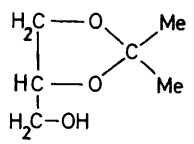
Nucleophilic Substitution in Glycerol Derivatives. Part VI.[1] Halogenodeoxygenation of 2-Phenyl-1,3-dioxan-5-ol to give 1,3-Dioxans and 1,3-Dioxolans [2]

By **Rajindra Aneja** * and **Alan P. Davies**, Lipid Chemistry Group, Unilever Research Laboratory, Colworth/Welwyn, The Frythe, Welwyn, Herts.

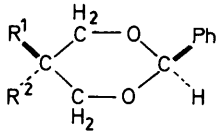
The reaction of *cis*-2-phenyl-1,3-dioxan-5-yl toluene-*p*-sulphonate with lithium bromide in boiling acetonitrile gives *trans*-5-bromo-2-phenyl-1,3-dioxan as the brominated product. However, the reaction between *cis*-2-phenyl-1,3-dioxan-5-ol and triphenylphosphine–carbon tetrabromide yields three products, *cis*-4-bromomethyl-2-phenyl-1,3-dioxolan, its *trans*-diastereoisomer and *trans*-5-bromo-2-phenyl-1,3-dioxan, in the proportions 45:48:7, respectively; the corresponding reaction with carbon tetrachloride gives the chloro-analogues of the three products. These rearrangements under essentially neutral conditions suggest that greater caution should be exercised in the use of acetal derivatives of glycerol as intermediates in the synthesis of pure glycerides.

BENZYLIDENEGLYCEROL, isopropylideneglycerol, and other acetal derivatives of glycerol are used widely as intermediates in syntheses, especially of glycerides.[3] These compounds are highly susceptible to molecular rearrangements under acidic conditions, but are generally stable and immune from such rearrangements under neutral and basic conditions.[4] We report some isomerisations of benzylideneglycerol derivatives caused by reagents which are believed to operate under mild, essentially neutral reaction conditions. These rearrangements were observed during a wider study of the behaviour of glycerol derivatives towards nucleophilic reagents.[1,2,5,6] Results for nucleophilic substitution by carboxylate [5] and halide ions [6] acting on diglyceride sulphonates were described recently. We have now compared the reactions between 1,3-benzylideneglycerol (I) (2-phenyl-1,3-dioxan-5-ol) and triphenylphosphine–carbon tetrahalide reagents with the reactions of representative sulphonate ester derivatives of (I) with halide ions as nucleophiles. Molecular rearrangements were observed in the former reactions.† Formally, they are ring contractions of 1,3-dioxans to 1,3-dioxolans, and are reminiscent of the transformations of pyranose to furanose rings in carbohydrate chemistry.[8]

Substrates and Nucleophiles.—2-Phenyl-1,3-dioxan-5-ol is normally prepared by the condensation of glycerol and benzaldehyde. Mixtures of 1,3-dioxan and 1,3-dioxolan derivatives are formed, but on equilibration and simultaneous crystallisation in the presence of mineral acid, *cis*-2-phenyl-1,3-dioxan-5-ol (I) can be obtained as the major product.[9] In contrast, acid-catalysed reaction of glycerol with acetone gives 4-hydroxymethyl-2,2-dimethyl-1,3-dioxolan (II) as the major product. Consequently, it is easier and more relevant to study the dioxolan series as the 2,2-dimethyl derivatives, and the dioxan series as the 2-phenyl derivatives. Nucleophilic substitution reactions have been described for several derivatives of 4-hydroxymethyl-2,2-dimethyl-1,3-dioxolan,[10] but relatively little has been published about 1,3-dioxans. We, therefore, focused attention on *cis*-2-phenyl-1,3-dioxan-5-ol (I). As in our studies with the glycerol ester derivatives,[1,5,6] sulphonate ester was chosen as the leaving group and chloride and bromide ions were used as the nucleophiles. In comparative experiments the reactions of (I) with



(II)



(I) R^1 = OH, R^2 = H
(III) R^1 = *p*-$MeC_6H_4 \cdot SO_3$, R^2 = H
(IV) R^1 = $MeSO_3$, R^2 = H
(V) R^1 = H, R^2 = OBz
(VI) R^1 = H, R^2 = Br

triphenylphosphine and carbon tetrachloride or carbon tetrabromide were also investigated. Reactions of these reagents [11-13] with alcohols normally give a result identical with the aforementioned two-step process through the sulphonate derivatives.

† In a concurrent independent study, Borremans and Anteunis [7] have made almost identical observations.

[1] Part V, R. Aneja and A. P. Davies, *Chem. Phys. Lipids*, 1973, **11**, in the press.
[2] Preliminary account, R. Aneja and A. P. Davies, *J.C.S. Chem. Comm.*, 1972, 722.
[3] See, *e.g.*, T. Malkin and T. H. Bevan, *Progr. Chem. Fats and other Lipids*, 1957, **4**, 63.
[4] See B. Seradarevich, *J. Amer. Oil. Chemists' Soc.*, 1967, **44**, 381.
[5] R. Aneja and A. P. Davies, *Tetrahedron Letters*, 1972, 4497; R. Aneja, A. P. Davies, J. A. Knaggs, and C. A. Rose, to be published.
[6] R. Aneja, A. P. Davies, and J. A. Knaggs, *J.C.S. Chem. Comm.*, 1973, 110; R. Aneja, J. S. Chadha, and J. A. Knaggs, *Chem. Phys. Lipids*, 1973, **11**, 89; see also R. Aneja and J. S. Chadha, *Biochim. Biophys. Acta*, 1971, **239**, 84.
[7] F. Borremans and N. Anteunis, *Bull. Soc. chim. belges*, 1971, **80**, 595.
[8] See *e.g.*, C. L. Stevens, R. P. Glinski, K. G. Taylor, P. Blumbergs, and F. Sirokman, *J. Amer. Chem. Soc.*, 1966, **88**, 2073; N. K. Kochetkov, A. I. Usov, and K. S. Adamyants, *Tetrahedron*, 1971, **27**, 549; S. Hanessian, *Chem. Comm.*, 1966, 796.
[9] P. E. Verkade and J. D. van Roon, *Rec. Trav. chim.*, 1942, **61**, 831; see A. J. Showler and P. A. Darley, *Chem. Rev.*, 1967, **67**, 427.
[10] (*a*) E. Baer and H. O. L. Fischer, *J. Amer. Chem. Soc.*, 1948, **70**, 609; (*b*) J. B. Lee and T. J. Nolan, *Canad. J. Chem.*, 1966, **44**, 1331.
[11] A. J. Burn and J. I. G. Cadogan, *J. Chem. Soc.*, 1963, 5788.
[12] J. B. Lee and I. M. Downie, *Tetrahedron*, 1967, **23**, 359; I. M. Downie, J. B. Holmes, and J. B. Lee, *Chem. and Ind.*, 1966, 900.
[13] R. G. Weiss and E. I. Snyder, *J. Org. Chem.*, 1970, **35**, 1627, and references therein.

cis-2-Phenyl-1,3-dioxan-5-yl toluene-*p*-sulphonate [14] (III) was prepared by the reaction of (I) with toluene-*p*-sulphonyl chloride and pyridine. The methanesulphonate (IV) was prepared in a similar way.[15] Both have a chair conformation with an equatorial phenyl and an axial sulphonate group; the 220 MHz ^{1}H n.m.r. spectrum of each shows the C-5 proton absorption as a triplet with a small (1·5—1·7 Hz) coupling constant [16] similar to that shown by the C-5 proton in (I) and such a conformation for (I) has been rigorously established by i.r. and dipole moment data.[17]

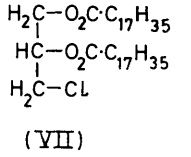
Reaction of Halide Ions with cis-2-*Phenyl*-1,3-*dioxan*-5-*yl Sulphonates*.—The reaction of the toluene-*p*-sulphonate (III) with lithium chloride in boiling acetonitrile under dry conditions produced no change, even after 50 h. Reactions of the methanesulphonate (IV) with lithium chloride or bromide in acetonitrile or in benzene under reflux results in a rapid release of benzaldehyde. In retrospect, this must be ascribed to a trace of moisture in the reaction mixture, present in spite of precautions to ensure anhydrous conditions. A brominated product was formed in low yield (<8%) in the initial runs of the reaction of (III) with lithium bromide in boiling acetonitrile, but under absolutely anhydrous conditions, a 46% yield of a brominated product, m.p. 83—86°, was obtained. Attempts to resolve and fractionate it further by g.l.c. were unsuccessful and the product was therefore accepted as a single compound.

It has been reported [15] that the reaction of 2-phenyl-1,3-dioxan-5-yl methanesulphonate (IV) with benzoate ions simply causes substitution with inversion of configuration, to give the *trans*-benzoate (V). By analogy, the reaction of (III) with lithium bromide should lead to the *trans*-bromo-derivative (VI). Our product, $C_{10}H_{11}BrO_2$, showed mass spectral peaks at *m/e* 243 and 240·9856 corresponding to the $[M - H]^+$ isotopic ions for $C_{10}H_{11}BrO_2$, and at *m/e* 167 and 165 for $[M - C_6H_5]^+$. In the n.m.r. spectrum, the relatively large chemical shift difference between the equatorial and the axial protons at C-4 and C-6 (*ca.* 1 p.p.m.) and the splitting of the C-5 proton signal (J 10·5 and 4·5 Hz) are significantly different from the corresponding values in the *cis*-compounds (I), (III), and (IV), but are comparable to the values for *trans*-2-phenyl-1,3-dioxan-5-yl benzoate [15] (V) and the corresponding palmitate,[4] and confirm the *trans* structure for (VI).* Interestingly, the reaction of lithium bromide in boiling acetone for 24 h with *cis*-2-methyl-1,3-dioxan-5-yl toluene-*p*-sulphonate has been reported [7] to yield a mixture of *cis*- and *trans*-5-bromo-2-methyl-1,3-dioxans.

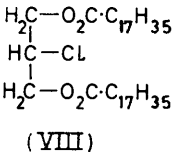
Action of Triphenylphosphine–Carbon Tetrahalide Reagent on the Alcohol (I).—*cis*-2-Phenyl-1,3-dioxan-5-ol (I), treated with carbon tetrachloride and triphenylphosphine in refluxing carbon tetrachloride gave a product in 40% yield. Similarly, with carbon tetrabromide in refluxing benzene, a product was isolated in 50% yield.

The reaction of an alcohol with carbon tetrachloride and triphenylphosphine [11] is a convenient general method for the conversion of alcohols into alkyl chlorides; [12,13] alkyl bromides are formed when carbon tetrabromide is used. The reaction occurs rapidly under mild, essentially neutral conditions, and results in inversion of configuration at the reacting centre; chloroform and triphenylphosphine oxide are by-products. Accordingly, the reaction of (I) with *e.g.* carbon tetrachloride may be expected to yield the *trans*-form of (X).

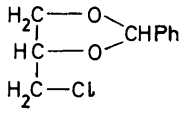
Elemental analysis of the product from the carbon tetrachloride reaction indicated that it was a monochlorodeoxy-derivative ($C_{10}H_{11}ClO_2$). Hydrogenolytic debenzylation followed by stearoylation gave a mixture of 1,2-distearoyl-3-chlorodeoxy-*rac*-glycerol (VII) (*ca.* 93 parts) and 1,3-distearoyl-2-chlorodeoxyglycerol (VIII) (*ca.* 7 parts),[19] showing that the product was a mixture of 2-phenyl-4-chloromethyl-1,3-dioxolan (IX) and 2-phenyl-5-chloro-1,3-dioxan (X) in the proportions 93 : 7.



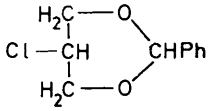
(VII)



(VIII)



(IX)



(X)

G.l.c. of the product from the carbon tetrabromide reaction resolved it into one minor and two major components. The minor component (*ca.* 7% of the total product) was identical in g.l.c. behaviour with the product (VI) from the reaction of the toluene-*p*-sulphonate (III) and lithium bromide. Coupled g.l.c.-mass spectrometry showed that all three components had peaks at *m/e* 241 and 243 corresponding to the two isotopic ions for $[M - H]$, at *m/e* 165 and 167 corresponding to $[M - C_6H_5]^+$, and at *m/e* 105 for $C_6H_5C{\equiv}O^+$. The mass spectra of the two major components were identical and very similar to that of the minor component. The spectrum of the minor component was identical with that of the product (VI) from the reaction of the toluene-*p*-sulphonate (III) and lithium bromide. Hence, as in the chlorodeoxy-series, the dioxolans

* The observed coupling constants agree with the values for $J_{4ax,5ax}$ and $J_{4eq,5ax}$ obtainable from the relevant torsion angles in the chair conformation of *trans*- (VI), according to ref. 18.

[14] L. W. Hessel, O. E. van Lohuiyzen, and P. E. Verkade, *Rec. Trav. chim.*, 1954, **73**, 842.

[15] N. Baggett, N. A. Bukhari, A. B. Foster, J. Lehmann, and J. M. Webber, *J. Chem. Soc.*, 1963, 4157.

[16] Compare and contrast refs. 4 and 15.

[17] N. Baggett, J. S. Brimacombe, A. B. Foster, M. Stacey, and D. H. Whiffen, *J. Chem. Soc.*, 1960, 2574.

[18] M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11.

[19] R. Aneja, A. P. Davies, and J. A. Knaggs, to be published.

predominate and the dioxan derivative is a minor constituent of the total product.

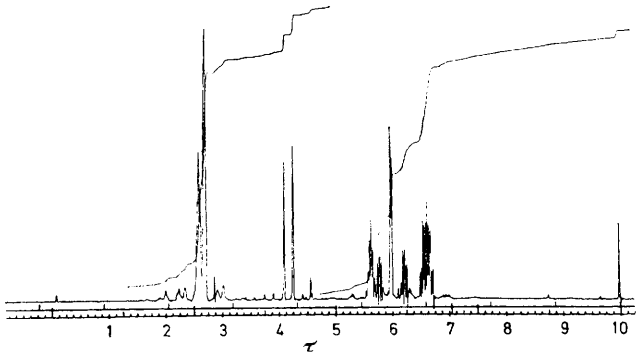


FIGURE 1 220 MHz ^{1}H N.m.r. spectrum of the bromodeoxy-products [(XI) + (XII) + (VI)] from the reaction of *cis*-2-phenyl-1,3-dioxan-5-ol (I) with triphenylphosphine and carbon tetrachloride

The 220 MHz n.m.r. spectrum (Figure 1) of the total bromodeoxy-product shows two signals at τ 4·09 and 4·25 and a very weak signal at 4·50 in the benzylic proton region. Comparison with the 100 MHz spectrum shows that the three signals are singlets. If their assignment to O·C*H*Ph·O is correct, the three singlets must arise from three different molecular species. Now the 1,3-dioxolan structure already deduced can exist as the *cis*- (XI) and the *trans*- (XII) diastereoisomers (and their mirror images). For similar diastereoisomeric pairs the PhC*H* resonance has been found to occur at lower field in the *cis*-isomer than in the *trans*-isomer.[20,21] Hence, the singlets at τ 4·09 and 4·25 may be assigned to the 2-proton in (XI) and (XII), respectively, and the weak singlet at τ 4·50 to the 2-proton in structure (VI) (or its *cis*-diastereoisomer). Similar assignments may be made for the chlorodeoxy-products.

The recognition of two diastereoisomeric species as the major constituents in these products permits complete analysis of the n.m.r. signals (Figure 2) arising from the protons of the glycerol residue. For the bromodeoxy-product, this consists of three complex multiplets centred at τ 5·64 (9 lines), 6·0 (10 lines), and 6·3 (14 lines). The splitting patterns are far more complex than those expected for the AA'BCC' system [22] of the glycerol residue of either diastereoisomer. However, by a judicious choice of line separations from the observed spectrum, a theoretical spectrum was obtained for each of the two diastereoisomers (XI) and (XII) by iterative calculation and refining to the best fit.[23] Superposition of the two calculated spectra gave a composite result identical with the observed spectrum (Table and Figure 2).

By similar reasoning, the chlorodeoxy-product was deduced to be an equimolar mixture of the *cis*- (XIII) and the *trans*- (XIV) dioxolan with a small amount (*ca.* 7%) of the dioxan derivative (X).

Finally, for reasons to be discussed later, a benzene solution of the bromodioxan (VI) was heated under reflux with (i) triphenylphosphine–carbon tetrachloride and (ii) triphenylphosphine. In neither reaction was isomerisation of (VI) to dioxolans detected.

Mechanism of the Rearrangement.—It is accepted now that in the reaction of alcohols with triphenylphosphine

Observed and calculated n.m.r. data for the dioxolans (XI) and (XII)

	Chemical shifts (τ)		
	Observed	Calculated	
Protons	(XI) + (XII)	(XI) (*cis*)	(XII) (*trans*)
2-H	4·09, 4·25	4·11	4·27
4-H	5·64	5·64	5·65
5'-H	5·80, 6·00	5·79	6·00
5-H	6·23, 6·00	6·25	6·00
6'-H	6·66	6·56	6·61
6-H	6·66	6·67	6·71
	Coupling constants (Hz)		
	Observed *	Calculated	
Protons	(XI) × (XII)	(XI) (*cis*)	(XII) (*trans*)
5,5'	8·7, 8·7	−8·8	−8·7
5,4	6·4, 5·5	6·4	5·5
5',4	6·4, 5·5	6·5	5·5
6,6'	10·4, 10·6	−10·4	−10·5
6,4	4·8, 5·0	4·9	4·9
6',4	4·2, 3·9	4·2	3·7

* Line separations.

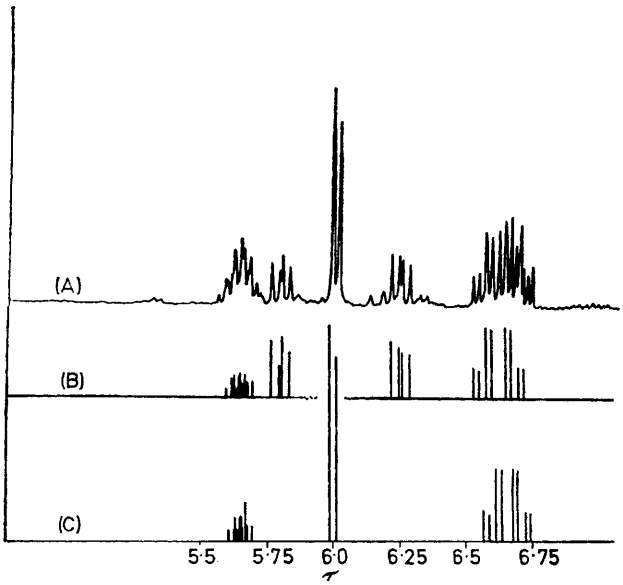


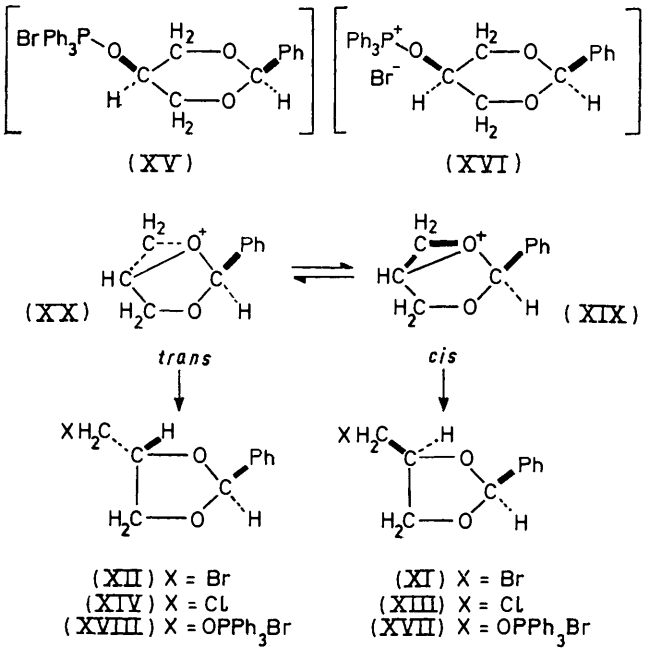
FIGURE 2 (A) Expanded scale (τ 5·5—6·57) display of the n.m.r. spectrum given in Figure 1, together with the calculated spectra (B) for the *cis*-dioxolan (XI) and (C) for the *trans*-dioxolan (XII)

and carbon tetrahalides, a halogenoalkoxytriphenylphosphorane [*e.g.* (XV)] is an intermediate. Evidence is accumulating which suggests that in the fragmentation of such phosphoranes, all bond forming and bond breaking is synchronous and presumably concerted.[6]

[20] T. D. Inch and N. Williams, *J. Chem. Soc.* (*C*), 1970, 263.
[21] M. Anteunis and Y. Rommelaere, *Bull. Soc. chim. belges*, 1970, **79**, 523.
[22] H. van Koningsveld, *Rev. Trav. chim.*, 1970, **89**, 801.
[23] Program LAOCN3 by S. Castellano and A. A. Bothner-by was employed (*J. Chem. Phys.*, 1964, **41**, 3863).

This fragmentation can be treated [24] as a symmetry allowed $[_{\sigma}2_s + _{\sigma}2_a]$ thermal pericyclic process. This treatment neatly rationalises the observed strong propensity for substitution with inversion. However, a concerted process precludes concomitant isomerisation and skeletal rearrangement. An earlier view of the mechanism,[25] requiring an S_N2-type attack by halide ion at C-5 in a phosphonium halide intermediate [*e.g.* (XVI)] is not satisfactory either, because it predicts the same product, *e.g.* (VI), as is obtained in the reaction of lithium bromide with the toluene-*p*-sulphonate (III). Finally, formation of (VI) in the substitution reaction followed by rearrangement to dioxolans cannot be involved because (VI) is not affected by triphenylphosphine and carbon tetrabromide under the usual reaction conditions. It must be concluded, therefore, that the dioxan-to-dioxolan rearrangement occurs independently of and prior to the substitution reaction. Presumably this involves isomerisation of the bromoalkoxytriphenylphosphorane (XV) derived from the dioxan-5-ol to the isomeric dioxolan derivatives (XVII) and (XVIII).

The rearrangement of (XV) into dioxolan isomers could proceed *via* the diastereoisomeric bicyclic dioxolanium cations (XIX) and (XX) with $[OPPh_3Cl]^-$ or its equivalent as the counter-ion in an intimate ion-pair. No doubt this ionisation is assisted by the ring oxygen atoms. The necessary intramolecular interaction of the ring oxygen atoms with C-5 is geometrically feasible in



the boat or the skew boat conformation of (XV). Finally, fragmentation of (XV), (XVII), and (VIII) by the concerted pathway leads to the products (VII), (XI), and (XII).

EXPERIMENTAL

M.p.s were determined with a Mettler FPI apparatus and are corrected. ^{1}H N.m.r. spectra were recorded for solutions in [^{2}H]chloroform with tetramethylsilane as internal standard at 220 MHz on a Varian HR 220 spectrometer. I.r. spectra were recorded for thin films on a Perkin-Elmer 257 spectrophotometer. G.l.c. analysis was carried out on a Perkin-Elmer F11 instrument. The progress of reactions and of chromatographic separations, and the purity of intermediates and the final products were checked by t.l.c. on silica gel GF 254 plates, with (i) chloroform–methanol and (ii) hexane–ether as developing solvents. Compounds containing aromatic chromophores were located by illumination with 254 nm u.v. light (dark spots on a green background); others were located by charring with 50% aqueous sulphuric acid. Elemental analyses were performed by Dr. F. Pascher of Bonn and Dr. F. B. Strauss of Oxford.

cis-2-*Phenyl*-1,3-*dioxan*-5-*ol* (I).—This material, prepared [9] from glycerol and an excess of benzaldehyde, had m.p. 83·9° (lit.,[9] 82·5—83·5°); τ 2·55 (2H, d, *o*-Ph), 2·68 (3H, m, *m*,*p*-Ph), 4·55 (1H, s, C*H*Ph), 5·92 (2H, 4 lines, *J* 1·5 and 12 Hz, CH_2·O), 6·05 (2H, 4 lines, *J* 1·5 and 12 Hz, CH_2·O), 6·50 (1H, t, *J* 1·5 Hz, C*H*·OH), and 6·57 (1H, OH).

cis-2-*Phenyl*-1,3-*dioxan*-5-*yl Toluene*-p-*sulphonate* (III).—This compound, prepared from *cis*-2-phenyl-1,3-dioxan-5-ol and toluene-*p*-sulphonyl chloride in pyridine solution, had m.p. 122·4° (lit.,[14] 124·5—125·5°); τ 2·18 (2H, d, *J* 7 Hz, *o*-C_6H_4·SO_2), 2·52—2·73 (7H, m, *m*-C_6H_4·SO_2 and Ph), 4·55 (1H, s, C*H*Ph), 5·54 (1H, t, *J* 1·7 Hz, C*H*·OTs), 5·80 (2H, 4 lines, *J* 1·6 and 13 Hz, CH_2·O), 5·96 (2H, 4 lines, *J* 1·6 and 13 Hz, CH_2·O), and 7·64 (3H, s, Me).

cis-2-*Phenyl*-1,3-*dioxan*-5-*yl Methanesulphonate* (IV).—A solution of *cis*-2-phenyl-1,3-dioxan-5-ol (1·8 g, 1 mmol) in dichloromethane was added to a stirred solution of methanesulphonyl chloride (2 g, 1·7 mmol) in pyridine (10 ml) and dichloromethane (10 ml) at 0°. The mixture was allowed to warm to room temperature and stirred for a further 48 h. Dichloromethane (200 ml) was added; the mixture was washed with 0·1N-sulphuric acid (3 × 50 ml) and then dried ($MgSO_4$). Subsequent filtration and evaporation gave a white solid. Column chromatography on Kieselgel (100 g) (elution with dichloromethane) gave *cis*-2-phenyl-1,3-dioxan-5-yl methanesulphonate as a white solid (2·0 g, 78%), by t.l.c. (in ether). Crystallisation from ethanol gave white needles (1·6 g), m.p. 130—133° (lit.,[15] 134—135°); τ 2·50—2·66 (5H, m, Ph), 4·48 (1H, s, C*H*Ph), 5·34 (1H, t, *J* 1·5 Hz, C*H*·OMs), 5·58 (2H, 4 lines, *J* 1·5 and 12·5 Hz, CH_2·O), 5·86 (2H, 4 lines, *J* 1·5 and 13·0 Hz, CH_2·O), and 6·91 (3H, s, Me) (Found: C, 51·5; H, 5·25; S, 12·35. $C_{11}H_{14}O_5S$ requires C, 51·15; H, 5·45; S, 12·4%).

Reaction of Lithium Chloride with 2-*Phenyl*-1,3-*dioxan*-5-*yl Toluene*-p-*sulphonate* (III).—A mixture of dry lithium chloride (420 mg, 10 mmol) and *cis*-2-phenyl-1,3-dioxan-5-yl toluene-*p*-sulphonate (668 mg, 2 mmol) in dry acetonitrile was heated under reflux in anhydrous conditions for 50 h. T.l.c. revealed that no reaction had occurred.

Reaction of Lithium Bromide with cis-2-*Phenyl*-1,3-*dioxan*-5-*yl Toluene*-p-*sulphonate* (III).—A solution of *cis*-2-phenyl-1,3-dioxan-5-yl toluene-*p*-sulphonate (380 mg, 1·1 mmol) in acetonitrile (30 ml; redistilled from P_4O_{10}) was distilled to remove 15 ml of solvent. Lithium bromide (2·4 g, 28 mmol; dried at 100° and 0·1 mmHg) was added

[24] R. Aneja, A. P. Davies, and J. A. Knaggs, *Tetrahedron Letters*, in the press.
[25] I. M. Downie, J. B. Lee, and M. F. S. Matough, *Chem. Comm.*, 1968, 1350.

and the mixture was refluxed under dry conditions for 45 min. T.l.c. [eluant benzene or hexane–ether (1 : 1)] revealed that all the starting material had been consumed. The solvent was removed and the residue extracted with cold hexane. Evaporation of the extract to dryness gave a white solid (204 mg) containing the required product and benzaldehyde. Evacuation (0·1 mmHg) for 24 h removed the benzaldehyde, giving a white solid (127 mg, 46%). G.l.c. (10% DEGS; 175°) revealed that the product was a single component. It was sublimed at <80° and 0·05 mmHg to give pure trans-5-*bromo*-2-*phenyldioxan* (VI), m.p. 83—86°; *m/e* 243 and 240·9856 ($C_{10}H_{10}BrO_2$); τ 2·58 (2H, d, *J* 5 Hz, *o*-Ph), 2·67 (3H, d, *J* 5 Hz, *p,m*-Ph), 4·50 (1H, s, PhC*H*), 5·65 (2H, 4 lines, *J* 4·5 and 10·5 Hz, CH_2·O), 5·85 (1H, 5 lines, *J* 10·5 and 4·5 Hz, CHBr), and 6·21 (2H, 3 lines, *J* 11 and 10·5 Hz, CH_2·O) (Found: C, 49·25; H, 4·6; Br, 32·9. $C_{10}H_{11}BrO_2$ requires C, 49·4; H, 4·55; Br, 32·85%).

Reaction of cis-2-*Phenyl*-1,3-*dioxan*-5-*ol with Carbon Tetrabromide and Triphenylphosphine.*—A mixture of carbon tetrabromide (7·1 g, 21 mmol), triphenylphosphine (5·2 g, 20 mmol), and *cis*-2-phenyl-1,3-dioxan-5-ol (3·6 g, 20 mmol) in dry benzene (200 ml) was heated under reflux for 1 h, during which a precipitate of triphenylphosphine oxide separated. The mixture was evaporated to dryness, the residue was extracted with hexane, and this extract (6 g) was further purified as follows. A column of Kieselgel (120 g; 0·05—0·2 mm) was slurried in hexane and the extract was added in benzene–hexane (1 : 4). Elution with benzene–hexane (1 : 1) removed impurities; benzene–hexane (8 : 1) gave the pure product (t.l.c. in benzene) as a clear oil (2·36 g, 49%); distilled at 80° (bath temp.) and 0·1 mmHg. G.l.c. (10% DEGS; isothermal 180°) showed the presence of two major components and one minor (7%); τ 2·60—2·71 (5H, m, Ph), 4·11 and 4·27 (1H, two singlets, C*H*Ph), 5·57—5·68 (1H, 9 lines, O·CH_2·C*H*·CH_2), 5·75—5·80, 5·98, 6·01, and 6·21—6·27 (2H, 10 lines, CH_2·O), and 6·50—6·73 (2H, 14 lines, CH_2Br). The spectrum is consistent with a mixture (*ca.* 1 : 1) of *cis*- and *trans*-4-bromomethyl-2-phenyl-1,3-dioxolans (see text). A very weak signal at τ 4·57 was attributed to PhC*H* in *trans*-5-bromo-2-phenyl-1,3-dioxan. The mass spectrum showed *m/e* 243 and 241 $[M - H]^+$ (Found: C, 49·05; H, 4·4; Br, 33·1. Calc. for $C_{10}H_{11}BrO_2$: C, 49·4; H, 4·55; Br, 32·9%).

Reaction of 2-*Phenyl*-1,3-*dioxan*-5-*ol with Carbon Tetrachloride–Triphenylphosphine.*—The reaction of triphenylphosphine (2·7 g, 10 mmol) with *cis*-2-phenyl-1,3-dioxan-5-ol (1·8 g, 10 mmol) in refluxing carbon tetrachloride gave an oil (810 mg) after purification as described for 4-bromomethyl-2-phenyl-1,3-dioxolan; τ 2·52—2·64 (5H, m, Ph), 4·02 and 4·18 (1H, two singlets, C*H*Ph), 5·5—5·61 (1H, 9 lines, C*H*·CH_2·O), 5·68—5·75, 5·86, 5·89, and 6·05—6·14 (2H, 10 lines, CH_2·O), and 6·25—6·52 (2H, 10 lines, CH_2Cl). The spectrum is consistent with a mixture (*ca.* 1 : 1) of *cis*- and *trans*-4-chloromethyl-2-phenyl-1,3-dioxolan (see text). A weak signal at τ 4·39 was assigned to PhC*H* of 5-chloro-2-phenyl-1,3-dioxan (Found: Cl, 17·85. Calc. for $C_{10}H_{11}ClO_2$: Cl, 17·7), *m/e* 197·0362 ($[M - 1]^+$ requires 197·0364).

1,2-*Distearoyl*-3-*chlorodeoxyglycerol.*—A solution of 4-chloromethyl-2-phenyl-1,3-dioxolan (see before) (230 mg) in ethanol (50 ml) was hydrogenated over palladium–charcoal (100 mg; 10%) until uptake ceased. The mixture was filtered and the filtrate evaporated to dryness; the residue of 3-chlorodeoxyglycerol (120 mg) was a gum. A mixture of this (85 mg, 0·9 mmol), stearoyl chloride (700 mg, 2·3 mmol), and pyridine (2 ml) in dichloromethane (12 ml) was stirred under dry conditions for 20 h, then evaporated to dryness, and the residue was taken up in ether. The solution was washed successively with 0·1N-sulphuric acid, 10% sodium hydrogen carbonate solution, and water, dried ($MgSO_4$), and evaporated to dryness (525 mg). Traces of stearic acid and anhydride were removed by elution in ether through a column of alumina (5 g; Woelm, grade II). The product (387 mg) was purified further by chromatography on Kieselgel (16 g). Elution with benzene–hexane (1 : 1) gave chromatographically pure *product* (320 mg), which after repeated crystallisation from acetone at 22° had m.p. 55—56° (175 mg); τ 4·80 (1H, 5 lines, *J* 5·5 Hz, glycerol CH), 5·66 (1H, 4 lines, *J* 4·5 and 12 Hz, CH_2·O·COR), 5·80 (1H, 4 lines, *J* 6·0 and 12 Hz, CH_2·O·COR), 6·36 (2H, 7 lines, *J* 5 Hz, CH_2Cl), 7·66 and 7·70 (4H, two triplets, CH_2·CO·O), 8·75 ((CH_2), and 9·11 ((CH_3). A weak signal at τ 5·73 can be assigned to the glycerol protons of the 1,3-diacyl-2-deoxychloro-isomer (Found: C, 73·15; H, 11·7; Cl, 5·5. $C_{39}H_{75}ClO_2$ requires C, 72·8; H, 11·75; Cl, 5·5%).

The mother liquor (149 mg) showed n.m.r. signals at τ 5·61—5·83 (3H, 5 lines). The signal at τ 5·70 may be assigned to CHCl and CH_2·O·COR, and the relative intensities correspond to a 85 : 15 mixture of 1,2-diacyl-3-chlorodeoxyglycerol and 1,3-diacyl-2-chlorodeoxyglycerol, respectively. Therefore, the reaction mixture (320 mg) contained 7% of 1,3-diacyl-2-chlorodeoxyglycerol.

Reaction of trans-5-*Bromo*-2-*phenyl*-1,3-*dioxan with Triphenylphosphine.*—A mixture of *trans*-5-bromo-2-phenyl-1,3-dioxan (8 mg, 0·06 mmol) and triphenylphosphine (13 mg, 0·05 mmol) was refluxed in dry benzene (2 ml) for 1 h. The solvent was removed and the residue dissolved in ether–hexane (1 : 1), and this solution was applied to a t.l.c. plate. After development in benzene, bands were located with 254 nm radiation and all except those containing triphenylphosphine and triphenylphosphine oxide were removed and extracted with chloroform. The solvent was removed and the residue was redissolved in hexane and analysed by g.l.c. (5 ft, 20% DEGS at 170°). One peak only was observed, the retention time of which was identical with that of the starting material.

Reaction of trans-5-*Bromo*-2-*phenyl*-1,3-*dioxan with Triphenylphosphine and Carbon Tetrabromide.*—The reaction between *trans*-5-bromo-2-phenyl-1,3-dioxan (13 mg, 0·09 mmol), triphenylphosphine (12 mg, 0·05 mmol), and carbon tetrabromide (37 mg, 0·11 mmol) in dry benzene (2 ml) under conditions identical to those just described, furnished unchanged starting material only.

We thank Dr. T. Bryce for obtaining the coupled g.l.c.–mass spectra, Mr. J. A. Knaggs for the n.m.r. calculations, Mr. T. Studley for reading the manuscript, and Professor W. D. Ollis, F.R.S., for discussions.

[3/1412 *Received*, 6*th July*, 1973]