

81. The (+)- and (-)-*o*-Tolyl-*p*-tolylcarbinols.

By M. P. BALFE, M. K. HARGREAVES, and J. KENYON.

Resolution of *o*-tolyl-*p*-tolylcarbinol into its optical antipodes has been achieved by fractional crystallisation of the quinine and the strychnine salts of its hydrogen phthalate. Some reactions of the acid ester are described.

RECRYSTALLISATION of the quinine salts of (\pm)-*o*-tolyl-*p*-tolylcarbinyl hydrogen phthalate yields the optically pure (-)-hydrogen phthalate. The pure (+)-hydrogen phthalate is obtained by converting the more soluble quinine salt into the corresponding strychnine salt which is, in turn, recrystallised. Decomposition of the (+)- and the (-)-hydrogen phthalate yields respectively the (+)- and the (-)-carbinol.

o-Tolyl-*p*-tolylcarbinyl hydrogen phthalate reacts with dilute sodium hydroxide solution and with sodium toluene-*p*-sulphinate in a manner similar to, but considerably slower than, that of *p*-methoxydiphenylcarbinyl hydrogen phthalate (Part II, *J.*, 1942, 605). The reaction between the hydrogen phthalate and anhydrous formic acid affords the di-(*o*-tolyl-*p*-tolylcarbinyl) ether.

EXPERIMENTAL.

o-Tolyl *p*-Tolyl Ketone.—A mixture of *o*-toluoyl chloride (80 g.), anhydrous aluminium chloride (80 g.), and dry toluene (320 g.) was warmed for 2 days on the water-bath and then set aside for a week, and the complex decomposed with ice and hydrochloric acid. The dried toluene layer was distilled, and the fraction, b. p. 181—182°/18 mm., collected. With care the material so prepared is obtained colourless, and has n_D^{20} 1.5908 (cf. Scharwin and Schorygin, *Ber.*, 1903, **36**, 2025); the yield is up to 105 g. (67—96%).

o-Tolyl-*p*-tolylcarbinol.—(a) *From o-tolyl p-tolyl ketone by Pondorff's method.* Cleaned aluminium (11 g.) and mercuric chloride (0.5 g.) were added to dry isopropyl alcohol (120 c.c.). After 2.5 hours isopropyl alcohol (120 c.c.) was added and, when all the aluminium had dissolved, *o*-tolyl *p*-tolyl ketone (41.3 g.) dissolved in isopropyl alcohol (200 c.c.) was added. After separation of acetone in the usual manner the carbinol (18 g., 43%) was isolated by extraction with ether.

(b) *By Grignard's method.* *o*-Tolyl bromide (20 g.), dissolved in an equal volume of dry ether, was slowly run on to magnesium (3 g.) covered with dry ether. When reaction had ceased, an ethereal solution of *p*-tolualdehyde (14 g.) was run in slowly with vigorous stirring. On completion of the reaction, the mixture was poured on ice and ammonium chloride; the yield was 5 g. (20%). The (\pm)-*o*-tolyl-*p*-tolylcarbinol separated from light petroleum in rhombs, m. p. 59—60° (Found: C, 84.6; H, 7.5. $C_{15}H_{18}O$ requires C, 84.9; H, 7.6%).

(\pm)-*o*-Tolyl-*p*-tolylcarbinyl α -naphthylurethane. A mixture of the carbinol (5.25 g.) and α -naphthyl isocyanate (4 g.) was warmed for a few minutes and set aside. The resulting urethane, after recrystallisation from light petroleum and then from ethanol, formed needles, m. p. 124° (Found: N, 3.4. $C_{26}H_{23}O_2N$ requires N, 3.7%).

(\pm)-*o*-Tolyl-*p*-tolylcarbinyl *p*-nitrobenzoate. A solution of the carbinol (9.3 g.) and *p*-nitrobenzoyl chloride (9.5 g.) in dry pyridine (10 c.c.) and carbon tetrachloride (20 c.c.) slowly deposited the ester, which separated from alcohol in fine needles (10.2 g.), m. p. 117—118° (Found: N, 3.4. $C_{22}H_{19}O_4N$ requires N, 3.8%).

(\pm)-*o*-Tolyl-*p*-tolylcarbinyl Hydrogen Phthalate.—A solution of *o*-tolyl-*p*-tolylcarbinol (106 g.) and phthalic anhydride (74 g.) in pyridine (40 g.) and toluene (40 g.) was warmed, set aside for 14 days, and then extracted with ice-cold hydrochloric acid; (\pm)-*o*-tolyl-*p*-tolylcarbinyl hydrogen phthalate (180 g.) crystallised from the toluene solution. The crude hydrogen phthalate (132 g., 72%) was freed from phthalic acid by extraction with chloroform. The ester after three crystallisations from ether—light petroleum formed prisms, m. p. 129° (Found, by rapid titration with dilute NaOH: *M*, 362. $C_{23}H_{20}O_4$ requires *M*, 360).

(-)-*o*-Tolyl-*p*-tolylcarbinyl Hydrogen Phthalate.—A solution of the (\pm)-hydrogen phthalate (124 g.) and quinine (111.6 g.) in hot ethanol was allowed to cool and diluted with water to incipient crystallisation. The quinine salt (94 g.) of (-)-*o*-tolyl-*p*-tolylcarbinyl hydrogen phthalate slowly crystallised. After four recrystallisations from ethanol (96%) it was decomposed by addition of ice-cold 5*N*-hydrochloric acid to a suspension of the salt in acetone, the mixture was then extracted with ether, and the ethereal extract washed with dilute hydrochloric acid and then with water and dried. The hydrogen phthalate separated from ether—light petroleum in small rhombs, m. p. 126°, $[\alpha]_D^{17}$ -49.7° (*l*, 2; *c*, 2.000 in chloroform). Further recrystallisation from carbon disulphide produced no significant change in the rotatory power.

(+)-*o*-Tolyl-*p*-tolylcarbinyl Hydrogen Phthalate.—The mother-liquor from the first crop of quinine salt was decomposed, yielding (+)-*o*-tolyl-*p*-tolylcarbinyl hydrogen phthalate (48 g.) having $[\alpha]_D^{19}$ +20° in chloroform. This acid ester (48 g.) and strychnine (42 g.) were dissolved in boiling 96% ethyl alcohol, and the solution was cooled and diluted with water. After $\frac{1}{2}$ hour, crystals (m. p. 120—122°; 44 g.) of the strychnine salt of (+)-*o*-tolyl-*p*-tolylcarbinyl hydrogen phthalate were deposited. This salt was recrystallised twice from 96% alcohol, then decomposed as described above. The resulting (+)-*o*-tolyl-

p-tolylcarbiny hydrogen phthalate separated from carbon disulphide in needles, $[\alpha]_D^{19.6} + 49.4^\circ$ (*l*, 2; *c*, 2.000 in chloroform). Its specific rotatory powers in various solvents were as follows :

Solvent.	<i>l</i> .	<i>c</i> .	$[\alpha]_D^{20}$.	Solvent.	<i>l</i> .	<i>c</i> .	$[\alpha]_D^{20}$.
Acetic acid	1	3.40	+27.1°	Chloroform	2	2.00	49.7°
Acetone	2	1.50	29.7	Benzene	2	1.80	61.0
Ethyl alcohol	2	1.80	30.9				

(+)- and (-)-*o*-Tolyl-*p*-tolylcarbinols.—(-)-*o*-Tolyl-*p*-tolylcarbiny hydrogen phthalate, $[\alpha]_D^{17} - 49.7^\circ$ (2 g.), was added to a solution of sodium ethoxide [from sodium (0.6 g.) in warm 96% alcohol (15 g.)]. The mixture was heated on a steam-bath for some minutes, until a thick white precipitate was produced. After being cooled in ice the product was diluted with water, and the carbinol (0.6 g.) filtered off and recrystallised from ether-light petroleum; it formed needles, m. p. 47–48°, $[\alpha]_D^{21} - 25.2^\circ$ (*l*, 2; *c*, 0.600 in carbon disulphide). The (+)-carbinol (0.6 g.), similarly obtained from the (+)-hydrogen phthalate (2 g.) of $[\alpha]_D^{19.6} + 49.4^\circ$, formed prisms, m. p. 48–49°, $[\alpha]_D^{20} + 24.1^\circ$ (*l*, 2; *c*, 1.100 in carbon disulphide).

Some Reactions of o-Tolyl-p-tolylcarbiny Hydrogen Phthalate.—(1) *With sodium toluene-p-sulphinat*e. Sodium toluene-*p*-sulphinat (0.75 g.), dissolved in 20 c.c. of water, was added to the hydrogen phthalate (1.5 g.) in 8 c.c. of a saturated solution of sodium hydrogen carbonate, and the mixture warmed on the steam-bath. After $\frac{1}{2}$ hour, needles (0.8 g.) of *p*-tolyl *o*-tolyl-*p*-tolylcarbiny sulphone were deposited which, after recrystallisation from alcohol and then twice from acetic acid, had m. p. 152–152.5° (Found : C, 75.15; H, 6.5; S, 8.7. $C_{22}H_{22}O_2S$ requires C, 75.4; H, 6.3; S, 9.1%). At room temperature a similar reaction takes some 16 weeks for completion.

Sodium toluene-*p*-sulphinat (0.09 g.) in *N*-sodium hydroxide (0.5 c.c.) was added to (+)-*o*-tolyl-*p*-tolylcarbiny hydrogen phthalate ($[\alpha]_D^{19} + 20^\circ$; 0.18 g.) dissolved in 96% ethyl alcohol (10 c.c.). The rotatory power of the solution changed as follows (*l*, 2; *t*, 20°) :

Time, days	0	0.25	1	2	3	4	11	22	34
<i>a</i>	0.54°	0.51°	0.46°	0.45°	0.44°	0.43°	0.41°	0.37°	0.31°

After 34 days the mixture was warmed on the steam-bath, it racemised within 2 hours.

(2) *With anhydrous formic acid*. A solution of (\pm)-*o*-tolyl-*p*-tolylcarbiny hydrogen phthalate (2 g.) in anhydrous formic acid (30 g.), after being kept for several hours, was poured into ice-water and extracted with ether. The ethereal extract was washed several times with aqueous sodium hydroxide, then dried, and the ether removed until crystals of *di*-(*o*-tolyl-*p*-tolylcarbiny) ether separated (0.11 g.) as needles, m. p. 138–139° (Found : C, 88.4; H, 7.5. $C_{30}H_{30}O$ requires C, 88.7; H, 7.35%). When (+)-*o*-tolyl-*p*-tolylcarbiny hydrogen phthalate ($[\alpha]_D^{19} + 20^\circ$ in chloroform; 0.23 g.) was dissolved in anhydrous formic acid (10 c.c.), racemisation was complete in 20 minutes.

(3) *With dilute sodium hydroxide solution*. A solution of (\pm)-*o*-tolyl-*p*-tolylcarbiny hydrogen phthalate (1.6 g.) in 0.3*N*-sodium hydroxide solution (10 c.c.) on storage deposited *di*-(*o*-tolyl-*p*-tolylcarbiny) phthalate (1.0 g.) as needles, m. p. 117.5° (Found : C, 82.2; H, 6.0. $C_8H_8O_4$ requires C, 82.3; H, 6.1%).

Thanks are expressed to Professor E. R. H. Jones, F.R.S., for laboratory facilities, and to Imperial Chemical Industries Limited for a grant.

BATTERSEA POLYTECHNIC, LONDON, S.W.11.

[Received, October 10th, 1950.]