloro-, 9-chloro-, and 7,9-dichloro-dibenz[*b,f*][1,4]-oxazepines as the primary products. Mechanisms of the primary and subsequent reactions are discussed.

DURING studies of the synthesis and other aspects of the chemistry [1,2] of the potent irritant and lachrymator, dibenz[*b,f*][1,4]oxazepine (1) it was sometimes convenient to decontaminate glassware and reaction residues with the commercial chlorinating and bleaching agent FiClor † [sodium dichloroisocyanurate (2)]. Because of solubility considerations, decontaminations were carried out in aqueous alcohol or in chloroform–water mixtures. It was observed that although the dibenz[*b,f*][1,4]oxazepine (1) was destroyed by FiClor both in aqueous alcohol (homogeneous conditions) and in chloroform–water (heterogeneous conditions) the products differed. Since, despite its many commercial applications,‡ studies of the organic chemistry of FiClor are few, it was pertinent, therefore, to study the FiClor–dibenz[*b,f*][1,4]oxazapine interaction under homogeneous and heterogeneous conditions both to identify the products and to elucidate why the preferred reactions varied with reaction conditions.

For clarity, the experimental work concerned with the separation and identification of reaction products will be described only in the Experimental section. The main discussion will be focused on the results from the gas chromatographic analyses.

RESULTS AND DISCUSSION

Reaction of FiClor and Dibenz[b,f][1,4]*-oxazepine under Homogeneous Conditions* (*Scheme* 1).—An aqueous solution of FiClor (2) was added to a dilute solution of (1) in water containing 3% ethanol. The course of the ensuing reactions was monitored by gas-chromatographic analysis of chloroform extracts of aliquots withdrawn from the reaction mixture at various times. Before extraction with chloroform, the excess of (2) in each aliquot was decomposed by addition of aqueous potassium iodide in the presence of potassium thiosulphate. In the absence of thiosulphate, iodination of some of the reaction products occurred.

No dibenz[*b,f*][1,4]oxazepine (1) could be detected in the reaction solution after 5 min and the results in Table 1 show that the major initial product was salicylaldehyde (4) with smaller amounts of the phenoxazine (5) and the lactam (3). Although (3) and (5) were essentially stable under the reaction conditions and were not easily chlorinated, salicylaldehyde underwent rapid further chlorination to afford mixtures of chlorinated phenols and chlorinated salicylaldehydes, in reaction sequences which included the facile replacement of CHO by Cl in salicylaldehyde and derived products. The loss of salicylaldehyde from the reaction mixture was not reflected by a corresponding increase in trichlorophenol or other chlorinated derivatives (Table 1). It was shown subsequently that FiClor rapidly converts (7)—(12) into trichlorophenol (13) which is further converted into the quinone (14). The quinone (14) was not detected in the experiment summarised in Table 1 since it is not extractable by chloroform from reaction aliquots treated with potassium iodide and potassium thiosulphate. It was isolated, however, following treatment of trichlorophenol with FiClor, and was detected by gas chromatography and t.l.c. in chloroform extracts from reaction mixtures of (1) and (2) which were not quenched with potassium iodide.

TABLE 1

Variation of product distribution with time in the reaction of dibenz[*b,f*]oxazepine with sodium dichloroisocyanurate

		% Yield after time *t*/min			
Product	R_t */s	5	60	120	200
(7)	100	0.3	0.2		
(4)	150	82	19	9.6	3.5
(10)	230		1.3	1.3	0.7
(8)	305		12	8.8	3.2
(13)	591		4.8	3.1	1.1
(5)	1 336	7	6.5	6.2	6.1
(3)	1 407	1.1	1.0	1.1	0.7

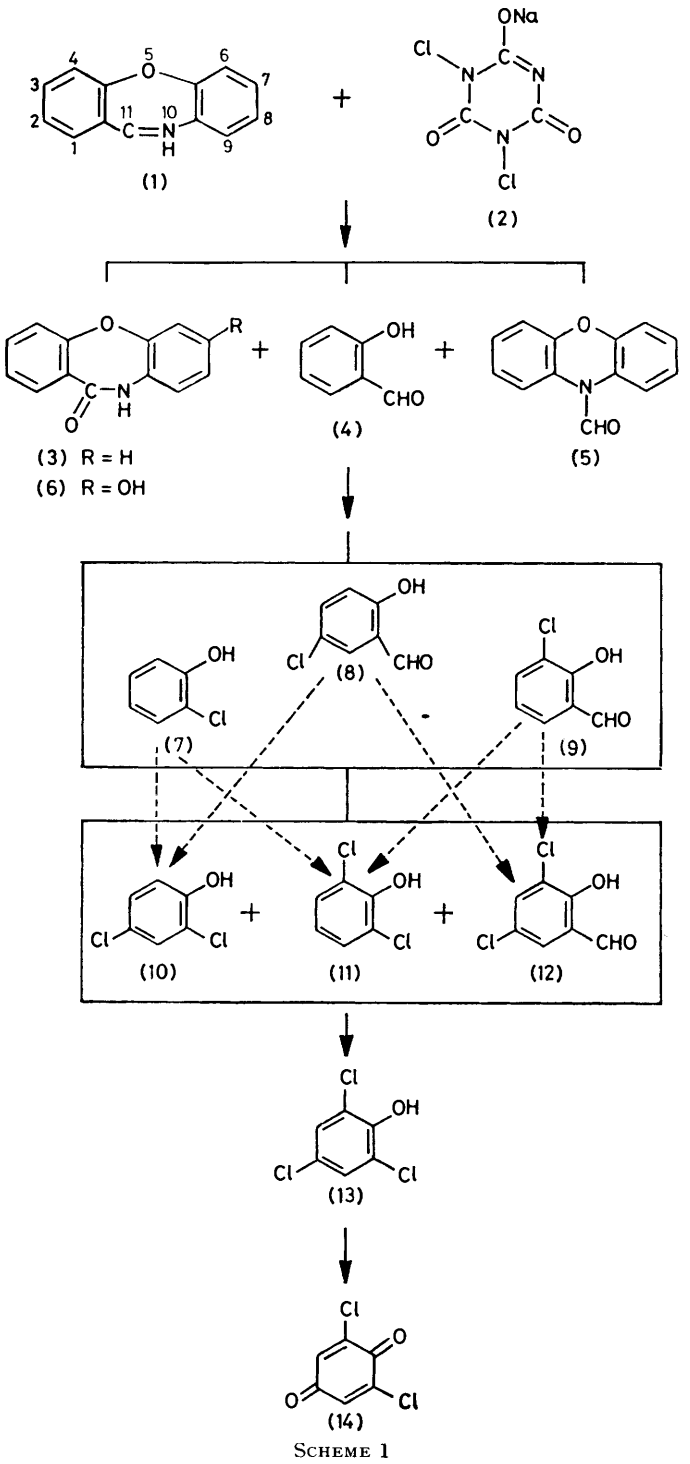
* Gas-chromatographic retention time; see Experimental section for gas-chromatographic conditions.

The compounds which have been isolated or detected as products from treatment of (1) with (2) are shown in Scheme 1. The hydroxy-derivative (6) was not amenable to g.c. assay but was isolated in trace amounts during preparative experiments to isolate products for their unequivocal identification (see Experimental section). The reaction sequences by which (4) is converted into (14) will be discussed later in the paper.

On the assumption (which will be discussed later) that

† FiClor refers to Fi-Clor clearon which is sodium dichloroisocyanurate dihydrate and is supplied by Chlor Chem Ltd. of Widnes, Lancs.

‡ FiClor is used mainly as a chlorine-releasing agent in bleaching process or for sterilisation. It has also found use in felt-proofing keratin fibres and cross-linking polyvinylalcohol fibres.

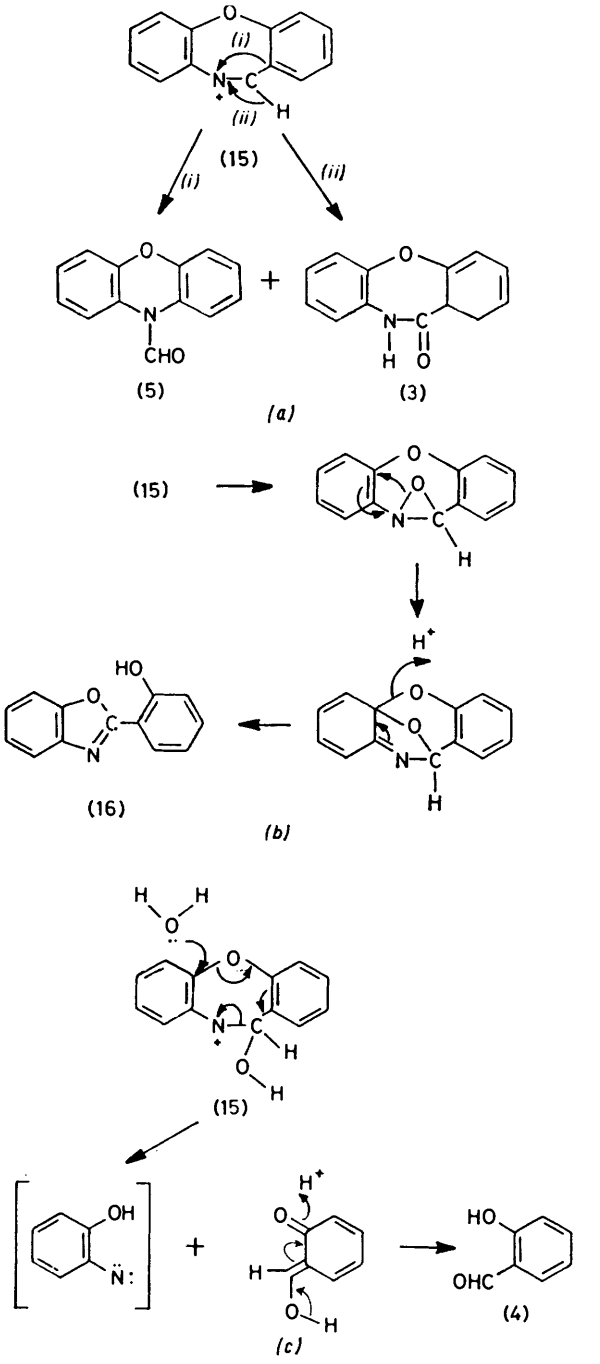


SCHEME 1

the oxidation of the azomethine group in (1) leads to the intermediate (15), it is probable that (3) and (5) are formed by the mechanism shown in Scheme 2(*a*); *i.e.* the oxidation follows essentially the same pathways as those described previously [2] for peracid oxidations of (1). However, whereas the peracid oxidations, in which the amount of water present was small, afforded significant amounts of the benzoxazole (16), probably by the mechanism illustrated in Scheme 2(*b*), under aqueous oxidation conditions salicylaldehyde becomes the major product probably by the mechanism in Scheme 2(*c*).

Support for the similarity of the oxidation routes for FiClor and peracids was provided by direct comparison of the initial reaction products of (1) with aqueous FiClor and with aqueous *m*-chloroperbenzoic acid (Table 2). With both oxidants salicylaldehyde was the major product, and under aqueous conditions with peracid much less benzoxazole was formed than previously.[2]

Further evidence, consistent with the mechanism



SCHEME 2

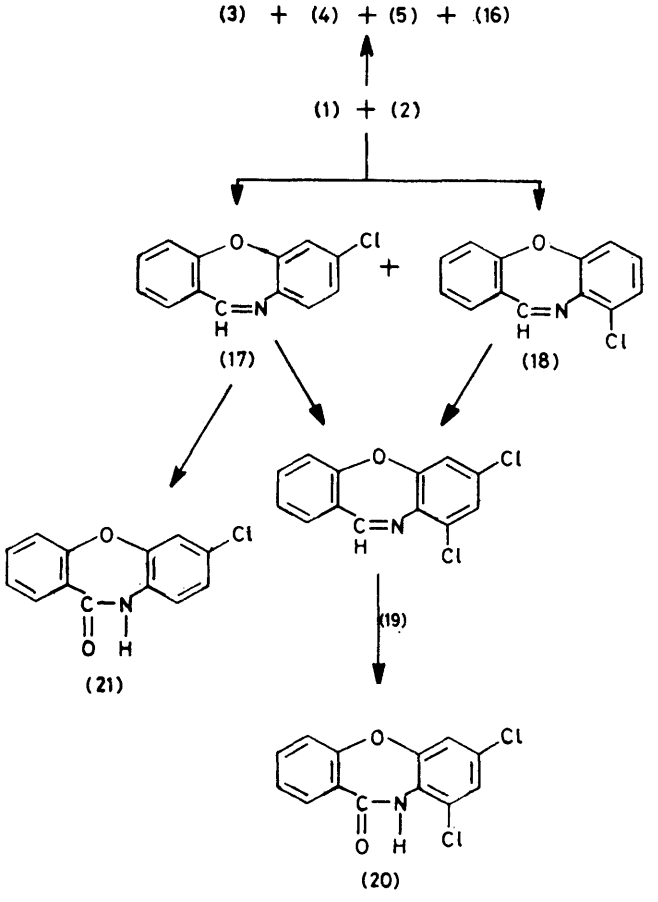
TABLE 2

Comparison of yields of products in the reaction of dibenz-[*b*,*f*][1,4]oxazepine with sodium dichloroisocyanurate (A) and *m*-chloroperbenzoic acid (B)

	% Yield	
Product	A (after 5 min)	B (after 15 min)
(4)	82	66
(5)	7	15
(3)	1	Trace
(16)		14

proposed for salicylaldehyde formation, was provided when the salicylaldehyde isolated from the reaction of (1) and (2) in $H_2{}^{18}O$ was found to be enriched in ^{18}O in one oxygen atom. That ^{18}O-enrichment was in the carbonyl oxygen and not in the phenolic oxygen was shown when derivatisation of the salicylaldehyde as its phenylhydrazone resulted in complete removal of ^{18}O.

In the many experiments carried out to investigate the reaction of (1) with aqueous FiClor no trace of any simple low-molecular-weight compounds containing nitrogen have been detected other than those such as (3), (5), and (16) in which tricyclic ring systems are retained. It must therefore be assumed that following decomposition by the processes illustrated in Scheme 2(*c*), polymerisation of the nitrogen containing fragments must occur.



SCHEME 3

Reaction of FiClor and Dibenz[b,f][1,4]*oxazepine under Heterogeneous Conditions* (*Scheme* 3).—*A two phase* mixture of (1) in chloroform and (2) in water was stirred vigorously. At various times aliquots of the chloroform layer were removed, washed with a solution containing potassium iodide and potassium thiosulphate, and examined by gas chromatography. The products detected are shown in Scheme 3, and in Table 3 the different product concentrations with time are given. Since, unlike for the homogeneous reaction between (1) and (2), fragmentation of the tricyclic ring system did not occur, good mass balances were obtained particularly in the early stages of the reaction.

Attention is drawn to the following points. (*a*) The products which may be attributed to oxidative attack on the azomethine group [the lactam (3), salicylaldehyde (4), phenoxazine (5), and benzoxazole (16)] are those

TABLE 3

Variation of product distribution with time in the reaction of (1) and (2) in chloroform–water (heterogeneous conditions)

		% Yield at time *t*/h					
Product	R_t *	1	2.5	5	10	24	36
(4)	63	1.0	0.8				
(1)	134	0.1					
(16)	169	11	12	12	11	5	4
(17)	212	1.4					
(5)	227	1.7	1.1	1.3	1.1	1.2	1.1
(18)	286	38	40	33	31	11	9.9
(3)	340	12	12	12	11	10	10
(19)	400	31	33	33	32	38	34
(20)	565	2.5	2.3	2.1	2.0	6.4	7.6
(21)	611	0.4	0.5	0.4	0.6	0.4	0.3

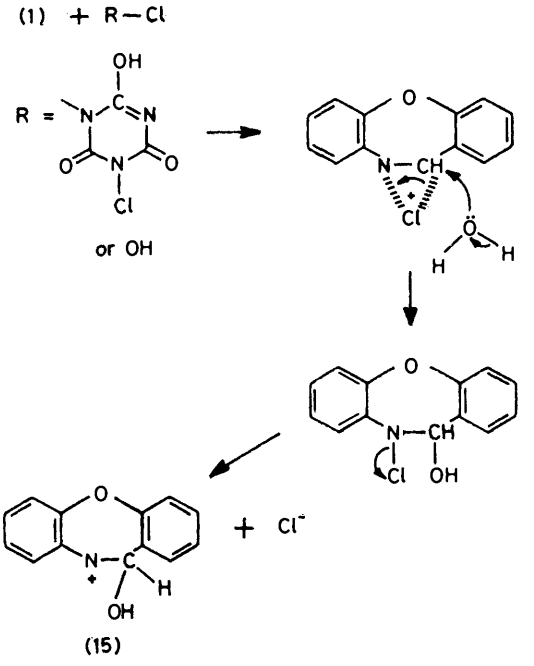
* Gas-chromatographic retention time; gas-chromatographic conditions are given in the Experimental section.

described previously as products of peracid or aqueous FiClor oxidations. These products [except (4)] are relatively resistant to nuclear chlorination by FiClor as shown by their persistance in the reaction mixture (Table 3) and in their behaviour to FiClor in control experiments. (*b*) Nuclear chlorination occurs at least preponderantly, if not exclusively, in those products in which the azomethine group is intact. (*c*) Oxidation of the azomethine group in products chlorinated at C-9, or at C-7 and C-9, is slow compared to oxidation in dibenzoxazepines which do not contain chlorine. In control experiments with FiClor (17) gave a trace of (21) but preponderantly the dichloro-derivative (19) which was then slowly converted into (20). The 9-chloro-derivative (18), however, gave no corresponding lactam and was converted sequentially into (19) and (20).

Comparison of the Mechanisms of Homogeneous and Heterogeneous Reactions.—The reaction between (1) and (2) is complex, with marked differences between the products formed in aqueous solution and those formed in the two-phase, chloroform–water system. In the absence of detailed physicochemical studies no firm conclusions as to reaction mechanisms may be drawn, although tentative suggestions based on the product analyses described earlier are possible.

The chemistry of trichloroisocyanuric acid resembles that of other *N*-halogenoimides, such as *N*-chloro- and *N*-bromo-succinimide,[3,4] and presumably (2) can behave similarly. It has been proposed that *N*-halogenoimides act as a source of hypohalous acid in aqueous solution [5] but, whilst the reactions between (1) and (2), and (1) and hypochlorous acid, in aqueous solution afford similar product distributions, under heterogeneous conditions there are marked differences.

This observation suggests that (2) does not act as a source of hypochlorous acid in aqueous solution. It is suggested that both reagents act as a source of electropositive chlorine and that the reaction in aqueous solution proceeds according to Scheme 4 *via* addition of water to



SCHEME 4

the initially formed chloronium ion, followed by loss of chloride ion, to afford (15). In aqueous solution (15) undergoes hydrolysis to afford preponderantly salicylaldehyde rather than intramolecular rearrangement, as previous discussed,[2] to afford (3), (5), and (16). Similarly *m*-chloroperbenzoic acid oxidation in dilute aqueous solution affords a similar product distribution *via* (15).

The high solubility of (1), and the derived products, in chloroform dictates that processes requiring water must occur at the interface of the two phase system or else utilise dissolved water. Consequently processes such as the intramolecular rearrangement of (15) to afford (3), (5), and (16) become important, whilst only a low yield of salicylaldehyde is obtained. Since *N*-halogenoimides can act as free-radical halogenating agents in non-polar solvents,[6] whilst chloroform tends to stabilise charged species, *e.g.* Cl^+, to a lesser extent than water, suggests that the aromatic nuclear chlorination products (17)—(19) may arise *via* a free radical mechanism. This supposition is supported by the observation that in a water–chloroform mixture toluene is converted to benzyl chloride by (2) and further, reaction of (1) with trichloroisocyanuric acid in chloroform afforded mainly the chlorination products (17)—(19) with little concomitant oxidation of the azomethine group.

Detailed mechanistic considerations are complicated by the fact that with FiClor in aqueous chloroform the lactams produced are converted into *N*-chloro-derivatives such as (22) (under the usual work-up conditions employed, these derivatives are reconverted into lactams and so were not measured quantitatively in any experiments). In chloroform such derivatives act similarly to *e.g.* trichloroisocyanuric acid, and convert (1) into (17)—(19), but no evidence has been obtained to indicate that these derivatives increase the chlorinating activity of FiClor in aqueous chloroform.

Chlorination of Salicylaldehyde.—The experimental studies on the chlorination of salicylaldehyde with FiClor in aqueous ethanol summarised in Table 4 bear out the fact that the reactions for conversion of (4) into (13) shown in Scheme 1 all occur. The key feature, that the formyl group is replaced directly by chlorine and not by hydrogen with chlorination taking place elsewhere in the molecule, was established when 3-chlorosalicylaldehyde afforded 2,6-dichlorophenol as the only dichlorophenol.

Other instances [7] in which deformylation occurs in substituted benzaldehydes where there is activation by electron-releasing substituents in the *ortho*- and *para*-positions have been reported and experiments in this

TABLE 4

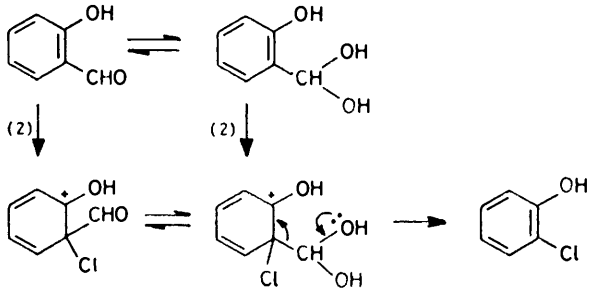
Reaction products of salicylaldehydes with chlorophenols with FiClor

Starting material	2-Chloro-phenol	Salicyl-aldehyde	3-Chloro-salicyl-aldehyde	5-Chloro-salicyl-aldehyde	3,5-Dichloro-salicyl-aldehyde	2,6-Dichloro-phenol	2,4-Dichloro-phenol	2,4,6-Tri-chlorophenol
Salicylaldehyde	+	+	trace	+	trace	+ *	+	+
2-Chlorophenol	+	—	—	—	—	trace	+	+
3-Chlorosalicyl-aldehyde	—	—	+	—	+	+	—	+
5-Chlorosalicyl-aldehyde	—	—	—	+	+	—	+	+
2,4-Dichlorophenol	—	—	—	—	—	—	+	+
2,6-Dichlorophenol	—	—	—	—	—	+	—	+
3,5-Dichlorosalicyl-aldehyde	—	—	—	—	+	—	—	+
2,4,6-Trichlorophenol	—	—	—	—	—	—	—	+

* As a shoulder on 5-chlorosalicylaldehyde.

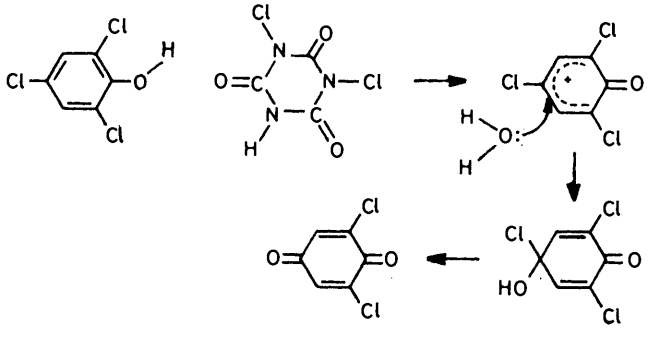
laboratory with FiClor and benzaldehyde or *m*-hydroxybenzaldehyde in which no deformylation occurred, and with FiClor and *p*-hydroxybenzaldehyde where deformylation did occur, confirm the early work.

A possible mechanism for the deformylation reaction which involves attack of electrophilic chlorine at the aromatic carbon carrying the formyl group, followed by elimination of formic acid from the hydrated aldehyde is shown in Scheme 5.



SCHEME 5

Oxidation of 2,4,6-*Trichlorophenol to* 2,6-*Dichloro*-p-*benzoquinone*.—The facile oxidation of 2,4,6-trichlorophenol (13) to 2,6-dichloro-*p*-benzoquinone (14) serves to illustrate the electrophilic properties of (2). It seems likely that (2) is able to abstract a hydride ion from the phenol to yield a keto-cation as shown in Scheme 6 which is readily attached at the *para*-position by water to give the quinone following elimination of hydrogen chloride. Similar keto-cations have been suggested during the oxidation of trihalogenoanisoles to *p*-benzoquinones.[8] Although it has been claimed[5] that 2,4,6-trichlorophenol and trichloroisocyanuric acid form a charge-transfer complex, and although the formation of



SCHEME 6

the benzoquinone (14) from (13) could result from the intermediacy of such a complex, no evidence for a charge-transfer complex was obtained in the present work.

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 157 spectrophotometer as KBr discs unless otherwise stated. N.m.r. spectra were measured with a JEOL JNM-4-H-100 n.m.r. spectrometer at 100 MHz for solutions in deuteriochloroform unless otherwise stated. Mass spectra were run on a Micromass 7070F spectrometer at 70 eV (source temperature 200 °C). G.l.c. was performed on a Perkin-Elmer F17 with F.I.D. detector equipped with an Infotronics 304/40 electronic integrator; 6 ft × 3.5-mm glass columns, nitrogen at 30 ml min^{-1} as carrier, and an injection temperature of 300 °C were used unless otherwise stated. All solutions were dried over magnesium sulphate.

Isolation and Identification of Products from the Reaction of Dibenz[b,f][1,4]*oxazepine* (1) *and Sodium Dichloroisocyanurate* (2) *in Aqueous Ethanol* (*Homogeneous Reaction*).—Compound (1) (100 mg) in ethanol (30 ml) was diluted to 1 l with water and (2) (450 mg) in water (20 ml) was added in one portion. After 1 h a solution of potassium iodide (1 g) and potassium thiosulphate (3 g) in water (10 ml) was added. The mixture was extracted with chloroform, the extract was dried and concentrated, and the residue was chromatographed over silica gel in chloroform to afford three fractions. Fraction A, R_F >0.2, was rechromatographed in cyclohexane–ether (9 : 1) to afford salicylaldehyde (R_F 0.7), *N*-formylphenoxazine [2] (R_F 0.1), and a mixed fraction (R_F 0.2—0.6) which was rechromatographed in light petroleum (b.p. 40—60 °C)–ether (9 : 1) to afford 5-chlorosalicylaldehyde (R_F 0.5), 2,4-dichlorophenol (R_F 0.2), and 2,4,6-trichlorophenol (R_F 0.1). Fraction B, R_F 0.1—0.2, was rechromatographed in chloroform–ethyl acetate (8 : 2) to afford dibenz[*b*,*f*][1,4]oxazepin-11(10*H*)-one [2] (R_F 0.7) and 7-hydroxydibenz[*b*,*f*][1,4]oxazepin-11(10*H*)-one [9] (6) (R_F 0.2). Fraction C, R_F <0.1, was obtained by eluting with chloroform–methanol (9 : 1) and was rechromatographed in chloroform–methanol (9 : 1) to give an unidentified material (1.6 mg); $\nu_{max.}$ 1 670 cm^{-1} (C=O), *m*/*e* 261 [M^+], possibly a chlorohydroxylactam.

The residue was also examined by m.s.–g.c. using a 3% OV–17 on Gas Chrom Q column, temperature-programmed from 80 °C (held for 1 min) to 240 °C at 15° min^{-1}, with helium as carrier gas (30 ml min^{-1}). Compounds detected were *o*-chlorophenol, R_t 170 s; salicylaldehyde, R_t 222 s; 2,4-dichlorophenol, R_t 306 s; 2,6-dichlorophenol, R_t 315 s; 5-chlorosalicylaldehyde, R_t 396 s; 3-chlorosalicylaldehyde, R_t 381 s; 2,4,6-trichlorophenol, R_t 408 s; 3,5-dichlorosalicylaldehyde, R_t 441 s; *N*-formylphenoxazine, R_t 768 s; and dibenz[*b*,*f*][1,4]oxazepin-11(10*H*)-one (3), R_t 876 s. 7-Hydroxydibenz[*b*,*f*][1,4]oxazepin-11(10*H*)-one (6) and the unidentified material from fraction C could not be gas-chromatographed. 2-(2-Hydroxyphenyl)benzoxazole(16),[10] R_t 713 s, was not detected.

Estimation of the Variation of Product Distribution with Time in the Reaction of (1) *with* (2).—Compound (1) (10 mg) in ethanol (3 ml) was diluted to 100 ml with water and (2) (45 mg) in water (2 ml) was added in one portion. Aliquots (25 ml) were withdrawn after various times and 1 ml of a standard solution of potassium iodide (1 g) and potassium thiosulphate (3 g) in water (10 ml) was added. The mixture was extracted with chloroform (5 ml) and each extract was analysed quantitatively by g.l.c. using a 6% Dexsil 300 GC on Gas Chrom Q column, temperature-programmed from 140 (held for 8 min) to 300 °C at 10° min^{-1}. The results are summarised in Table 1. 2,6-Dichlorophenol, R_t 289 s; 3-chlorosalicylaldehyde, R_t 493 s; and 3,5-dichlorosalicylaldehyde, R_t 744 s were also detected but in amounts too small for quantitative estimation.

Formation of 2,6-*Dichloro*-p-*benzoquinone*.—Compound (1) (10 mg) in ethanol (3 ml) was diluted to 100 ml with water and treated with (2) (45 mg) in water (2 ml) for 5 h. The mixture was extracted with chloroform and the extract analysed by g.l.c. using a 6% Dexsil 300 GC on Gas Chrom Q column at 140 °C; 2,6-dichloro-*p*-benzoquinone (R_t 395 s) was detected.[11]

Reaction of (1) *with* (2) *in* ^{18}O-*Enriched Water*.—Compound (1) (106 μg) in ethanol (30 μl) was added to water (1 ml, enriched with 20.9% ^{18}O) and 2% aqueous (2) (50 μl) was added. After 5 min potassium iodide–potassium thiosulphate solution (0.5 ml) was added and the mixture was extracted with chloroform (0.5 ml). The mixture was analysed by m.s.–g.c. using a 3% OV–17 on Gas Chrom Q column at 80 °C and helium as carrier gas (30 ml min^{-1}). The splitting pattern of salicylaldehyde (R_t 323 s) showed a peak at *m/e* 124 [$M^+ + 2$] which was 14% of the *m/e* 122 peak [M^+], but no peak at *m/e* 126 [$M^+ + 4$].

The chloroform extract was treated with phenylhydrazine in chloroform and the products analysed by m.s.–g.c. using a 3% OV–17 on Gas Chrom Q at 215 °C and helium as carrier gas (30 ml min^{-1}). The splitting pattern of salicylaldehyde phenylhydrazone showed a peak at *m/e* 212 [M^+], but < 2% enhancement of the *m/e* 214 peak [$M^+ + 2$].

Isolation and Identification of Products from the Reaction of (1) *with* (2) *in Chloroform–Water* (*Heterogeneous Conditions*).—A mixture of (1) (1 g) in chloroform (50 ml) and (2) (3 g) in water (50 ml) was stirred vigorously for 5 h. The chloroform layer was separated, shaken with potassium iodide–potassium thiosulphate (50 ml), dried, concentrated, and chromatographed over silica gel in chloroform to afford 2-(2-hydroxyphenyl)benzoxazole (16) (R_F 0.9); 9-*chlorodibenz*[b,f][1,4]*oxazepine* (18) (R_F 0.7); 7,9-*dichlorodibenz*[b,f]*oxazepine* (19) (R_F 0.6); 7,9-*dichlorodibenz*[b,f][1,4]*oxazepin*-11-*one* (20) (R_F 0.5); and a mixture of dibenz[*b,f*][1,4]oxazepin-11(10*H*)-one (3) with 7-chlorodibenz[*b,f*][1,4]oxazepin-11(10*H*)-one (21) (R_F 0.1), separated by fractional crystallisation from ethanol.

Compound (1) (1 g) in chloroform (25 ml) was vigorously stirred with (2) (3.0 g) in water (50 ml). Aliquots (5 ml) were withdrawn, shaken with potassium iodide–potassium thiosulphate (10 ml) and analysed quantitatively by g.l.c. using a 3% OV–17 on Gas Chrom Q column at 240 °C. 9-*Chlorodibenz*[b,f][1,4]*oxazepine* (18), m.p. 124—127 °C, was prepared from 2,6-dichloronitrobenzene [12] by the method of Wardrop [1] (Found: C, 67.95; H, 3.6; N, 6.2. $C_{13}H_8ClNO$ requires C, 68.3; H, 3.5; N, 6.1%); $\nu_{max.}$ 1 600 cm^{-1} (CH=N), δ 6.90—7.50 (7 H, complex) and 8.62 (1 H). 7,9-*Dichlorodibenz*[b,f]*oxazepine* (19), m.p. 166—168 °C, was prepared from 2,4,6-trichloronitrobenzene [13] by the method of Wardrop [1] (Found: C, 59.4; H, 2.6; N, 5.3. $C_{13}H_7Cl_2NO$ requires C, 59.1; H, 2.65; N, 5.3%); $\nu_{max.}$ 1 630 cm^{-1} (CH=N); δ 8.60 (1 H) and 6.00—6.50 (6 H, complex).

7,9-*Dichlorodibenz*[b,f][1,4]*oxazepin*-11(10H)-*one*. 7,9-Dichlorodibenz[*b,f*][1,4]oxazepine (0.1 g), sodium dichromate (0.3 g), and acetic acid (10 ml) were heated under reflux for 0.5 g, poured into water, filtered, and the precipitate recrystallised from ethanol to afford 7,9-*dichlorodibenz*[b,f][1,4]*oxazepin*-11(10H)-*one* (20) (88 mg, 80%), m.p. 212—214 °C (Found: C, 55.6; H, 2.4; N, 4.9. $C_{13}H_7Cl_2NO_2$ requires C, 55.7; H, 2.5; N, 5.0%); $\nu_{max.}$ 3 250 (NH), and 1 700 cm^{-1} (C=O); δ(DMSO) 7.30–7.80 (complex).

Reaction of (1) *with* m-*Chloroperbenzoic Acid in Aqueous Ethanol*.—Compound (1) (10 mg) in ethanol (3 ml) was diluted to 100 ml with water and treated with a solution of *m*-chloroperbenzoic acid (20 mg) in water (2 ml) for 0.25 h. The mixture was extracted with chloroform (5 ml) and quantitatively analysed by g.l.c. using a 6% Dexsil 300 GC on Gas Chrom Q column temperature-programmed from 140 (held 8 min) to 300 °C at 10° min^{-1}; the results are summarised in Table 2.

The Reaction of (2) *with Salicylaldehyde and Derived Products*.—Salicylaldehyde (10 mg) in ethanol (3 ml) was diluted to 100 ml with water. The solution was treated with (2) (25 mg) in water (2 ml) for 1 h. The reaction mixture was quenched with potassium iodide–potassium thiosulphate (1 ml) and extracted with chloroform. The extract was dried and concentrated, and the residue was examined qualitatively by g.l.c. using a 10% SE 30 column at 145 °C; the results are summarised in Table 4.

Reaction of Toluene with (2) *in Chloroform–Water*.—A mixture of toluene (1 g) in chloroform (25 ml) and (2) (3 g) in water (50 ml) was stirred vigorously for 24 h. The chloroform layer was analysed by g.l.c. using a 3% OV–17 on Gas Chrom Q column at 130 °C. Chlorotoluene (R_t 78 s), 36 μg ml^{-1}, and benzyl chloride (R_t 109 s), 705 μg ml^{-1}, were detected.

Reaction of (1) *with Trichloroisocyanuric Acid*.—A mixture of (1) (0.45 g) and trichloroisocyanuric acid (0.15 g) in chloroform (20 ml) was stored for 0.5 h, washed with potassium iodide–potassium thiosulphate (10 ml), dried, concentrated, and chromatographed over silica gel ($CHCl_3$); 9-*chlorodibenz*[b,f][1,4]*oxazepine* (18) was isolated.

Reaction of (1) *with a Chloroform Extract of* (2).—A solution of (2) (2 g) in water (50 ml) was extracted with chloroform (10 ml), the extract dried over magnesium sulphate, and (1) (30 mg) was added. The mixture was stored for 2 h, washed with potassium iodide–potassium thiosulphate (10 ml), and analysed by g.l.c. using a 3% OV–17 on Gas Chrom Q at 240 °C. The results are in Table 5.

TABLE 5

Compound	R_t/s	Concentration/ μg ml^{-1}
(1)	134	2 591
(17)	212	75
(5)	227	5
(18)	286	121
(3)	340	64
(19)	400	56

10-*Chlorodibenz*[b,f][1,4]*oxazepin*-11(10H)-*one*.—A mixture of dibenz[*b,f*][1,4]oxazepin-11(10*H*)-one (0.1 g) in chloroform (10 ml) and (2) (1 g) in water (10 ml) was vigorously stirred for 2 h, separated, dried, and concentrated to afford 10-chlorodibenz[*b,f*][1,4]oxazepin-11(10*H*)-one; $\nu_{max.}$ (liquid film) 1 680 cm^{-1} (C=O); δ 7.10—8.10 (complex); *m/e* 245 (M^+). The product in chloroform was shaken with potassium iodide–potassium thiosulphate, dried, concentrated, and recrystallised from ethanol to give the lactam (3), m.p. 214 °C.

Reaction between 10-*Chlorodibenz*[b,f][1,4]*oxazepin*-11(10H)-*one and* (1).—A mixture of (1) (100 mg) and 10-chloro-10,11-dihydrodibenz[*b,f*][1,4]oxazepin-11-one (100 mg) in chloroform (20 ml) was stored for 2 h, washed with potassium iodide–potassium thiosulphate (10 ml), dried, concentrated, and the residue separated by chromatography over silica gel to afford 9-*chlorodibenz*[b,f][1,4]*oxazepine* (18).

Reaction of 3-*Hydroxybenzaldehyde with* (2).—A solution of 3-hydroxybenzaldehyde (10 mg) in ethanol (3 ml) was diluted to 100 ml with water and (2) (30 mg) in water (2 ml) was added. The mixture was stored for 24 h and extracted with chloroform. The dried extract was analysed by g.l.c. using a 3% OV–17 on Gas Chrom Q column, temperature-programmed from 130 (held for 5 min) to 270 °C, at 15° min^{-1}. Detected were 2-chloro-5-hydroxybenzaldehyde, (R_t 636 s) and 2-chloro-3-hydroxybenzaldehyde (R_t 438 s).

The expected deformylation products *m*-chlorophenol (R_t 91 s), 2,3-dichlorophenol (R_t 215 s) and 3,4-dichlorophenol (R_t 539 s) were not detected.

Reaction of 4-*Hydroxybenzaldehyde with* (2).—A solution of 4-hydroxybenzaldehyde (10 mg) in ethanol (3 ml) was diluted to 100 ml with water and treated with (2) (30 mg) in water (2 ml) for 5 h. The mixture was extracted with chloroform and the dried extract was analysed by g.l.c. using a 3% OV–17 on Gas Chrom Q column, temperature-programmed from 130 (held for 5 min) to 270 °C at 15° min^{-1}. Detected were 2,4-dichlorophenol (R_t 206 s), *p*-chlorophenol (R_t 249 s), 2,6-dichloro-*p*-benzoquinone (R_t 388 s), and 2,4,6-trichlorophenol (R_t 461 s).

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