Alkyl–Oxygen Fission in Carboxylic Esters. Part XIV. 4-Methyldiphenylmethyl and 2 : 4 : 6-Trimethyldiphenylmethyl Compounds.*

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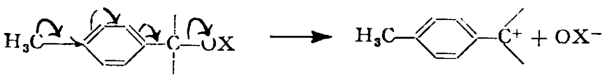
4-Methyldiphenylmethanol and 2 : 4 : 6-trimethyldiphenylmethanol have been resolved by fractional crystallisation of the alkaloidal salts of their hydrogen phthalic esters. These alcohols and their esters, by virtue of inductive and hyperconjugative electron release from the methyl groups, undergo unimolecular alkyl–oxygen fission reactions more readily than the corresponding diphenylmethyl compounds, but less readily that the analogous methoxy-substituted compounds.

Earlier papers in this series have demonstrated that the introduction of α-aryl groups into the alkyl group of alcohols and their carboxylic esters greatly increases the tendency of these compounds to react by a unimolecular alkyl–oxygen fission mechanism. This is particularly marked when the aryl group carries *ortho-* and/or *para*-electron-releasing substituents, such as alkoxy-groups (Part XII, *J.*, 1953, 3619), alkylthio-groups (Part VIII, *J.*, 1951, 382), or dialkylamino-groups (Parts III and V, *J.*, 1946, 797, 807; Balfe, Kenyon, and Thain, *J.*, 1952, 790). No systematic study has hitherto been reported of the effect of *ortho-* or *para*-alkyl substituents on the reactivity of such 1-arylmethanols.

It would be expected that inductive and hyperconjugative electron release by the alkyl groups would facilitate unimolecular heterolysis of the alkyl–oxygen bond, as it does of the alkyl–halogen bond in the analogous alkyl halides (Hughes, Ingold, and Taher, *J.*, 1940, 949), *e.g.*:



Evidence supporting this was given by Balfe, Hargreaves, and Kenyon (*J.*, 1951, 375) who showed that 2 : 4′-dimethyldiphenylmethyl hydrogen phthalate was more reactive by a unimolecular alkyl–oxygen fission mechanism than was diphenylmethyl hydrogen phthalate. The introduction in the α-position of alcohols of the 2 : 4 : 6-trimethylphenyl group has been shown to promote alkyl–oxygen heterolysis; for example, a solution of di-(2 : 4 : 6-trimethylphenyl)methanol in concentrated sulphuric acid shows a van't Hoff factor $i = 4{\cdot}04$, indicating the formation of the stable dimesitylcarbonium ion (Deno and Newman, *J. Amer. Chem. Soc.*, 1951, **73**, 3644). 4-Methyldiphenylmethanol and 2 : 4 : 6-trimethyldiphenylmethanol have now been resolved *via* their hydrogen phthalic esters, and the tendency of the alcohols and their esters to undergo unimolecular alkyl–oxygen fission has been investigated.

Earlier workers failed to resolve 4-methyldiphenylmethanol (Cohen, Marshall, and Woodman, *J.*, 1915, **107**, 887; Reis and Schneider, *Z. Krist.*, 1929, **69**, 62), but we find that the brucine salt of the hydrogen phthalate is optically pure after three crystallisations from ethyl acetate. The alcohol, and its hydrogen phthalate, hydrogen succinate, formate, acetate, and benzoate, under mildly acid conditions all undergo reactions characteristic of alkyl–oxygen fission; for example, they alkylate alcohols, phenols, carboxylic acids, sodium toluene-*p*-sulphinate (giving the *p*-tolyl sulphone), and acetyl chloride (giving the alkyl chloride). In all these reactions, the optically active reactant gives inactive products, indicating the presence of carbonium ions as the reaction intermediate. In sodium hydroxide solution, some disproportionation of the hydrogen phthalate occurs, to give the dialkyl phthalate and phthalic acid.

2 : 4 : 6-Trimethyldiphenylmethanol was resolved by fractional crystallisation of the strychnine salt of its hydrogen phthalate from acetone. This alcohol and its hydrogen phthalate display an approximately equal reactivity by a unimolecular alkyl–oxygen

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* Part XIII, *J.*, 1954, 779.

fission mechanism to that of the corresponding 4-methyldiphenylmethyl compounds. Under acid conditions they alkylate carboxylic acids, alcohols, thiocresol, sodium toluene-*p*-sulphinate, and acetyl chloride; optically active reactants give racemic products. Hydrolysis of the optically active hydrogen phthalate in aqueous sodium hydroxide of concentration less than 0·5N proceeds with some racemisation, and in 0·3N-aqueous sodium hydroxide at room temperature hydrolysis is accompanied by the formation of some dialkyl phthalate.

Construction of molecular models shows that, whereas the 4-methyldiphenylcarbonium ion may become planar with the incursion of very little deformation of bond angles, the 2 : 4 : 6-trimethyldiphenylcarbonium ion cannot assume a planar configuration. In the latter case, if the mesityl group is coplanar with the bonds about the reaction centre, the phenyl group is forced into a plane almost at right angles to that of the rest of the molecule. Resonance stabilisation of the carbonium ion therefore probably involves only the mesityl group, just as only one mesityl group is involved in the stabilisation of the dimesityl-carbonium ion (Deno and Newman, *loc. cit.*).

EXPERIMENTAL

4-*Methylbenzophenone.*—A mixture of benzoyl chloride (67 g.) and toluene (67 g.) was added, during 2 hr., to a stirred suspension of aluminium chloride (100 g.) in toluene (150 g.). After 2 hr. at 100°, and 2 days at room temperature, the solution was worked up in the usual manner, giving 4-methylbenzophenone (yield, 90%), as a pale yellow oil, b. p. 310—320°, m. p. 59·5° after crystallisation from light petroleum.

4-*Methyldiphenylmethanol.*—Zinc dust (85 g.) was added slowly to a stirred solution of the ketone (85 g.) and potassium hydroxide (85 g.) in 96% ethanol (400 c.c.). After 1 hr. at 100°, the solution gave, in almost quantitative yield, 4-methyldiphenylmethanol, as needles, m. p. 51—53°, from light petroleum. The above method of preparation is markedly superior to that involving the Grignard reaction between *p*-bromotoluene and benzaldehyde.

Esters of 4-*Methyldiphenylmethanol.*—A mixture of the alcohol (83 g.), phthalic anhydride (66 g.), and pyridine (35 g.), after 3 hr. at 45—55°, was diluted with an equal volume of acetone, and decomposed by the addition of a slight excess of dilute hydrochloric acid. Dilution with water gave 4-*methyldiphenylmethyl hydrogen phthalate* (125 g.) which separated from ether–light petroleum or from aqueous ethanol as clusters of needles, m. p. 120—122° (Found, by rapid titration with 0·1N-NaOH : equiv., 345. $C_{22}H_{18}O_4$ requires equiv., 346).

A mixture of the alcohol (19·8 g.), succinic anhydride (10 g.), and pyridine (7·7 g.), after 5 hr. at 55—60°, yielded the *hydrogen succinate* (20 g.) as needles from ether–light petroleum; m. p. 100—100·5° (Found : equiv., 301. $C_{18}H_{18}O_4$ requires equiv., 298).

The alcohol (20 g.) in 98% formic acid (30 c.c.) was kept at 100° for 45 min. An ethereal extract yielded the *formate* as needles (from methanol) (20 g.), m. p. 52—53° (Found, by hydrolysis : equiv., 225. $C_{15}H_{14}O_2$ requires equiv., 226). The (—)-alcohol (see below) yielded the (±)-formate.

The (—)-alcohol (4·2 g.), $[\alpha]_D^{22}$ −14·8° (*l*, 2; *c*, 1·34 in CS_2), pyridine (2 g.), and acetic anhydride (2·2 g.), after 5 days, yielded the *acetate* (4·0 g.), b. p. 154—156°/2 mm., $[\alpha]_D^{22}$ −16·8° (*l*, 2; *c*, 2·538 in C_6H_6) (Found, by hydrolysis : equiv., 251. $C_{16}H_{16}O_2$ requires equiv., 240). Similarly the (—)-alcohol (0·5 g.) was heated under reflux in glacial acetic acid (20 c.c.), by which time the solution was optically inactive; the (±)-acetate was isolated (0·585 g.) (Found : equiv., 243).

After 16 hr., a mixture of the alcohol (10 g.), pyridine (4 g.), and benzoyl chloride (6·5 g.) yielded the *benzoate* as clusters of small needles (from ethanol) (15 g.), m. p. 81—82° (Found, by hydrolysis : equiv., 301. $C_{21}H_{18}O_2$ requires equiv., 302).

(+)- *and* (—)-4-*Methyldiphenylmethyl Hydrogen Phthalate.*—From a solution of the (±)-hydrogen phthalate (52·5 g.) and brucine (65·2 g.) in ethyl acetate (250 c.c.), the crystalline salt [48 g.; m. p. 119—120° (decomp.)] separated as needles during 21 days. Two further crystallisations from ethyl acetate gave the optically pure brucine salt (22 g.), m. p. 102—105°. Decomposition of this salt gave the (+)-hydrogen phthalate (5 g.), m. p. 114—114·5°, $[\alpha]_D$ +18·5° (*l*, 2; *c*, 1·15 in C_6H_6). No increase in rotatory power was effected by further recrystallisation of the brucine salt of this ester.

Part of the hydrogen phthalate (5·0 g.), $[\alpha]_D$ −9·7° (*l*, 2; *c*, 2·06 in C_6H_6), which was recovered from the first two mother-liquors of brucine salts, was dissolved in ethyl acetate and added to a suspension of quinidine (4·75 g.) in ethyl acetate (15 c.c.). The clear solution soon deposited the quinidine salt as crystals (7·0 g.), m. p. 145—148°. Recrystallisation gave a salt, m. p. 145—145·5°, which was decomposed to yield the (−)-hydrogen phthalate, m. p. 114—114·5°, $[\alpha]_D$ −16·4°(*l*, 2; *c*, 1·3 in C_6H_6).

(+)-4-*Methyldiphenylmethanol.*—The (+)-hydrogen phthalate (1·5 g.) was dissolved in a solution of sodium (0·7 g.) and water (1 c.c.) in absolute ethanol (100 c.c.); after 15 min. at 100°, sodium phthalate separated. Addition of water gave (+)-4-methyldiphenylmethanol (0·7 g.) as a crystalline precipitate, m. p. 61—63°, $[\alpha]_D$ +26·9° (*l*, 2; *c*, 1·378 in CS_2). Cohen, Marshall, and Woodman (*loc. cit.*) were unable to resolve 4-methyldiphenylmethanol *via* its hydrogen phthalate They therefore resolved 4-methyldiphenylmethylamine by crystallisation of its bromocamphorsulphonate and, on treatment of the apparently optically pure amine hydrochloride with sodium nitrite, obtained the partially active alcohol, $[\alpha]_D^{20}$ −1·4° (*l*, 2; *c*, 8·904 in ethanol).

Reactions of 4-*Methyldiphenylmethanol.*—(i) *With sodium toluene*-p-*sulphinate.* After 1 hr., a solution of the alcohol (1·7 g.) and sodium toluene-*p*-sulphinate (2·0 g.) in formic acid (50 c.c., 98—100%) gave 4-*methyldiphenylmethyl* p-*tolyl sulphone* (2·0 g.), m. p. 159—160°, in quantitative yield (Found: S, 9·5. $C_{21}H_{20}O_2S$ requires S, 9·5%). Similarly, when the alcohol (0·633 g.) and toluene-*p*-sulphinic acid (0·516 g.) were boiled with water (15 c.c.), the sulphone was isolated quantitatively.

(ii) *With methanol.* The alcohol was recovered unchanged after 30 hours' heating under reflux in anhydrous or 25% aqueous methanol, but in the presence of 0·5N-hydrochloric acid, it was converted during 16 hr. into the (±)-methyl ether, b. p. 160—165°/10 mm., in quantitative yield.

(iii) *With hydrochloric acid and acetyl chloride.* The alcohol (5·0 g.) was triturated with cold concentrated hydrochloric acid (50 c.c.). The oil which was immediately formed was left for 12 hr. in a vacuum-desiccator, and distilled, yielding 4-methyldiphenylmethyl chloride (5·1 g.), b. p. 160—164°/6—7 mm., n_D^{24} 1·5865 (Found: Cl, 16·3. Calc. for $C_{14}H_{13}Cl$: Cl, 16·4%). The reaction of acetyl chloride alone similarly yielded the chloride, but in the presence of pyridine gave the acetate, b. p. 190—194°/10—12 mm. (Found, by hydrolysis: equiv., 242).

Reactions of 4-*Methyldiphenylmethyl Esters.*—(i) *With sodium toluene*-p-*sulphinate.* A solution of the hydrogen phthalic ester (2·0 g.) and sodium toluene-*p*-sulphinate (1·23 g.) in 0·3N-sodium hydroxide (19 c.c.) deposited crystals of the sulphone (1·8 g.) during 12 days. Recrystallisation from acetic acid gave 4-methyldiphenylmethyl *p*-tolyl sulphone as very small needles, m. p. 159—160° (Found, S, 9·5. Calc. for $C_{21}H_{20}O_2S$: S, 9·5%). The (−)-hydrogen phthalate gave the (±)-sulphone. Under similar conditions, the hydrogen succinate also gave the sulphone, in 78% yield. The formate, acetate, and benzoate reacted with sodium toluene-*p*-sulphinate at room temperature in formic acid solution, but not in acetic acid solution, to give the sulphone. The same (±)-sulphone was obtained in excellent yield when the hydrogen phthalate, formate, benzoate, or (−)-acetate was heated under reflux for 15 min. with an aqueous solution of toluene-*p*-sulphinic acid.

(ii) *With methanol.* The hydrogen phthalic ester (3·0 g.) was heated under reflux with anhydrous methanol (40 c.c.) for 40 hr., yielding phthalic acid (0·62 g.; m. p. 188—190°) (Found: equiv., 83. Calc. for $C_8H_6O_4$: equiv., 83) and methyl 4-methyldiphenylmethyl ether (0·7 g.; b. p. 150—154°/8 mm.) (Found: C, 85·6; H, 7·2. Calc. for $C_{15}H_{16}O$: C, 84·9; H, 7·5%). Under similar conditions, the (−)-hydrogen phthalate yielded the inactive ether. Likewise, the hydrogen succinate was converted into the methyl ether. The acetate and benzoate were recovered from anhydrous methanol, and in 14—28% aqueous methanol underwent partial hydrolysis. From solution in methanol containing 14% of 0·5N-aqueous hydrochloric acid, after boiling for 12 hr., the methyl ether was isolated in excellent yield. However, the formate, after 24 hr. in boiling anhydrous methanol, was converted quantitatively into the alcohol, and from neutral or acidic aqueous methanol gave the methyl ether.

(iii) *With phenol.* The hydrogen phthalate (3·5 g.) and phenol (1·0 g.) were heated under reflux in dry chloroform. Phthalic acid (1·42 g.), m. p. 195° (decomp.) (Found: equiv., 82), was precipitated during 20 hr. The filtrate yielded 4-*methyldiphenylmethyl phenyl ether* (2·49 g.), b. p. 190—200°/7 mm., n_D^{20} 1·5910 (Found: C, 87·0; H, 6·8. $C_{20}H_{18}O_4$ requires C, 87·5; H, 6·5%).

(iv) *With carboxylic acids.* The hydrogen phthalate (3·0 g.), dissolved in 90% formic acid, after 15 min. at 100°, yielded 4-methyldiphenylmethyl formate (1·9 g., from methanol,), m. p. 50—52°, mixed m. p. with 4-methyldiphenylmethanol, 40—44° (Found: C, 79·7; H, 6·1. Calc. for $C_{15}H_{14}O_2$: C, 79·6; H, 6·2%). The (−)-hydrogen phthalate gave the (±)-formate.

During 3 months, the hydrogen phthalate reacted with cold glacial acetic acid to yield 4-methyldiphenylmethyl acetate (1·38 g.). The hydrogen succinate (1·0 g.) in 98% formic acid (10 c.c.), after 2 days at room temperature, gave the formate in 90% yield; in acetic acid, reaction was incomplete (30%) after 3 months at room temperature, but after 24 hours' heating under reflux the acetate was isolated in 69% yield.

The (–)-acetate (0·68 g.) in 98% formic acid (20 c.c.), after 5 days, yielded the (±)-formate (0·63 g.), m. p. 50—52°. The benzoate (0·82 g.) dissolved in 98% formic acid (10 c.c.) on gentle warming; next day it yielded the formate (0·6 g.), m. p. and mixed m. p. 51—52°. On being heated under reflux in glacial acetic acid (10 c.c.) for 24 hr., the benzoate (0·73 g.) was converted into the acetate (0·57 g.) (Found : equiv., 239).

(v) *With hydrochloric acid.* The hydrogen phthalate (1·0 g.) was triturated with concentrated hydrochloric acid (10 c.c.). After 12 hr., an oil had separated, which was extracted with ether, yielding 4-methyldiphenylmethyl chloride (0·22 g.), b. p. 160—166°/7 mm., n_D^{25} 1·5864 (Found : Cl, 16·3%). The aqueous layer yielded phthalic acid (0·31 g.), m. p. 190° (decomp.). The hydrogen phthalate was recovered after solution in acetyl chloride for 6 days. The acetate (0·50 g.), on trituration with concentrated hydrochloric acid (10 c.c.), was similarly converted into the chloride (0·44 g.), b. p. 160—165°/7 mm. (Found : Cl, 16·9%).

(vi) *With aqueous sodium hydroxide.* Solutions of the hydrogen phthalate or hydrogen succinate in 0·1—0·3N-sodium hydroxide yielded the alcohol in *ca.* 90% yield after a few days. Under the following conditions, however, some disproportionation occurred, giving the neutral ester. The hydrogen phthalate (1·0 g.) in 0·1N-sodium hydroxide (34 c.c.), after 2·5 hr. at 65°, yielded an oil which, from methanol, gave 4-methyldiphenylmethanol (0·2 g.), m. p. 50°, and impure di-(4-methyldiphenylmethyl) phthalate (0·34 g.), as a viscous oil which could not be crystallised (Found, by hydrolysis: equiv., 259. Calc. for $C_{36}H_{30}O_4$: equiv., 263). Disproportionation also occurred when the hydrogen phthalate (3·0 g.) was heated under reflux in chloroform (50 c.c.) for 34 hr.; the hydrogen phthalate (0·63 g.), m. p. 120—122°, phthalic acid (0·53 g.), m. p. 190° (decomp.), and the neutral phthalate (1·5 g.) (Found, by hydrolysis: equiv., 255) were isolated. The hydrogen succinate (1·0 g.) in 0·1N-sodium hydroxide (40 c.c.) after 6 days yielded an oil (0·294 g.) which did not solidify. From the aqueous layer, the hydrogen succinate (0·6 g.), m. p. 98—100°, was recovered. The oil was identified as *di-(4-methyldiphenylmethyl) succinate* by quantitative hydrolysis (Found : equiv., 244. $C_{32}H_{30}O_4$ requires equiv., 239), from which the alcohol (0·07 g.), m. p. 50—52°, was isolated.

2 : 4 : 6-*Trimethyldiphenylmethanol.*—The Grignard reaction between bromomesitylene (20 g.), magnesium (2·4 g.), and benzaldehyde (10·5 g.) gave 2 : 4 : 6-trimethyldiphenylmethanol (18 g.), which was purified through its hydrogen phthalate.

(±)-2 : 4 : 6-*Trimethyldiphenylmethyl Hydrogen Phthalate.*—A mixture of the unpurified alcohol (18 g.), phthalic anhydride (12 g.), and pyridine (6·5 g.) in benzene (13 c.c.), after 2 hr. at 60—65° and 16 hr. at room temperature, yielded 2 : 4 : 6-*trimethyldiphenylmethyl hydrogen phthalate* (27 g., 90%) as rhombs (from ether–light petroleum), m. p. 159—160° (Found : equiv., 375. $C_{24}H_{21}O_4$ requires equiv., 374). From chloroform the hydrogen phthalate gave efflorescent crystals containing about 1 mol. of chloroform, which melted first at 89—92° (decomp.) and then resolidified and melted again at 158—160°.

(+)-2 : 4 : 6-*Trimethyldiphenylmethyl Hydrogen Phthalate.*—A warm solution of the (±)-hydrogen phthalate (80 g.) and strychnine (69 g.) in acetone (200 c.c.) overnight deposited the crystalline salt (65 g.). After 5 recrystallisations from acetone this salt (35 g.), m. p. 138—141° (decomp.), was decomposed with aqueous ammonia, yielding the (+)-hydrogen phthalate, m. p. 125—126° (from benzene), $[\alpha]_D^{20}$ +89·1° (*l*, 1; *c*, 3·74 in $CHCl_3$). The m. p. and rotatory power of this ester were unchanged on further recrystallisation.

(+) *and* (–)-2 : 4 : 6-*Trimethyldiphenylmethanol.*—The above (+)-hydrogen phthalate (10 g.) was dissolved in a solution of sodium (3·5 g.) and water (5 c.c.) in ethanol (150 c.c.); after 15 min. at 100°, sodium phthalate separated. Addition of water gave (+)-2 : 4 : 6-trimethyldiphenylmethanol (5·7 g.), m. p. 67—69°. Recrystallisation from light petroleum yielded the *alcohol* in large prisms (4·5 g.), m. p. 70—70·5°, $[\alpha]_D^{20}$ +148·8° (*l*, 2; *c*, 1·250 in $CHCl_3$) (Found: C, 85·1; H, 8·0. $C_{16}H_{18}O$ requires C, 85·0; H, 8·0%). From this alcohol, the (+)-hydrogen phthalate was regenerated, having m. p. 125—126°, $[\alpha]_D^{19}$ +88·7° (*l*, 1; *c*, 2·57 in $CHCl_3$). The hydrogen phthalate from the mother-liquors of brucine salts was crystallised from ether–light petroleum, and the (±)-ester slowly separated. The oily (–)-hydrogen phthalate from the filtrate was hydrolysed, yielding (–)-2 : 4 : 6-trimethyldiphenylmethanol (10 g.; from light petroleum), m. p. 70—70·5°, $[\alpha]_D^{20}$ –147·9° (*l*, 2; *c*, 1·305 in $CHCl_3$).

(±)-, (+)-, *and* (−)-2 : 4 : 6-*Trimethyldiphenylmethyl Benzoate.*—The (±)-alcohol reacted with benzoyl chloride in the presence of pyridine to give the (±)-benzoate in 90% yield, as shining needles, m. p. 93—94°. Louise (*Ann. Chim. Phys.*, 1885, **6**, 209) reports m. p. 92°. Similarly, the (+)-alcohol gave the (+)-benzoate, m. p. 79—80°, $[\alpha]^{20}_{D}$ +44·8° (*l*, 2; *c*, 1·280 in C_6H_6), and the (−)-alcohol gave the (−)-benzoate, $[\alpha]^{18}_{D}$ −44·3° (*l*, 2; *c*, 2·008 in C_6H_6).

Reactions of 2 : 4 : 6-*Trimethyldiphenylmethanol.*—(i) *With sodium toluene*-p-*sulphinate.* A mixture of the alcohol (2·25 g.) and sodium toluene-*p*-sulphinate (2·15 g.) in acetic acid (40 c.c.) containing concentrated sulphuric acid (0·5 c.c.) was heated on the steam-bath for 30 min. and rapidly became purple. Nexy day, water was added, and p-*tolyl* 2 : 4 : 6-*trimethyldiphenylmethyl sulphone* (3·3 g.) was isolated as needles (from ethanol), m. p. 147—148° (Found : C, 75·5; H, 6·8; S, 8·8. $C_{23}H_{24}O_2S$ requires C, 75·8; H, 6·7; S, 8·8%). The same reagents in formic acid solution, in the absence of sulphuric acid, similarly yielded the sulphone.

(ii) *With acids.* The alcohol (5 g.), after being heated under reflux with 50% sulphuric acid (100 c.c.) for 2 days, yielded di-(2 : 4 : 6-trimethyldiphenylmethyl) ether, m. p. 137—138° (from ether–light petroleum). Louise (*loc. cit.*) records m. p. 137°. After 1·5 days in boiling acetic acid solution (20 c.c.), the (+)-alcohol (0·55 g.) was converted into the (±)-acetate (0·50 g.), b. p. 136—138°/0·8 mm., which could not be solidified (Found : C, 80·7; H, 7·7. Calc. for $C_{18}H_{20}O_2$: C, 80·6; H, 7·5%). Louise (*loc. cit.*) reports m. p. 52°. After 16 hr. at room temperature, a solution of the (+)-alcohol (1·0 g.) in 98% formic acid (8 c.c.) gave the *formate* (1·1 g.), m. p. 66·5—67·5° (Found : C, 80·1; H, 7·1. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·1%). The (+)-alcohol (0·5 g.) was heated on the steam-bath for 5 min. with trichloroacetic acid (1·0 g.), and gave 2 : 4 : 6-*trimethyldiphenylmethyl trichloroacetate* (90%), m. p. 92—93° (Found : C, 58·4; H, 4·7; Cl, 29·5. $C_{18}H_{17}O_2Cl_3$ requires C, 58·2; H, 4·6; Cl, 28·4%).

(iii) *With acetyl chloride.* Acetyl chloride (2 c.c.) was added to the (+)-alcohol (0·5 g.) which dissolved rapidly, giving a deep purple solution. The (±)-*chloride* (0·34 g.) was isolated, having b. p. 138—140°/0·8 mm. (Found : C, 78·5; H, 7·3; Cl, 14·1%; equiv., by hydrolysis, 246. $C_{16}H_{17}Cl$ requires C, 78·5; 7·0; Cl, 14·5%; equiv., 245). From the hydrolysate, ethyl 2 : 4 : 6-trimethyldiphenylmethyl ether was isolated, m. p. 29—30°.

Reactions of 2 : 4 : 6-*Trimethyldiphenylmethyl Esters.*—(i) *With sodium toluene*-p-*sulphinate.* A solution of the hydrogen phthalate (2·0 g.) and sodium toluene-*p*-sulphinate (1·1 g.) in aqueous sodium hydroxide (25 c.c. of 0·2N), after 2 days at 50° deposited the *p*-tolyl sulphone which, recrystallised (from ethanol; 1·7 g.), had m. p. 147—148°. The (+)-ester gave the (±)-sulphone.

(ii) *With thio*-p-*cresol.* A solution of the hydrogen phthalate (3·5 g.) in acetone (15 c.c.) was added to a suspension of thio-*p*-cresol (1·15 g.) in formic acid (7 c.c.). Within a few minutes, phthalic acid (1·2 g.) was deposited. Next day, water was added to the solution, yielding p-*tolyl* 2 : 4 : 6-*trimethyldiphenylmethyl sulphide* (3 g.), which separated from acetic acid or ethanol as leaflets, m. p. 93—94° (Found : C, 82·8; H, 7·1; S, 10·0. $C_{23}H_{24}S$ requires C, 83·1; H, 7·2; S, 9·7%). The (+)-ester gave the (±)-sulphide. A solution of the sulphide (1·0 g.) in acetic acid (15 c.c.) containing hydrogen peroxide (4·0 c.c. of 90-vol.), after 9 hr. at 60°, on cooling deposited *p*-tolyl 2 : 4 : 6-trimethyldiphenylmethyl sulphone, m. p. 145—147°, undepressed on admixture with the specimen prepared from sodium toluene-*p*-sulphinate.

(iii) *With ethanol.* A solution of the (+)-hydrogen phthalate (0·5 g.) in 96% ethanol (40 c.c.) was heated under reflux for 20 hr., by which time it was optically inactive. (±)-Ethyl 2 : 4 : 6-trimethyldiphenylmethyl ether (0·2 g.), b. p. 131—133°/0·5 mm., m. p. 30—31°, was isolated (Found : C, 85·0; H, 8·8. Calc. for $C_{18}H_{22}O$: C, 85·0; H, 8·8%). Louise (*loc. cit.*) reports m. p. 32°. The benzoate (2 g.) was recovered after being heated under reflux in 96% ethanol (20 c.c.) for 56 hr., but the formate, after 6 hours' heating or 6 weeks at room temperature, gave the ethyl ether in 80% yield.

(iv) *With carboxylic acids.* A solution of the (+)-hydrogen phthalate (0·38 g.) in 98% formic acid (10 c.c.) rapidly became turbid. After 15 min. the solution was diluted with ice-cold sodium hydroxide solution, yielding (±)-2 : 4 : 6-trimethyldiphenylmethyl formate (0·2 g.), m. p. and mixed m. p. 66—67°. The (+)-hydrogen phthalate (2 g.) in acetic acid (20 c.c.) after 5 hr. at 100° gave the (±)-acetate (1·0 g.), b. p. 135—136°/0·6 mm. A mixture of the (+)-hydrogen phthalate (0·3 g.) and trichloroacetic acid (0·5 g.) was ground with gentle heating, forming a thick slurry which changed to a purple semi-solid. After 5 min. at 100°, aqueous sodium hydroxide was added, yielding (±)-2 : 4 : 6-trimethyldiphenylmethyl trichloroacetate (from light petroleum; 0·25 g.), m. p. and mixed m. p. 92—93°.

(v) *With acetyl chloride.* A solution of the (+)-hydrogen phthalate (2·0 g.) in acetyl chloride (1·0 c.c.) rapidly set to a purple semi-solid. After being kept overnight *in vacuo* over potassium hydroxide, a light petroleum extract yielded, on distillation, (±)-2 : 4 : 6-trimethyldiphenylmethyl chloride (0·6 g.), b. p. 138—140°/0·8 mm.

(vi) ***With aqueous sodium hydroxide.*** Solutions of the (+)-hydrogen phthalate (0·6 g.) in aqueous sodium hydroxide (10 mols.) of various concentrations were heated on the steam-bath for 5 min. and the liberated alcohol was isolated by extraction with light petroleum. The following results were obtained :

NaOH, N	2	1	0·5	0·25
Optical purity of alcohol, %	100	98·5	88·1	81·7

Under milder conditions, some neutral phthalate was also formed as an oil which could not be purified. A solution of the (+)-hydrogen phthalate (1·9 g.) ($[\alpha]_D^{20}$ +89·2° in $CHCl_3$) in aqueous sodium hydroxide (15·7 c.c. of 0·3N), after 8 hr. at 60°, deposited a neutral oil (1·3 g.), $[\alpha]_D^{20}$ +70·0° (*l*, 1; *c*, 1·46 in $CHCl_3$), which, by quantitative hydrolysis, was shown to consist of 81% of the dialkyl phthalate and 19% of the alcohol. Hydrolysis of this mixture of neutral phthalate and alcohol with sodium ethoxide in ethanol gave the alcohol possessing 68·5% of its maximum optical activity.

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