84. *Alkyl–Oxygen Fission in Carboxylic Esters. Part VIII. Esters of* p-*Methylthio- and* p-*Methylsulphonyl-diphenylcarbinols.*

By M. P. Balfe, R. E. Dabby, and J. Kenyon.

The (—)-hydrogen phthalate of *p*-methylthiodiphenylcarbinol yields, by methods previously described, a half-racemised neutral dicarbinyl phthalate and the racemic *p*-tolyl sulphone. It reacts with acetic acid to yield the (±)-acetate, with concurrent racemisation of the unreacted phthalate, and on hydrolysis with aqueous alkali yields a partly racemised carbinol; optically pure (—)-carbinol is obtained on hydrolysis of the (—)-hydrogen phthalate in alcoholic alkali. These reactions are characteristic of the unimolecular mechanism of alkyl–oxygen fission. Oxidation of the *p*-methylthio- to the *p*-methylsulphonyl derivative introduces an electron-attracting *p*-substituent in place of the electron-releasing methylthio-group, and the (+)-hydrogen phthalate of *p*-methylsulphonyldiphenylcarbinol accordingly does not undergo reactions involving alkyl–oxygen fission.

Reductions of *p*-methylthiobenzophenone under acid or alkaline conditions and of *p*-methylsulphonylbenzophenone under acid conditions yield the corresponding *p*-substituted diphenylcarbinols, but when *p*-methylsulphonylbenzophenone is reduced under alkaline conditions, the methylsulphonyl group is removed and unsubstituted diphenylcarbinol is produced.

(—)-*p*-Methylthiodiphenylcarbinol and certain of its derivatives undergo reactions involving alkyl–oxygen fission similar to those of derivatives of methoxyphenyl-phenyl- and -α-naphthyl-carbinol, described and discussed in Parts II (*J.*, 1942, 605) and IV (*J.*, 1946, 803). The (—)-hydrogen phthalate yields the (—)-carbinol on hydrolysis with alcoholic alkali, and extensively racemised (—)-carbinol on hydrolysis in aqueous alkali; it also yields the (±)-carbinol on hydrolysis by sulphuric acid in acetone solution. From a solution of the (—)-hydrogen phthalate in an equimolecular proportion of aqueous sodium hydroxide, the neutral ester, di-(*p*-methylthiophenyl)carbinyl phthalate, separates, and from this on hydrolysis with alcoholic alkali the carbinol is obtained with half the rotatory power of that obtained from the hydrogen phthalate. The (—)-hydrogen phthalate, dissolved in an equimolecular proportion of aqueous sodium hydroxide, reacts with sodium toluene-*p*-sulphinate to yield the (±)-*p*-tolyl sulphone. It yields the (±)-chloride (chloro-*p*-methylthiodiphenylmethane) on reaction with acetyl chloride. The (—)-carbinol reacts with acetyl chloride in presence of pyridine to yield the (—)-acetate, and in the absence of pyridine to yield the (±)-chloride. The chloride is also obtained by triturating the carbinol, and a number of its derivatives, with concentrated hydrochloric acid; these reactions are accompanied by complete racemisation.

Solutions of (—)-*p*-methylthiodiphenylcarbinyl hydrogen phthalate in acetic acid undergo racemisation at 100° ($t_{\frac{1}{2}}$ = 14 minutes) and at room temperature ($t_{\frac{1}{2}}$ = 100 hours) with formation of the (±)-acetate and concurrent racemisation of the unreacted fraction of the phthalate. Solutions in ethyl alcohol react similarly at 100°, yielding the (±)-ethyl ether. Solutions of the carbinol in acetic acid also yield the (±)-acetate at 100° ($t_{\frac{1}{2}}$ = 2 hours) and undergo a very slow racemisation at room temperature.

(+)-*p*-Methylsulphonyldiphenylcarbinol is obtained by oxidation of (—)-*p*-methylthiodiphenylcarbinol with hydrogen peroxide. It yields a (+)-hydrogen phthalate identical with that obtained by oxidation of (—)-*p*-methylthiodiphenylcarbinyl hydrogen phthalate. Hydrolysis of this (+)-phthalate with aqueous alkali yields (+)-*p*-methylsulphonyldiphenylcarbinol without any racemisation. (±)-*p*-Methylsulphonyldiphenylcarbinyl hydrogen phthalate does not yield the neutral dicarbinyl phthalate, nor does it react with sodium toluene-*p*-sulphinate, when dissolved in an equimolecular proportion of aqueous sodium hydroxide. These observations illustrate how the electron-releasing tendency of the *p*-methylthio-group, which promotes alkyl–oxygen fission in derivatives of *p*-methylthiodiphenylcarbinol, is converted into an electron-attracting tendency when the methylthio-group is oxidised to the sulphone. The same effect is illustrated by the inertness of *p*-bromomethylsulphonylbenzene towards magnesium, whereas *p*-bromomethylthiobenzene readily forms the Grignard reagent.

When reduced in acid conditions (zinc and acetic acid), both *p*-methylthio- and *p*-methylsulphonyl-benzophenone yield the corresponding diphenylcarbinols. Under alkaline conditions (zinc dust and sodium hydroxide, or sodium amalgam), *p*-methylthiobenzophenone yields *p*-methylthiodiphenylcarbinol, but *p*-methylsulphonylbenzophenone yields diphenylcarbinol, with fission of the bond between the sulphur atom and the aromatic nucleus. Electron-accession to this carbon–sulphur bond is assisted by the *p*-carbonyl group, but reduction can only occur if this accession is followed either by addition of protons to the resulting anionic sites, which is impossible in the present examples, or by fission of the bond joining these sites. Presumably the fact that this fission occurs only with the *p*-methylsulphonyl derivative and under alkaline conditions, is related to the comparative stability of the methylsulphinate anion (cf. Birch, *Faraday Soc. Discussions*, 1947, **2**, 247).

EXPERIMENTAL.

Thioanisole, prepared by the action of methyl sulphate on sodium thiophenoxide in aqueous solution (yield 91%), had b. p. 82°/18 mm.; d_4^{20} 1·053; n_D^{20} 1·5835. *p*-Bromothioanisole, prepared by the action of bromine on a solution of thioanisole in carbon disulphide, separates from methanol in glistening plates, m. p. 37·5° (yield 92%).

p-*Methylthiobenzophenone*.—Powdered aluminium chloride (112 g.) was added during 45 minutes to a mechanically stirred mixture of thioanisole (93 g.), benzoyl chloride (87 c.c.), and carbon disulphide (300 c.c.); the temperature of the reaction mixture was kept below 20° during the mixing, and subsequently raised to 40—45° for an hour. The solid product was filtered off, washed with carbon disulphide, and decomposed with hydrochloric acid, decomposition being completed by heating on the steam-bath. When the hot reaction mixture was poured on crushed ice, the ketone set to a crystalline mass which, after being washed with sodium hydroxide and dried, weighed 153 g. and had m. p. 75—76°. p-*Methylthiobenzophenone* separates from ether–light petroleum in rhombs, or from methanol in prismatic needles, m. p. 78°. It distils unchanged, b. p. 221°/11 mm. (Found: C, 73·3; H, 5·4; S, 13·4. $C_{14}H_{12}OS$ requires C, 73·6; H, 5·3; S, 14·0%).

p-*Methylthiodiphenylcarbinol*—(*a*) Zinc dust (46 g.) was added to a solution of *p*-methylthiobenzophenone (46 g.) and sodium hydroxide (46 g.) in ethyl alcohol (300 c.c.), and the mixture heated under reflux for 5—6 hours, and filtered whilst hot; the residue was washed with boiling alcohol (30 c.c.), and the filtrate diluted with water, p-*methylthiodiphenylcarbinol*, m. p. 92—93° (46 g.), being obtained. It separates from ether–light petroleum in silky needles, m. p. 94° (96%) (Found: C, 72·8; H, 6·2; S, 14·0. $C_{14}H_{14}OS$ requires C, 73·0; H, 6·1; S, 14·1%). A parallel result was obtained by the action of sodium amalgam on an alcoholic solution of the ketone.

(*b*) Benzaldehyde (1·0 g.) in ethereal solution was added to a Grignard reagent prepared from *p*-bromothioanisole (2·1 g.); the resulting methylthiodiphenylcarbinol (yield 45%) had m. p. 94° alone or when mixed with the carbinol from method (*a*). Methylthiodiphenylcarbinol, after being heated at 145° for an hour, was recovered unchanged. It does not react with methyl iodide.

(±)-*Methylthiodiphenylcarbinyl Hydrogen Phthalate*.—To a solution of phthalic anhydride (37 g.) in pyridine (40 g.), the carbinol (57·5 g.) was added, and the mixture—which became homogeneous in 15 minutes—was kept at 50—60° for 3 hours. The viscous product was dissolved in acetone (150 c.c.), and the solution decomposed by the addition of hydrochloric acid (100 c.c.) diluted with water (2 l.). The precipitated oily material soon set to a crystalline solid, m. p. 118—120°. The *hydrogen phthalate* separates from benzene–light petroleum or carbon disulphide in hemispherical clusters of needles, m. p. 123—124° (90%) (Found, by titration with 0·1N-NaOH: *M*, 378. $C_{23}H_{18}O_4S$ requires *M*, 378). When a solution of the acid ester (0·500 g.) in alcoholic potash was heated under reflux for 30 minutes, 30·28 c.c. were neutralised (Calc.: 30·32 c.c.), whence *M* = 378; the neutralised solution of the hydrolysed ester yielded the carbinol (0·300 g. Calc., 0·304 g.), m. p. 94°.

(−)-*Methylthiodiphenylcarbinyl Hydrogen Phthalate*.—A solution of the (±)-acid ester (95 g.) and quinine (95 g.) in warm alcohol (200 c.c.; 96%) after being kept overnight deposited the crystalline quinine salt; this after three crystallisations from the same solvent yielded optically pure quinine (−)-methylthiodiphenylcarbinyl phthalate (40 g.) as glistening needles, m. p. 116—117°. Decomposition of this in acetone solution with hydrochloric acid yielded the (−)-acid ester (19·5 g.), which separates from carbon disulphide in fibrous needles, m. p. 96—97°. Rotatory powers are given in the table.

Specific rotatory powers of (−)-methylthiodiphenylcarbinyl hydrogen phthalate.

Solvent	g./100 c.c. of soln.	*t*.	$[\alpha]_{6438}$	$[\alpha]_{5893}$	$[\alpha]_{5780}$	$[\alpha]_{5461}$	$[\alpha]_{5086}$	$[\alpha]_{4800}$	$[\alpha]_{4358}$
CS_2	2·501	18°	−25·0°	−30·6°	−31·6°	−33·4°	−45·0°	−53·0°	−75·0°
C_6H_6	5·002	19	−21·3	−22·0	−24·0	−27·5	−34·3	−44·3	−56·0
$COMe_2$	4·998	19	−9·0	−10·0	−10·9	−15·2	−16·5	−17·5	−27·5
$CHCl_3$	5·011	18·5	−9·0	−9·6	−11·4	−13·4	−15·0	−20·0	−27·4
MeOH	5·003	15	−8·0	−9·5	−11·0	−13·5	−16·0	−18·5	−25·0
MeOAc	5·013	18	−6·5	−7·1	−7·4	−8·0	−10·0	−13·0	−17·5

(−)-*Methylthiodiphenylcarbinol*.—The (−)-acid ester (2 g.) was dissolved in a solution of sodium ethoxide [from sodium (0·5 g.) in absolute alcohol (20 c.c.)], and the whole heated gently for a few minutes. On dilution with water the (−)-*carbinol* separated as a crystalline solid, and recrystallised from carbon disulphide in clusters of short needles (1·0 g.), m. p. 56—57°, $[\alpha]_D^{20}$ −13·5° (*l*, 2; *c*, 6·000 in carbon disulphide). Reconversion of this carbinol into its hydrogen phthalate yielded a product possessing a rotatory power almost identical with that of the original acid ester, indicating absence of racemisation.

When, however, aqueous sodium hydroxide of high or low concentration is used to effect the hydrolysis the liberated alcohol is extensively racemised.

Acetate. To a solution of the carbinol (2·3 g.; $[\alpha]_D$ −8·6° in carbon disulphide) in pyridine (2 g.) was added acetic anhydride (1·1 g.)—or acetyl chloride (0·8 g.)—and the mixture gently warmed for a few minutes. The resulting (−)-*acetate* (1·9 g.) had b. p. 221°/15 mm., d_4^{21} 1·144, n_D^{20} 1·5912, $[\alpha]_D^{20}$ −29·4° (*l*, 2; *c*, 3·756 in carbon disulphide) [Found: C, 70·3; H, 6·2%; *M*, 272 (by hydrolysis). $C_{16}H_{16}O_2S$ requires C, 70·6; H, 5·9%; *M*, 272].

The (±)-*acetate* was obtained when the (−)-carbinol (1 g.) was heated with glacial acetic acid (15 c.c.) for several hours on the steam-bath. It had b. p. 221°/15 mm., n_D^{20} 1·5912 [Found: *M*, 273 (by hydrolysis)].

Reactions of (−)-Methylthiodiphenylcarbinyl Hydrogen Phthalate.—(i) *Formation of di(methylthiodiphenylcarbinyl) phthalate.* (*a*) A solution of the (−)-hydrogen phthalate (3 g.; $[\alpha]_D$ −27·0° in carbon disulphide) in sodium hydroxide (27 c.c.; 0·3N.) after some 40 minutes began to deposit the neutral *phthalate*; this, after 3 days, was removed as a glassy mass (2·1 g.; calc., 2·3 g.), m. p. 40—45°, which could not be obtained crystalline. It had $[\alpha]_D$ −23·6° in carbon disulphide (*c*, 2·501; *l*, 2) [Found: *M*, 596 (by hydrolysis). $C_{36}H_{30}O_4S_2$ requires *M*, 590]. By hydrolysis with potassium hydroxide in absolute alcohol the neutral ester yielded (−)-methylthiodiphenylcarbinol, m. p. 90—91°, $[\alpha]_D$ −4·4° in carbon disulphide. Hydrolysis of the original (−)-hydrogen phthalate under similar conditions yielded a (−)-carbinol of approximately twice the rotatory power, *i.e.*, $[\alpha]_D$ −8·6°, and m. p. 56—57°.

(*b*) A solution of the (±)-hydrogen phthalate (3·78 g.) in chloroform (25 c.c.) after being heated under reflux for 5 hours had deposited phthalic acid (0·55 g.). From the filtrate there were isolated unchanged acid ester (1·5 g.) and the neutral phthalate (1·5 g.) (Found, by hydrolysis; *M*, 594).

(ii) *Formation of methylthiodiphenylcarbinyl* p-*tolyl sulphone.* A solution of the (−)-hydrogen phthalate (0·5 g.; $[\alpha]_D$ −17·0°) in sodium hydroxide (4·5 c.c.; 0·3N.) was rapidly filtered into a solution of sodium toluene-*p*-sulphinate (0·28 g.) in water (5 c.c.). Separation of the crystalline *sulphone* began after some 30 minutes and was complete within 24 hours. The sulphone (0·25 g.) was optically inactive and separated from methanol in needles, m. p. 172° alone and when mixed with sulphone prepared in a similar manner from the (±)-hydrogen phthalate (Found: S, 16·9. $C_{21}H_{20}O_2S_2$ requires S, 17·3%).

(iii) *Formation of ethyl (±)-methylthiodiphenylcarbinyl ether.* A solution of the (−)-hydrogen phthalate (4 g.; $[\alpha]_D$ −30·6° in carbon disulphide) in absolute alcohol (70 c.c.) was heated under reflux for 45 minutes; the mixture yielded the (−)-hydrogen phthalate (1·4 g.), the rotatory power of which had fallen to $[\alpha]_D$ −22·4°, and the (±)-*ethyl ether* (1·7 g.), b. p. 206—208°/15 mm., n_D^{20} 1·5910, d_4^{21} 1·0891 (Found: C, 74·2; H, 7·3. $C_{16}H_{18}OS$ requires C, 74·4; H, 7·0%). When the heating was prolonged to 4 hours the (−)-ester was converted completely into the (±)-ether.

(iv) *Formation of (±)-methylthiodiphenylcarbinyl acetate.* A solution of the (−)-hydrogen phthalate (1 g.; $[\alpha]_D$ −30·6°) in glacial acetic acid (20 c.c.) when kept for an hour at room temperature yielded (−)-hydrogen phthalate (0·45 g.) with $[\alpha]_D$ −21·8° and (±)-methylthiodiphenylcarbinyl acetate (0·36 g.), b. p. 216°/14 mm., n_D^{20} 1·5912.

(v) *Hydrolysis with sulphuric acid.* The (−)-hydrogen phthalate (1 g.; $[\alpha]_D$ 20° −30·6° in carbon disulphide) was heated under reflux for 3 hours in acetone (15 c.c.) containing sulphuric acid (0·5 c.c.) and water (4 c.c.). (±)-Carbinol (0·5 g.), m. p. and mixed m. p. 94°, was formed [the neutral (−)-dicarbinyl phthalate yielded (±)-carbinol in a similar experiment]. From a similar solution of the (−)-hydrogen phthalate in acetone and sulphuric acid, after 2 days at room temperature, 0·75 g. of hydrogen phthalate with $[\alpha]_D^{20}$ −24·8° (in carbon disulphide) was extracted by sodium carbonate, and the residue yielded ±)-carbinol (0·1 g.; m. p. 94°).

Preparation of Methylthiodiphenylcarbinyl Chloride.—*From the carbinol.* (i) By use of concentrated hydrochloric acid. The (−)-carbinol (2 g.) when triturated with the acid (40 c.c.) gradually changed to a liquid which, in turn, solidified. The resulting (±)-*methylthiodiphenylcarbinyl chloride* separated from light petroleum and a little ether in needles, m. p. 56° (Found: Cl, 14·1. $C_{14}H_{13}SCl$ requires Cl, 14·2%). (ii) By use of acetyl chloride. The (−)-carbinol (1 g.) dissolved readily in acetyl chloride (1 g.) and yielded the (±)-chloride, m. p. 56°.

From esters. The optically active acetate, hydrogen phthalate, and neutral phthalate of methylthiodiphenylcarbinol when triturated with concentrated hydrochloric acid at room temperature yielded, in each case, (±)-methylthiodiphenylcarbinyl chloride, m. p. 56°. The (+)-hydrogen phthalate (1·9 g.) on reaction with acetyl chloride (0·7 c.c.) yielded (±)-chloride (1·2 g.), m. p. and mixed m. p 56°.

Reactions of Methylthiodiphenylcarbinyl Chloride.—(i) With water, this gave the carbinol, m. p. 94°, and (ii) with absolute alcohol the ethyl ether, b. p. 212°/20 mm., n_D^{20} 1·5910. (iii) With sodium benzoate it yielded the *benzoate*, hemispherical clusters of needles, m. p. 59° alone and mixed with a specimen prepared directly from the carbinol (Found: C, 75·6; H, 5·5. $C_{21}H_{18}O_2S$ requires C, 75·45; H, 5·4%). (iv) With sodium toluene-*p*-sulphinate it afforded the sulphone, m. p. 172°, and (v) with potassium hydrogen phthalate the hydrogen phthalate (m. p. and mixed m. p. 123—124°) together with a small proportion of carbinol (m. p. 94°).

(±)-p-*Methylsulphonyldiphenylcarbinol*—(*a*) A mixture of methylthiodiphenylcarbinol (1 g.), glacial acetic acid (20 c.c.), and hydrogen peroxide (3·3 c.c.; 90-vol.) after being kept for 2 days at room temperature was mixed with an excess of dilute sodium hydroxide solution. The precipitated p-*methylsulphonyldiphenylcarbinol* separated from hot water or methanol in glistening plates (1 g.), m. p. 125—125·5° (Found: C, 64·0; H, 5·5; S, 12·2. $C_{14}H_{14}O_3S$ requires C, 64·1; H, 5·3; S, 12·2%).

(*b*) A mixture of methylthiobenzophenone (2 g.) in acetic acid (25 c.c.) and potassium permanganate (2·2 g.), after being heated on the steam-bath for 40 minutes, was decolorised with sulphur dioxide and diluted with water. The precipitated p-*methylsulphonylbenzophenone* separated from alcohol in glistening plates (2·1 g.), m. p. 141° (Found : S, 11·8. $C_{14}H_{12}O_3S$ requires S, 12·3%). When the permanganate was replaced by hydrogen peroxide a similar result was obtained. This ketone (4 g.) on reduction with aluminium (0·5 g.) and anhydrous *iso*propyl alcohol (30 c.c.) during 2 hours yielded *p*-methylsulphonyldiphenylcarbinol, glistening plates (3·7 g.) (from ethanol), m. p. 125—125·5° alone and when mixed with the product from (*a*) or with the product obtained when the ketone was reduced with zinc dust and acetic acid.

Reduction of p-*Methylsulphonylbenzophenone to Diphenylcarbinol.*—A mixture of the ketone (4 g.), ethyl alcohol (150 c.c.), and sodium amalgam (80 g. of 5%) was heated under reflux for 2 hours, and the alcoholic solution diluted with water. The resulting crystalline material, which was sulphur-free, separated from ether–light petroleum in long, silky needles, m. p. 66—67° alone or when mixed with an authentic specimen of diphenylcarbinol. A similar result was obtained when a mixture of the ketone (1 g.), ethanol (30 c.c.), sodium hydroxide (5 g.), and zinc dust (5 g.) was left overnight at room temperature.

Oxidation of (−)-*Methylthiodiphenylcarbinol to* (+)-p-*Methylsulphonyldiphenylcarbinol.*—A solution of (−)-methylthiodiphenylcarbinol (3·6 g.; $[\alpha]_D$ −4·5° in methylene chloride) in glacial acetic acid (75 c.c.) and hydrogen peroxide (15 c.c.; 90-vol.) after being kept for 6 days and dilution with dilute sodium hydroxide deposited (+)-p-*methylsulphonyldiphenylcarbinol*, which separated from methylene chloride in glistening plates (3·0 g.), m. p. 146—147°, $[\alpha]_D^{19}$ +45·1° (*l*, 2; *c*, 5·025 in methylene chloride).

(+)-p-*Methylsulphonyldiphenylcarbinyl Hydrogen Phthalate.*—(*a*) A mixture of the (+)-carbinol (1·5 g.), phthalic anhydride (0·84 g.), and pyridine (1 g.) was heated on the steam-bath for 2 hours and worked up in the usual way. The resulting *hydrogen phthalate* separated from methylene chloride–ligroin in plates (2·1 g.), m. p. 105—107°, $[\alpha]_D^{18}$ +37·0° (*l*, 2; *c*, 5·113 in methylene chloride) (Found, by titration : *M*, 415. $C_{22}H_{18}O_6S$ requires *M*, 410).

(*b*) *By oxidation of* (−)-*methylthiodiphenylcarbinyl hydrogen phthalate.* A solution of the (−)-ester (3 g.; $[\alpha]_D$ −22·5° in carbon disulphide solution) in glacial acetic acid (30 c.c.) and hydrogen peroxide (10 c.c.) was kept for 3 days and diluted with water. The precipitated sulphonyl ester separated from methylene chloride–ligroin in plates (2·9 g.), m. p. 106—108°, $[\alpha]_D^{19}$ +36·6° in methylene chloride. By hydrolysis with sodium hydroxide it yielded (+)-*p*-methylsulphonyldiphenylcarbinol, $[\alpha]_D^{18}$ +44·8° in methylene chloride.

Hydrolysis of (+)-p-*Methylsulphonyldiphenylcarbinyl Hydrogen Phthalate.*—(a) *In anhydrous alcohol.* The (+)-ester (0·5 g.), heated with an alcoholic solution of sodium ethoxide, yielded (+)-*p*-methylsulphonyldiphenylcarbinol, which separated from methylene chloride in glistening plates (0·25 g.), m. p. 146—147°, $[\alpha]_D^{19}$ +45·0° (*l*, 2; *c*, 2·203 in methylene chloride).

(b) *In aqueous solution.* The (+)-ester (0·5 g.) in sodium hydroxide (15 c.c. of 0·3N.), heated on the steam-bath for 30 minutes, yielded the (+)-carbinol (0·3 g.), m. p. 146—147°, $[\alpha]_D^{19}$ +44·8° (*l*, 2; *c*, 2·221 in methylene chloride).

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BATTERSEA POLYTECHNIC, LONDON, S.W.11.

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