86. *Alkyl–Oxygen Fission in Carboxylic Esters. Part X. Phthalates of Di-*p*-methoxyphenylcarbinol and of* tert.*-Alcohols.*

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Di-*p*-methoxyphenylcarbinol does not react with phthalic anhydride in presence of pyridine. Reaction occurs, however, in the presence of triethylamine, yielding a mixture of the acid and the neutral phthalate. It is suggested that the stronger base overcomes the effect of the two electron-releasing *p*-substituents which hinder the separation of the proton from the hydroxyl group. *tert.*-Alcohols, however, do not react with phthalic anhydride even in the presence of triethylamine.

Evidence is put forward that aralkyl groups are more firmly held in symmetrically substituted neutral phthalates than in other esters.

DI-*p*-METHOXYPHENYLCARBINOL does not react with phthalic anhydride in the presence of pyridine at 40° or 100°; nor can its hydrogen phthalate be formed by reaction of the potassium-derivative of the carbinol with phthalic anhydride, or by the reaction (Houben, *Ber.*, 1906, **39**, 1736) of the carbinylmagnesium bromide with phthalic anhydride. The esterification normally involves separation of a proton from the carbinol (Gerrard, *J.*, 1940, 218; Balfe, Kenyon, *et al.*, *J.*, 1942, 605). In view of the presence in the carbinol of two electron-releasing *p*-substituents, it was thought possible that this alcohol could be esterified by an acid-catalysed reaction, involving separation of the hydroxyl ion. However, such reactions yielded only products of the action of acid on the carbinol, *viz.*, bisdi-*p*-methoxyphenylcarbinyl ether, *pp'*-dimethoxybenzophenone, and di-*p*-methoxyphenylmethane. Alternatively, it appeared possible that, since the electron-releasing substituents lessen the ease of removal of the proton (as in the comparison of the dissociation constants of benzoic and anisic acids, Ingold, *J.*, 1933, 1124), the esterification might be promoted by the use of a stronger base than pyridine ($K_b = 2{\cdot}4 \times 10^{-9}$), by virtue of the greater affinity of the stronger base for the proton. It has in fact been found that in the presence of triethylamine ($K_b = 6{\cdot}4 \times 10^{-9}$) the esterification proceeds readily, some of the neutral dicarbinyl phthalate being formed along with the acid ester. Triethylamine also accelerates the formation of the urethane from di-*p*-methoxyphenylcarbinol with phenyl *iso*cyanate.

The hydrogen phthalate of di-*p*-methoxyphenylcarbinol, like that of *p*-methoxyphenyl-1-naphthylcarbinol (*J.*, 1946, 803), is converted into the neutral ester with particular ease; from its solution, *e.g.*, in chloroform, phthalic acid is deposited slowly in the cold, rapidly on warming. It does not yield a clear solution in aqueous alkali, the neutral ester being immediately deposited, nor can it be exactly titrated in alcoholic solution on account of partial hydrolysis. The neutral ester, however, is comparatively stable towards, or in, cold alkaline solutions. Though this is a general characteristic of esters, the comparison, in the present example, with the ready dismutation of the acid ester, suggests that the carbinyl cation is less easily separated from the neutral ester than from the acid ester. The suggestion is supported by the observation that the neutral ester is converted into the *p*-tolyl sulphone very much more slowly than is the acid ester, under comparable conditions.

In Part II (*J.*, 1942, 605) it is shown that the reaction which leads to the formation of the neutral di-*p*-methoxyphenylcarbinyl phthalate is not diverted by added anions (benzoate or octyl hydrogen phthalate), and these observations are also in agreement with the suggestion that the carbinyl radicals are more firmly held in the symmetrical di-ester than in other esters.

Since *tert.*-alcohols do not, as a rule, yield hydrogen phthalates by reaction with the acid anhydride in presence of pyridine, the reaction in presence of triethylamine has been investigated. No reaction occurred with linaloöl, ethylmethylphenylcarbinol, or triphenylcarbinol. Triphenylcarbinol may be unreactive in this sense on account of a very strong tendency to react by the opposite mechanism (separation of the hydroxyl ion), and so may ethylmethylphenylcarbinol, the hydrogen phthalate of which does not yield the corresponding neutral ester or sulphone because the carbinyl cations at once break down to αβ-dimethylstyrene. Alkyl–oxygen fission is less likely in linaloöl; the inertness of the *tert.*-alcohols may therefore be due in part to steric hindrance.

EXPERIMENTAL.

*Di-*p*-methoxyphenylcarbinyl Hydrogen Phthalate.*—A solution of the carbinol (Schackenberg and Scholl, *Ber.*, 1903, **36**, 655) (2·4 g.), phthalic anhydride (1·5 g., 1 mol.), and triethylamine (2 c.c., 1·5 mols.) in dry, peroxide-free dioxan (3 c.c.) was heated at 40° for 6 hours, then diluted with an equal volume of acetone, made slightly acid with hydrochloric acid, and further diluted with ice-water. The precipitate solidified (3·6 g.; m. p. 105—110°) and by crystallisation from benzene–light petroleum (1 : 1; 60 c.c.) was separated into the ***hydrogen phthalate*** (0·4 g.), m. p. 131—132° (Found : C, 70·5; H, 5·0. $C_{23}H_{20}O_6$ requires C, 70·4; H, 5·1%) and bisdi-*p*-methoxyphenylcarbinyl phthalate (2·0 g.), m. p. 110—115° (see below). In a similar experiment, but with one-third of the above quantities and without heating, the temperature of the mixture rose from 20° to 30° during 10 minutes. After a further 15 minutes, the mixture was treated as above, yielding a solid (1·1 g.), m. p. 118—120° which was raised to 128—129° by washing with benzene; *i.e.*, an improved yield of the hydrogen phthalate was obtained.

Solutions of the hydrogen phthalate in benzene or chloroform rapidly deposited phthalic acid, and the neutral ester was isolated from each solution. A cold solution of the hydrogen phthalate (0·161 g.) in acetone–ethyl alcohol–water required 7·59 c.c. of 0·1N-aqueous sodium hydroxide for titration to the phenolphthalein end-point (equivalent to titration of the carboxyl groups and 85% of the ester groups). Sodium hydroxide solution (5·0 c.c.; 0·1 N.) was then added, and the mixture heated at 90° for 2 hours, and the excess of alkali titrated; 1·10 c.c. had been consumed, equivalent to reaction with 17% of the ester groups. In other experiments, proportions of the ester groups ranging between 47 and 85% were titrated by the cold alkali.

*Di-*p*-methoxyphenylcarbinyl Phenylurethane.*—(i) A mixture of the carbinol (2·4 g.) and phenyl *iso*cyanate (1·2 g., 1 mol.) was gently warmed, then sealed for 10 days, the original emulsion then having solidified. The solid (3·5 g.) was recrystallised thrice from carbon tetrachloride–light petroleum, yielding the *urethane*, m. p. 111—112° (Found : C, 72·3; H, 5·9; N, 3·7. $C_{22}H_{21}O_4N$ requires C, 72·7; H, 5·8; N, 3·9%). (ii) The carbinol (1·2 g.) was added slowly to a mixture of phenyl *iso*cyanate (0·6 g., 1 mol.) and dry triethylamine (0·7 c.c.). The clear solution became warm and after 5 minutes set solid (0·8 g.; m. p. 90—96°). Recrystallised as above, the urethane had m. p. 109—111°, alone or mixed with the first specimen.

*Bisdi-*p*-methoxyphenylcarbinyl Phthalate.*—The material of m. p. 110—115°, after recrystallisation from light petroleum (b. p. 60—80°), yielded the neutral *phthalate*, m. p. 114—115° (Found : C, 73·7; H, 5·6%; equiv., by hydrolysis with hot alcoholic potassium hydroxide, 621. $C_{38}H_{34}O_8$ requires C, 73·8; H, 5·5%; equiv., 618). A cold solution of the neutral ester in aqueous alcohol, made just alkaline to phenolphthalein with sodium hydroxide, retained its colour for several hours, indicating absence of hydrolysis. The neutral ester (0·4 g.) in ethyl ether (20 c.c.) was shaken with aqueous sodium hydroxide (10 c.c. of 0·3N.) for 1½ hours. The ethereal layer was separated, dried (Na_2SO_4), and concentrated, yielding the unchanged neutral ester (0·3 g.), m. p. and mixed m. p. 112—113°.

*Di-*p*-methoxyphenylcarbinyl* p*-Tolyl Sulphone.*—(i) *From the carbinyl hydrogen phthalate.* The hydrogen phthalate (0·39 g.) was added to a solution of sodium toluene-*p*-sulphinate (0·32 g.) in acetone (4 c.c.) and water (1·5 c.c.) at 20°. After 1 minute the clear solution was poured into water. The oil which separated was extracted with ether, and the extract dried and concentrated, yielding the *sulphone* (0·35 g., 92%), m. p. 95—100°, raised by recrystallisation from ether–light petroleum to 109—110° (Found: S, 8·3. $C_{22}H_{22}O_4S$ requires S, 8·4%).

(ii) *From the neutral dicarbinyl phthalate.* A solution of the neutral ester (0·31 g.) in acetone (4 c.c.) was added to a solution of sodium toluene-*p*-sulphinate (0·32 g.) in water (1·5 c.c.). The mixture, after 10 minutes at 20°, was poured into water and treated as above, yielding unchanged neutral ester (0·22 g., 71%), m. p. and mixed m. p. 113—114°, and the *p*-tolyl sulphone (0·04 g., 5%), m. p. 96—98°; after recrystallisation, m. p. and mixed m. p. 105—106°.

Ethylmethylphenylcarbinyl Hydrogen Phthalate.—Powdered potassium (2·6 g.) was dissolved in a solution of the alcohol (11 g., 1·1 mol.) in benzene (20 c.c.). A warm solution of phthalic anhydride (10 g., 1 mol.) in benzene (60 c.c.) was added. After 30 minutes at 80° and 18 hours at room temperature, the mixture was poured into water. The separated benzene layer was washed with aqueous sodium hydrogen carbonate, and the combined aqueous layers were acidified with hydrochloric acid. The precipitated oil solidified (12 g., 60%), m. p. 105—110°; recrystallised from ether–light petroleum it yielded the *hydrogen phthalate*, m. p. 113—115° (Found: equiv., 300. $C_{17}H_{18}O_4$ requires equiv., 298), decomposing to phthalic acid and an unsaturated substance of b. p. 184—186° (Tiffeneau, *Ann. Chim.*, 1907, **10**, 362, records b. p. 186—187° for αβ-dimethylstyrene).

The solid (0·2 g.) which separated during 3 days from a solution of the hydrogen phthalate (0·5 g.) and N-sodium hydroxide (1·7 c.c.; 1 mol.) in water (10 c.c.) was unchanged hydrogen phthalate, m. p. and mixed m. p. 113—115°. Unchanged hydrogen phthalate (0·45 g.; m. p. and mixed m. p. 113—115°) also separated during 3 days from a mixture of the hydrogen phthalate (1·0 g.) in N-sodium hydroxide (3·3 c.c.; 1 mol.) and sodium toluene-*p*-sulphinate (0·85 g., 1·5 mols.) in water (17 c.c.).

A solution of the hydrogen phthalate (2 g.) in N-sodium hydroxide (6·7 c.c.; 1 mol.) was heated under reflux for 2 hours. The oil which separated was extracted with chloroform, and ozonised oxygen was passed through the dried extract. The ozonide was decomposed with water, and volatile products were swept by carbon dioxide into a solution of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid. The dinitrophenylhydrazone of acetaldehyde (0·1 g.) was precipitated; m. p. and mixed m. p. after recrystallisation from ethyl alcohol, 165—167°. From the non-volatile fraction, the 2 : 4-dinitrophenylhydrazone of acetophenone (0·35 g.) was obtained, m. p. and mixed m. p. after recrystallisation from nitrobenzene, 235—240°.

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