124. *Alkyl–Oxygen Fission in Carboxylic Esters. Part II. Derivatives of* p-*Methoxybenzhydrol.*

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p-Methoxybenzhydrol, its esters, and ethers undergo a remarkable variety of interconversions when treated with various carboxylic acids or alcohols in excess. Many of its derivatives in which an alkyl–oxygen bond is present give *p*-methoxybenzhydryl chloride when triturated with cold concentrated hydrochloric acid. That alkyl–oxygen fission takes place in these reactions is demonstrated either by the constitution of the products or by the occurrence of racemisation when the reacting compound is optically active.

Alkyl–oxygen fission is also involved in two new reactions of *p*-methoxybenzhydryl hydrogen phthalate. One is the formation of p-*tolyl*-p-*methoxybenzhydrylsulphone* when sodium *p*-toluenesulphinate is added to an aqueous solution of sodium *p*-methoxybenzhydryl phthalate. The second is the separation of the neutral ester from a solution of the hydrogen phthalate in an equimolecular proportion of aqueous sodium hydroxide. It is suggested that the initial stage in both these reactions is ionic alkyl–oxygen fission of the hydrogen phthalate, with racemisation of the resulting *p*-methoxybenzhydryl kation, which then undergoes reaction to give the products in question. Some aspects of the mechanism of the formation of the neutral ester, however, remain obscure.

The preparation of (+)-*p*-methoxybenzhydrol is described.

ALKYL–OXYGEN fission, which is facilitated by increase in the electron-releasing properties of the alkyl group,* can be observed in derivatives of phenylmethylcarbinol and even more readily in those of anisylmethylcarbinol (a communication on these experiments is in preparation); in derivatives of *p*-methoxybenzhydrol it occurs with great ease.

The tendency towards racemisation during the alkaline hydrolysis of hydrogen phthalic esters of some types of optically active alcohols affords an indication of the readiness of esters of these alcohols to react by alkyl–oxygen fission. Some racemisation occurs when dilute alkali is used for hydrolysis of esters of substituted allyl alcohols (Part I, this vol., p. 556), but retention of optical purity is complete (acyl–oxygen fission) when 5N-aqueous sodium hydroxide is employed.

The hydrolysis of (+)-p-*methoxybenzhydryl hydrogen phthalate* even by 10N-aqueous sodium hydroxide results in extensive racemisation; the alcohol of highest rotatory power was obtained when hydrolysis was carried out in ethyl alcohol containing about 2% of water. When the solvent contains 20% of water the hydrolysis is accompanied by much racemisation. The rotatory powers of (+)-*p*-methoxybenzhydrol and its hydrogen phthalate are given in Table I.

TABLE I.

Specific rotatory powers of p-*methoxybenzhydrol and its hydrogen phthalate* (l = 2).

Substance.	Solvent.	*c*, %.	Temp.	$[\alpha]_{6438}$.	$[\alpha]_{5893}$.	$[\alpha]_{5780}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.
Hydrol	CS_2	2·420	13·5°	+38·2°	+47·85°	+49·1°	+59·0°	+120·7°
Acid ester	C_6H_6	2·487	17	+42·5	+52·3	+52·7	+61·9	+119·7
	$CHCl_3$	2·055	18·5	+31·6	+37·0	+35·0	+43·1	+ 78·4
	CH_3OH	2·500	17	—	+28·0	—	—	—
	CS_2	0·340	19	+62·7	+71·2	—	—	—

The ease with which alkyl–oxygen fission occurs in *p*-methoxybenzhydrol and its derivatives is indicated by the readiness of formation of *p*-methoxybenzhydryl chloride, on trituration with cold concentrated hydrochloric acid, not only from the alcohol but also from its esters and ethers. The (+)alcohol and the (−)hydrogen phthalate give the *dl*-chloride, which has also been obtained by this method from the dl-*acetate*, -*benzoate*, and -*methyl ether* and from *dl*-*p*-methoxybenzhydryl ether. The *dl*-chloride is also obtained by the action of acetyl chloride, at room temperature or on gentle warming, on (+)-*p*-methoxybenzhydrol, *dl*-*p*-methoxybenzhydryl acetate, and *dl*-*p*-methoxybenzhydryl ether; these reactions all involve alkyl–oxygen fission.

The reaction of the alcohol with acetyl chloride is a notable example of its tendency to undergo alkyl–oxygen fission, the carbonium kation combining with anionic chlorine. In the more common type of reaction—

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* The experiments of Chattaway (J., 1936, 355) form an interesting contrast with those described in the present series of papers. Whereas esters of, *e.g.*, aliphatic alcohols react with ammonia to give the acid amide and the alcohol, Chattaway found that γγγ-trichloro-α-nitro-β-acetoxypropane on treatment with ammonia yields ammonium acetate and γγγ-trichloro-α-nitro-β-aminopropane. The α- and γ-electron-attracting substituents impose so strong a positive charge on the carbinol carbon atom that the unshared electrons of the nitrogen atom in the ammonia are attracted to this carbon atom rather than to the >C=O carbon atom of the acid residue. This mechanism involves alkyl–oxygen fission, but not by the unimolecular mechanism, involving racemisation, which characterises the reactions which we are now discussing. A bimolecular mechanism, involving inversion of configuration, if the carbinol carbon atom were optically active, seems more probable.

acetylation—a proton is separated from an alkoxy-residue and the carbon–oxygen bond is not disturbed. *p*-Methoxybenzhydrol reacts with acetyl chloride by the latter mechanism in the presence of pyridine, yielding the acetate, which indicates that, as suggested by Gerrard (J., 1940, 218), the function of the pyridine in such reactions is to promote removal of the proton from the hydroxyl group, rather than to cause ionic fission of the acid chloride.

The chloride itself undergoes typical reactions of halides with unusual readiness. At room temperature water affords *p*-methoxybenzhydryl ether and a small proportion of the alcohol, sodium hydroxide gives the alcohol, potassium hydrogen phthalate gives the hydrogen phthalic ester, and the hydrol in presence of pyridine yields *p*-methoxybenzhydryl ether. Optically active *p*-methoxybenzhydryl chloride could not be prepared, presumably because of the lability of the chlorine atom. Treatment of the (+)alcohol with thionyl chloride and pyridine, one of the most reliable procedures for preparing optically active chlorides from secondary alcohols, gives a racemic chloride in this case.

(—)-*p*-Methoxybenzhydryl hydrogen phthalate on warming with methyl alcohol yields readily and quantitatively *dl*-*p*-methoxybenzhydryl methyl ether: the racemisation is clear evidence that alkyl–oxygen fission occurs. *dl*-*p*-Methoxybenzhydrol and its normal phthalate also yield the methyl ether on heating with methyl alcohol, presumably by the same mechanism. Similarly, the methyl ether and the benzoate of *dl*-*p*-methoxybenzhydrol yield the acetate when warmed with glacial acetic acid. On the other hand, *p*-methoxybenzhydryl ether does not react when heated with acetic acid or acetic anhydride.

The reactions of *p*-methoxybenzhydryl esters and ethers have not been exhaustively studied, but the examples given above indicate that almost any one of these may be converted into another by treatment with an excess of the appropriate reagent. The alkyl–oxygen bond is so weak that the course of the reactions is controlled by the relative concentrations of the reactants and by phase considerations (separation of insoluble products) rather than by considerations of bond strength.

Optically active *p*-methoxybenzhydrol becomes racemised, without undergoing chemical decomposition, when heated in water, a result which again indicates alkyl–oxygen fission. Its combination with phthalic anhydride in the presence of pyridine—no combination occurs in its absence—results in little, if any, racemisation, indicating that this reaction occurs by the mechanism corresponding to acyl–oxygen fission. The hydrogen phthalate of optically active *p*-methoxybenzhydrol, like that of αγ-dimethylallyl alcohol (Part I, *loc. cit.*), undergoes racemisation in solvents with which it reacts (acetic acid and methyl alcohol) and in nitromethane solution, and also in solution in benzene in which the hydrogen phthalate of αγ-dimethylallyl alcohol is optically stable.

Sodium (—)-*p*-methoxybenzhydryl phthalate reacts in aqueous solution with sodium *p*-toluenesulphinate, yielding dl-p-*tolyl*-p-*methoxybenzhydrylsulphone*. The carbon–sulphur is stronger than the carbon–oxygen bond, and the sulphone can be recovered unchanged from hot glacial acetic acid or after heating with concentrated hydrochloric acid. The irreversible formation of the carbon–sulphur bond appears to be the underlying cause of the formation of the sulphone, since from sodium *p*-methoxybenzhydryl phthalate and sodium benzoate (1 mol.) in aqueous solution the neutral phthalic ester (see below) and not *p*-methoxybenzhydryl benzoate is formed. In the reaction with sodium benzoate an equilibrium presumably exists between the hydrogen phthalate and the benzoate of *p*-methoxybenzhydrol.

The reaction with sodium *p*-toluenesulphinate (1 mol.) appears to be characteristic of esters which undergo alkyl–oxygen fission very readily. *Sulphones* are also obtained under these conditions from the hydrogen phthalates of anisylmethylcarbinol and of benzhydrol but not from those of αγ-dimethylallyl alcohol or phenylmethylcarbinol, though both the latter compounds undergo this type of fission in certain circumstances. The hydrogen phthalates of the *tert.*-alcohol phenylmethylethylcarbinol or of octan-2-ol also do not yield sulphones by this method, nor does the methyl ether of *p*-methoxybenzhydrol on heating under reflux in methyl-alcoholic solution with sodium *p*-toluenesulphinate.

In unpublished experiments with anisylmethylcarbinol, Dr. K. Nandi observed that its hydrogen phthalate, on treatment with dilute aqueous alkali, gave the neutral phthalate. Similar observations have been made with (+)-*p*-methoxybenzhydryl hydrogen phthalate: when this ester is dissolved in 0·15N-sodium hydroxide (1 mol.), separation of an oil begins within a few minutes and is complete after 18 hours, the aqueous solution containing only sodium phthalate. The oil can be separated into *p*-methoxybenzhydrol of low dextrorotation and dextrorotatory di-*p*-methoxybenzhydryl phthalate. Hydrolysis of this neutral ester with alcoholic sodium hydroxide gives dextrorotatory *p*-methoxybenzhydrol with approximately half the rotatory power of the optically pure alcohol. From a solution of (+)-*p*-methoxybenzhydryl hydrogen phthalate and potassium hydrogen phthalate (5 mols.) in 0·3N-sodium hydroxide (1 mol.), a similar oil separates, but in this case both the alcohol and the neutral ester isolated from it are optically inactive.

Our interpretation of these results is that, in the absence of added anions, ionic fission of the acid phthalate ion produces a racemised *p*-methoxybenzhydryl kation. This combines with a second *p*-methoxybenzhydryl phthalate anion to yield the neutral ester, which is insoluble in the aqueous medium. The neutral ester contains one *p*-methoxybenzhydryl radical which has been racemised during its migration, and one which, not having been detached from the phthalate radical, retains its optical purity. Therefore, the alcohol obtained by hydrolysis of the neutral ester possesses half the maximum rotatory power of (+)-*p*-methoxybenzhydrol. Along with the neutral ester some almost racemic alcohol is deposited, formed by interaction of *p*-methoxybenzhydryl kations with hydroxyl ions or water molecules of the solvent. (It appears that the neutral ester continues to change after its deposition because, when it is left in contact with the supernatant aqueous layer for 12 days before being separated, the proportion of free alcohol present increases, while the alcohol obtained by hydrolysis of the ester is optically inactive.) When phthalate ions are present in excess, most of the liberated kations combine with them to yield racemic *p*-methoxybenzhydryl hydrogen phthalate. From this in turn a neutral ester is slowly formed which on hydrolysis yields a racemic alcohol because both its *p*-methoxybenzhydryl radicals have been through a phase of ionic fission involving their racemisation.

It appears that the formation of the neutral ester is a rapid process. When the hydrogen phthalate is dissolved in aqueous sodium hydroxide (1 mol.) as described above, and the solution kept for 10 minutes before sodium *p*-toluenesulphinate is added, very little sulphone (which is the major product when phthalate and sulphinate solutions are mixed immediately) is formed, the bulk of the acid ester being in this case converted into the neutral ester. The mechanism of formation of the neutral ester is, however, not completely elucidated. The explanation suggested above implies that it involves an intermolecular rearrangement and is supported by the formation of *p*-tolyl-*p*-methoxybenzhydrylsulphone when sodium *p*-toluenesulphinate is added to a freshly prepared solution of the hydrogen phthalic ester in aqueous sodium hydroxide (1 mol.).

However, when the rearrangement occurs in the presence of an excess of octyl hydrogen phthalate (even when the octyl and the *p*-methoxybenzhydryl hydrogen phthalates are dissolved together in the aqueous alkali), the octyl ester does not take part in the reaction and is recovered unchanged from the solution. The product of the reaction is di-*p*-methoxybenzhydryl phthalate, a result which would appear to be inconsistent with an intermolecular mechanism, and on hydrolysis it yields racemic *p*-methoxybenzhydrol, in contrast to the production of a partially active alcohol when the reaction is carried out in the absence of octyl hydrogen phthalate, as described above.

Further, the hydrogen phthalates of phenylmethylcarbinol, γ-phenyl-α-methylallyl alcohol, and benzhydrol when dissolved in equimolecular proportions of aqueous sodium hydroxide remain unchanged; when the solutions are heated, the corresponding alcohols are liberated. On the other hand, all three hydrogen phthalates are known to be capable of undergoing reactions involving alkyl–oxygen fission. The tendency to this type of reaction is greater in derivatives of *p*-methoxybenzhydrol, but it is not obvious how, on this fact alone, an explanation of the complete absence of neutral ester formation from the less reactive hydrogen phthalic esters can be based.

EXPERIMENTAL.

p-Methoxybenzhydrol was prepared by the addition during 6 hours of an ethereal solution of anisaldehyde (122 g., 0·9 mol.) to a Grignard reagent (prepared from bromobenzene, 157 g.), cooling in ice, and decomposing the solid addition compound with ice and ammonium chloride. The dried ethereal extract, evaporated below 60° to small bulk and diluted with light petroleum, deposited the carbinol (150 g.; 78%) in bulky masses of short needles, m. p. 63—65°. After recrystallisation from ether–light petroleum, it separated in rosettes of transparent, prismatic rods, m. p. 66—67° (Adams, Wirth, and French, *J. Amer. Chem. Soc.*, 1918, **40**, 430, give m. p. 68°). In acetic acid solution, chromic acid smoothly oxidised it to *p*-methoxybenzophenone, glassy, prismatic rods, m. p. 61—62°.

dl-p-*Methoxybenzhydryl Hydrogen Phthalate.*—A mixture of the alcohol (10·7 g.), phthalic anhydride (7·5 g.), and pyridine (7 g.) was kept at 55—60° for 4—5 hours. The resulting viscous liquid was diluted with an equal volume of acetone and decomposed with a slight excess of cold dilute hydrochloric acid; the precipitated pasty solid rapidly hardened, and after an hour the resulting crystalline acid *ester* was collected and dried (18·0 g.), m. p. 98—99°. It separated from carbon disulphide in bulky masses of short needles, m. p. 102—103° (decomp.) (Found, on rapid titration with 0·1N-NaOH : *M*, 365. $C_{22}H_{18}O_5$ requires *M*, 362).

Equimolecular amounts of the carbinol (5·3 g.) and phthalic anhydride (3·7 g.) were kept at 120—130° for 4 hours, during which phthalic acid (0·6 g.) separated. No acid phthalic ester was formed under these conditions; the only compound, other than unchanged material, to be isolated was *p*-methoxybenzhydryl ether.

(+)-p-*Methoxybenzhydryl Hydrogen Phthalate.*—A solution of the *dl*-ester (143 g.) and cinchonidine (96·6 g.) in acetone (250 c.c.) after standing overnight deposited the cinchonidine salt of the dextrorotatory hydrogen phthalate. This, after three recrystallisations from ethyl acetate, yielded cinchonidine (+)-*p*-methoxybenzhydryl phthalate (87 g.), bulky clusters of short needles, m. p. 143—144° (decomp.). This salt, mixed with about twice its weight of acetone, was then decomposed with cold dilute hydrochloric acid, and the resulting (+)-p-*methoxybenzhydryl hydrogen phthalate* precipitated by addition of water. It separates from carbon disulphide in bulky clusters of short needles, m. p. 103—103·5° (Found, by rapid titration with 0·1N-NaOH : *M*, 365). Rotatory powers are in Table I.

(+)-p-*Methoxybenzhydrol.*—To a solution of the (+)acid ester (1·81 g.) in cold absolute ethanol (100 c.c.) was added sodium hydroxide (0·9 c.c. of 50%), and the whole heated rapidly on the steam-bath; after 3 mins. a bulky precipitate of sodium hydrogen phthalate had separated. Addition of water resulted in a clear solution from which, on dilution with 3 vols. of water, (+)-*p*-methoxybenzhydrol separated in bulky masses of long, hairy needles (1·05 g.), m. p. 58—59°. Rotatory powers are in Table I. Unless the water content of the alcoholic sodium hydroxide is kept low, racemisation occurs; *e.g.*, in a similar experiment where 10 c.c. of absolute alcohol and 2·5 c.c. of 5N-sodium hydroxide were employed, the resulting *p*-methoxybenzhydrol had only $[\alpha]_{5893}$ +9·4° in carbon disulphide solution.

Hydrolysis of (−)-p-*Methoxybenzhydryl Hydrogen Phthalate with Concentrated Aqueous Sodium Hydroxide.*—The ester (5·4 g., $[\alpha]_{5893}$ −10·2° in benzene) was triturated with sodium hydroxide solution (30 c.c. of 5N); a pasty solid separated which was largely the carbinol, since it dissolved readily in cold methyl alcohol (in which the neutral ester is but sparingly soluble). It was freed from traces of neutral ester by heating the methyl-alcoholic solution after adding a few drops of 50% aqueous sodium hydroxide. The resulting (−)-*p*-methoxybenzhydrol, m. p. 58—61°, had $[\alpha]_{5893}$ −5·5° in carbon disulphide. A second specimen of the hydrogen phthalate ($[\alpha]_{5893}$ −11·6°) was hydrolysed in alcoholic solution (60 c.c.) containing sodium hydroxide (8 c.c. of 5N). The resulting (−)-*p*-methoxybenzhydrol (3·1 g., m. p. 60—62°) had $[\alpha]_{5893}$ −10·4° in carbon disulphide.

A comparison of these two results suggests that the production of the alcohol in concentrated aqueous alkali is the result of two consecutive reactions : (i) conversion of the acid phthalate into the half racemised neutral phthalate; (ii) rapid hydrolysis of the latter.

When 1·8 g. of the (+)phthalate were hydrolysed with 2·5 c.c. of 5N-sodium hydroxide in 10 c.c. of 98% ethyl alcohol, the resulting *p*-methoxybenzhydrol had $[\alpha]^{18°}_{5893}$ +9·4° (*c*, 2·5; *l*, 2) in carbon disulphide solution.

Conversion of (+)-p-*Methoxybenzhydrol into its* (+)*Hydrogen Phthalate.*—The hydrol (0·8 g.; $[\alpha]_{5893}$ +46·8° in carbon disulphide) obtained by hydrolysis in alcoholic solution of its hydrogen phthalate ($[\alpha]_{5893}$ +44·5° in benzene) was heated with phthalic anhydride (0·57 g.) and pyridine (0·6 g.) for an hour at 50—60°. The resulting *p*-methoxybenzhydryl hydrogen phthalate (0·8 g.) had $[\alpha]_{5893}$ +38·4° in benzene solution.

Racemisation of (+)-p-*Methoxybenzhydrol in Hot Aqueous Solution.*—The hydrol (0·56 g.; $[\alpha]_{5893}$ +17·4° in carbon disulphide) was heated with distilled water (750 c.c.) on the steam-bath, and its rotatory power determined at intervals:

Time of heating, hrs.	0	0·5	10	30
$[\alpha]_{5893}$ in CS_2	+17·4°	14·2°	7·0°	0·00°

The resulting *dl*-*p*-methoxybenzhydrol melted sharply at 65—66°. In a separate experiment the *dl*-alcohol (1 g.) was heated with distilled water (500 c.c.) on the steam-bath for over 100 hours, but was recovered unchanged, m. p. 66°.

Racemisation of (+)-p-*Methoxybenzhydryl Hydrogen Phthalate in Various Solvents at Room Temperature.*—A specimen of the ester had $[\alpha]_{5893}$ +44·5° (*c*, 1·75; *l*, 2) in absolute ethyl alcohol immediately after dissolution; the solution was optically inactive when examined 2 months later. Another specimen of the ester ($[\alpha]_{5893}$ −15·7° in benzene) had $[\alpha]_{5893}$ −2·8° (*c*, 1·0; *l*, 2) in glacial acetic acid when freshly dissolved; after 24 hours the solution was optically inactive. Other observations are given in Table II. From all the solutions referred to in this paragraph phthalic acid was eventually deposited.

TABLE II.

Solvent (*l*, 2) *c* (g./100 c.c.)	Methyl alcohol. 2·50				Nitromethane. 1·3		Benzene. 2·55			
	Time, hrs.	$[\alpha]_{5893}$.	Time, hrs.	$[\alpha]_{5893}$.	Time hrs.	$[\alpha]_{5893}$.	Time, hrs.	$[\alpha]_{5893}$.	Time, hrs.	$[\alpha]_{5893}$.
	0	+28·0°	169	3·4°	0	+17·7°	0	+38·4°	216	14·0°
	24	21·8	192	2·2	2	11·5	48	35·8	264	13·4
	48	17·2	216	1·6	3	7·7	72	32·0	288	11·0
	72	13·1	240	1·1	8	4·2	96	28·2	336	8·8
	120	7·6	288	0	19	0	120	26·4	456	6·8
	144	6·0					144	22·4	528	6·4
							168	21·4	912	4·4
							192	18·4	1656	1·8

Reaction of p-*Methoxybenzhydryl Hydrogen Phthalate with Acetic Acid.*—The ester (3 g.; $[\alpha]_{5893}$ +45·4° in benzene; *c*, 2·5) was dissolved in glacial acetic acid (60 c.c.); the solution had $\alpha_{5893}^{18°}$ + 2·96° (*l*, 2). After 5 hours the solution, which then had $\alpha_{5893}^{18°}$ +1·47° (*l*, 2), was poured into water, and the oil which separated was extracted with ether. Extraction of the ethereal solution with dilute ammonia yielded the hydrogen phthalate (1·3 g.) with $[\alpha]_{5893}$ +35·0° (*c*, 4·88; *l*, 2) in benzene. Evaporation of the washed ethereal solution yielded *p*-methoxybenzhydryl acetate (0·5 g.), b. p. 190—195°/20 mm.

p-*Methoxybenzhydryl Chloride.*—A. *Preparation by means of concentrated aqueous hydrochloric acid.* (i) From *dl*-*p*-methoxybenzhydrol. The *dl*-alcohol (2 g.), triturated with hydrochloric acid (10 c.c.), rapidly changed into a liquid which, in turn, soon set to a crystalline powder; this was filtered off, washed with hydrochloric acid, and dried in a vacuum over quicklime (2 g., m. p. 59—60°). Recrystallisation from light petroleum gave *dl*-*p*-methoxybenzhydryl chloride in bulky clusters of soft, long needles, m. p. 62—63°. When 0·2708 g., dissolved in alcohol (10 c.c.), was warmed for a few minutes with an excess of 0·1N-sodium hydroxide, it neutralised 11·65 c.c. of the alkali (Equiv., 232. Calc.: 232·5) (Bartlett and Nebel, *J. Amer. Chem. Soc.*, 1940, **62**, 1345, who prepared this compound by the action of hydrogen chloride on the alcohol, give m. p. 62—63°).

(ii) From (+)-*p*-methoxybenzhydrol. A specimen of the (+)alcohol (0·50 g.; $[\alpha]_{5893}$ +17·4° in carbon disulphide) was triturated with hydrochloric acid (5 c.c.) as described in (i); the resulting chloride (0·54 g.) without further crystallisation had m. p. 62—63° and was optically inactive in carbon disulphide solution (*c*, 2·5; *l*, 2).

(iii) From *dl*-*p*-methoxybenzhydryl hydrogen phthalate. When the *dl*-ester (3·62 g.) was triturated with hydrochloric acid (10 c.c.) its crystalline character underwent an immediate change and the temperature of the mixture rose slightly. After 10 mins.' trituration the solid (3·95 g.) was filtered off, washed with hydrochloric acid, and dried. It was separated by extraction with boiling light petroleum into phthalic acid (1·60 g.; calc., 1·66 g.) and *p*-methoxybenzhydryl chloride (m. p. 62—63°; 2·20 g.; calc., 2·32 g.).

(iv) From (−)-*p*-methoxybenzhydryl hydrogen phthalate. A specimen of the (−)ester (1·81 g., $[\alpha]_{5893}$ −18·2° in benzene), treated with hydrochloric acid (5 c.c.) as in (iii), yielded phthalic acid (0·81 g.) and *dl*-p-methoxybenzhydryl chloride (m. p. 61—62°, 1·10 g.) which was optically inactive in carbon disulphide solution (*c*, 2·5; *l*, 2).

(v) From *dl*-*p*-methoxybenzhydryl acetate. The acetate (0·5 g.), triturated with hydrochloric acid (2 c.c.), gradually changed into a crystalline solid, m. p. 57—59°. This separated from light petroleum in bulky clusters of fine needles (0·3 g.), m. p. 62—63° alone or when mixed with authentic *p*-methoxybenzhydryl chloride.

(vi) From *dl*-*p*-methoxybenzhydryl ether of m. p. 120°. The finely powdered ether (1·00 g.) was triturated with hydrochloric acid (6 c.c.), and the mixture warmed to about 50° for a few minutes until the crystals melted. On cooling, the molten liquid set at once to a hard crystalline mass (1·15 g.; calc., 1·16 g.); after being powdered and dried, it had m. p. 62—63° alone or mixed with an authentic specimen of *p*-methoxybenzhydryl chloride. This reaction proceeds immediately at room temperature, but unless the reaction product is warmed the crystals of ether become coated with a protecting layer of *p*-methoxybenzhydryl chloride.

(vii) From *p*-methoxybenzhydryl methyl ether. This ether (0·4 g.) was triturated in concentrated hydrochloric acid (2 c.c.). An oil formed which rapidly solidified. This chloride (0·35 g.) separated from light petroleum in needles, m. p. 61—62°; mixed m. p. 62—63°.

(viii) From *p*-methoxybenzhydryl benzoate. The ester (1 g.) was triturated with concentrated hydrochloric acid (1 c.c.). The dried product (1·1 g.) separated from light petroleum in small needles, m. p. 60—61°; mixed m. p. with an authentic specimen of *p*-methoxybenzhydryl chloride, 62—63°. Benzoic acid was recovered from the light petroleum filtrates.

B. *Preparation by means of acetyl chloride.* (i) From *dl*-*p*-methoxybenzhydrol. The *dl*-alcohol (1·0 g.) dissolved readily in acetyl chloride (1 c.c.) with some evolution of heat, but not of hydrogen chloride, and the solution rapidly became semi-solid. The product, after standing overnight in an evacuated desiccator containing sodium hydroxide, had m. p. 60—61° and separated from light petroleum in needles, m. p. 62—63° (1·0 g.) alone or mixed with authentic *p*-methoxybenzhydryl chloride. It is clear that no significant amount of acetylation had occurred.

(ii) From (+)-*p*-methoxybenzhydrol. When experiment (i) was repeated upon a carbinol (0·5 g.) with $[\alpha]_{5893}$ +17·4°

in carbon disulphide, the resulting *dl-p*-methoxybenzhydryl chloride (0·55 g.) was optically inactive in carbon disulphide solution (*c*, 2·5; *l*, 2).

(iii) From *dl-p*-methoxybenzhydryl ether. The powdered ether (1·0 g.) dissolved rapidly in warm acetyl chloride (1 c.c.) and the solution at once set to a crystalline mass. After standing in a vacuum over sodium hydroxide for 2 days the resulting dry powder was completely soluble in hot light petroleum, and separated therefrom on cooling in needles (1·0 g.), m. p. 62—63°, alone or mixed with authentic *p*-methoxybenzhydryl chloride.

(iv) From *dl-p*-methoxybenzhydryl acetate. A solution of the acetate (0·5 c.c.) in cold acetyl chloride (1 c.c.) was placed in a desiccator containing sodium hydroxide. Next day, the solid residue was crystallised from light petroleum, needles (0·3 g.), m. p. 62—63°, of *p*-methoxybenzhydryl chloride being obtained.

C. *Preparation by means of thionyl chloride and pyridine.* Thionyl chloride (0·65 g.) was added slowly to an ice-cold solution of *p*-methoxybenzhydrol (1·07 g., $[\alpha]_{5893}$ +29·0° in carbon disulphide) in pyridine (0·40 g.). After a vigorous reaction, the whole set solid within 5 minutes. Extraction with warm, light petroleum removed the chloride. The first crop (m. p. 60—61°; 0·12 g.) was optically inactive in carbon disulphide (*c*, 2·40; *l*, 1).

Reactions of dl-p-*Methoxybenzhydryl Chloride.*—(i) *With cold water.* A solution of the chloride (0·8 g.) in ether (25 c.c.) was shaken with water three times: the first two washings were acid to Congo-red but the third was not. The dried ethereal solution deposited glassy rhombs of *p*-methoxybenzhydryl ether (0·5 g.), m. p. 119—120°; a small second crop (needles, m. p. 55—60°) consisted probably of *p*-methoxybenzhydrol mixed with traces of the ether.

(ii) *With sodium hydroxide.* Sodium hydroxide (2 c.c. of 3N) was added to a solution of the chloride (0·8 g.) in acetone (5 c.c.). After an hour, addition of water precipitated an oil which rapidly set to a mass of crystalline plates. These (0·7 g.) had m. p. 65—66°, alone or mixed with authentic *p*-methoxybenzhydrol.

(iii) *With potassium hydrogen phthalate.* The finely powdered salt (1·02 g.) was added to a solution of *p*-methoxybenzhydryl chloride (1·17 g.) in dry acetone (15 c.c.), and the gently warmed suspension triturated at intervals during 3 hours. The reaction mixture was diluted with water, extracted with ether, and the ethereal solution extracted with dilute ammonia. Addition of hydrochloric acid to the alkaline extract precipitated *p*-methoxybenzhydryl hydrogen phthalate as a fine crystalline powder (1·1 g.), m. p. 98—99° alone or mixed with a specimen prepared directly from the alcohol.

(iv) *With* dl-p-*methoxybenzhydrol.* A few drops of pyridine were added to a solution of *p*-methoxybenzhydryl chloride (0·23 g.) and *p*-methoxybenzhydrol (0·21 g.) in dry ether. Next day the solution was washed with dilute acid, dried, and evaporated. Crystallisation of the residue from acetone yielded *p*-methoxybenzhydryl ether (0·3 g.) in glassy rhombs, m. p. 119—120°.

Preparation of dl-p-*Methoxybenzhydryl Acetate.*—(i) A mixture of the *dl*-alcohol (5·3 g.), acetic anhydride (3 g.), and pyridine (2 g.), after standing for 2 days at room temperature, was dissolved in ether, and the solution washed successively with dilute acid, sodium carbonate, and water. The resulting dl-p-*methoxybenzhydryl acetate* (5 c.c.) had b. p. 182—183°/4 mm. (0·3548 G. on hydrolysis with 0·1N-sodium hydroxide, neutralised 13·90 c.c. $C_{16}H_{16}O_3$ requires 13·85 c.c.). It showed no tendency to crystallise when kept in a refrigerator for several weeks.

(ii) Acetyl chloride (2 g.) was added dropwise to a mixture of the *dl*-alcohol (5·3 g.) and pyridine (2 g.) cooled in ice, and the mixture warmed for 30 minutes. The product was decomposed with ice, extracted with ether, and washed as before; b. p. 168—170°/2 mm., $n_D^{10^\circ}$ 1·5649.

(iii) A mixture of the *dl*-alcohol (4 g.) and acetic anhydride (2 g.) was heated on the steam-bath for 3 hours and worked up. The main product had b. p. 172—173/3 mm., $n_D^{10^\circ}$ 1·5672. An undistilled residue (about 1 g.) separated from methyl alcohol in small rhombs (0·5 g.), m. p. 119—120° alone or mixed with *p*-methoxybenzhydryl ether.

(iv) *dl-p*-Methoxybenzhydrol (3 g.) in acetic anhydride (10 c.c.) was heated for 3 hours on a steam-bath. Direct distillation gave the acetate (3 c.c.), b. p. 185—186°/5 mm., $n_D^{10^\circ}$ 1·5640.

(v) A solution of (+)-*p*-methoxybenzhydrol in acetic acid after being heated on the steam-bath for 5 hours was optically inactive.

(vi) A solution of *dl-p*-methoxybenzhydryl methyl ether (2 g.) in glacial acetic acid (30 c.c.) was heated for 6 hours, and the acetic acid distilled off. The residue had b. p. 210°/20 mm. (1·5 g.) and was shown to be *p*-methoxybenzhydryl acetate by hydrolysis to sodium acetate and *p*-methoxybenzhydrol (1·1 g.), m. p. 64—65°.

p-*Methoxybenzhydryl Benzoate.*—(i) Benzoyl chloride (6·4 g.) was slowly added to an ice-cold solution of *p*-methoxybenzhydrol (8·56 g.) in pyridine (4 c.c.), and the mixture warmed for 0·5 hour at 50—60°. Decomposition with ice-cold dilute hydrochloric acid gave a solid *benzoate* (8·3 g.); this separated from ethyl alcohol in clusters of small needles, m. p. 57—58° (Found: C, 79·1; H, 5·8. $C_{21}H_{18}O_3$ requires C, 79·2; H, 5·7%).

(ii) *p*-Methoxybenzhydrol (2·14 g.) was converted into its chloride and dissolved in acetone (20 c.c.). Sodium benzoate (1·44 g.) in water (10 c.c.) was added, giving an immediate precipitate of sodium chloride. After several hours, the solution was diluted, depositing an oil, which solidified on cooling. The benzoate separated from ethyl alcohol in small needles, m. p. 58° alone and when mixed with the ester from experiment (i).

p-*Methoxybenzhydryl Ether.*—Recrystallised *p*-methoxybenzhydrol (m. p. 66—67°, 4 g.) distilled at 196—198°/11 mm., leaving a residue (0·5 g.). The distillate set to a hard, crystalline mass, m. p. 67°, of unchanged carbinol. The residue, dissolved in warm ether, yielded crystalline rhombs which, after recrystallisation from ether or alcohol, formed well-defined, rhombic, glassy plates, m. p. 120°, of *p*-methoxybenzhydryl ether (Kohler and Patch, *J. Amer. Chem. Soc.*, 1916, **38**, 121, give m. p. 120°) [Found: C, 81·95; H, 6·35; OMe, 13·9; *M* (Rast), 390. Calc.: C, 81·95; H, 6·34; OMe, 15·1%; *M*, 410]. This compound is unaffected by bromine in carbon tetrachloride solution, by benzoyl chloride and pyridine, by boiling acetic anhydride, or by boiling in water or in methyl alcohol for 92 hours. When, however, the methyl alcohol contained a few drops of sulphuric acid, the ether was quantitatively converted into *p*-methoxybenzhydryl methyl ether (m. p. 26—27°) by 4 hrs.' heating.

Preparation of p-*Methoxybenzhydryl Methyl Ether.*—(i) *From* (−)-p-*methoxybenzhydryl hydrogen phthalate.* A solution of the (−)-ester (7·24 g., $[\alpha]_{5893}$ −2·4° in benzene) in dry methyl alcohol (200 c.c.) was distilled during 2·5 hrs. The residue was separated into phthalic acid (3·3 g.; calc., 3·32 g.) and p-*methoxybenzhydryl methyl ether* (4 c.c.), b. p. 195°/17 mm., m. p. 28—29°. The latter separates from ether–light petroleum in glassy tablets, m. p. 29°. It was optically inactive both in the homogeneous state (*l*, 0·25) and in ethereal solution (*c*, 4·7; *l*, 2) (Found: C, 78·8; H, 7·0. $C_{15}H_{16}O_2$ requires C, 79·0; H, 7·0%).

(ii) *From di*-dl-p-*methoxybenzhydryl phthalate.* After standing in an open vessel for about 20 days, a solution of the ester (2·5 g.) in methyl alcohol (60 c.c.) left a residue, partly crystalline and partly oily. This was completely separated by extraction with cold petrol into phthalic acid and the very soluble *p*-methoxybenzhydryl methyl ether; after evaporation of the solvent, the latter formed glassy, irregular rhombs, m. p. 29° alone and mixed with the specimen prepared in (i).

(iii) *From* dl-p-*methoxybenzhydrol.* A solution of the alcohol (5 g.) in dry methanol (100 c.c.) was slowly distilled during 6 hours, and the oily residue kept in a vacuum for an hour. On inoculation with *p*-methoxybenzhydryl methyl ether it rapidly set to a crystalline mass of glassy, irregular rhombs, m. p. 29° alone and when mixed with the methyl ether prepared in (i). It separated from petrol in rhombs, m. p. 29°.

o-Methoxybenzhydrol (m. p. 35°) and α-naphthylanisylcarbinol (m. p. 88°) do not react with methyl alcohol under these conditions.

Interaction of p-*Methoxybenzhydryl Chloride and Sodium* p-*Toluenesulphinate.*—Solutions of the sulphinate (1 g.) in warm water (4 c.c.) and the chloride (0·78 g.) in acetone (10 c.c.) were mixed, and sufficient acetone added to render the whole homogeneous. Sodium chloride began to separate immediately. After a few minutes water was added, and the resulting clear solution, on further dilution, deposited a crystalline precipitate. This when dried (1·2 g.; calc., 1·18 g.) had m. p. 159—160°; crystallisation from boiling alcohol (120 c.c.) afforded p-*tolyl*-p-*methoxybenzhydrylsulphone* in clusters of prismatic needles, m. p. 160° (Found : S, 8·7. $C_{21}H_{20}O_3S$ requires S, 9·1%). It was recovered unchanged after being heated for several hours on the steam-bath with glacial acetic acid or concentrated hydrochloric acid.

Interaction of (—)-p-*Methoxybenzhydryl Hydrogen Phthalate and Sodium* p-*Toluenesulphinate.*—The phthalate (1·81 g., $[\alpha]_{5893}$ —15·7° in benzene) was rapidly dissolved in sodium hydroxide (18 c.c. of 0·3N), and the solution filtered into a solution of sodium *p*-toluenesulphinate (1·1 g.) in water (25 c.c.); a bulky crystalline precipitate soon began to form, and separation appeared to be complete after some 20 mins. The dried precipitate (1·8 g.), m. p. 159—160°, was optically inactive in chloroform solution (*c*, 5; *l*, 2). It separates from ether or alcohol in clusters of prismatic needles, m. p. 160° alone or mixed with *p*-tolyl-*p*-methoxybenzhydrylsulphone prepared as described above.

If the hydrogen phthalate is dissolved in the sodium hydroxide, and the solution kept for 10 mins. before it is added to the solution of the sulphinate, only a trace of sulphone is formed, but the neutral phthalate is deposited, as in the absence of sodium *p*-toluenesulphinate.

Experiments with Hydrogen Phthalates of Other Alcohols.—Each ester (0·005 mol.) was dissolved in 0·3N-sodium hydroxide (17 c.c.) and filtered into a solution of sodium *p*-toluenesulphinate (1·07 g., 0·005 mol.) in water (15 c.c.), the mixture being left at room temperature. During 4 weeks no deposit separated in the experiments with the hydrogen phthalates of the following alcohols : *m*-methoxybenzhydrol, anisyl alcohol, phenylmethylethylcarbinol, phenylmethylcarbinol, αγ-dimethylallyl alcohol, octan-2-ol. From the hydrogen phthalate of *o*-methoxybenzhydrol, a crystalline deposit separated slowly during 6 days, whereas from that of *p*-methoxybenzhydrol the deposition is complete after 1 hour.

A solution of (—)anisylmethylcarbinyl hydrogen phthalate (3·0 g. of $[\alpha]_{5893}$ —18·0° in ethyl alcohol) in sodium hydroxide (35 c.c. of 0·3N) was filtered into a solution of sodium *p*-toluenesulphinate (2·15 g.) in water (25 c.c.). The solution rapidly turned cloudy and began to deposit a fine crystalline precipitate of p-*tolyl*-α-*anisylethylsulphone.* After a week, this was filtered off, washed, and dried. It (1·6 g.) was optically inactive in chloroform solution. It separates from alcohol as a crystalline powder, m. p. 119—120° (Found : S, 11·0. $C_{16}H_{18}O_3S$ requires S, 11·0%).

To a solution of benzhydryl hydrogen phthalate (1·66 g.) in 0·3N-sodium hydroxide (18 c.c.), sodium *p*-toluenesulphinate (1·07 g.) dissolved in water was added. The solution remained clear after 2 weeks at room temperature. It was then heated on the steam-bath for about 10 hrs. during which a crystalline precipitate (1·30 g.) separated. This p-*tolylbenzhydrylsulphone*, after two crystallisations from ethyl alcohol, had m. p. 190—191°; yield 0·9 g. (Found : S, 10·0. $C_{20}H_{18}O_2S$ requires S, 10·0%).

Action of Dilute Aqueous Sodium Hydroxide on (+)-p-*Methoxybenzhydryl Hydrogen Phthalate.*—A solution of the ester (7·24 g.) in cold sodium hydroxide (280 c.c. of 0·15N) began to turn milky after a few minutes, and after 18 hours, a layer of very viscous oil had separated. The clear supernatant liquid was decanted—a portion neutralised with hydrochloric acid gave no precipitate, showing that the hydrogen phthalate had been completely decomposed—evaporated to small bulk, and acidified; the resulting phthalic acid weighed 2·40 g. The oil was dissolved in ether, and the ethereal solution washed with water, dried, and evaporated. The residue (4·93 g.) was extracted with hot methyl alcohol (15 c.c.), and the whole rapidly cooled; the neutral ester (A) at once separated as an oil (2·73 g.). The decanted methyl-alcoholic extract, diluted with water, yielded crude *p*-methoxybenzhydrol, which was spread on porous earthenware to remove adhering oil. This (1·8 g.) was separated by several crystallisations from carbon disulphide and light petroleum into *p*-methoxybenzhydrol (1·4 g.; $[\alpha]_{5893}$ +3·4° in carbon disulphide) and the oily neutral ester (about 0·2 g.).

The viscous oil (A) had $[\alpha]_{5893}$ +23·5° in carbon disulphide (*c*, 5·0; *l*, 2); it (2·40 g.) was dissolved in warm absolute alcohol, mixed with sodium hydroxide (1 c.c. of 50%), and heated on the steam-bath for 30 mins. On addition of water, the crystalline sodium hydrogen phthalate which had separated dissolved, and the resulting clear solution was diluted with an equal volume of water and left in an open beaker for 2 days. The (+)-*dl*-*p*-methoxybenzhydrol (1·88 g.; calc., 1·85 g.), m. p. 62—63°, which had separated had $[\alpha]_{5893}$ +19·0° in carbon disulphide. The alkaline liquor yielded phthalic acid (0·55 g.; calc., 0·71 g.).

This experiment constitutes an approximate analysis of the neutral ester; the amounts of *p*-methoxybenzhydrol and phthalic acid obtained are in good agreement with the theoretical but suggest that the neutral ester was not completely free from admixed carbinol. It is probable also that the carbinol of $[\alpha]_{5893}$ +3·4° was not completely free from neutral ester; *dl*-*p*-methoxybenzhydrol tends to separate when *d* + *dl*-carbinol is fractionally crystallised from carbon disulphide, so it was not feasible to recrystallise the carbinol further. As these two factors act in opposite directions, it is probable that the rotatory power given is close to the true value.

This experiment was repeated with a hydrogen phthalic ester (7·26 g.) of $[\alpha]_{5893}$ +44·0° and 0·3N-sodium hydroxide. The (+)-*dl*-carbinol obtained had $[\alpha]_{8593}$ +2·4° (*c*, 2·5; *l*, 2) in carbon disulphide; the neutral ester had $[\alpha]_{5893}$ +18·4° and on hydrolysis yielded *p*-methoxybenzhydrol, $[\alpha]_{5893}$ +17·2° (*c*, 2·5; *l*, 2), both in carbon disulphide.

In a similar experiment, using hydrogen phthalate (3·62 g.) of $[\alpha]_{5893}$ —10·0° in benzene, the oil was left in contact with the supernatant water for 12 days. During this time, the proportion of crystalline deposit (*p*-methoxy-benzhydrol) increased. The oil was then separated, hydrolysed as described above, and the solution diluted with water. The alcohol which separated (0·75 g., m. p. 58—63°) was optically inactive in carbon disulphide solution. Phthalic acid (0·6 g.) was recovered on acidifying the alkaline solution after removal of the alcohol.

Action of Dilute Sodium Hydroxide on (—)-p-*Methoxybenzhydryl Hydrogen Phthalate in Presence of Sodium Phthalate.*—A solution of the (—)-hydrogen phthalate (3·69 g., $[\alpha]_{5893}$ —15·7° in benzene) in sodium hydroxide (34 c.c. of 0·3N) was filtered quickly into a solution of potassium hydrogen phthalate (10·2 g.; 5 mols.) in sodium hydroxide (170 c.c. of 0·3N). At the end of 4 hrs., a fibrous, crystalline precipitate was suspended in the liquid and a lower layer of viscous oil had separated. Filtration yielded the crystalline *p*-methoxybenzhydrol (0·45 g.), m. p. 59—62°, mixed m. p. with an authentic specimen, 62—63°; it was optically inactive in carbon disulphide solution. The oily neutral ester, hydrolysed with alcoholic sodium hydroxide, gave the alcohol (1·15 g.), which was optically inactive in carbon disulphide solution.

Action of Dilute Aqueous Sodium Hydroxide on dl-p-*Methoxybenzhydryl Hydrogen Phthalate in Presence of Sodium Benzoate.*—The phthalate (1·81 g., 1 mol.) was dissolved in 0·3N-sodium hydroxide (18 c.c.; 1 mol.), and the solution added to a solution of sodium benzoate (0·7 g., 1 mol.) in water (10 c.c.). Di-*p*-methoxybenzhydryl phthalate separated as an oil, as in the corresponding experiment in the absence of sodium benzoate. Benzoic acid (0·5 g.) was recovered by acidification of the aqueous layer, indicating that the sodium benzoate had not reacted.

Action of Dilute Sodium Hydroxide on (—)-p-*Methoxybenzhydryl Hydrogen Phthalate in Presence of* (+)-β-*Octyl Hydrogen Phthalate.*—(i) A solution of the (—)hydrogen phthalate (3·6 g., $[\alpha]_{5893}$ —15·7°) in sodium hydroxide (34 c.c. of 0·3N) was filtered into a solution of (+)-β-octyl hydrogen phthalate (13·9 g., 5 mols.) in sodium hydroxide (170 c.c. of 0·3N).

The solution soon began to turn cloudy owing to separation of oily globules. After a week the oil was removed by extraction with ether, and then hydrolysed in alcoholic sodium hydroxide solution. The resulting *p*-methoxybenzhydrol (1·76 g.) had m. p. 61—63° and was optically inactive in carbon disulphide solution. The (+)octyl hydrogen phthalate (12·5 g., m. p. 74°) was recovered unchanged.

(ii) (+)-*p*-Methoxybenzhydryl hydrogen phthalate (3·6 g., $[\alpha]_{5893}$ +52·3° in benzene) and (+)octyl hydrogen phthalate (13·9 g.) were dissolved together in sodium hydroxide (205 c.c., 0·3N). From the filtered solution an oil began to separate rapidly; after 18 hrs. it was removed by extraction with ether and hydrolysed with alcoholic sodium hydroxide. The resulting *p*-methoxybenzhydrol (1·4 g., m. p. 58—59°) was optically inactive in carbon disulphide solution. The (+)octyl hydrogen phthalate (12 g.), m. p. 74°, was recovered unchanged, and no octyl alcohol was obtained when the alkaline liquor, from which the *p*-methoxybenzhydrol had been removed, was distilled in a current of steam.

Benzhydryl hydrogen phthalate was prepared by heating a mixture of benzhydrol (7 g.), phthalic anhydride (6 g.), and pyridine (4 g.) at 60—70° for 5 hours. The resultant viscous liquid was diluted with acetone and decomposed with ice-cold dilute hydrochloric acid; the precipitated oily phthalate solidified on standing, and the crystals were filtered off and dried (11 g.). They separated from methylene chloride in small needles, m. p. 157—158°, not raised by further recrystallisation (Fessler and Shriner, *J. Amer. Chem. Soc.*, 1936, **58**, 1385, give m. p. 164—165°) (Found, by titration with sodium hydroxide : *M*, 330. Calc. : *M*, 332).

A solution of *dl*-phenylmethylcarbinyl hydrogen phthalate in 0·3N-sodium hydroxide remained perfectly clear after 5 weeks, and when acidified yielded the unchanged ester.

A solution of benzhydryl hydrogen phthalate (4·05 g.) in sodium hydroxide (45 c.c. of 0·3N) on standing for 2 weeks deposited some crystals of sodium benzhydryl phthalate which redissolved on warming, but otherwise no apparent change occurred. The solution was then heated on the steam-bath for about 10 hours; an oil separated, and on cooling it set to a crystalline mass of benzhydrol (2·2 g.; calc., 2·3 g.), m. p. 58—64°, raised to 65—66° by one crystallisation.

A solution of γ-phenyl-α-methylallyl hydrogen phthalate (2·3 g.) in sodium hydroxide (35 c.c.) after 2 days had deposited an oil and become acidic. A further 10 c.c. of sodium hydroxide was added, and the oil extracted with ether. On inoculation with *dl*-γ-phenyl-α-methylallyl alcohol it set to a crystalline mass, m. p. 29—30°. Acidification of the alkaline liquor yielded phthalic acid (1·3 g.), showing that hydrolysis was complete.

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