Alkyl–Oxygen Fission in Carboxylic Esters. Part XIII. The Resolution and Reactions of* 1 : 2 : 2 : 2-*Tetraphenylethanol. Crystalline Solvent Complexes of* (+)-1 : 2 : 2 : 2-*Tetraphenylethyl Hydrogen Phthalate.*

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By the usual procedure (±)-1 : 2 : 2 : 2-tetraphenylethanol can be converted into its (+)- and (−)-hydrogen phthalic esters, which by interaction with lithium aluminium hydride yield the (+)- and the (−)-ethanol, respectively.

The hydrogen phthalate reacts, somewhat slowly, with alkali to yield, not the original ethanol, but its decomposition products triphenylmethane and benzaldehyde: under acid conditions the principal product is tetraphenylethylene. The optically active forms of the hydrogen phthalate readily yield stable crystalline complexes containing one molecule of solvent. In marked contrast the (±)-hydrogen phthalate exhibits no such tendency to complex-formation.

As part of our study of the hydrolysis of carboxylic esters we have examined the behaviour of 1 : 2 : 2 : 2-tetraphenylethyl hydrogen phthalate. This ester is formed in excellent yield by combination of the alcohol with phthalic anhydride at 100° in the presence of pyridine: by fractional crystallisation of its brucine salt it is separated, easily and almost quantitatively, into its (+)- and (−)-isomerides. This separation is greatly facilitated by the marked difference in solubility of the (+)- and (±)-isomerides. Rotatory powers are given in Table 1.

A solution of the hydrogen phthalate in aqueous alcoholic sodium hydroxide (2·5 mols.) remains unchanged for many weeks at room temperature but when heated on the steam-bath for several hours it slowly undergoes decomposition according to the equation

$$NaO_2C\cdot C_6H_4\cdot CO_2\cdot CHPh\cdot CPh_3 + NaOH \longrightarrow C_6H_4(CO_2Na)_2 + CHPh_3 + PhCHO$$

and no trace of the original alcohol can be detected.

Table 1. *Specific rotatory powers of* (+)-1 : 2 : 2 : 2-*tetraphenylethyl hydrogen phthalate in various solvents at* 18° (*c*, 1·500; *l*, 1).

Solvent	6439 Å	5893 Å	5790 Å	5461 Å	5086 Å	4800 Å	4358 Å
Acetone	+86·1°	+107°	+114°	+137°	+155°	+180°	+245°
Ethanol	82·6	103	107	115	130	147	221
Ethylbenzene	61·7	65	75	85	94	101	117

No variation of $[\alpha]_{5893}$ was observed when *c*, in acetone solution, was increased from 0·4 to 2·7: the values of $[\alpha]_{5893}$ in solvents other than acetone are independent of whether the solutions are made with the unsolvated ester or with its acetone complex provided that *c* is calculated on the basis of unsolvated ester (see below). Replacement of sodium hydroxide by sodium carbonate resulted in no reaction: even after 50 hours' heating the hydrogen phthalate was recovered unchanged.

In view of these results 1 : 2 : 2 : 2-tetraphenylethanol was heated under reflux with aqueous alcoholic sodium hydroxide: after 5 min. the solution yielded triphenylmethane and benzaldehyde, each isolated in 65% yield. This decomposition was observed by Delacre (*Bull. Acad. roy. Belg.*, 1890, **20**, 109), and it has now been shown to occur under conditions favourable to ester hydrolysis. The reaction is rapid in alcoholic solution and its rate is not appreciably affected by dilution with water but is dependent upon alkali concentration. Similar decomposition occurs in dry benzene solution at room temperature in presence of sodium ethoxide.

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Thus it seems likely that the formation of triphenylmethane and benzaldehyde during reactions of 1 : 2 : 2 : 2-tetraphenylethanol and its hydrogen phthalate is dependent on the release of the anion $Ph_3C{\cdot}CHPh{\cdot}O^-$ which results from acyl–oxygen fission. The sodium salt of the hydrogen phthalate in aqueous solution when mixed with sodium toluene-*p*-sulphinate remained unchanged during 6 months—the non-formation of sulphone confirms that esters of this alcohol show little or no tendency to react by alkyl–oxygen fission under alkaline conditions. When conditions are such that the alkoxide anion is not released then the group remains intact, *e.g.*, the esterification of the ethanol with phthalic anhydride in the presence of pyridine results in no significant side-reaction; furthermore the product of interaction of the alcohol with ethylmagnesium iodide—during which the calculated amount of ethane is evolved—regenerates the unchanged alcohol on decomposition with water.

It therefore seems highly probable that the hydrolysis of 1 : 2 : 2 : 2-tetraphenylethyl hydrogen phthalate by aqueous alkali occurs by acyl–oxygen fission.

Since alkaline hydrolysis failed to yield the ethanol from its hydrogen phthalate, hydrolysis by acid was tried and here again the reaction proved abnormal, the product being tetraphenylethylene. It was shown by Skell and Hauser (*J. Amer. Chem. Soc.*, 1942, **64**, 2633) that this ethanol in benzene solution with dry hydrogen bromide gives high yields of tetraphenylethylene. It is thus probable that acid hydrolysis of 1 : 2 : 2 : 2-tetraphenylethyl hydrogen phthalate involves alkyl–oxygen fission.

On the other hand when a solution of the hydrogen phthalate in formic acid containing an equivalent amount of sodium toluene-*p*-sulphinate was heated for a few minutes no sulphone was formed, the main product being again tetraphenylethylene. It is thus possible that no carbonium ion exists long enough to react with an anion of such high co-ordinating power as the sulphinate ion : this result supports the suggestion by Skell and Hauser (*loc. cit.*) that rearrangement is simultaneous with fission of the alkyl–oxygen bond:

$$R{\cdot}CO{\cdot}O{\cdot}CHPh{\cdot}CPh_3 \longrightarrow R{\cdot}CO{\cdot}\overset{-}{O} + \overset{+}{C}HPh{\cdot}CPh_3 \xrightarrow[\text{rapid}]{\text{very}} Ph_2C{=}CPh_2 + \overset{+}{H}$$

Reaction of (+)-1 : 2 : 2 : 2-*Tetraphenylethyl Hydrogen Phthalate with Lithium Aluminium Hydride.*—The isolation of an optically active tertiary alcohol from its hydrogen phthalate by means of lithium aluminium hydride has been described by Doering and Zeiss (*J. Amer. Chem. Soc.*, 1950, **72**, 147), and this reaction has now been applied in parallel manner to (+)- and (−)-1 : 2 : 2 : 2-tetraphenylethyl hydrogen phthalate. Rotatory powers are in Table 2.

TABLE 2. *Specific rotatory powers of* (—)-1 : 2 : 2 : 2-*tetraphenylethanol in various solvents at* 20° (*c*, 1·300; *l*, 1).

Solvent	6439 Å	5893 Å	5780 Å	5461 Å	5086 Å	4800 Å	4358 Å
Acetone	−59·0°	−69·5°	−72·0°	−81·0°	−96·0°	−116°	−146°
Ethanol	59·5	61·9	76·5	86·7	105	126	154
Benzene	84·2	105	119	143	168	209	252

Retention of full optical activity by the liberated ethanols (proved by reconversion into hydrogen phthalates possessing their original rotatory powers) indicates clearly that cleavage of the esters has occurred at the acyl–oxygen bond exclusively.

Molecular Compounds of Optically Active 1 : 2 : 2 : 2-*Tetraphenylethyl Hydrogen Phthalate.*—A most interesting development of this investigation has been the isolation of a series of compounds in which the optically active forms of 1 : 2 : 2 : 2-tetraphenylethyl hydrogen phthalate occur in combination with a molecular proportion of a solvent.

A solution of the (+)- or (—)-form of the hydrogen phthalate in a solvent, other than a paraffin hydrocarbon, deposits crystals of the hydrogen phthalate which contain, in most cases, 1 mol. of the solvent, *e.g.*, acetone, thus rendering it tedious to obtain a solvent-free compound. The most convenient method of doing this is to heat the hydrogen phthalate–acetone complex in a current of air until it has lost weight corresponding to 1 mol. of acetone and acquired a m. p. 181—182°: this material separates from (much) light petroleum in needles, m. p. 183°.

The various crystalline complexes were kept at 95—100° for some 20 min. to remove adhering solvent and then titrated with standard alkali; the equivalent weight corresponded to 498 + *M* where *M* is the molecular weight of the solvent—results are given in Table 3.

Possibly the most significant behaviour of these compounds is the following. When acetone solutions of the (+)- and the (−)-hydrogen phthalate, each of which separately would deposit needles, m. p. 118—122°, of the solvated compound, are mixed, the large flat prisms, m. p. 219°, of the (±)-hydrogen phthalate which separate contain no solvent of crystallisation.

TABLE 3.

Solvent	Crystalline form	M. p.	Equiv. Found	Equiv. Calc.[*]
Acetone	Needles	118—122°	558	556
Ethyl ether	,,	110—112	570	572
Ethyl *n*-propyl ether	,,	87—89	580	586 [†]
n-Butyl ether	Prisms	136—140	550	630
Benzene	,,	140—145	574	576
Toluene	Plates	110—112	556	590
Ethylbenzene	Needles	106—108	560	604 [‡]
Nitrobenzene	Hexagonal plates	110—112	625	621
Methanol	Prismatic needles	126—128	532	530
Ethanol	Needles	135—140	540	544
tert.-Butanol	Prisms	145—148	565	572
Chloroform	Prismatic needles	116—120	600	620
Carbon tetrachloride	,, ,,	181—183	530	652
Acetic acid	,, ,,	114—116	330	279 [§]
Carbon disulphide	Needles	132—137	518	574 [‖]

[*] For 1 : 1-complex.

[†] Owing to its low m. p. this compound was dried in a vacuum desiccator at room temp.

[‡] This expt. was repeated with slight modifications as follows: the crystalline complex which separated from ethylbenzene–light petroleum was placed in a stream of air at room temp. for 10 min.: it then had m. p. 100—102° (decomp.) and equiv. 590. After heating at 95° for 10, 30, and 60 min. the equiv. was 567, 540, and 520, respectively. The final product sintered at 108° and melted at 179—180°.

[§] This compound separates from the acetic acid solution on addition of water: the equivalent corresponds to hydrogen phthalate : solvent ratio of 3 : 2.

[‖] Best prepared by the addition of much light petroleum to a warm dilute solution in carbon disulphide. More concentrated solutions set to a granular gel.

The pronounced readiness of the (+)- or (−)-hydrogen phthalate to combine with acetone is illustrated by the following: From concentrated solutions in dry ethanol the hydrogen phthalate separated in needles containing one equivalent of the solvent but from aqueous ethanolic solutions no definitely crystalline material could be separated. However, when acetone was added to these aqueous alcoholic solutions the crystalline hydrogen phthalate readily separated as the acetone complex.

EXPERIMENTAL

Benzopinacol was prepared in very good yield by the method (i) given in *Org. Synth.* Coll. Vol. II, p. 71, or (ii) of Gomberg and Bachmann (*J. Amer. Chem. Soc.*, 1927, **49**, 241) and converted into β-benzopinacolone, also in good yield, by Gomberg and Bachmann's method (*loc. cit.*).

1 : 2 : 2 : 2-Tetraphenylethanol was prepared from β-benzopinacolone most conveniently by Levy and Lagrave's method (*Bull. Soc. chim.*, 1928, **43**, 440) with the modification of adding the pinacolone, not intermittently as a solid, but continuously as an ethereal suspension. It separates from ethanol in prisms, m. p. 152°.

(±)-1 : 2 : 2 : 2-*Tetraphenylethyl Hydrogen Phthalate*.—A mixture of the ethanol (20 g.), phthalic anhydride (11·5 g.), and pyridine (15 c.c.) was heated on the steam-bath for 8 hr. Next day the resultant solid was dissolved in hot acetone (1500 c.c.), and the cooled and stirred solution acidified with hydrochloric acid and slowly diluted with water. The resulting fine crystalline *product* (24 g.) separated from *n*-butyl acetate (250 c.c.) in prisms, m. p. 221—223° (decomp.) [Found, by titration with $Ba(OH)_2$: *M*, 500. $C_{23}H_{27}O_4$ requires *M*, 498].

(+)-1 : 2 : 2 : 2-*Tetraphenylethyl Hydrogen Phthalate*.—A solution of the (±)-hydrogen phthalate (50 g.) and brucine (40 g.) in hot acetone (1300 c.c.), after cooling, deposited the brucine salt (70 g.), m. p. 162—167°; after digeston with boiling methyl acetate (1200 c.c.) this salt (35 g.) had m. p. 162—164° and was almost optically pure brucine salt of (+)-1 : 2 : 2 : 2-tetraphenylethyl hydrogen phthalate (*A*) (see below). This salt's being but sparingly soluble in suitable solvents renders fractional crystallisation a laborious and wasteful process. On the other hand there is a wide difference in solubility—as well as in melting point—between the (±)- and the (+)- or (−)-hydrogen phthalates, thus making the separation of the optically pure compound from admixed racemic material a simple and efficient procedure. Accordingly a combination of the two procedures was adopted similar to that used for the resolution of 1-phenylethanol by Downer and Kenyon (*J.*, 1939, 1156); brief details are as follows.

The brucine salt (35 g.), suspended in cold acetone (200 c.c.), was acidified (dropwise; stirring) with hydrochloric acid: water was then added to dissolve the precipitated brucine hydrochloride. The solution soon deposited the hydrogen phthalate, small needles, m. p. *ca.* 120° (decomp.): this, by crystallisation from acetone–light petroleum yielded optically pure (+)-1 : 2 : 2 : 2-*tetraphenylethyl hydrogen phthalate* (14·8 g.), as needles, m. p. 118—122° (decomp.) [Found: *M* (by titration), 557. $C_{34}H_{26}O_4,Me_2CO$ requires *M*, 556].

The filtrate, after addition of a few drops of water, yielded optically impure (+)-hydrogen phthalate (4 g.), m. p. 195° (decomp.). A further crop of the brucine salt, by similar treatment, yielded optically pure (+)-hydrogen phthalate (5·4 g.).

(−)-1 : 2 : 2 : 2-*Tetraphenylethyl Hydrogen Phthalate*.—The more soluble fractions of the brucine salt, by similar treatment, yielded optically pure (−)-1 : 2 : 2 : 2-*tetraphenylethyl hydrogen phthalate*, needles (22·1 g.), m. p. 118—122° (decomp.) (Found: *M*, 555). The combined yield of optically pure (+)- and (−)- hydrogen phthalate was 42·3 g. (this includes about 10% of combined acetone) = 76%: some 7 g. of largely (±)-hydrogen phthalate were recovered.

(+)- *and* (−)-1 : 2 : 2 : 2-*Tetraphenylethanol*.—The (+)-hydrogen ester (2 g.) was introduced, by extraction from a Soxhlet apparatus, into a flask containing anhydrous ether (100 c.c.) and lithium aluminium hydride (0·8 g.): the extraction was complete after 9 hr., and the heating was continued for a further 3 hr. Working up in the usual way yielded (+)-1 : 2 : 2 : 2-tetraphenylethanol, which separated from light petroleum in prisms (1·0 g.), m. p. 120—121°, $[\alpha]_D$ +61·0° (*c*, 1·00 in acetone; *l*, 1).

Similarly the (−)-hydrogen ester yielded (−)-1 : 2 : 2 : 2-tetraphenylethanol as prisms (1·2 g.), m. p. 120—121°, $[\alpha]_D$ −60·0° (*c*, 0·900 in acetone; *l*, 1).

A mixture of equal amounts of the (+)- and the (−)-ethanol had m. p. 149—151°, alone and when mixed with (±)-1 : 2 : 2 : 2-tetraphenylethanol, m. p. 152°.

A mixture of the (−)-ethanol (0·1 g.), phthalic anhydride (0·05 g.), and pyridine (1 c.c.) when heated for 10 hr. yielded the (−)-hydrogen phthalate (as its acetone complex), needles, m. p. 118—122° (decomp.) alone and mixed with an authentic specimen.

In a similar manner, but with avoidance of acetone, the (+)-ethanol yielded the (+)-hydrogen phthalate, which, without crystallisation, had m. p. 170—171°, $[\alpha]_D$ +102° (*c*, 0·800 in acetone; *l*, 1).

Reactions of (−)-1 : 2 : 2 : 2-*Tetraphenylethyl Hydrogen Phthalate*.—(i) *With sodium hydroxide*. A solution of the (−)-acid ester (1 g.) in 0·2N-alcoholic sodium hydroxide (25 c.c.; 2·5 mol.) was heated on the steam-bath. After 2 hr. sodium phthalate (0·3 g.) had separated, and dilution of the filtrate with water yielded triphenylmethane (0·33 g.; m. p. and mixed m. p. 94°). Addition of 2 : 4-dinitrophenylhydrazine to the filtrate yielded benzaldehyde 2 : 4-dinitrophenylhydrazone (0·4 g.; m. p. and mixed m. p. 237°). From the filtrate there was isolated unchanged (−)-hydrogen phthalate (as its acetone complex) (0·2 g.; m. p. 110°). These quantities represent yields of over 80%. This reaction occurs at room temp. but much more slowly. The (+)-acid ester was recovered after being heated for 50 hr. with (*a*) aqueous sodium carbonate or (*b*) in acetone (20 c.c.) containing hydrochloric acid (0·1N; 10 c.c.).

(ii) *With ethanolic hydrochloric acid*. A solution of the (−)-acid ester (0·5 g.) in ethanol (15 c.c.) containing hydrochloric acid (0·2 c.c.) was heated under reflux for 6 hr. and then diluted with water. The precipitated crystalline material was separated by fractional crystallisation from ethanol into (*a*) unchanged (−)-acid ester (0·25 g.), (*b*) tetraphenylethylene (0·02 g.), m. p. 221—223° (alone and mixed with an authentic specimen, and (*c*) the neutral ester—*ethyl*

1 : 2 : 2 : 2-*tetraphenylethyl phthalate* (0·06 g.), irregular prisms, m. p. 178—179°, $[\alpha]_D$ −136° (*c*, 0·800 : *l*, in acetone) (Found : C, 81·7; H, 5·8. $C_{36}H_{30}O_4$ requires C, 82·3; H, 5·5%).

This neutral ester was also prepared from the (−)-acid ester by (*a*) the action of cold ethanolic hydrogen chloride and (*b*) the action of ethyl iodide on the potassium salt. Both products had m. p. 178—179°, alone or mixed with the original specimen, the structure of which is thus confirmed.

The corresponding ethyl ester of the (+)-hydrogen phthalate had m. p. 178—179°; a mixture with the corresponding (−)-ethyl ester had m. p. 160—162°.

(iii) *With methyl(or ethyl)magnesium iodide.* Even after being heated under reflux for 3 hr. with Grignard reagent (6 mol.) the (−)-acid ester was largely recovered together with some tetraphenylethylene (5—20%).

(iv) *With formic acid.* A solution of the (+)-acid ester (0·1 g.) in formic acid (90%; 4 c.c.) after 2 hr. on the steam-bath yielded tetraphenylethylene (0·06 g.), m. p. 223—225° alone and mixed with an authentic specimen. When heated with glacial acetic acid at 100° for 8 hr. the acid ester was unchanged: hot aqueous acetic acid (50%), however, slowly effects the decomposition.

Non-formation of p-*Tolyl Sulphone.*—A solution of the (+)-hydrogen phthalate (0·5 g.) in ethanol (5 c.c.), neutralised with sodium hydroxide, was mixed with a solution of sodium toluene-*p*-sulphinate (0·5 g.) in water (10 c.c.). After 6 months the solution yielded unchanged (+)-hydrogen phthalate (0·4 g.), m. p. and mixed m. p. 118—120°.

When a solution of the two components in formic acid was heated on the steam-bath for 30 min. the main product was tetraphenylethylene. No trace of sulphone was observed in either experiment.

Reactions of 1 : 2 : 2 : 2-*Tetraphenylethanol.*—(i) *With sodium hydroxide.* A solution of the tetraphenylethanol (1 g.) in ethyl alcohol (20 c.c.) containing sodium hydroxide (50%; 1 c.c.) was heated under reflux for 5 min. and yielded triphenylmethane (0·45 g.) and benzaldehyde (as its 2 : 4-dinitrophenylhydrazone; 0·58 g.). A similar solution, after 10 days at room temperature, gave the same products in 30% yield.

(ii) *With alcoholic hydrochloric acid.* A solution of the tetraphenylethanol (0·5 g.) in ethyl alcohol (10 c.c.) containing hydrochloric acid (0·6 c.c.) when heated under reflux for 6 hr. yielded tetraphenylethylene (0·1 g.) and the unchanged ethanol (0·3 g.).

(iii) *With methylmagnesium iodide* (*in anisole solution*). When the tetraphenylethanol was treated with Grignard reagent, methane (20 c.c. : calc. 21 c.c.) was liberated; the resulting magnesium complex, after being mixed with acid, yielded the original ethanol quantitatively.

(iv) *The action of heat.* The ethanol (1 g.) when heated at 200—210° for 5 min. yielded triphenylmethane (0·5 g.), and benzaldehyde (as its 2 : 4-dinitrophenylhydrazone; 0·75 g.) in 95% yield. At 180° no decomposition occurred during 5 min.

(v) *With sodium ethoxide in benzene solution.* A mixture of benzene (20 c.c.), absolute ethanol (1 c.c.), and sodium (excess) was heated under reflux, and the solution filtered into a solution of the ethanol (1 g.) in benzene (10 c.c.). Next morning the solution yielded benzaldehyde (as its dinitrophenylhydrazone) and triphenylmethane (0·5 g.), m. p. 92—93° (alone and mixed); the yield was 72%.

Solvent Complexes of (+)- *and* (−)-1 : 2 : 2 : 2-*Tetraphenylethyl Hydrogen Phthalate.*—During investigation of the resolution of the (±)-hydrogen phthalate an unusual property of the optically active forms of this compound was encountered, namely the readiness with which they combine with solvents. The solvent molecules appear to be, in some cases at least, firmly bound in the crystal structure as is shown by the following results.

(i) The (+)-hydrogen phthalate, obtained by decomposition with acid of the less soluble brucine salt, separates from acetone–light petroleum in needles, m. p. 118—122° (decomp.) [Found, by titration of its acetone solution with aqueous baryta : equiv., 558. Calc. for the pure (unsolvated) ester : equiv., 498].

These crystals, when heated at 95° for 1 hr. suffered neither loss in weight nor alteration of m. p. : after being heated at 90—100°/20 mm. for 5 hr. they had lost 7% in weight but the m. p. was unchanged : after a short period at 108—110°/20 mm. no melting occurred but there was an additional loss in weight of 4%. The crystals now had m. p. 180—181°, $[\alpha]_D$ +103° (in acetone), equiv., 490.

(ii) The (−)-hydrogen phthalate [needles from acetone–light petroleum, m. p. 118—122° (decomp.), 14·8 g.] was heated at 95°/20 mm. but suffered no loss in weight during 2 hr. It was then reheated under the same pressure with a slow stream of air passing over it and through an acidified solution of 2 : 4-dinitrophenylhydrazine. No reaction was visible in the hydrazine solution until the bath-temperature reached 109°, then a heavy yellow precipitate separated rapidly. This precipitate, after recrystallisation, formed needles, m. p. 125—126°, alone or mixed with authentic acetone 2 : 4-dinitrophenylhydrazone.

After 4 hr. the hydrogen phthalate had lost 1 mol. of acetone; the m. p. had risen to 182—188°, and the equivalent fallen to 499; $[\alpha]_D$ +107° (*c*, 2·160 in acetone; *l*, 1).

When these solvent-free crystals were finely powdered and mixed with acetone hard masses were formed, reminiscent of the behaviour of anhydrous sodium carbonate on addition of water; the solid dissolved when heated and the resulting solution, after addition of light petroleum, yielded the crystalline ester, m. p. 118—122° (decomp.) (Found: equiv., 554. Calc. for $C_{34}H_{26}O_4,COMe_2$: equiv. 556).

The corresponding (+)-hydrogen phthalate behaved similarly.

When the solvent-free (+)-hydrogen phthalate (0·5 g.; m. p. 182—183°) was added to cold benzene (2 c.c.) a clear solution resulted; this, within 1 min., deposited small prisms (0·5 g.), m. p. 140—145° (decomp.) (see Table 3), of a benzene complex (0·5 g.), which dissolved readily in cold acetone (2 c.c.): the solution, on being scratched, deposited the (+)-hydrogen phthalate–acetone complex as needles, m. p. 118—122° (decomp.).

Crystallisation of (–)-1 : 2 : 2 : 2-*Tetraphenylethyl Hydrogen Phthalate in a Solvent-free Condition.*—A solution of the (–)-hydrogen phthalate, either solvent-free or its acetone complex (3·5 g.) in boiling petroleum (b. p. 100—120°; 600 c.c.) on cooling deposited needles, m. p. 183° (3·0 g.), $[\alpha]_D$ –107° (*c*, 1·990 in acetone; *l*, 1) (Found: equiv., by titration, 500. Calc. 498).

The Solvating Properties of the (+)- *and the* (–)-1 : 2 : 2 : 2-*Tetraphenylethyl Hydrogen Phthalate contrasted with the Non-solvation of the* (±)-*Isomeride.*—Equal weights (0·5 g.) of the (+)- and the (–)-hydrogen phthalate (each dissolved in 15 c.c. of acetone) were mixed; the solution slowly deposited large flat prisms of the (±)-isomeride, m. p. 219° alone and mixed with an authentic specimen (Found: equiv., 501. Calc., for solvent-free compound: equiv., 498). The isomeride was optically inactive.

Determinations of Molecular Weight.—A solution of (+)-1 : 2 : 2 : 2-tetraphenylethyl hydrogen phthalate (0·2318 g.) in nitrobenzene (24·0 g.) gave a depression of freezing point of 0·133°, whence $M = 510$. The corresponding (±)-compound (0·3495 g.) in nitrobenzene (23·8 g.) gave a depression of 0·170°, whence $M = 610$ (Calc. for $C_{34}H_{26}O_4$: M, 498).

Barium Salts of (–)- *and* (±)-1 : 2 : 2 : 2-*Tetraphenylethyl Hydrogen Phthalate.*—A solution of the (–)-hydrogen phthalate (0·5 g.) in warm acetone was neutralised with baryta: the crystals (0·5 g.) which slowly separated formed rosettes of fine needles, m. p. 213—216° (decomp.), from aqueous acetone. The corresponding (±)-isomeride also had m. p. 213—216°.

Each of these *salts*, when heated in a current of air as previously described, yielded acetone 2 : 4-dinitrophenylhydrazone, corresponding to 1·7 mol. of acetone [Found: M, by estimation of Ba (–)-isomeride, 1245; (±)-isomeride, 1235. $(C_{34}H_{25}O_4)_2Ba,2COMe_2$ requires M, 1247].

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