Reaction of 1,3-Dioxolans with Iodine Monochloride: the Scope and Mechanism of Formation of 1,3-Dioxolan-2-ylium Dichloroiodates(I)

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Treatment of a series of 2-substituted-4,4,5,5-tetramethyl-1,3-dioxolans with iodine monochloride afforded the appropriate 2-substituted-4,4,5,5-tetramethyl-1,3-dioxolan-2-ylium dichloroiodate(I) salts in excellent yields. In contrast to the stable 2-aryl-substituted salts, the 2-alkyl and unsubtituted derivatives were relatively labile. While 2-phenyl-1,3-dioxolan and 2-phenyl-1,3-dioxan afforded low yields of unstable salts, crystalline products could not be isolated from 4,5-disubstituted dioxolans. The reaction was inhibited by electron-withdrawing 4- and 5-substituents. From a study of the effects of photolysis and added iodine, the mechanism is proposed to involve a hydride ion transfer. Possible reasons for the formation of dichloroiodate(I) rather than monohalide salts, are outlined. The stability of the 2-aryl-substituted salts is discussed in terms of charge distribution in the cation and possible aryl–anion interactions.

While numerous methods for the preparation of resonance-stabilised 1,3-dioxolan-2-ylium salts have been documented,[1,2] in only a few instances have they been generated directly from simple 2-alkyl- or 2-aryl-1,3-dioxolans. Ethyl bromide and silver tetrafluoroborate,[3] trityl tetrafluoroborate[4] or hexachloroantimonate,[5] 2,4,6-trichlorophenyldiazonium tetrafluoroborate,[6] and recently bromine[7] have been used as reagents for this purpose. The first three reactions appear to involve abstraction of a hydride ion from the dioxolan, while the diazonium species is suspected to react *via* a free-radical mechanism.[8] The mechanism by which bromine reacts has not been elaborated.

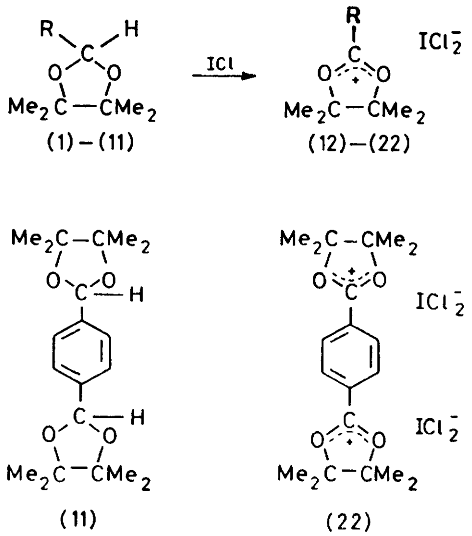
We recently reported[9] that halogens and interhalogens oxidise 2-phenyl-4,4,5,5-tetramethyl-1,3-dioxolan (4) to the appropriate 2-phenyl-4,4,5,5-tetramethyl-1,3-dioxolan-2-ylium polyhalide salt. The reaction of iodine monochloride with dioxolans was subsequently investigated in greater detail, and we now report on the scope and mechanism of this process.

RESULTS AND DISCUSSION

Scope of the Reaction of ICl *with* 1,3-*Dioxolans and Related Species*.—The effect of different ring-substituents on the reaction was determined by reacting ICl with, first, a series of 2-substituted-4,4,5,5-tetramethyl-1,3-dioxolans (Scheme 1 and Table 1). All the dioxolans listed reacted vigorously affording the dichloroiodate(I) salts (12)—(22) in excellent yields.

The salts (12)—(14) were hygroscopic and decomposed rapidly at room temperature. With the exception of (14), which also crystallised with difficulty, they were all considerably more stable at 0 °C. In contrast, the 2-aryl-substituted salts (15)—(22) were stable for several months at room temperature.

Secondly, the effect of substitution at the 4- and 5-positions of the dioxolan ring was briefly investigated (Table 2). 2-Phenyl-1,3-dioxolan (23) and the corresponding dioxan (30) afforded the unstable salts (31) and (32), respectively, in low yield. The decomposition product from (31) was 2-chloroethyl benzoate. The dioxolans (24)—(26) gave unstable oils which failed to crystallise. Hydrolysis of these oils produced hydroxy- and chloro-alkyl benzoates which indicates that the appropriate 2-phenyl-1,3-dioxolan-2-ylium cations were in fact formed, but not precipitated. Further evidence for the formation of these carbocations was obtained from the downfield shifts apparent in the ^{1}H n.m.r. spectrum of the oil derived from (25). The dioxolans (26) and (27) and dioxolone (28) were not as readily oxidised since starting material and benzaldehyde were recovered after aqueous work-up. Although relatively little starting material and benzaldehyde were recovered from the benzodioxolan (29) upon work-up, no 2-hydroxyphenyl benzoate was obtained, which suggests that the dioxolanylium cation was not formed.



Scheme 1

Inhibition of the oxidation process in the case of (27)—(29) is most probably due to the presence of electron-withdrawing groups on the 4- and 5-positions, since they would diminish the ability of the dioxolanyl oxygen atoms to stabilise the incipient positive charge at the 2-

position by conjugative interaction. This conjugative interaction is also most effective when the dioxolanylium ring is planar, since overlap between the oxygen and trigonal carbon P_z orbitals is then at a maximum.[10] Owing to the geometrical constraints of the *trans*-fused system, a planar dioxolanylium ring cannot be achieved from the dioxolan (26). Hence the relatively slow rate of oxidation of (26) is probably due to the fact that the activation energy for the oxidation process is raised since a strained, puckered dioxolanylium ring must be formed. An *X*-ray crystallographic study[11] has revealed that the dioxolanylium ring is non-planar even in the *cis*-fused 2-methyl-4,5-tetramethylene-1,3-dioxolan-2-ylium cation.

TABLE 1

Reaction of 2-substituted-4,4,5,5-tetramethyl-1,3-dioxolans with iodine monochloride

Substrate	R	Product	Isolated yield (%)
(1)	H	(12)	63
(2)	Me	(13)	85
(3)	Pr^n	(14)	98
(4)	Ph	(15)	90
(5)	C_6H_4Me-*o*	(16)	93
(6)	C_6H_4Me-*p*	(17)	97
(7)	C_6H_4OH-*p*	(18)	55
(8)	C_6H_4OMe-*p*	(19)	62
(9)	C_6H_4Cl-*p*	(20)	90
(10)	$C_6H_4NO_2$-*p*	(21)	92
(11)		(22)	75

The generally greater stability in solution of the 4- and 5-substituted cations, particularly the tetramethyl species (12)—(22), in comparison with the cation (31), is attributable to steric hindrance presented by the substituents towards attack by chloride at the C-4 and C-5 positions.

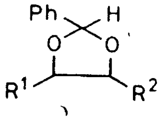
TABLE 2

Reaction of 4- and 5-substituted-2-phenyl-1,3-dioxolans and some derivatives with iodine monochloride

Substrate	Products [%]
(23)[a]	(31) [30]
(23)	2-hydroxyethyl benzoate[b] [23]
	2-chloroethyl benzoate[b] [72]
(24)	unstable oil
	(33)[b] [27]
	(34)[b] [13]
	(35)[b] [58]
	(36)[b] [2]
(25)	unstable oil
	(37)[b] [97]
(26)	unstable oil
	benzaldehyde[b] [24]
	(38)[b] [68]
(27)	(27)[b] [42]
	benzaldehyde[b] [9]
	(39)[b] [33]
	(40)[b] [13]
(28)	benzaldehyde[b] [88]
(29)	(29)[b] [9]
	benzaldehyde[b] [8]
(30)	(32) [33]

[a] Reaction time 5 min.; in all other cases 1 h. [b] Obtained after aqueous work-up. Yields from n.m.r. of crude product by integration against an added internal standard.

Mechanistic Studies.—The iodine monochloride oxidation of 1,3-dioxolans could involve either a direct hydride-ion transfer to ICl [Scheme 2, pathway (*a*)], or a free-radical process[12] [pathway (*b*)]. A comparison of the relative rates of reaction of 2-phenyl-4,4,5,5-tetramethyl-1,3-dioxolan (4) and its *p*-methoxy- and *p*-nitro-substituted derivatives [(8) and (10), respectively] with ICl revealed that the methoxy-substituent facilitated the reaction while it was inhibited by the nitro-group (Figure 1).



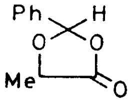
(23) $R^1 = R^2 = H$

(24) $R^1 = Me, R^2 = H$

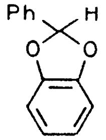
(25) $R^1 = R^2 = Me$

(26) $R^1 = R^2 = [CH_2]_4$ (*trans*)

(27) $R^1 = R^2 = CO_2Me$ (*trans*)



(28)



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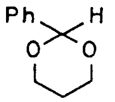

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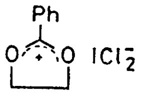
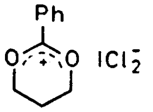
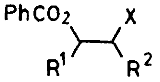


(31)



(32)



(33) $R^1 = H, R^2 = Me, X = OH$

(34) $R^1 = H, R^2 = Me, X = Cl$

(35) $R^1 = Me, R^2 = H, X = OH$

(36) $R^1 = Me, R^2 = H, X = Cl$

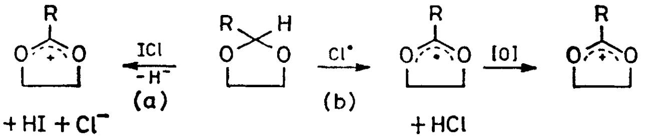
(37) $R^1 = R^2 = Me, X = OH$

(38) $R^1 = R^2 = [CH_2]_4$ (*trans*); $X = OH$

(39) $R^1 = R^2 = CO_2Me, X = OH$

(40) $R^1 = R^2 = CO_2Me, X = Cl$

It was also established that the oxidation process is even more sensitive to variations in the electron density at C-2 caused by substituents at the 4- or 5-positions. Thus the dioxolone (28) and apparently the benzodioxolan (29), both of which contain electron-withdrawing groups in conjugation with the oxygen atoms, failed to undergo oxidation under the same conditions as when dioxolans (10) and even (11) were smoothly converted. In addition, 4-chloromethyl-2-phenyl-1,3-dioxolan and



SCHEME 2

4,5-*trans*-bis(methoxycarbonyl)-2-phenyl-1,3-dioxolan (27) both reacted more slowly than 4-methyl-2-phenyl-1,3-dioxolan (24) and 4,5-dimethyl-2-phenyl-1,3-dioxolan (25), respectively. Furthermore, the oxidation is also sensitive to conformational effects as evidenced by the lower reactivity of the *trans*-fused dioxolan (26).

These results do not allow a clear distinction to be drawn between the two mechanistic pathways, since although hydrogen abstractions by chlorine atoms are generally exothermic and thus unselective,[13] the occurrence of charge separation in the transition state cannot be ruled out. However, if chlorine atoms did participate, such great sensitivity to conformational constraints and small changes in the electron density at C-2 as brought about even by non-conjugated substituents at C-4 or C-5, would not have been expected. Furthermore, products arising from hydrogen abstraction from other active sites present in several of the dioxolans, would have been expected.[12,14]

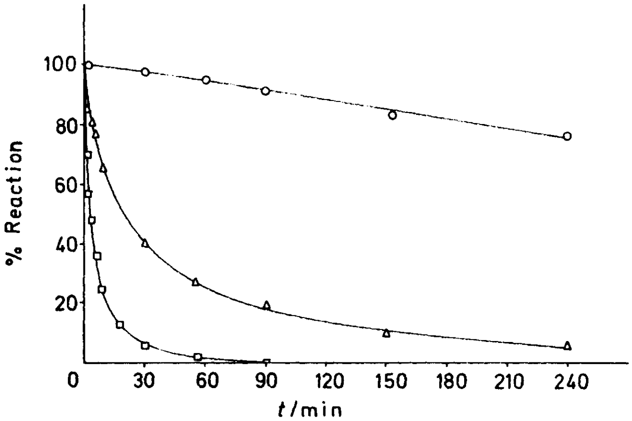


FIGURE 1 Relative rates of reaction of dioxolans with ICl; (○) 2-(*p*-nitrophenyl-4,4,5,5-tetramethyl-1,3-dioxolan (10); (△) 2-phenyl-4,4,5,5-tetramethyl-1,3-dioxolan (4); and (□) 2-(*p*-methoxyphenyl)-4,4,5,5-tetramethyl-1,3-dioxolan (8)

Photolysis of the reaction mixture of 2-phenyl-4,4,5,5-tetramethyl-1,3-dioxolan (4) and ICl decreased the rate relative to the reaction in the dark, while the rate of the dark reaction was increased by addition of iodine (Figure 2). These results support the hydride-ion transfer mechanism [pathway (*a*)] on the basis of the following rationale. Iodine monochloride may dissociate homolytically to iodine and chlorine atoms [equation (E1)]. Dissociation would be facilitated by irradiation,[12] thus effectively increasing the concentration

$$\mathrm{ICl} \rightleftharpoons \mathrm{I^{\cdot}} + \mathrm{Cl^{\cdot}} \qquad \text{(E1)}$$

$$\mathrm{ICl} \xrightarrow{h\nu} \mathrm{I^{\cdot}} + \mathrm{Cl^{\cdot}} \qquad \text{(E2)}$$

$$\mathrm{ICl} + \mathrm{I_2} \rightleftharpoons 3\mathrm{I^{\cdot}} + \mathrm{Cl^{\cdot}} \qquad \text{(E3)}$$

of chlorine atoms at the expense of undissociated ICl. Since the reaction is slowed by irradiation, undissociated ICl is clearly the dominant reactive species. Iodine is acknowledged to be an excellent radical trap,[15] and exogeneous iodine is thus likely to disturb the equilibrium by trapping chlorine atoms [equation (E3)], thereby effectively increasing the concentration of undissociated ICl relative to that in equation (E1). As the dioxolan failed to react at a perceptible rate with iodine alone under these conditions, the rate enhancement observed upon addition of iodine to the ICl reaction further strengthens the proposition that the dioxolan is oxidised by undissociated iodine monochloride, probably in a process involving a hydride-ion transfer. The hydriodic acid liberated reacts rapidly with excess of ICl, producing iodine and HCl.

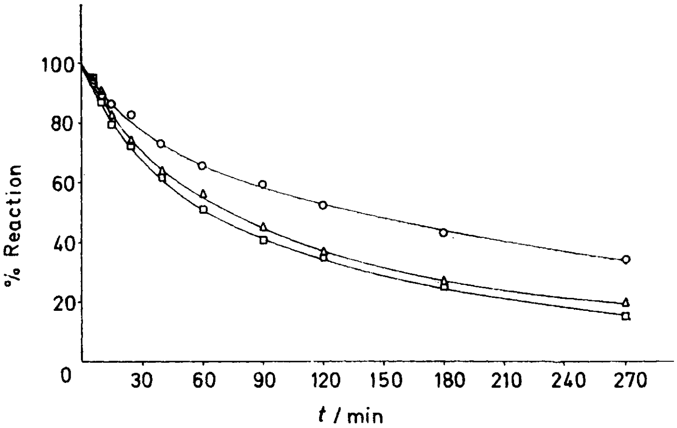
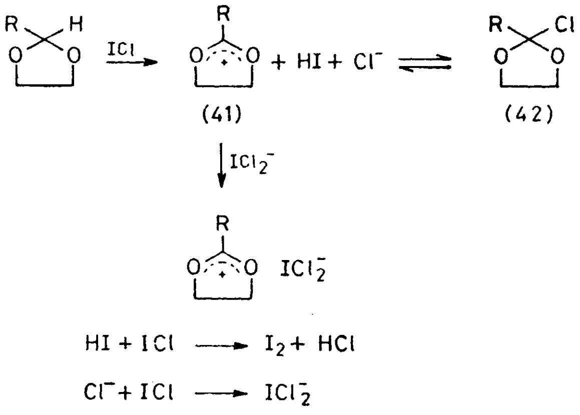


FIGURE 2 Relative rates of reaction of 2-phenyl-4,4,5,5-tetramethyl-1,3-dioxolan (4) with ICl at 0 °C; (△) in the dark; (○) under irradiation; and (□) in the dark with iodine

Owing to the stability of the resonance-stabilised 1,3-dioxolan-2-ylium cation (41) and the relatively low nucleophilicity of the chloride ion, a covalent C–Cl bond in an intermediate such as (42) would be expected to display high ionic character and low stability (Scheme 3).



SCHEME 3

While 2-chloro-1,3-dioxolans have been detected spectroscopically at low temperatures,[14a,16] 2-halogeno-1,3-dioxolans, with the exception of 2-chloro-2-phenyl-1,3-benzodioxolan,[17] are generally not isolable, and in fact the structures of several 2-halogeno-1,3-dioxolans reported previously have subsequently been revised.[18] On the other hand, any purely ionic association of the relatively small and hard [19] monohalide ion with the relatively large and soft [19] cation (41) would be weak. Since the chloride ion in the above reaction is poorly solvated (solvent $CHCl_3$ or CH_2Cl_2), it rapidly combines with unreacted ICl to form the larger (softer) dichloroiodate(I) ion, which associates more strongly with the large carboxonium ion. This is in agreement with Perst's observation [2] that oxonium and carboxonium ions form stable salts generally only with large complex anions of low polarisability and which possess weak nucleophilic properties (*e.g.* BF_4^-, $SbCl_6^-$, ClO_4^-, HSO_4^-, *etc.*). The same rationale can be applied to the reaction of 2-phenyl-4,4,5,5-tetramethyl-1,3-dioxolan with all the halogens and interhalogens described earlier.[9]

In sharp contrast, oxazolinium ions can be isolated as simple halide salts.[1] The greater stability of oxazolinium relative to dioxolanylium ions has been attributed to the higher efficiency of nitrogen, relative to oxygen, at stabilising the positive charge. Indeed, available evidence [1] indicates that the structure of an oxazolinium ion is best represented by localising the charge predominantly on the less electronegative nitrogen atom. In comparison with a dioxolanylium ion, the charge on an oxazolinium ion is thus less diffuse (harder) and a much stronger association with a smaller (harder) monohalide ion can occur.

The anomalous stability of 2-chloro-2-phenyl-1,3-benzodioxolan [17] can be ascribed to destabilisation of the 2-phenyl-1,3-benzodioxolan-2-ylium cation as a result of delocalisation of the oxygen lone pairs onto the benzene ring. Consequently the charge is localised to a greater extent on the 2-carbon, which renders the latter more electrophilic (harder) and thus able to form a relatively strong covalent bond with the small chloride ion.

The trihalide salts that we,[9] along with the one example of Plénat and his co-workers,[7] have isolated incorporate the simplest anions yet reported in isolable carboxonium salts; the smallest anions previously noted have concontained at least five atoms (*e.g.* BF_4 and ClO_4).[1,2]

Stability of Salts (15)—(22).—The enhanced stability of the 2-aryl-substituted salts (15)—(22) merits further discussion. It is debatable whether this can be attributed to conjugative interaction between the aryl and dioxolanylium π-systems. There is a considerable body of evidence which suggests that such interactions make a relatively small contribution to the stabilities of 1,3-dioxolan-2-ylium cations [1,20,21] and related benzylic cations containing one or two oxygen or nitrogen atoms as α-substituents.[22] Conversely, some evidence for significant conjugative interactions in 2-phenyl-1,3-dioxolan-2-ylium cations has also been presented.[23] However, coplanarity of the aromatic ring and the trigonal cationic centre, which is a prerequisite for conjugative interaction, is not certain in any of these cases.

The crystal structure of the salt (15) was recently determined [24] and the phenyl and dioxolanyl rings shown to be coplanar with a connecting bond length of 1.47(2) Å. While this bond length is significantly shorter than the value of 1.51 ($\pm$0.01) Å which is regarded as the best estimate [25] for a pure σ-bond between two trigonal carbon atoms, the difference represents a π-bond order of only 0.24.[25]

Further evidence that the aryl system plays a secondary role to the oxygen atoms in the conjugative stabilisation of 2-aryl-1,3-dioxolan-2-ylium cations is afforded by consideration of the effects of various substituents on the relative rates of oxidation of dioxolans as described previously. The oxidation process is much more severely inhibited when electron-withdrawing groups are located on the 4- and 5-positions, which affects the conjugative ability of the oxygen atoms, than when placed on the phenyl ring. Thus (27) was oxidised slowly and (28) not at all, while under similar conditions the *p*-nitro-substituted dioxolan (10) was smoothly oxidised in high yield to the carbocation. Even more dramatic is the stability of the dication (22) and the facility with which it is formed. Assuming sequential rather than simultaneous formation of the two carbocations in (22), the presence of the first-formed carbocation (for which a σ_p value of +0.97 can be estimated) [20] neither inhibits formation of the second cation nor markedly lowers the stability of the dication as a whole. Clearly, if significant conjugative interaction occurred between the cation and the phenyl ring, it is highly unlikely that the dication (22) would have formed so readily in an oxidation process whose rate has been shown to be highly sensitive to the effect of electron-withdrawing groups on the 4- and 5-positions. Also, an examination of models has revealed that, owing to severe steric interactions between the *o*-methyl substituent and an oxygen atom in the salt (16), the two rings are unlikely to be coplanar, thus preventing any resonance delocalisation of positive charge onto the aromatic ring. Yet the stability of this salt is not discernibly lower than that of the *para*-isomer (17). In contrast, there is evidence that buckling of the dioxolan ring, which would reduce conjugation between the oxygen atoms and the carbocation at C-2, has a marked effect on the stability of the incipient carbocation in (26).

However, the crystal structure of the salt (15) [24] does reveal that the iodine atom of the anion lies 3.713 Å from the mean plane through the phenyl ring, and is almost symmetrically located with respect to the ring, with non-bonded I · · · C distances ranging from 3.87 to 4.06 Å. It is thus possible that some stabilising interaction occurs between the orbitals of the phenyl and anion systems.

The contrasting instability of the salt (31) would seem to be due to the absence of the methyl groups and their stabilising +*I* effect on the carbocation. It is also possible either that interaction between the anion and aromatic ring such as that suggested for (15) does not occur in (31), or its lower stability could simply be due to a lower crystal-lattice energy.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus. I.r. spectra were recorded on Unicam SP1000 and Perkin Elmer 297 spectrophotometers. 60-MHz ^{1}H N.m.r. spectra were recorded on a Perkin-Elmer R12A spectrometer with $SiMe_4$ as internal standard. G.l.c. analyses were carried out on a Becker-Packard 420 chromatograph equipped with an Autolab 6300 digital integrator. Column A contained 1% Si Dow 11 with Carbowax XXX 60—70 mesh; Column B Fluorosilicone oil FS 1265 on AW-DMCS Chromosorb W 80—100 mesh (1.5 : 98.5); and Column C 1% Si Dow 11 on Supelcort 60—80. Elemental analyses were determined in the Micro-analytical Laboratories of the University of Cape Town. Mass spectra were recorded at the C.S.I.R. in Pretoria.

Syntheses.—Unless otherwise stated, all the dioxolans were synthesised by the standard procedure[26] of condensing an aldehyde with a diol, with concomitant removal of water, in the presence of toluene-*p*-sulphonic acid, and characterised by comparison with published data. Those dioxolans listed below have, with the exception of (27), (29), and the last entry, not been previously reported.

2-(o-*Methylphenyl*)-4,4,5,5-*tetramethyl*-1,3-*dioxolan* (5) was synthesised according to the standard procedure; b.p. 108—111 °C at 2 mmHg; δ(CCl_4) 1.18 (s, 6 H), 1.26 (s, 6 H), 2.34 (s, 3 H), 6.04 (s, 1 H), 6.97—7.25 (m, 3 H), and 7.43—7.70 (m, 1 H) (Found: C, 76.0; H, 9.1. $C_{14}H_{20}O_2$ requires C, 76.33; H, 9.15%).

2-(p-*Hydroxyphenyl*)-4,4,5,5-*tetramethyl*-1,3-*dioxolan* (7). A solution of ethanethiol (8.0 ml) in dry dimethylformamide (100 ml) was added to a suspension of sodium hydride (5.3 g of a 60% suspension) in dry dimethylformamide (50 ml) under nitrogen. The solution was stirred for 5 min, then a solution of 2-(*p*-methoxyphenyl)-4,4,5,5-tetramethyl-1,3-dioxolan (10.0 g) in DMF (50 ml) was added and refluxed for 4 h. After cooling, the solution was acidified (glacial acetic acid), then neutralised (sodium hydrogencarbonate) and extracted (ether). The ether extracts were dried and concentrated to a solid which crystallised from benzene–light petroleum as 2-(p-*hydroxyphenyl*)-4,4,5,5-*tetramethyl*-1,3-*dioxolan* (7) (6.2 g, 67%), m.p. 143 °C; δ(CCl_4) 1.18 (s, 6 H), 1.24 (s, 6 H), 5.79 (s, H), 6.69 (d, 2 H), 7.19 (d, 2 H), and 7.80 (s, OH) (Found: C, 70.4; H, 7.8. $C_{13}H_{18}O_3$ requires C, 70.25; H, 8.16%).

2-(p-*Chlorophenyl*)-4,4,5,5-*tetramethyl*-1,3-*dioxolan* (9) was synthesised according to the standard procedure; b.p. 146 °C at 1 mmHg; δ(CCl_4) 1.13 (s, 6 H), 1.24 (s, 6 H), 5.83 (s, 1 H), and 7.30 (s, 5 H) (Found: C, 64.8; H, 7.2. $C_{13}H_{17}ClO_2$ requires C, 64.86; H, 7.12%).

p-*Bis*(4,4,5,5-*tetramethyl*-1,3-*dioxolan*-2-*yl*)*benzene* (11) was synthesised according to the standard procedure; m.p. 120 °C (light petroleum); δ($CDCl_3$) 1.22 (s, 12 H), 1.30 (s, 12 H), 5.96 (s, 2 H), and 7.47 (s, 4 H) (Found: C, 71.95; H, 9.15. $C_{20}H_{30}O_4$ requires C, 71.82; H, 9.04%).

2-*Phenyl*-4,5-trans-*tetramethylene*-1,3-*dioxolan* (26) was synthesised according to the standard procedure; b.p. 166—167 °C at 1.5 mmHg; δ(CCl_4) 1.10—2.30 (m, 8 H), 3.05—3.40 (m, 2 H), 5.90 (s, 1 H), and 7.11—7.46 (m, 5 H) (Found: C, 76.6; H, 8.1. $C_{13}H_{16}O_2$ requires C, 76.44; H, 7.90%).

4,5-*trans*-Bis(methoxycarbonyl)-2-phenyl-1,3-dioxolan (27) was synthesised from benzaldehyde and dimethyl D-(+)-tartrate (Fluka).

5-*Methyl*-2-*phenyl*-1,3-*dioxolan*-4-*one* (28) was synthesised by acid-catalysed condensation of benzaldehyde and 2-hydroxypropanoic acid; b.p. 119—120 °C at 2.3 mmHg δ(CCl_4) 1.49 and 1.52 (two d, 3 H), 4.33 (q, 1 H), 6.19 and 6.41 (two s, 1 H), and 7.33 (s, 5 H); $\nu_{max.}$ (CCl_4) 1 810, 1 229, and 1 195 cm^{-1} (Found: C, 66.8; H, 5.6. $C_{10}H_{10}O_3$ requires C, 67.41; H, 5.66%).

2-Phenyl-1,3-benzodioxolan (29) was synthesised by the method of Capon and Page.[27]

4-*Chloromethyl*-2-*phenyl*-1,3-*dioxolan*.—Anhydrous tin(IV) chloride (5.0 ml, 0.04 mol) followed by a solution of epichlorohydrin (45 ml, 0.57 mol) in chloroform (60 ml) were added dropwise to a stirred solution of benzaldehyde (30 g, 0.28 mol) in chloroform (200 ml) whose temperature was maintained at 0—5 °C. The solution was then stirred at room temperature for 48 h. Anhydrous sodium carbonate (20 g) followed by water (50 ml) were then added. The chloroform layer was then decanted, washed, dried (Na_2SO_4), and concentrated to an oil which upon distillation afforded a mixture of *cis*- and *trans*-4-chloromethyl-2-phenyl-1,3-dioxolan (42 g, 0.21 mol), b.p. 147—151 °C at 1.5 mmHg (lit.,[28] b.p. 154—159 °C at 10 mmHg; δ(CCl_4)[29] 3.30—3.65 (m, 2 H), 3.70—4.50 (m, 2 H), 5.71 and 5.89 (two s, 1 H), and 7.30 (s, 5 H).

Reactions of 1,3-*Dioxolans with Iodine Monochloride*.—*General procedure*. The reagent (2.0 ml, 40 mmol) was added slowly to a cooled, stirred solution of the dioxolan (8 mmol) in chloroform or dichloromethane (20 ml). Hydrogen chloride and iodine were evolved as the reaction proceeded. After further stirring at room temperature, ether (80 ml) was added and the resulting precipitate filtered off and washed thoroughly with ether. In some instances the salt was purified further by dissolution in acetonitrile and re-precipitation with ether. The halide content was determined by dissolving a known weight of the salt in an aqueous ethanolic solution of sodium metabisulphite, followed by potentiometric titration with silver nitrate.

Those reactions which failed to precipitate a solid were repeated and then quenched (aqueous $Na_2S_2O_3$). Normal work-up gave oils which were analysed as described below.

4,4,5,5-Tetramethyl-1,3-dioxolan (1) (0.5 h) gave hygroscopic yellow crystals of 4,4,5,5-*tetramethyl*-1,3-*dioxolan*-2-*ylium dichloroiodate*(I) (12) (1.65 g, 5.07 mmol, 63%) which decomposed readily at room temperature, but were stable for several days at 0 °C; δ($MeNO_2$) 1.82 (s, 12 H) and 9.20 (s, 1 H) (Found: Cl, 21.2; I, 37.8. $C_7H_{13}Cl_2IO_2$ requires Cl, 21.69; I, 38.81%).

Alkaline hydrolysis of (12) gave pinacol monoformate; δ(CCl_4) 1.20 (s, 6 H), 1.52 (s, 6 H), 2.70 (s, OH), and 8.03 (s, 1 H); $\nu_{max.}$ (CCl_4) 3 605, 3 480, 2 999, 1 731 (shoulder at 1 706), 1 200, 1 165, 1 141, and 1 102 cm^{-1} (Found: C, 57.7; H, 9.6. $C_7H_{14}O_3$ requires C, 57.52; H, 9.65%).

2,4,4,5,5-Pentamethyl-1,3-dioxolan (2) (0.5 h) gave yellow crystals of 2,4,4,5,5-*pentamethyl*-1,3-*dioxolan*-2-*ylium dichloroiodate*(I) (13) (2.31 g, 6.77 mmol, 85%), m.p. 73—74 °C which decomposed slowly at room temperature (Found: Cl, 20.7; I, 36.6. $C_8H_5Cl_2IO_2$ requires Cl, 21.43; I, 38.35%).

Alkaline hydrolysis gave pinacol monoacetate; δ(CCl_4) 1.14 (s, 6 H), 1.44 (s, 6 H), 1.96 (s, 3 H), and 3.20 (s, OH); $\nu_{max.}$ (CCl_4) 3 620, 3 460, 1 736, 1 710, 1 257, and 1 162 cm^{-1}.

2-n-Propyl-4,4,5,5-tetramethyl-1,3-dioxolan (3) (0.5 h) gave extremely hygroscopic yellow crystals of 2-*n*-*propyl*-4,4,5,5-*tetramethyl*-1,3-*dioxolan*-2-*ylium dichloroiodate*(I) (14) (2.90 g, 7.97 mmol, 98%), m.p. 62—62.5 °C, which decomposed on standing.

Alkaline hydrolysis gave *pinacol monobutyrate*; δ(CCl$_4$) 0.95 (t, 3 H), 1.13 (s, 6 H), 1.44 (s, 6 H), 1.55 (m, 2 H), 2.20 (m, 2 H), and 3.10 (s, OH); $\nu_{\text{max.}}$ (CCl$_4$) 3 620, 3 460, 1 737, 1 709, and 1 147 cm^{-1} (Found: C, 63.7; H, 10.4. C$_{10}$H$_{20}$O$_3$ requires C, 63.80, H, 10.71%).

2-Phenyl-4,4,5,5-tetramethyl-1,3-dioxolan (4) (1 h) gave bright yellow crystals of 2-*phenyl*-4,4,5,5-*tetramethyl*-1,3-*dioxolan*-2-*ylium dichloroiodate*(I) (15) (2.90 g, 7.19 mmol, 90%), m.p. 118—120 °C; δ(MeNO$_2$), 1.93 (s, 12 H) and 7.75—8.50 (m, 5 H); $\nu_{\text{max.}}$ (CH$_2$Cl$_2$) 1 600m, 1 520s, 1 463s, and 1 122s cm^{-1} (Found: C, 38.7; H, 4.3; Cl, 18.4; I, 32.3. C$_{13}$H$_{17}$Cl$_2$IO$_2$ requires C, 38.74; H, 4.25; Cl, 17.59; I, 31.48%).

2-(*o*-Methylphenyl)-4,4,5,5-tetramethyl-1,3-dioxolan (5) (1 h) gave bright yellow crystals of 2-(o-*methylphenyl*)-4,4,5,5-*tetramethyl*-1,3-*dioxolan*-2-*ylium dichloroiodate*(I) (16) (3.09 g, 7.42 mmol, 93%), m.p. sublimes at 135—150 °C; δ(CDCl$_3$–CH$_2$Cl$_2$) 1.89 (s, 12 H), 2.75 (s, 3 H) and 7.50—8.30 (m, 4 H) (Found: C, 40.15; H, 4.7. C$_{14}$H$_{19}$Cl$_2$IO$_2$ requires C, 40.31; H, 4.59%).

2-(*p*-Methylphenyl-4,4,5,5-tetramethyl-1,3-dioxolan (6) (1 h) gave a light brown precipitate of 2-(p-*methylphenyl*)-4,4,5,5-*tetramethyl*-1,3-*dioxolan*-2-*ylium dichloroiodate*(I) (17) (3.24 g, 7.78 mmol, 97%) which turned pale yellow upon re-precipitation from dichloromethane with diethyl ether, m.p. 116—117.5 °C (partial melt, re-solidification), 140—152 °C; δ(CDCl$_3$–CH$_2$Cl$_2$), 1.89 (s, 12 H), 2.58 (s, 3 H), 7.58 (d, 2 H), and 8.21 (d, 2 H) (Found: C, 39.5; H, 4.6. C$_{14}$H$_{19}$Cl$_2$IO$_2$ requires C, 40.31; H, 4.59%).

2-(*p*-Hydroxyphenyl)-4,4,5,5-tetramethyl-1,3-dioxolan (7) (0.5 h) gave a pale yellow precipitate of 2-(p-*hydroxyphenyl*)-4,4,5,5-*tetramethyl*-1,3-*dioxolan*-2-*ylium dichloroiodate*(I) (18) (1.85 g, 4.42 mmol, 55%), m.p. 118—119 °C (Found: C, 37.3; H, 4.1. C$_{13}$H$_{17}$Cl$_2$IO$_3$ requires C, 37.23, H, 4.09%).

2-(*p*-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3-dioxolan (8) (1 h) gave a yellow precipitate of 2-(p-*methoxyphenyl*-4,4,5,5-*tetramethyl*-1,3-*dioxolan*-2-*ylium dichloroiodate*(I) (19) (2.13 g, 4.92 mmol, 62%), m.p. 119—120 °C (Found: C, 38.6; H, 4.4. C$_{14}$H$_{19}$Cl$_2$IO$_3$ requires C, 38.82; H, 4.42%).

2-(*p*-Chlorophenyl)-4,4,5,5-tetramethyl-1,3-dioxolan (9) (1 h) gave a pale yellow precipitate of 2-(p-*chlorophenyl*)-4,4,5,5-*tetramethyl*-1,3-*dioxolan*-2-*ylium dichloroiodate*(I) (20) (3.14 g, 7.17 mmol, 90%), m.p. sublimed from 170 °C (Found: C, 35.5; H, 3.7. C$_{13}$H$_{16}$Cl$_3$IO$_2$ requires C, 35.68; H, 3.69%).

2-(p-Nitrophenyl)-4,4,5,5-tetramethyl-1,3-dioxolan (10) (1 h) gave a light brown precipitate of 2-(p-*nitrophenyl*)-4,4,5,5-*tetramethyl*-1,3-*dioxolan*-2-*ylium dichloroiodate*(I) (21) (3.27 g, 7.29 mmol, 92%). Recrystallisation (MeCN) gave yellow crystals, m.p. sublimed at 181—182 °C (Found: C, 34.8; H, 3.5; N, 2.8. C$_{13}$H$_{16}$Cl$_2$INO$_4$ requires C, 34.85; H, 3.60; N, 3.13%).

p-Bis(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)benzene (11) (1.34 g, 4.00 mmol) was treated with iodine monochloride (2.0 ml, 40 mmol) for 1 h. The resultant yellow solid, p-*bis*-(4,4,5,5-*tetramethyl*-1,3-*dioxolan*-2-*ylium*-2-*yl*)*benzene bis*[*dichloroiodate*(I)] (22), was re-precipitated from nitromethane with diethyl ether (2.24 g, 3.08 mmol, 75%), m.p. 123—127 °C (Found: C, 33.35; H, 4.0; Cl, 19.2; I, 35.0. C$_{20}$H$_{28}$Cl$_4$I$_2$O$_4$ requires C, 32.99; H, 3.88; Cl, 19.48; I, 34.86%).

2-Phenyl-1,3-dioxolan (23) (5 min) gave hygroscopic yellow crystals of 2-*phenyl*-1,3-*dioxolan*-2-*ylium dichloroiodate*(I) (31) (0.82 g, 2.36 mmol, 30%) which readily decomposed, both in the solid phase and in solution, to 2-chloroethyl benzoate (Found: Cl, 19.9; I, 36.7%. C$_9$H$_9$Cl$_2$IO$_2$ requires Cl, 20.43; I, 36.57%). Hydrolysis afforded pure 2-hydroxyethyl benzoate (identical with an authentic specimen).

The reaction was repeated and after 1 h no precipitate was obtained. Work-up (aqueous Na$_2$S$_2$O$_3$) gave an oil which was shown, by comparison with authentic specimens (t.l.c., n.m.r., i.r.), to consist of the mixture of benzoates reported in Table 2.

4-Methyl-2-phenyl-1,3-dioxolan (24) (1 h) gave an unstable oil which failed to solidify. The reaction was repeated and aqueous Na$_2$S$_2$O$_3$ work-up gave an oil which was shown (t.l.c., n.m.r., i.r.) to consist of the mixture of benzoates[30] reported in Table 2.

4,5-Dimethyl-2-phenyl-1,3-dioxolan (25) (1 h) gave an unstable oil which failed to solidify; δ(CDCl$_3$) 1.65—2.20 (m, 6 H), 5.60 and 6.10 (two m, 2 H), and 7.50—8.50 (m, 5 H) (all signals poorly resolved). The reaction was repeated and aqueous Na$_2$S$_2$O$_3$ work-up gave 2-(3-hydroxybutyl) benzoate (37) (1.51 g, 7.8 mmol, 97%) identical with an authentic specimen.

2-Phenyl-4,5-*trans*-tetramethylene-1,3-dioxolan (26) (1 h) gave an unstable oil which failed to solidify. The reaction was repeated on a one-third scale, and aqueous Na$_2$S$_2$O$_3$ work-up gave an oil which was shown (n.m.r.) to contain the products reported in Table 2. The mixture was chromatographed (preparative t.l.c.) to give *trans*-cyclohexane-1,2-diol monobenzoate (38) (0.27 g), m.p. 90—92 °C (light petroleum–chloroform) (lit.,[31] m.p. 92—93 °C); $\nu_{\text{max.}}$ (CHCl$_3$) 3 500, 1 720, and 1 281 cm^{-1}; δ(CDCl$_3$) 0.70—2.30 (m, 8 H), 3.10 (s, OH), 3.65 (m, 1 H), 4.78 (m, 1 H), 7.18—7.60 (m, 3 H), and 7.90—8.15 (m, 2 H).

4,5-*trans*-Bis(methoxycarbonyl)-2-phenyl-1,3-dioxolan (27) in a one-third scale reaction (1 h) failed to give a precipitate upon addition of ether. The reaction was repeated and aqueous Na$_2$S$_2$O$_3$ work-up gave an oil (0.81 g) which was shown (n.m.r., t.l.c.) to contain the products reported in Table 2. The mixture was chromatographed (preparative t.l.c.) to give starting material and benzaldehyde, and also dimethyl D-(+)-tartrate monobenzoate (39), m.p. 77—79 °C (benzene–light petroleum) (lit.,[32] m.p.78 °C); δ(CCl$_4$) 3.34 (d, *J* 7.7 Hz, OH), 3.74 (s, 3 H), 3.79 (s, 3 H), 4.75 (dd, *J* 7.7 and 2.7 Hz, 1 H), 5.57 (d, *J* 2.7 Hz, 1 H), 7.30—7.60 (m, 3 H), and 7.90—8.15 (m, 2 H); $\nu_{\text{max.}}$ (CCl$_4$) 3 550 (sharp) 1 779, 1 753 (shoulder at 1 740), and 1 260 cm^{-1}: and [2-*chloro*-1,2-*bis*(*methoxycarbonyl*)]*ethyl benzoate* (40), b.p. 160 °C (bath temperature) at 0.3 mmHg; δ(CCl$_4$) 3.77 (s, 3 H), 3.81 (s, 3 H), 4.87 (d, *J* 4.3 Hz, 1 H), 5.75 (d, *J* 4.3 Hz, 1 H), 7.20—7.63 (m, 3 H), and 7.88—8.14 (m, 2 H); $\nu_{\text{max.}}$ (CCl$_4$) 1 780, 1 742, and 1 253 cm^{-1} (Found: C, 52.15; H, 4.35%; M^+, 300, 302. C$_{13}$H$_{13}$ClO$_6$ requires C, 51.93; H, 4.36%; M, 300.7).

5-Methyl-2-phenyl-1,3-dioxolan-4-one (28) (1 h) failed to evolve HCl. Aqueous Na$_2$S$_2$O$_3$ work-up gave only benzaldehyde (0.72 g, 7.1 mmol, 88%).

2-Phenyl-1,3-benzodioxolan (29) (1 h) failed to precipitate any solid or oil. Aqueous Na$_2$S$_2$O$_3$ work-up afforded a dark oil (2.2 g) containing starting material and benzaldehyde, but no benzoate esters (n.m.r., i.r.).

2-Phenyl-1,3-dioxan (30) (0.67 g, 4.09 mmol) with ICl (1.0 ml) for 5 min gave unstable and hygroscopic yellow crystals of 2-*phenyl*-1,3-*dioxan*-2-*ylium dichloroiodate*(I) (32) (0.48 g, 1.33 mmol, 33%) (Found: Cl, 19.0; I, 36.9. C$_{10}$H$_{11}$Cl$_2$IO$_2$ requires Cl, 19.64; I, 35.15%). Hydrolysis afforded 3-hydroxypropyl benzoate (identical with an authentic specimen).

Rate Studies.—(a) *Reaction of* 2-*phenyl*-4,4,5,5-*tetramethyl*-1,3-*dioxolan* (4) *and its* p-*methoxy*- (8) *and* p-*nitro*- (10) *derivatives with iodine monochloride*. A solution of the dioxolan (1.00 mmol) and iodine monochloride (5.00 mmol) in chloroform (100 ml) was stirred in the dark at 0 °C (±0.1 °C). Aliquots (2.0 ml) were withdrawn at intervals and the reaction quenched by addition to a 20% aqueous sodium thiosulphate solution (2.0 ml) containing 10% sodium carbonate. The chloroform layer was separated, dried (sodium carbonate), and analysed (g.l.c., columns A, B, and C, respectively). The results are represented in Figure 1.

(b) *Reaction of* 4-*methyl- and* 4-*chloromethyl*-2-*phenyl*-1,3-*dioxolan with iodine monochloride*. The procedure followed was identical with that described in (a), except that 3.74 mmol of dioxolan and 18.5 mmol of iodine monochloride was used, and the reaction temperature was 25.0 °C (±0.1 °C). G.l.c. analyses were carried out on column A.

After 2 min, 4-methyl-2-phenyl-1,3-dioxolan had reacted completely. The rate of disappearance of 4-chloromethyl-2-phenyl-1,3-dioxolan was as follows [min (mmol)]: 2 (0.29), 5 (0.12), 10 (0.02), and 15 (0.0).

(c) *Reaction of* 4,5-*trans-bis*(*methoxycarbonyl*)-2-*phenyl*-1,3-*dioxolan*(27) *and* 4,5-*dimethyl*-(*mixture of* cis *and* trans)-2-*phenyl*-1,3-*dioxolan* (25) *with iodine monochloride*. A solution of the dioxolan (1.00 mmol) and iodine monochloride (4.00 mmol) in dichloromethane (20 ml) was stirred at 0 °C for 10 min. Work-up in the usual manner gave an oil which was analysed by n.m.r. spectroscopy (trichloroethylene as internal standard). 4,5-trans-*Bis*(*methoxycarbonyl*)-2-*phenyl*-1,3-*dioxolan* afforded unreacted dioxolan (0.61 mmol) and benzaldehyde (0.33 mmol). The isomeric mixture of 4,5-dimethyl-2-phenyl-1,3-dioxolans gave unreacted dioxolan (0.09 mmol), benzaldehyde (0.13 mmol), and 2-n-(3-hydroxy)butyl benzoate (37) (0.79 mmol).

(d) *Reaction of* 2-*phenyl*-4,4,5,5-*tetramethyl*-1,3-*dioxolan with iodine monochloride at* 0 °C *in the dark, under irradiation* (1 000-W *tungsten lamp*), *and in the dark in the presence of iodine* (25 *mmol*). The procedure followed was identical with that described in (a), except that the volume of solvent used was 150 ml. G.l.c. analyses were carried out on column C at 200 °C. The results are represented in Figure 2. In a blank experiment the dioxolan was treated with iodine (12.76 g; 50.2 mmol). G.l.c. analysis revealed that after 6.5 h no reaction had occurred.

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REFERENCES

[1] C. U. Pittman, jun., S. P. McManus, and J. W. Larsen, *Chem. Rev.*, 1972, **72**, 357.

[2] H. Perst, ' Oxonium Ions in Organic Chemistry,' Academic Press, New York, 1971.

[3] H. Meerwein, V. Hederich, and K. Wunderlich, *Arch. Pharm.*, 1958, **291**, 541.

[4] H. Meerwein, V. Hederich, H. Morschel, and K. Wunderlich, *Annalen*, 1960, **635**, 1; C. B. Anderson, E. C. Friedrich, and S. Winstein *Tetrahedron Letters*, 1963, 2037.

[5] Z. Jedlinski, J. Lukaszczyk, J. Dudek, and M. Gibas, *Macromolecules*, 1976, **9**, 622.

[6] H. Meerwein, H. Allendörfer, P. Beekmann, F. Kunert, H. Morschel, F. Pawellek, and K. Wunderlich, *Angew. Chem.*, 1958, **70**, 211.

[7] A. Bazbouz, J. Coste, H. Christol, and F. Plénat, *Tetrahedron Letters*, 1979, 11.

[8] R. Werner and C. Rüchardt, *Tetrahedron Letters*, 1969, 2407.

[9] A. Goosen and C. W. McCleland, *J.C.S. Chem. Comm.*, 1979, 751.

[10] H. Paulsen and R. Dammeyer, *Chem. Ber.*, 1973, **106**, 2324.

[11] H. Paulsen and R. Dammeyer, *Chem. Ber.*, 1976, **109**, 605.

[12] C. C. Kelly, W. H. S. Yu, and M. H. J. Wijnen, *Canad. J. Chem.*, 1970, **48**, 603.

[13] D. C. Nonhebel, J. M. Tedder, and J. C. Walton, ' Radicals,' Cambridge University Press, Cambridge, 1979, p. 69.

[14] (*a*) D. R. Maudling and B. G. Roberts, *J. Org. Chem.*, 1972, **37**, 1458; (*b*) J. Jonas, T. P. Forrest, M. Kratochvil, and H. Gross, *ibid.*, 1968, **33**, 2126.

[15] T. E. Stevens and W. E. Emmons, *J. Amer. Chem. Soc.*, 1958, **80**, 338; M. Ahktar, D. H. R. Barton, and P. G. Sammes, *ibid.*, 1965, **87**, 4601; R. D. Rieke and N. A. Moore, *J. Org. Chem.*, 1972, **37**, 413.

[16] M. S. Newman and C. H. Chen, *J. Org. Chem.*, 1973, **38**, 1173; H. Gross, J. Freiburg, and B. Costisella, *Chem. Ber.*, 1968, **101**, 1250.

[17] H. Gross and J. Rusche, *Chem. Ber.*, 1966, **99**, 2625.

[18] K. Heyns, W.-P. Trautwein, F. Garrido Espinosa, and H. Paulsen, *Chem. Ber.*, 1966, **99**, 1183.

[19] R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533; *J. Chem. Educ.*, 1968, **45**, 581, 643.

[20] H. Hart and D. A. Tomalia, *Tetrahedron Letters*, 1966, 3389.

[21] K. B. Gash and G. U. Yuen, *J. Org. Chem.*, 1969, **34**, 720.

[22] J. W. Larsen, S. Ewing, and M. Wynn, *Tetrahedron Letters*, 1970, 539; G. A. Olah, P. W. Westerman, and D. A. Forsyth, *J. Amer. Chem. Soc.*, 1975, **97**, 3419; B. Ancian, F. Membrey, and J. P. Doucet, *J. Org. Chem.*, 1978, **43**, 1509.

[23] Y. Chiang, A. J. Kresge, P. Salomaa, and C. I. Young, *J. Amer. Chem. Soc.*, 1974, **96**, 4494; O. Bouab, G. Lamaty, C. Moreau, O. Pomares, P. Deslongchamps, and L. Ruest, *Canad. J. Chem.*, 1980, **58**, 567.

[24] M. R. Caira and J. F. de Wet, submitted for publication in *Acta Cryst.*, (Part B)

[25] C. A. Coulson, in 'Physical Chemistry, an Advanced Treatise,' vol. 5, eds. H. Eyring, D. Henderson, and W. Jost, Academic Press, New York, 1970, p. 400.

[26] E. Willy, G. Binsch, and E. L. Eliel, *J. Amer. Chem. Soc.*, 1970, **92**, 5394.

[27] B. Capon and M. I. Page, *J.C.S. Perkin II*, 1972, 522.

[28] G. K. Chizh, V. M. Vishnevetskii, N. K. Moshchinskaya, L. F. Konovalova, and V. G. Ivanov, *J. Org. Chem. U.S.S.R.*, 1972, **8**, 745.

[29] R. Aneja and A. P. Davies, *J.C.S. Perkin I*, 1974, 141.

[30] Y. Kamiya and S. Takemura, *Chem. Pharm. Bull.*, 1974, **22**, 201; T. G. Back, D. H. R. Barton, and B. L. Rao, *J.C.S. Perkin I*, 1977, 1715.

[31] Heilbron, ' Dictionary of Organic Compounds,' 4th edn., Eyre and Spottiswoode Ltd., London, 1965.

[32] Beilstein, ' Handbuch der Organischen Chemie,' Teil 9, Band II, p. 149.