1059. *Preparation of Some Chromans from* 1,3-*Diaryloxypropanes. Part II*[1]

By L. W. Deady, R. D. Topsom, and J. Vaughan

The scope of the previously reported aluminium chloride catalysed decomposition of 1,3-diaryloxypropanes to give chromans and phenols has now been investigated. The substituents that can be employed on the aromatic nuclei are probably limited to alkyl, aryl, alkoxy-, and halogeno-groups. Within these limits the method provides a simple and useful synthesis for 6- and 8-substituted chromans. Decompositions of *m*-substituted 1,3-diaryloxypropanes give mixtures of the respective 5- and 7-substituted chromans which can be separated by preparative gas chromatography in favourable cases. Kinetic results support a synchronous mechanism. The investigation has been extended to 1,2-diphenoxyethane and 1,4-diphenoxybutane, both of which give the ω-chloroalkyl phenyl ether rather than ring-closure.

We previously reported[1] that the readily prepared 1,3-diphenoxypropane decomposes smoothly in the presence of aluminium chloride to give phenol and chroman. A similar reaction occurred with 1,3-di-*p*-tolyloxy- and 1,3-di-*p*-chlorophenoxy-propane. The good

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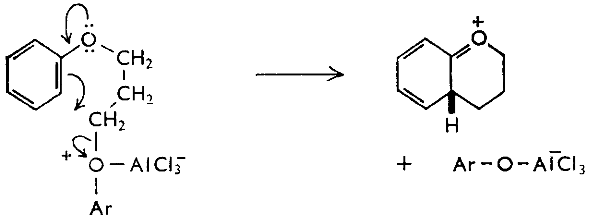
[1] The Paper by L. W. Deady, R. D. Topsom, and J. Vaughan, *J.*, 1963, 2094, is considered as Part I.



yields obtained suggested that this simple method of chroman synthesis might be of wide utility. We here report an investigation of the scope of this reaction, including phenyl and naphthyl compounds, various aryl substituents, and variation in the central bridging chain. We have also investigated the mechanism.

EXPERIMENTAL

Analyses were carried out by the Microanalytical Laboratory of the University of Otago. The analytical gas chromatograph had columns packed with 10% w/w Apiezon L on Celite 545; the column temperature was 200°. The Beckman Megachrom preparative gas chromatograph employed had columns packed with 35% w/w Apiezon J on C22 firebrick, and was used with a column temperature of 210°. Infrared spectra were determined as liquid smears on a Perkin-Elmer model 221 or 137 spectrograph with sodium chloride optics.

Substituted Diaryloxyalkanes (Table 1).—*Method A.* This was described in Part I of this series.[1] *Method B.* Ethanol (150 ml. per mole of phenol) was added to the reaction mixture to increase the solubility of the phenoxide ion. After extraction as in method *A*, the products were washed free from excess phenoxide with hot water, and recrystallised. *Method C.* The reaction was conducted as method *A* but the product (a liquid) was extracted with ether and subsequently distilled. *Method D.* As method *C* except that the material left, after evaporation of the organic solvents, was purified by recrystallisation.

TABLE 1

Di(substituted-phenoxy)alkanes, ArO·[CH$_2$]$_n$·OAr

No.	Subst.	n	Method	Yield (%)	M. p.† or b. p.	Cryst. from	Found (%)		Formula	Reqd. or calc. (%)	
							C	H		C	H
1	H	3	*A*	76	60°	EtOH					
2	2-Me *‡	3	*C*	65	164—170/1 mm.		79·8	7·9	$C_{17}H_{20}O_2$	79·65	7·85
3	3-Me *	3	*A*	62	57	EtOH	79·3	7·45	$C_{17}H_{20}O_2$	79·65	7·85
4	4-Me	3	*A*	77	91	EtOH					
5	2-Cl *	3	*A*	68	75—76	AcOH	61·0	4·9	$C_{15}H_{14}Cl_2O_2$	60·6	4·7
6	3-Cl *‡	3	*C*	68	180—183/1 mm.		60·9	5·05	$C_{15}H_{14}Cl_2O_2$	60·6	4·7
7	4-Cl	3	*A*	82	120—121	AcOH					
8	2-MeO	3	*A*	65	109	EtOH					
9	3-MeO *‡	3	*C*	55	210—215/1 mm.		70·8	7·1	$C_{17}H_{20}O_4$	70·8	7·0
10	4-MeO	3	*A*	78	85—86	EtOH	70·75	7·3	$C_{17}H_{20}O_4$	70·8	7·0
11	2-Br *	3	*A*	62	103	EtOH	46·95	3·85	$C_{15}H_{14}Br_2O_2$	46·65	3·6
12	4-Br	3	*A*	81	142—143	AcOH					
13	2-C_6H_5 *	3	*D*	43	59·5	EtOH	85·35	6·35	$C_{27}H_{24}O_2$	85·25	6·35
14	4-C_6H_5 *	3	*B*	84	150	AcOH	85·5	6·45	$C_{27}H_{24}O_2$	85·25	6·35
15	4-NO_2	3	*B*	61	128—129	C_6H_6					
16	4-CHO	3	*B*	80	130	C_6H_6					
17	2,3-Benzo	3	*A*	53	97	EtOH	83·85	6·25	$C_{23}H_{20}O_2$	84·1	6·15
18	3,4-Benzo	3	*A*	56	146	C_6H_6					
19	H	2	*A*	59	96	EtOH					
20	2,3-Benzo	2	*A*	40	127	AcOH					
21	H	4	*A*	92	98	EtOH					

* New compounds. † M. p.s agree with literature figures except for No. 17 (L. Gatterman, *Annalen*, 1907, **357**, 313, gives m. p. 103—104°). ‡ No. 2, n_D^{19} 1·5539; No. 6, n_D^{20} 1·5763; No. 9, n_D^{20} 1·5628.

Di(phenoxymethyl) ether. This compound, m. p. 98° (from ethanol), was similarly prepared (92%) by method *A* from di(chloromethyl) ether.

1,3,-*Di*-p-*aminophenoxypropane.* Reduction of the corresponding di(nitrophenoxy)-propane afforded [2] this compound, m. p. 104° (from benzene).

Decomposition of Diaryloxypropanes.—The decompositions were carried out by refluxing (4 hr.) the diether in benzene (1·5 l. per mole of diether) with 1·3 moles of aluminium chloride.

TABLE 2

Substituted chromans

Subst.	Yield (%)	B. p./mm.	n_D (temp.)	Found (%) C	Found (%) H	Formula	Reqd. or calc. (%) C	Reqd. or calc. (%) H
H	72	102—104°/20	1·5505(17°)					
5-Me[b]	76·5[c]	71—72/1	1·5488(21)	81·25	7·45	$C_{10}H_{12}O$	81·05	8·15
6-Me	92	103—105/16	1·5442(15)	81·15	8·15	$C_{10}H_{12}O$	81·05	8·15
7-Me	76·5[c]	67—68/1	1·5440(20)	80·35	8·1	$C_{10}H_{12}O$[h]	81·05	8·15
8-Me	73	64—67/2	1·5460(20)	81·0	8·25	$C_{10}H_{12}O$	81·05	8·15
5-Cl[a]	54[c]	—[e]	—					
6-Cl	70	86—89/1	1·5653(15)	64·2	5·35	C_9H_9ClO	64·15	5·35
7-Cl[b]	54[c]	91/1	—	64·6	5·65	C_9H_9ClO	64·15	5·35
8-Cl	55	93/2	1·5709(20)	63·9	5·3	C_9H_9ClO	64·15	5·35
6-Br	50	140—142/16	1·5860(16)	51·4	4·3	C_9H_9BrO	50·7	4·25
8-Br[b]	35	100—104/1	1·5847(20)					
5-MeO[a] ...	67·5[c]	—	1·5602(23)	73·55	7·55	$C_{10}H_{12}O_2$	73·15	7·35
6-MeO[a] ...	84	92/1	1·5500(19)	72·85	7·35	$C_{10}H_{12}O_2$	73·15	7·35
7-MeO	67·5[c]	133/16	1·5519(13)	73·55	7·3	$C_{10}H_{12}O_2$	73·15	7·35
8-MeO	—[d]	—						
6-C_6H_5[a] ...	81	151/1[f]	—	85·55	6·7	$C_{15}H_{14}O$	85·7	6·7
8-C_6H_5[a] ...	61	144—145/1	1·6223(17)	85·75	6·5	$C_{15}H_{14}O$	85·7	6·7
5,6-Benzo	82·5	132/1[g]	—	84·95	6·4	$C_{13}H_{12}O$	84·75	6·55
7,8-Benzo	82·5	134/1	1·6373(20)	85·05	6·65	$C_{13}H_{12}O$	84·75	6·55

[a] New compounds. [b] Compounds not previously reported but not obtained pure. [c] Mixture of 5- and 7-isomers. [d] Not isolated but dinitro-derivative prepared (see Table 3). [e] All converted into the nitro-derivative (Table 3). [f] M. p. 41—42° (from light petroleum). [g] M. p. 40° (from ethanol). [h] O Found 10·5, calc. 10·8%.

The chromans (Table 2) were isolated as previously described. 1,3-Di-*p*-formyl-, 1,3-di-*p*-nitro-, and 1,3-di-*p*-amino-phenoxypropane were recovered unchanged after attempted decompositions under these conditions. Chroman itself was obtained as a by-product in the preparation of both 6- and 8-bromochroman. It was identified by its physical properties, infrared spectrum, and conversion into 6-nitrochroman, identical with an authentic specimen.

1,3-*Di*-(m-*substituted-phenoxy*)*propanes.* These compounds were decomposed and the chroman fraction isolated as described above. The fraction contained a mixture of the appropriate 5- and 7-substituted chromans, and the relative amounts were determined by gas chromatography. The two isomers were then separated, in each case, by preparative gas chromatography. The retention times of each pair were similar, and considerable "tailing" of the first peak occurred. Thus, while the first isomer to come off the column could be obtained pure, the second was contaminated by the first. Additional passages through the chromatograph would probably remove this contaminant if necessary. 7-Chloro- and 7-methoxy-chroman were eluted before their corresponding 5-isomers, but 5-methylchroman had a smaller retention time than 7-methylchroman. Readily purified derivatives (Table 3) were, however, obtained from each compound. The individual compounds were identified by their infrared spectra. Each of the 5-substituted compounds had a strong peak in the range 12·9—13·0 μ, characteristic of 3 adjacent aromatic C–H bonds, while their 7-substituted isomers had a strong peak in the range 12·1—12·5 μ, characteristic of 2 adjacent aromatic C–H bonds.

1,3-*Di*-o-*methoxyphenoxypropane.* Distillation of the non-phenolic material (11·5 g.) obtained from the decomposition of this compound (80 g.) gave a fraction (6·1 g.) of b. p. 65—112°/1 mm. The fraction consisted (gas chromatography) of two major and nine minor components. The sample of b. p. 128—145°/16 mm. gave a nitro-derivative having analysis figures in accord with a dinitromethoxychroman (Table 3). The acidic compounds isolated were: *o*-methoxyphenol, b. p. 55—57°/1 mm., $n_D^{14·5}$ 1·5468; 3-*chloropropyl* o-*hydroxyphenyl ether*, b. p. 106—114°/1 mm., m. p. 45—46° after three recrystallisations from aqueous ethanol,

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[2] M. W. Partridge and W. F. Short, *J.*, 1947, 390.

TABLE 3

Nitro-derivatives of substituted chromans

Subst.	Deriv.	M. p. (solvent)	Found (%) C	H	Formula	Reqd. or calc.* (%) C	H
H	Mono	100° (EtOH)	60·35	5·1	$C_9H_9NO_3$	60·35	5·05
5-Me	Mono	99—100 (aq. EtOH)	62·3	5·9	$C_{10}H_{11}NO_3$	62·15	5·75
7-Me	Mono	74 (aq. EtOH)	62·3	6·0	$C_{10}H_{11}NO_3$	62·15	5·75
8-Me	Mono	67 (EtOH)	61·9	5·9	$C_{10}H_{11}NO_3$	62·15	5·75
5-Cl	Mono	90 (aq. EtOH)	50·85	4·1	$C_9H_8ClNO_3$	50·6	3·75
6-Cl	Mono	64 (EtOH)	50·3	4·05	$C_9H_8ClNO_3$	50·6	3·75
7-Cl	Mono	96 (EtOH)	50·8	4·15	$C_9H_8ClNO_3$	50·6	3·75
8-Cl	Mono	112—113 (EtOH)	50·9	4·35	$C_9H_8ClNO_3$	50·6	3·75
6-Br	Mono	102 (EtOH)	41·8	3·4	$C_9H_8BrNO_3$	41·85	3·1
8-Br	Mono	104 (EtOH)	42·15	3·25	$C_9H_8BrNO_3$	41·85	3·1
6-MeO	Mono †	80—81 (EtOH)	57·25	5·7	$C_{10}H_{11}NO_4$	57·4	5·3
	Di	142—143 (EtOH)	47·35	4·65	$C_{10}H_{10}N_2O_6$ ‡	47·25	3·95
7-MeO	Picrate	77 (EtOH)	48·95	4·1	$C_{16}H_{15}N_3O_9$	48·85	3·8
8-MeO	Di	173 (EtOH)	47·05	4·35	$C_{10}H_{10}N_2O_6$	47·25	3·95
8-C_6H_5	Mono	117—118 (EtOH)	70·4	5·4	$C_{15}H_{13}NO_3$	70·6	5·15

* All are new compounds with the exception of 6-nitrochroman. † Prepared by nitrating in acetic acid. ‡ O Found 38·0, reqd. 37·8%.

infrared spectrum having strong peaks at 2·9 (O–H stretch) and 13·3 μ (4 adjacent aromatic C–H bonds) (Found: C, 47·05; H, 4·35; O, 37·6. $C_9H_{11}ClO_2$ requires C, 47·25; H, 3·95; O, 37·8%); 1-(o-*hydroxyphenoxy*)-3-(o-*methoxyphenoxy*)*propane*, m. p. 76° (from aqueous ethanol) (Found: C, 69·85; H, 6·7; O, 24·0. $C_{16}H_{18}O_4$ requires C, 70·05; H, 6·55; O, 23·35%).

Decomposition of Related Diaryloxyalkanes.—1,4-*Diphenoxybutane*. Decomposition of this compound, as above, gave phenol as the only acidic product. Distillation of the non-phenolic material afforded 1,4-dichlorobutane (b. p. 46—48°/14 mm., n_D^{17} 1·4572, positive halogen test, infrared spectrum identical with that of an authentic sample), and 4-chlorobutyl phenyl ether [b. p. 140—142°/16 mm., $n_D^{18·5}$ 1·5255, positive halogen test; gave 1,4-diphenoxybutane when refluxed with an alkaline solution of phenol (lit.,[3a] b. p. 144°/20 mm., n_D^{20} 1·5230)].

Di(phenoxymethyl) ether. Decomposition of this triether was exothermic and gave mostly high-boiling acidic material (b. p. > 200°/1 mm.). The only volatile products were a small amount of phenol and some diphenylmethane [b. p. 136—140°/16 mm., $n_D^{26.5}$ 1·5751, solidified at room temperature, infrared spectra indicative of a monosubstituted benzene compound (lit.,[3b] m. p. 26—27°, n_D^{20} 1·5768) (Found: C, 92·45; H, 7·45. Calc. for $C_{13}H_{12}$: C, 92·85; H, 7·15%)].

1,2-*Diphenoxyethane*. The compound was recovered unchanged after attempted decomposition under the above conditions. Breakdown occurred on treatment with aluminium chloride in chlorobenzene (4·5 hr. at 105°), to give phenol and 2-chloroethyl phenyl ether [b. p. 108—116°/16 mm., solidified at room temperature, positive halogen test; gave 1,2-diphenoxyethane when heated with an alkaline solution of phenol (lit.,[3a] b. p. 108—110°/16 mm., m. p. >25°)].

1,2-*Di*-1-*naphthyloxyethane*. Decomposition in chlorobenzene (115°) gave 1-naphthol and 2-chloroethyl 1-naphthyl ether [b. p. 128—130°/1 mm., n_D^{20} 1·6110, positive halogen test; gave 1,2-di-1-naphthyloxyethane when heated with 1-naphthol in ethanolic sodium hydroxide solution (lit.,[3c] b. p. 145—147°/2 mm., n_D^{20} 1·6139)].

Nitro-chromans (Table 3).—Nitro-derivatives were, in general, readily prepared by dropwise addition of conc. nitric acid to the appropriate chroman. 6-Methyl-, 5-methoxy-, and 7-methoxy-chroman did not give solid derivatives under these conditions.

Rate Measurements.—*Reagents*. Various commercial samples of aluminium chloride were found to contain considerable amounts of alumina, and the catalyst was therefore prepared [4] from hydrogen chloride and aluminium. It was purified by sublimation and stored and handled under dry nitrogen. The benzene used was fractionated and stored over sodium.

Method. The decomposition was followed by the spectrophotometric estimation of the

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[3] (*a*) P. M. Frearson and E. S. Stern, *J.*, 1958, 3065; (*b*) K. v. Auwers and A. Fruhling, *Annalen*, 1921, **422**, 192; (*c*) W. R. Turner and G. H. Richter, *J. Amer. Chem. Soc.*, 1929, **51**, 3409.

[4] J. W. Mellor, " A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, London, 1924, vol. V, p. 312.

phenol formed. Stock solutions of known weights of the appropriate diether and aluminium chloride could be made up at room temperature and stored for several days at 0° without significant reaction. Solutions for individual runs were prepared by the addition of known amounts of benzene and, where necessary, of further diether. Aliquots (5 ml.) of this solution were sealed in glass tubes, with careful exclusion of moisture, and brought to the reaction temperature (73·0 ± 0·10) in a thermostatted bath. Tubes were removed from the bath at intervals, rapidly cooled, and broken, and the contents were wshed with ether (10 ml.) into hydrochloric acid (20 ml.; 3N). The organic layer was separated and the aqueous layer further extracted with ether (15 ml.). The total organic extract was then extracted with 10% aqueous sodium hydroxide (3 × 20 ml.) and the alkaline extract made up to a fixed volume (100 ml.). The concentration of phenoxide ion in this solution was determined by measurement of the optical density with a Beckman DK 2A ratio-recording spectrometer utilising the primary band at about 240 mμ. Reactions were followed to less than 40% completion, and the concentration of phenol formed was a linear function of time in most cases (see Discussion section). The zero-order rate constant, k_0, was determined from the slope; values were reproducible to about 2% in separate runs.

DISCUSSION

Preparation and Decomposition of Diaryloxypropanes.—The diaryloxypropanes were generally prepared in good yield by the reaction of phenols with 1,3-dibromopropane under heterogeneous conditions. Previous workers [5-7] added solvents such as ethanol to allow homogeneous reactions but this necessitated a later inconvenient dilution with water.

The decompositions proceeded smoothly unless electron-withdrawing substituents were present. Thus good yields of substituted chromans and phenols were obtained from alkyl- and aryl-substituted phenoxypropanes and from dinaphthyloxypropanes. That the breakdown of di-2-naphthyloxypropane gave only 5,6-benzochroman is not surprising, because the formation of the 6,7-benzo-product would involve ring-closure at the unreactive 3-position of the naphthalene nucleus. Di-*p*-formyl- and di-*p*-nitro-phenoxypropane failed to decompose under the reaction conditions, and di-*p*-aminophenoxypropane was similarly inert, presumably because the amino-group is co-ordinated with aluminium chloride under the reaction conditions. The reaction did proceed with halogeno-substituents but some concurrent dehalogenation was observed with both di(bromophenoxy)propanes employed. Nevertheless, the resultant yields of halogeno-chromans were much superior to those reported [8] by an alternative method. In each series, the yield of the 8-substituted chroman was less than that of its 6-isomer; this may be related to the decrease in the number of positions for closure and may also reflect a buttressing effect.

The formation of methoxychromans from two of the di(methoxyphenoxy)propanes was interesting, because anisole is known [9] to be dealkylated more readily than n-propyl phenyl ether. The good yields obtained are consistent with a reaction involving ring-closure synchronous with the splitting off of the phenol and thus proceeding with a lower energy than simple dealkylation. However, di-*o*-methoxyphenoxypropane did not give more than a trace of 8-methoxychroman and considerable demethylation occurred. This may result from the partial bonding of the aluminium chloride to both of the oxygen atoms attached *ortho* on one of the aromatic nuclei with a consequent decrease in its aid to the cyclisation reaction.

The 5- and 7-substituted chromans produced on the breakdown of di(*m*-substituted-phenoxy)propanes were separated by preparative gas chromatography although the second compound eluted in each case was contaminated by some of its isomer. A second elution would probably allow the collection of pure samples but this was not attempted here as the collector efficiency of the chromatograph used was low under the conditions necessary to achieve separation. The relative amounts of the two isomers obtained were estimated by

[5] J. Lohmann, *Ber.*, 1891, **24**, 2631.
[6] J. A. King and F. H. McMillan, *J. Amer. Chem. Soc.*, 1945, **67**, 336.
[7] F. H. McMillan, *J. Amer. Chem. Soc.*, 1952, **74**, 5229.
[8] P. Maitte, *Ann. Chim. (France)*, 1956, **9**, 431.
[9] B. W. Tronow and L. W. Ladigina, *Ber.*, 1929, **62**, *B*, 2844.

by analytical gas chromatography before separation. The ratios found (Table 4) were very similar to those observed for 5- and 7-substituted tetrahydroquinolines obtained[10] from the breakdown of 1,3-di(arylamino)propanes which, in turn, have been shown[10] to be similar to those obtained[11] for 5- and 7-substituted quinolines produced in the Skraup reaction.

TABLE 4

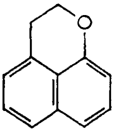
Relative amounts (%) of 5- and 7-substituted chromans obtained in the breakdown of di-(*m*-substituted-phenoxy)propanes *

Subst.	Chroman		Tetrahydroquinoline		Quinoline	
	5-	7-	5-	7-	5-	7-
Me	41	59	41	59	40	60
Cl	45	55	49	51	47	53
MeO	24	76	21	79	22	78

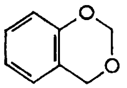
* The relative amounts of tetrahydroquinolines produced[10] on the breakdown of 1,3-di(*m*-substituted-phenylamino)propanes and of quinolines produced[11] from *m*-substituted anilines by the Skraup reaction are also shown.

These results suggest that all three reactions involve the cyclisation of similar entities. The Claisen rearrangement of allyl 3-methylphenyl ether, by contrast, gives[12] 53% of 2-allyl-3-methylphenol (corresponding to the 5-isomers in Table 4) and 47% of 2-allyl-5-methylphenol (corresponding to the 7-isomers).

Decomposition of Related Diaryloxyalkanes.—1,4-Diphenoxybutane decomposed under conditions similar to those above but the major products were phenol, 1,4-dichlorobutane, and 4-chlorobutyl phenyl ether, and no homochroman was detected. 1,2-Diphenoxyethane was almost inert under similar reaction conditions but decomposed at higher temperatures to give phenol and 2-chloroethyl phenyl ether, with no evidence for the formation of coumaran. The formation of a chroman involves substitution at an aromatic carbon atom, and this presumably implies a lateral attack on the aromatic ring. Models confirm that such attack is less favoured with these two systems. Di-1-naphthyloxyethane decomposed similarly at an increased temperature but no compound (I), which would result from closure at the 8-position in the naphthalene nucleus, was detected. This presumably reflects the lower electron availability at this position compared to one *ortho* to the ethereal oxygen atom. An attempt was also made to obtain compound (II) by a similar decomposition of di(phenoxymethyl) ether but the only volatile products obtained were small amounts of phenol and diphenylmethane.



(I)



(II)

Mechanism.—The evidence above favours a reaction involving ring-closure synchronous with the splitting off of the phenol. The relative absence of by-products, the mild conditions employed, the use of a non-polar solvent, and the primary alkyl group involved also suggest that a carbonium ion intermediate is unlikely. Further support for the synchronous mechanism comes from the relative reactivity of some of the substituted diethers.

Alkyl aryl ethers form[13] relatively strong 1 : 1 complexes with aluminium chloride, and this would be expected to occur with the diethers used. The presence of a second oxygen atom allows the co-ordination of a second aluminium chloride molecule. Only the first complex should be capable of direct breakdown to the products. Kinetic measurements did indeed show that, for a fixed concentration of diphenoxypropane, the rate of decomposition was at a maximum in the presence of a slight excess of aluminium chloride.

[10] I. K. Lewis, G. B. Russell, R. D. Topsom, and J. Vaughan, *J. Org. Chem.*, 1964, **29**, 1183.

[11] M. H. Palmer, *J.*, 1962, 3645.

[12] D. S. Tarbell and S. S. Stradling, *J. Org. Chem.*, 1962, **27**, 2724.

[13] J. W. Walker and A. Spencer, *J.*, 1904, **135**, 1106.

The rate fell when the catalyst concentration was either decreased, when the concentration of the first complex would fall, or increased, when the first complex would also decrease as the concentration of the second increased. It was also found (Table 5) that the initial rate of decomposition in the presence of a fixed concentration of aluminium chloride was almost independent of the diether concentration provided that this was in excess. This result is reasonable as the initial concentration of the first complex is almost equal to the aluminium chloride concentration under these conditions. The initial rate was found to be effectively zero-order for such reactions presumably because the concentration of the first complex does not vary greatly in the initial stages of the reaction, the amount used being regenerated by reacton between the excess diether and the aluminium chloride phenol complex formed in the reaction.

Rate measurements (Table 5) were made for a series of substituted diethers under conditions where [Diether] > [$AlCl_3$].

TABLE 5

Rate constants, k_0 (moles l.$^{-1}$ min.$^{-1}$), for the breakdown of di(substituted-phenoxy)-propanes (*D*, moles l.$^{-1}$) in benzene at 73·0°. [$AlCl_3$] = 0·406M

Subst.	H	H	H	*p*-Me	*p*-Me	*p*-Me	*m*-Me	*m*-Me	*p*-Cl	*p*-Cl	*m*-Cl	*m*-Cl
D	0·450	0·580	0·812	0·490	0·562	0·658	0·509	0·678	0·443	0·492	0·488	0·586
10^3k_0 ...	3·16	3·18	3·20	7·74	7·75	7·75	12·28	12·40	1·26	1·28	2·84	2·84

The relative order of reactivity of the substituted diphenoxypropanes is thus *m*-Me > *p*-Me > H > *m*-Cl > *p*-Cl. This order is in accord with that expected from a synchronous mechanism, as it reflects the electron availability at the position *ortho* to the ether group, that is, at the position of closure. Any mechanism involving a rate-determining fission of the ether linkage prior to ring-closure would be expected to give a different order (*m*-Cl > *p*-Cl > H > *m*-Me > *p*-Me).

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