35. *The Preparation and Rearrangement of Benzoates and Substituted Benzoates of Dibromopropanols.*

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Pure crystalline benzoates of 2 : 3-dibromopropan-1-ol and 1 : 3-dibromopropan-2-ol have been prepared: above 100° they partially rearrange to an oily mixture of the two. The liquids which previous investigators have described as pure must have been such mixtures. Various substituted benzoates of the dibromopropanols have been prepared, and the thermal rearrangement of some of them studied. Esters of the weaker aromatic acids rearrange more easily than those of the stronger acids. Although allyl esters of strong aromatic acids gave pure 2 : 3-dibromopropyl esters when treated with bromine in chloroform at room temperature, the corresponding esters of weaker acids gave mixed esters. Reaction mechanisms are discussed.

ACCOUNTS of the benzoates of 2 : 3-dibromopropan-1-ol and 1 : 3-dibromopropan-2-ol, which were required for another investigation, are unsatisfactory. Philippi and Seka [1] claimed to have prepared the former ester by heating 2 : 3-dibromopropanol with benzoyl chloride, and Hurd and Pilgrim [2] reported the similar preparation of the latter from 1 : 3-dibromopropan-2-ol. Edwards and Hodges,[3] however, found that the liquid products of these two syntheses had identical boiling points and infrared absorption spectra, whilst catalytic dehalogenation of either gave *n*-propyl benzoate. They concluded that both products were 2 : 3-dibromopropyl benzoate, which in one case was supposedly formed by

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[1] Philippi and Seka, *Annalen*, 1923, **433**, 88.
[2] Hurd and Pilgrim, *J. Amer. Chem. Soc.*, 1933, **55**, 1195.
[3] Edwards and Hodges, *J.*, 1953, 3427.

rapid rearrangement of the isomer or an intermediate complex, although no rigorous proof of the absence of the 1 : 3-dibromo-derivative was offered. On the basis of similar evidence they later formulated the liquid adduct from allyl bromide and benzoyl hypobromite as 2 : 3-dibromopropyl benzoate.[4] Yasnopolsky's claim [5] to have prepared 2 : 3-dibromopropyl benzoate, m. p. 86—88°, in poor yield by reaction of 2 : 3-dibromopropan-1-ol with benzoyl chloride in the presence of strong aqueous sodium hydroxide was not supported by analytical evidence and could not be substantiated in this laboratory.

It has now been found that both 2 : 3-dibromopropan-1-ol and 1 : 3-dibromopropan-2-ol can be esterified by heating them with benzoyl chloride without appreciable rearrangement provided excessively high temperatures are avoided. In each case equimolecular proportions of the reagents were heated together on the steam-bath until evolution of hydrogen chloride ceased, and the product was purified by crystallisation from methanol. Alternatively, heating could be avoided completely by carrying out the initial reactions at 0° in the presence of pyridine. Good yields were obtained by both routes. The melting point of 2 : 3-dibromopropyl benzoate was 33—34° and that of the isomer 32—33°: admixture of the isomers at room temperature caused liquefaction. When warmed with sodium iodide in acetone 2 : 3-dibromopropyl benzoate, in common with other vicinal dibromides,[6] caused iodine to be liberated, but the isomeric benzoate did not. Finally, the infrared absorption spectra of the two isomeric benzoates were distinctive (see p. 193).

Neither benzoate could be purified by distillation. When either crude ester, prepared in the presence or absence of pyridine, was distilled the product was a colourless oil, b. p. 120°/0·4 mm., which afforded correct analytical data but did not crystallise. The infrared spectra showed they were mixtures. Apparently either ester undergoes partial rearrangement to a mixture of the two when heated somewhat above 100°, so the liquids prepared by earlier investigators must have been such mixtures. In Philippi and Seka's preparation [1] the temperature of the initial reaction was high enough to cause isomerisation, but presumably later workers [2,3] would have obtained pure esters if they had isolated their products by crystallisation instead of distillation. Of the five absorption bands regarded by Edwards and Hodges [3] as characteristic of 2 : 3-dibromopropyl benzoate, that at 11·9 μ is actually characteristic of its isomer, those at 7·05, 8·5, and 9·75 μ are common to the spectra of both isomers, and that at 9·5 μ is shown by neither pure ester.

The remarkable ease with which the two benzoates undergo reversible thermal isomerisation made it desirable to confirm the spectral evidence by isolating the rearrangement products. Unfortunately, the isomeric benzoates would be difficult to separate because they have very similar solubilities in the common organic solvents, whilst distillation is of course precluded. In the hope of obtaining more readily separable isomers, sixteen substituted benzoates, of which twelve were new, were synthesised from the acid chlorides and the dibromopropanols at 0° in the presence of pyridine. Most of them could doubtless also be prepared by heating the reactants in the absence of a base at moderate temperatures: indeed 2 : 3-dibromopropyl *p*-cyanobenzoate has been prepared previously in this way.[7] As with the unsubstituted benzoates, only the 2 : 3-dibromopropyl esters liberated iodine when warmed with sodium iodide in acetone. (When testing nitrobenzoates in this way it was necessary to add water so as to destroy the coloured complexes which aromatic nitro-compounds give with sodium iodide in acetone [8] before the presence or absence of iodine could be observed.) The dibromopropyl *p*-anisates, *p*-chlorobenzoates, and 3 : 5-dinitrobenzoates were chosen for thermal isomerisation studies because of favourable solubility relations and distinctive melting points.

When solutions of 2 : 3-dibromopropyl *p*-anisate and its isomer in toluene were each refluxed for 24 hours isomerisation occurred to a small extent, the products being separated

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[4] Edwards and Hodges, *J.*, 1954, 761.

[5] Yasnopolsky, *J. Gen. Chem. U.S.S.R.*; 1954, **24**, 2033 (U.S. transln.).

[6] Finkelstein, *Ber.*, 1910, **43**, 1530.

[7] Chow and Gisvold, *J. Amer. Pharm. Assoc.*, 1952, **41**, 202.

[8] Shellman, *J. Org. Chem.*, 1957, **22**, 818; Blatt and Gross, *ibid.*, p. 1046.

by fractional crystallisation from methanol. A similar period of refluxing in xylene caused more extensive isomerisation, either pure anisate giving an equilibrium mixture from which about equal amounts of the two isomers were isolated. Since rearrangement proceeded equally well in the presence of calcium carbonate, it appeared to be truly thermal and not to require catalysis by acidic decomposition products.

The *p*-chlorobenzoates were somewhat less labile (unchanged in boiling toluene for 24 hours). In boiling xylene there was appreciable rearrangement, the equilibrium mixture, again containing about equal proportions of the isomers, being obtained after 72 hours. Isomerisation in boiling acetic acid was also examined because this solvent was a convenient one in which to prepare bisthiuronium salts from dibromo-esters:[9] considerable rearrangement was detected but side-reactions probably also occurred since the total recovery of crystalline material was rather poor.

Thermal isomerisation of the two 3 : 5-dinitrobenzoates could not be demonstrated: they were recovered after 24 hours' refluxing in either xylene or anisole, whilst in boiling *p*-cymene or nitrobenzene gross decomposition ensued.

There has been no opportunity to extend these thermal isomerisation studies to the dibromopropyl esters of aliphatic acids, but certain deductions can be drawn from published data. The retention of optical activity during the preparation of the propionate, hexanoate, and stearate from (+)-2 : 3-dibromopropan-1-ol proves that the esters had not become equilibrated with the symmetrical isomers, but it is not known to what thermal treatment the products had been subjected.[10] Of more significance, therefore, is that fact that 2 : 3-dibromopropyl lævulate apparently remained substantially a single compound after distillation at 208—210°/40 mm., since it gave only one semicarbazone and one phenylhydrazone.[11] Finally, the butyrates prepared from 2 : 3-dibromopropan-1-ol and 1 : 3-dibromopropan-2-ol were shown [3] to be distinct despite having been distilled at 118°/6·5 mm. It thus seems reasonable to suppose that the aliphatic esters of the dibromopropanols undergo thermal rearrangement less readily than the benzoates (isomerised at 120°/0·4 mm.). The apparent slow conversion of 2 : 3-dibromopropyl acetate into its isomer on prolonged heating in the presence of hydrogen chloride is probably, as Edwards and Hodges suggested,[3] an example of acid-catalysed rather then truly thermal rearrangement.

The observed order of ease of thermal rearrangement in the substituted benzoates (*p*-anisates $>$ *p*-chlorobenzoates $\gg$ 3 : 5-dinitrobenzoates) is the reverse of that to be expected if the acyloxy-group migrated as an anion, but would be consistent with a mechanism involving cyclisation to a resonating dioxolanium structure.[12] It is therefore suggested that thermal interconversion of isomeric dibromo-esters (I and III) in non-polar solvents containing no added acid may proceed by intramolecular rearrangement through the hypothetical ion-pair (II). Such an intermediate might be supposed to be formed more readily when the substituent (R) represents a suitable aromatic radical rather than when it is alkyl, since it might then be stabilised by contributions from additional resonance forms (*e.g.*, IV). It is, however, realised that, as in other cases of anionotropic rearrangement,[13] different mechanisms (including the acid-catalysed process advocated by Edwards and Hodges [3]) may be more appropriate under other conditions.

At the outset of the present investigation it was expected that addition of bromine to allyl esters would provide a useful alternative route to 2 : 3-dibromo-esters but, as mentioned in a preliminary note,[14] the reaction was found in several cases to be complex. The crude oil from the addition of bromine to allyl *p*-anisate in dry chloroform at room temperature was separated by treatment with methanol into 45% of the expected 2 : 3-dibromopropyl *p*-anisate and 32% of the isomeric ester from 1 : 3-dibromopropan-2-ol. A non-vicinal

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[9] Doyle, Hunter, and Nayler, unpublished work.

[10] Abderhalden and Eichwald, *Ber.*, 1914, **47**, 2880.

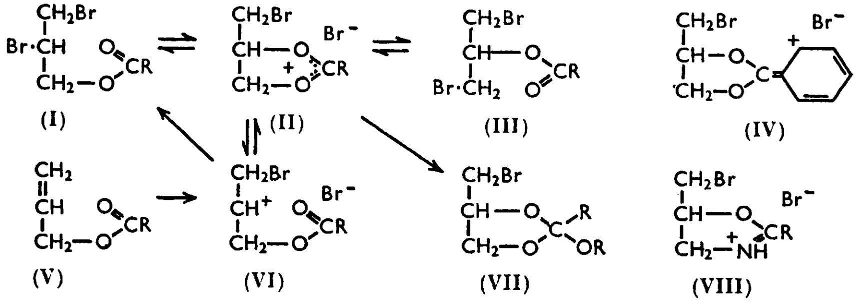
[11] Sah and Ma, *J. Amer. Chem. Soc.*, 1932, **54**, 3271.

[12] Winstein and Buckles, *J. Amer. Chem. Soc.*, 1942, **64**, 2780.

[13] Braude, Turner, and Waight, *Nature*, 1954, **173**, 863.

[14] Nayler, *Chem. and Ind.*, 1958, 863.

dibromide was similarly isolated in 14% yield from allyl *p*-chlorobenzoate, although the 2 : 3-dibromopropyl ester was the main product. These four crystalline dibromides were identified by comparison with authentic esters prepared from 2 : 3-dibromopropan-1-ol and 1 : 3-dibromopropan-2-ol. The oily nature of the crude dibromides obtained from allyl benzoate and *p*-toluate suggested that they too were probably mixtures, but allyl 2 : 4-dichlorobenzoate gave only the 2 : 3-dibromopropyl ester.



Dibromides have been prepared before from a number of allyl esters, but in no case has the isolation of more than one product been reported. The crystalline products from allyl palmitate,[15] *p*-nitrobenzoate,[16] and 3 : 5-dinitrobenzoate[16] must have been the normal 2 : 3-dibromopropyl esters because their melting points were different from those of the esters of 1 : 3-dibromopropan-2-ol, of which the palmitate and *p*-nitrobenzoate had been prepared previously[15,16] and the 3 : 5-dinitrobenzoate was obtained in the present work. Liquid dibromides have been less well characterised, but the product from allyl lævulate was evidently essentially a single compound, identical with that obtained from 2 : 3-dibromopropanol and lævuloyl chloride, since both specimens gave only one semicarbazone and one phenylhydrazone.[11]

Apparently allyl esters of aliphatic acids and the stronger aromatic acids (*e.g.*, *p*-nitro-, 3 : 5-dinitro-, and 2 : 4-dichloro-benzoic acid) give exclusively normal dibromides, whilst the tendency to form a mixture of vicinal and non-vicinal dibromides is characteristic of the weaker aromatic acid derivatives. The dibromides of the latter group are those which undergo ready thermal isomerisation, but the formation of a proportion of abnormal bromine adduct in such cases cannot be ascribed to this cause since the conditions are far too mild. Nevertheless, the correspondence suggests a similarity in reaction mechanism.

In suitable circumstances cyclisation might be supposed to compete with the second stage of the normal addition of bromine to an allyl ester (V $\longrightarrow$ VI $\longrightarrow$ I). A fairly high electron-density at the acyl-oxygen atom of the intermediate (VI) could be expected to favour formation of the hypothetical structure (II), as would a substituent (R) which could confer additional resonance stability on the cyclic structure. As in the thermal isomerisations, these requirements appear to be met when R represents an aryl radical containing neither a strongly electron-attracting group nor an *ortho*-substituent which would place steric restrictions on resonance. Participation of the ion-pair (II) in the addition of bromine to an allyl ester would result in the formation of a proportion of the non-vicinal dibromide (III).

The possible significance of cyclic intermediates in the addition of bromine to certain allyl derivatives has been discussed by Winstein and his collaborators. They concluded[17] that the structure (II; R = Me) did not participate in the addition of bromine to allyl acetate, because no ortho-ester (VII; R = Me) could be detected when the reaction was run in methanol. The oxazolinium bromides (VIII; R = Ph or C_6H_4·OMe-*p*), which may

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[15] Fairbourne and Cowdrey, *J.*, 1929, 129.

[16] Fairbourne and Foster, *J.*, 1926, 3146, 3148.

[17] Winstein and Goodman, *J. Amer. Chem. Soc.*, 1954, **76**, 4368.

be regarded as stable nitrogen analogues of the hypothetical intermediate (II), were, however, obtained, together with *N*-(2 : 3-dibromopropyl)-amides, in the addition of bromine to 3-benzamidopropene and its *p*-methoxy-derivative.[18]

EXPERIMENTAL

Infrared absorption spectra were kindly determined by Mr. H. D. C. Rapson and Mr. K. Austin using a Grubb-Parsons double-beam spectrometer. The specimens were examined as liquid films (the pure benzoates being first melted by gentle warming) between sodium chloride plates.

2 : 3-*Dibromopropyl Benzoate*.—Benzoyl chloride (14·1 g.) and 2 : 3-dibromopropan-1-ol (21·8 g.) were heated together on the steam-bath under reflux until evolution of hydrogen chloride ceased (3 hr.). The colourless oil was cooled, diluted with ether, washed with sodium hydrogen carbonate solution and then with water, and dried. After removal of the solvent under reduced pressure, the residual oil was rubbed with methanol at low temperature, whereupon it crystallised. The white solid was collected and washed with very cold methanol (yield 26·1 g., 81%; m. p. 31—32°). 2 : 3-*Dibromopropyl benzoate* was purified by dissolution in methanol (45 ml.) at room temperature, followed by strong cooling to give small colourless rods, m. p. 33—34° (Found: C, 37·8; H, 3·4. $C_{10}H_{10}O_2Br_2$ requires C, 37·3; H, 3·1%), $\nu_{max.}$ 7·05, 7·27, 7·6, 7·8, 8·0, 8·5, 8·7, 9·35, 9·75, 10·28, 10·7 μ.

2-*Bromo*-1-*bromomethylethyl Benzoate*.—Benzoyl chloride (7·0 g.) and 1 : 3-dibromopropan-2-ol (10·9 g.) were heated on the steam-bath for 9 hr. and the product was isolated as described for the isomer. Crude 2-*bromo*-1-*bromomethylethyl benzoate* (12·5 g., 75%), m. p. 29—30°, was purified by dissolution in methanol (25 ml.) at room temperature, followed by strong cooling to give hexagonal plates, m. p. 32—33° (Found: C, 37·6; H, 3·2. $C_{10}H_{10}O_2Br_2$ requires C, 37·3; H, 3·1%), $\nu_{max.}$ 7·04, 7·43, 7·53, 7·62, 7·85, 8·05, 8·35, 9·35, 9·75, 10·07, 10·45, 10·7, 11·9 μ. Admixture with 2 : 3-dibromopropyl benzoate at room temperature resulted in liquefaction.

Preparation of Dibromopropyl Esters in Presence of Pyridine.—The appropriate acid chloride (0·1 mole) in dry chloroform (30 ml.) was added during 15 min. to a stirred ice-cold mixture of pyridine (20 ml.), chloroform (30 ml.), and the dibromopropanol (21·8 g., 0·1 mole). The mixture was stirred at 0° for 1 hr., set aside overnight at room temperature, poured into ice-water, and acidified with hydrochloric acid. The layers were separated and the aqueous phase was twice extracted with chloroform. The combined chloroform solutions were washed with sodium hydrogen carbonate solution, then with water, dried, and evaporated under reduced pressure. Products, if oily, were triturated with methanol at low temperature. Details are in Table 1. 2-Bromo-1-bromomethylethyl 3 : 5-dinitrobenzoate was recrystallised from chloroform; in other cases methanol was used. Compounds melting below 40° were purified by dissolution in methanol at room temperature, followed by strong cooling. When the isomeric esters had similar m. p.s marked depression was observed on admixture. References in this paper to " authentic specimens " are to compounds prepared in this way.

Thermal Rearrangement of p-*Anisates and* p-*Chlorobenzoates*.—A solution of the ester (5 g.) in the dry solvent (30 ml.) (Table 2) was refluxed for the period stated, then evaporated under reduced pressure. The gummy residue was rubbed with methanol and set aside at room temperature for a few hours, and the white solid collected: it usually consisted of fairly pure 2-bromo-1-bromomethylethyl ester. The filtrate was cooled strongly to give a second crop which frequently contained both isomers, which were separated by further treatment with methanol. Concentration of the mother-liquor gave a third crop, usually consisting of fairly pure 2 : 3-dibromopropyl ester. Further purification of the various crops was effected in the usual way. The recoveries noted in Table 2 refer to materials which melt no more than a few degrees lower then the pure compounds and show no depression of m. p. on admixture with the latter.

Allyl Esters.—Allyl alcohol (8 g.) and *p*-toluoyl chloride (14·3 g.) were heated under reflux on the steam-bath for 4 hr., then distilled to give *allyl* p-*toluate* (59%), b. p. 117—120°/11 mm. A redistilled specimen had b. p. 117°/11 mm., n_D^{20} 1·5135 (Found: C, 75·4; H, 7·1. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·9%).

Similar procedures gave *allyl* p-*anisate* (89%), b. p. 78—80°/0·03 mm., n_D^{20} 1·5354 (Found:

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[18] Goodman and Winstein, *J. Amer. Chem. Soc.*, 1957, **79**, 4788.

C, 68·8; H, 6·6. $C_{11}H_{12}O_3$ requires C, 68·7; H, 6·3%), p-*chlorobenzoate* (74%), b. p. 129—130°/14 mm., n_D^{20} 1·5360 (Found: C, 61·2; H, 4·7; Cl, 18·3. $C_{10}H_9O_2Cl$ requires C, 61·1; H, 4·6; Cl, 18·0%), and 2 : 4-*dichlorobenzoate* (86%), b. p. 143—144°/14 mm., n_D^{19} 1·5533 (Found: C, 51·5; H, 3·4; Cl, 31·0. $C_{10}H_8O_2Cl_2$ requires C, 52·0; H, 3·5; Cl, 30·7%).

Addition of Bromine to Allyl Esters.—(a) *To allyl* p-*anisate.* Bromine (14·5 g.) in dry chloroform (20 ml.) was added dropwise to a stirred solution of allyl *p*-anisate (17·4 g.) in chloroform (35 ml.). When decolorisation was complete (30 min.) the solution was washed with sodium hydrogen carbonate solution, then with water, dried, and evaporated under reduced pressure. The residual oil was rubbed with several portions of methanol to leave 2-bromo-1-bromomethylethyl *p*-anisate (10·1 g., 32%), m. p. 90—93° raised to 94—96° by crystallisation from hot methanol and not depressed by admixture with an authentic specimen. From the mother-liquors there was recovered 2 : 3-dibromopropyl *p*-anisate (14·4 g., 45%), m. p. 32—33° raised to 38—39° by crystallisation from methanol below room temperature and not depressed by admixture with an authentic specimen.

TABLE 1.

Ester	Yield (%)	Form	M. p.	Formula	Found (%) C	Found (%) H	Required (%) C	Required (%) H
			2 : 3-*Dibromopropyl esters.*					
Benzoate	76	Rods	33—34°	$C_{10}H_{10}O_2Br_2$	37·8	3·4	37·3	3·1
p-*Toluate*	81	Needles	29—30	$C_{11}H_{12}O_2Br_2$	39·4	3·4	39·3	3·6
p-*Anisate*	78	Plates	38—39	$C_{11}H_{12}O_3Br_2$	37·5	3·5	37·5	3·4
o-*Chlorobenzoate*	79	Plates	32—33	$C_{10}H_9O_2Br_2Cl$	33·4	2·5	33·7	2·6
p-*Chlorobenzoate*	71	Prisms	30—31	$C_{10}H_9O_2Br_2Cl$	33·9	2·9	33·7	2·6
2 : 4-*Dichlorobenzoate*	67	Rhombs	39—40	$C_{10}H_8O_2Br_2Cl_2$	30·7	2·4	30·7	2·1
p-Cyanobenzoate	64	Prisms	78—79 *	$C_{11}H_9O_2NBr_2$	38·3	2·9	38·1	2·6
p-Nitrobenzoate †	57	Plates	53—54	$C_{10}H_9O_4NBr_2$	32·8	2·4	32·7	2·5
3 : 5-Dinitrobenzoate †	70	Plates	84—85	$C_{10}H_8O_6N_2Br_2$	29·5	2·3	29·2	2·0
			2-*Bromo*-1-*bromomethylethyl esters.*					
Benzoate	62	Plates	32—33	$C_{10}H_{10}O_2Br_2$	37·6	3·2	37·3	3·1
p-*Toluate*	59	Plates	41—42	$C_{11}H_{12}O_2Br_2$	39·6	3·9	39·3	3·6
p-*Anisate*	66	Plates	95—96	$C_{11}H_{12}O_3Br_2$	37·8	3·5	37·5	3·4
o-*Chlorobenzoate*	60	Rods	39—40	$C_{10}H_9O_2Br_2Cl$	33·9	2·9	33·7	2·6
p-*Chlorobenzoate*	83	Needles	107—108	$C_{10}H_9O_2Br_2Cl$	33·4	2·7	33·7	2·6
2 : 4-*Dichlorobenzoate*	68	Needles	73—75	$C_{10}H_8O_2Br_2Cl_2$	30·3	2·4	30·7	2·1
p-*Cyanobenzoate*	53	Needles	80—81	$C_{11}H_9O_2NBr_2$	38·3	3·0	38·1	2·6
p-Nitrobenzoate ‡	54	Needles	78—79	$C_{10}H_9O_4NBr_2$	32·6	2·6	32·7	2·5
3 : 5-*Dinitrobenzoate*	67	Plates	139	$C_{10}H_8O_6N_2Br_2$	29·2	2·2	29·2	2·0

* Not depressed by admixture with the product obtained by Chow and Gisvold's method.[7] † Previously prepared from the allyl esters and bromine.[16] ‡ Previously prepared from 1 : 3-dibromopropan-2-ol and *p*-nitrobenzoyl chloride in quinoline.[16]

TABLE 2. *Thermal rearrangements* (*reflux for* 24 *hr.*).

Ester	Solvent	Products (%) (I)	Products (%) (III)	Ester	Solvent	Products (%) (I)	Products (%) (III)
	p-*Anisates*				p-*Chlorobenzoates*		
I	Toluene	84	7	I	Toluene	92	0
III	,,	12	77	III	,,	0	91
I	Xylene	47	39	I	Xylene	66	24
I	,, *	42	38	III	,,	32	56
III	,,	45	41	I	,, †	47	42
III	,, *	44	40	III	,, †	44	41
				I	AcOH	20	26
				III	AcOH	13	34

* Stirred with $CaCO_3$ (5 g.). † 72 hr.

(b) *To allyl* p-*chlorobenzoate.* When bromine (17·5 g.) in chloroform (20 ml.) was added dropwise to allyl *p*-chlorobenzoate (21·5 g.) in chloroform (40 ml.) decolorisation was complete in 80 min. Working up as in (a) gave an oil which, when rubbed with methanol (100 ml.), slowly gave a white solid (4·67 g.), m. p. 99—103°. Concentrating and cooling the filtrate gave several further crops of low-melting solid (29·5 g. in all). The latter were combined and treated with methanol (160 ml.) whereupon the greater part dissolved, but a small residue was further crystallised from hot methanol to give 0·78 g. of material, m. p. 105—107°. The more soluble principal component, recovered from the mother-liquor, had m. p. 29—31° and crystallised from methanol below room temperature in prisms, m. p. 30—31°, not depressed by admixture with authentic 2 : 3-dibromopropyl *p*-chlorobenzoate. The combined crops (5·45 g., 14%) of the less soluble and higher-melting product were further crystallised from hot methanol to give the pure isomer, m. p. and mixed m. p. 107—108°.

(c) *To allyl* 2 : 4-*dichlorobenzoate.* Bromine (8·8 g.) in chloroform (20 ml.), added dropwise to allyl 2 : 4-dichlorobenzoate (12·6 g.) in chloroform (70 ml.), was decolorised in 6 hr. The crude oil, obtained as in (a), on treatment with cold methanol gave 2 : 3-dibromopropyl 2 : 4-dichlorobenzoate (13·5 g.), m. p. 38—39°. Recrystallised from methanol it had m. p. and mixed m. p. 39—40°.

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