[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

# Some Reactions of Tetraphenylphthalic Anhydride and Esters of Tetraphenylphthalic Acid

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*Received March 28, 1956*

Tetraphenylphthalic anhydride (1) is saponified with aqueous alkali at elevated temperature, (2) reacts spontaneously with (a) sodium methoxide in methanol, (b) aniline, to give the phthalanilic acid, (c) and alcohols to give the half esters. Base-catalyzed trans-esterification takes place smoothly. Previously suspected non-reactivity is explained on the basis of steric hindrance and low solubility.

It has been reported that ethyl tetraphenylphthalate is exceedingly difficult to saponify[3,4] and also that the propyl ester may be converted to the ethyl ester merely by recrystallization from ethanol.[5] The known facts about the chemistry of tetraphenylphthalic anhydride, tetraphenylphthalic acid, and esters of the acid are few. It was thus the purpose of this research to investigate the basic chemistry of this interesting group of compounds.

Tetraphenylphthalic anhydride reacts sluggishly with cold aqueous sodium hydroxide, readily with hot aqueous sodium hydroxide and may be titrated in pyridine solution with aqueous sodium hydroxide. Indeed, the latter conditions proved to be suitable for determination of the anhydride, the acid, and the half esters.

Sodium methoxide in methanol gave sodium methyl tetraphenylphthalate smoothly. Sodium hydroxide in ethanol similarly gave the half ethyl ester. The mono-ester was not saponified by means of sodium hydroxide in ethanol.

Refluxing the anhydride without a catalyst with methanol, ethanol, or hexanol gave the half-esters only. Pyridine or hydrochloric acid appeared to speed up the reaction. Long refluxing with hexanol in the presence of *p*-toluenesulfonic acid gave dihexyl tetraphenylphthalate. With butanol and the catalyst the diester was formed only in trace amounts even after 90 hours reflux. With potassium hydroxide in diethylene glycol, only one equivalent of base was consumed by the anhydride up to 100°, partial consumption of two equivalents was noted at 150°, and complete neutralization was observed at reflux (240°).

It is interesting to point out that the half-esters all exhibit the melting point of the anhydride, as does the acid.[3,4,6] For the methyl and ethyl half-esters, this was positively shown to be the case by melting larger samples of the half-esters, collecting the evolved liquids, and identifying them as methanol and ethanol, respectively. The residue in each case was identified as the anhydride by melting point and neutral equivalent.

Aniline reacts exothermally with tetraphenylphthalic anhydride to give tetraphenylphthalanilic acid. Heated above its melting point, the latter formed pentaphenylphthalimide.

The trans-esterification of various esters of tetraphenylphthalic acid was next investigated. No reaction took place between ethyl tetraphenylphthalate and hexanol unless sodium hexyloxide was present. *p*-Toluenesulfonic acid did not appear to be as useful, since after long reflux only ethyl hexyl tetraphenylphthalate had formed. Using the corresponding alkoxide as catalyst, the dipropyl, dicyclohexyl, and dicetyl esters were also prepared. However, it did not prove possible to convert the dicetyl ester to the diethyl ester in a similar manner; apparently the equilibrium is unfavorable for the new ester unless one of the alcohols can be removed.

The results reported have shown that tetraphenylphthalic anhydride, acid, and esters undergo reactions similar to those of phthalic anhydride, except that they are more sluggish. In the previous report of the inability to saponify the diethyl ester,[3] the alcoholic alkaline solution was an unfavorable reagent for the reaction, since it has been shown that half-ester formation will take place under the conditions. When fusion with potassium hydroxide was employed,[4] it is doubtful whether diethyl tetraphenylphthalate was soluble in it, thus evincing an erroneous conclusion as to the reactivity of the diethyl ester. The report of the facile trans-esterification[5] of the dipropyl ester to the diethyl ester must have been due to the long reflux time and to co-

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[1] From the thesis presented by George W. Thielcke to the Graduate Faculties of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the M.S. Degree, 1956.

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[3] W. Dilthey, I. Thewalt, and O. Trösken, *Ber.*, **67**, 1959 (1934).

[4] C. F. H. Allen and L. J. Sheps, *Can. J. Research*, **11**, 171 (1934).

[5] E. C. Schreiber and E. I. Becker, *J. Am. Chem. Soc.*, **72**, 4829 (1950).

[6] The free dicarboxylic acid reported in footnote 3 was obtained by boiling the anhydride with alcoholic potassium hydroxide. No analysis was reported. For two reasons it appears that the product probably was mistakenly called the free acid: (1) in our hands only the half-ester was obtained with this procedure; (2) the melting point cannot distinguish between the half-ester and the free acid.

distillation of propyl alcohol during the recrystallization.

## EXPERIMENTAL[7,8]

*Starting materials.* Tetraphenylphthalic anhydride was prepared as previously described,[9] m.p. 295–296°. Diethyl tetraphenylphthalate, m.p. 204–205°, was prepared from diethyl chloromaleate and tetracyclone.[10] Cyclohexanol, hexanol, and butanol were commercial products and were distilled before use. Commercial cetyl alcohol (Lorol 24) was recrystallized twice from methanol and converted to the acid phthalate which was recrystallized twice from petroleum naphtha.

*Anal.* Calc'd for $C_{24}H_{38}O_4$: Neut. equiv., 389. Found: Neut. equiv., 390, 387.

Saponification of the half-ester gave the cetyl alcohol which was recrystallized from methanol and finally distilled, b.p. 189–191° (15 mm.).

*Reaction of tetraphenylphthalic anhydride with sodium hydroxide.* The pink color of phenolphthalein in a mixture of 0.5 g. of tetraphenylphthalic anhydride and 0.3 ml. of 0.179*N* NaOH was not discharged on standing for 16 hours.

A mixture of 0.5248 g. of tetraphenylphthalic anhydride after refluxing with 20.00 ml. of 0.179 *N* NaOH required 7.04 ml. of 0.179 *N* HCl to neutralize excess alkali, giving a neutral equivalent of 226 (theory 226).

A solution of 0.5964 g. of tetraphenylphthalic anhydride in 40 ml. of pyridine required 14.82 ml. of 0.179 *N* NaOH giving a neutral equivalent of 225.

*Reaction of tetraphenylphthalic anhydride with sodium alkoxides.* A solution of tetraphenylphthalic anhydride in acetone was titrated with 0.556 *N* sodium methoxide in methanol using phenolphthalein as indicator. The neutral equivalent was 465 and 468 (theory 453).

Acidification of the solution and evaporation of most of the acetone followed by addition of water to incipient crystallization gave white crystals of *methyl hydrogen tetraphenylphthalate* which, after recrystallization from methanol, melted at 295–296°.

*Anal.* Calc'd for $C_{33}H_{24}O_4$: Neut. equiv., 485. Found: Neut. equiv., 482, 480.

A solution of 2.09 g. of tetraphenylphthalic anhydride in ethanol consumed 4.60 milliequivalents of sodium hydroxide in ethanol.

*Anal.* Calc'd for $C_{32}H_{20}O_3$: Neut. equiv., 453. Found: Neut. equiv., 456.

Acidification of the titrated solution and concentration to one-half volume gave 2.15 g. of white solid, m.p. 295–296°.

*Anal.* Calc'd for $C_{34}H_{26}O_4$: Neut. equiv., 499. Found: Neut. equiv., 498.

*Reaction of tetraphenylphthalic anhydride with alcohols.* Tetraphenylphthalic anhydride (4 g., 8.8 mmoles) was refluxed in 90 ml. of ethanol for 16 hours. The anhydride dissolved in three hours and cooling the solution gave white crystalline *ethyl hydrogen tetraphenylphthalate,* which melted 295–296° after recrystallization from 100 ml. of ethanol, 2.5 g. (5.0 mmole, 57%).

*Anal.* Calc'd. for $C_{34}H_{26}O_4$: Neut. equiv., 499. Found: Neut. equiv., 494.

When the mixture of anhydride and ethanol contained either 5 ml. of pyridine or 5 ml. of concentrated hydrochloric acid, the anhydride dissolved within one hour. The products obtained in these experiments had the same melting points and the same neutral equivalent, 496 and 492, respectively, as the products obtained without catalyst.

A solution of 4.0 g. (8.8 mmoles) of tetraphenylphthalic anhydride was refluxed in 100 ml. of methanol for 20 hours. The product obtained on cooling and filtering was recrystallized from methanol and air-dried to give 3.0 g. (6.2 mmoles, 70%) of white *methyl hydrogen tetraphenylphthalate,* m.p. 295–296°.

*Anal.* Calc'd for $C_{33}H_{24}O_4$: Neut. equiv., 485. Found: Neut. equiv., 483.

A mixture of 10.0 g. (0.021 mole) of tetraphenylphthalic anhydride was refluxed in 80 ml. of hexanol for 1.5 hours. After most of the excess alcohol was distilled at 100° (25 mm.), the residue was crystallized twice from carbon tetrachloride to give 8.25 g. (0.015 mole, 71%), of *hexyl hydrogen tetraphenylphthalate,* m.p. 295–296°.

*Anal.* Calc'd for $C_{38}H_{34}O_4$: Neut. equiv., 555. Found: Neut. equiv., 562.

A mixture of 4.25 g. (9.4 mmoles) of tetraphenylphthalic anhydride and 0.5 g. of *p*-toluenesulfonic acid in 90 ml. of hexanol was refluxed for 13 hours. The refluxing alcohol was carried by means of a funnel tube to the bottom of a water-cooled moisture trap packed with Drierite. After removal of most of the excess alcohol at reduced pressure, the product solidified and was recrystallized from 85% aqueous acetic acid to give 4.0 g. (6.3 mmoles, 67%) of white crystalline *dihexyl tetraphenylphthalate,* m.p. 161–163°, which did not depress the melting point of authentic dihexyl tetraphenylphthalate (see below).

A mixture of 4.0 g. (8.8 mmoles) of tetraphenylphthalic anhydride and 0.5 g. of *p*-toluenesulfonic acid in 100 ml. of butanol was refluxed under a drying trap as described for hexanol for 90 hours. After removing the excess alcohol at reduced pressure, the residue was crystallized twice from 90% acetic acid and once from petroleum naphtha affording 1.6 g. of impure compound, m.p. 287–294° (starting anhydride or butyl hydrogen tetraphenylphthalate). Concentration of the filtrate and recrystallization of the residue afforded 0.7 g. of *dibutyl tetraphenylphthalate,* m.p. 192–195° (reported,[5] m.p. 193–194°).

*Melting phenomena of the monoesters.* Methyl hydrogen tetraphenylphthalate (0.7 g.) was placed in a 20 × 120 mm. Pyrex test tube which had been drawn out to form two bulbs connected by an inverted U-tube. The bulb containing the ester was heated to 300–305° in a sulfuric acid bath while the empty bulb was cooled in an ice-water bath. About 0.2 ml. of liquid was collected in the cold bulb. This was diluted with 6 ml. of water and divided into three portions. After treatment with a hot copper spiral, one portion gave a positive resorcinol test for formaldehyde;[11] an untreated portion did not give the test. The third portion gave a negative iodoform test.

Ethyl hydrogen tetraphenylphthalate (1.0 g.) was treated similarly, affording about 0.2 ml. of liquid. This liquid gave a negative resorcinol test and a positive iodoform test indicating ethanol.

The residual solid from both experiments gave a neutral equivalent of 227 (theory, 226).

*Saponification of the anhydride.* A solution of 1.24 g. of tetraphenylphthalic anhydride in 100 ml. of ethanol and 25 ml. of 0.35 *N* NaOH (in ethanol) was refluxed for four hours. Neutralization and cooling gave an equivalent weight of 450 (theory 453), indicating that only one equivalent of alkali was consumed.

Acidification of the titrated solution gave 1.28 g. (94%) of white solid, m.p. 294–296°.

*Anal.* Calc'd for $C_{34}H_{26}O_4$: Neut. equiv., 499. Found: Neut. equiv., 484.

*Reaction with ammonia.* One gram (2.2 mmoles) of tetraphenylphthalic anhydride was added to 10 ml. of concen-

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(7) Analyses were performed by Dr. K. Ritter, Zürich, Switzerland.

(8) Temperatures were uncorrected.

(9) M. E. Synerholm, *J. Am. Chem. Soc.*, **67**, 1229 (1945).

(10) J. A. Romano, B.S. Thesis, Polytechnic Institute of Brooklyn, 1949.

(11) E. H. Huntress and S. P. Mulliken, *Identification of Pure Organic Compounds. Order I*, John Wiley and Sons, Inc., New York, N. Y., 1941, pp. 49, 427.

trated ammonia in a test tube. The temperature rose rapidly from 19° to 23°. After washing the solid with an additional 90 ml. of concentrated ammonia, 1:1 hydrochloric acid, water, and then air-drying, the crude product was refluxed for one-half hour with chloroform to remove unreacted anhydride. Then it was cooled, filtered, and washed with chloroform. Evaporation of the chloroform gave 0.17 g. of white residue which, upon treatment with aniline, gave the anilide, m.p. 278–279°.

The main product was insoluble in ethanol, butanol, toluene, and acetone. Recrystallization twice from 90% acetic acid afforded 0.25 g. of white crystals of tetraphenylphthalic acid, m.p. 293–295°, Neut. equiv., 236 (theory, 235).

*Reaction with aniline.* Tetraphenylphthalic anhydride (12 g., 0.027 mole) in 200 ml. of chloroform was treated with 3 ml. (3.1 g., 0.033 mole) of freshly distilled aniline. Crystals began separating after 6 minutes. After standing four hours, the last hour in the refrigerator, the colorless crystals were collected, washed with chloroform, and air-dried. Recrystallization of 5 g. from 100 ml. of chloroform afforded 2.0 g. of *tetraphenylphthalanilic acid.* The product melted with shrinking and resolidification at 278–279° and finally melted over a wide range over 300°.

*Anal.* Calc'd for $C_{38}H_{27}NO_3$: Neut. equiv., 546. Found: Neut. equiv., 543.

*Pentaphenylphthalimide.* A test tube containing 2.0 g. (3.7 mmoles) of tetraphenylphthalanilic acid was heated at 290–295° until frothing ceased and only a clear straw-colored liquid remained. The liquid solidified on cooling and was recrystallized four times from xylene to give 0.7 g. of the colorless product, m.p. 327–346°. Further recrystallization gave a m.p. 348–353°.

Tetraphenylphthalanilic acid (5 g., 0.011 mole) and 10 ml. of aniline were refluxed for one hour. Upon cooling, the mixture solidified and was extracted with dilute hydrochloric acid, filtered, and dried to give 6 g. of nearly white solid. Three recrystallizations from xylene gave 2.5 g. (0.0047 mole, 53%) of colorless product, m.p. 355–357°. A mixture melting point with the previously obtained material melted at 350–356°.

*Anal.* Calc'd for $C_{38}H_{25}NO_2$: C, 86.50; H, 4.78; N, 2.66. Found: C, 86.68; H, 5.15; N, 2.38.

*Dihexyl tetraphenylphthalate.* A mixture of 10 g. (0.019 mole) of diethyl tetraphenylphthalate in 100 ml. of hexanol in a 500-ml. flask equipped with a thermometer well and a total reflux, variable take-off head was refluxed for two hours. The condenser jacket was filled with hot water, and the take-off cock was kept closed so that any vapors would be collected in a cold trap attached to the still head outlet. No reaction occurred. As this point 0.025 g. of sodium hexyloxide in 2.0 ml. of hexanol was added. Distillate was immediately collected and the reaction appeared to be complete in from 15 to 20 minutes. After a total reflux period of one hour, 1.9 ml. of distillate had been collected (theory, 2.2 ml.), $n_D^{25}$ 1.3640. After distilling the remaining hexanol *in vacuo*, the solid product was recrystallized from 90% acetic acid to give 3.56 g. (5.6 mmoles, 29%) of colorless ester, m.p. 162–163°. Two further recrystallizations raised the melting point to 163.5–164.0°.

*Anal.* Calc'd for $C_{44}H_{46}O_4$: C, 82.72; H, 7.26. Found: C, 82.63; H, 7.50.

The ester is soluble in benzene, carbon tetrachloride, cyclohexane, and petroleum naphtha.

*Ethyl hexyl tetraphenylphthalate via trans-esterification.* A solution of 10 g. (0.019 mole) of diethyl tetraphenylphthalate in 80 ml. of hexanol containing 0.4 g. of *p*-toluenesulfonic acid was refluxed in a modified Thompson-Oakdale apparatus for 100 hours. About 35 ml. of heterogeneous distillate were collected. The size of the lower aqueous layer (4 ml.) indicated that some hexanol had probably dehydrated.

Upon cooling the reaction mixture 4.2 g. of a solid, "A," separated and was collected, m.p. 146–153°. From the filtrate 2.9 g. of a white solid, "B," was obtained, m.p. 144–146°. After five additional recrystallizations, from 85–90% acetic acid for each fraction, there was obtained 1.5 g. of white solid from "A," m.p. 149–150°, which did not depress the melting point, 149–150°, of the 1.4 g. obtained from "B." The total yield, therefore, was 2.9 g. (27%).

*Anal.* Calc'd for $C_{40}H_{38}O_4$: C, 82.45; H, 6.57. Found: C, 82.48; H, 6.86.

*Ethyl hexyl tetraphenylphthalate via half ester.* Hexyl acid tetraphenylphthalate (4 g., 7.2 mmoles) in benzene was refluxed with 1.0 g. (4.3 mmoles) of silver oxide. The benzene removed a small quantity of water formed during the reaction. The mixture was filtered from residual silver oxide and treated directly with 1.0 ml. (1.9 g., 12.4 mmoles) of ethyl iodide. After one hour's standing, a yellow turbidity developed and after one hour's reflux a copious yellow precipitate formed and coagulated. The precipitate (1.16 g., 68%) was filtered, washed with benzene, and the combined filtrates were concentrated to a sirupy residue which was recrystallized from 80% acetic acid to give 2.7 g. (4.9 mmoles, 64%) of white crystals, m.p. 149–150°. A mixture melting point with the product of the preceding paragraph melted 149.5–150.5°.

*Dicyclohexyl tetraphenylphthalate.* In the same apparatus as used for the preparation of the dihexyl ester, a mixture of 10 g. (0.019 mole) of di-ethyl tetraphenylphthalate and 0.044 g. of sodium cyclohexyloxide in 100 ml. of cyclohexanol was refluxed for six hours. During this time an additional 0.022 g. of catalyst was added; 1.4 ml. of ethanol was recovered. Removal of part of the cyclohexanol induced crystallization and upon cooling 11.0 g. of crude product, m.p. 235–242°, was collected. Three recrystallizations from 95% acetic acid gave a small crop of white crystals, m.p. 243–244°.

*Anal.* Calc'd for $C_{44}H_{42}O_4$: C, 83.25; H, 6.67. Found: C, 82.94; H, 6.64.

*Dicetyl tetraphenylphthalate.* A mixture of 35 g. of cetyl alcohol, 10.0 g. (0.019 mole) of diethyl tetraphenylphthalate, 50 ml. of xylene (freshly distilled from sodium), and 1.0 ml. of sodium ethoxide containing 0.0216 g. of sodium was rerefluxed as described above. After one hour 3.4 ml. (theory, 3.2 ml.) of liquid was collected in the trap. A 0.4-ml. portion of this liquid was insoluble in water and had $n_D^{21}$ 1.485 (xylenes, $n_D$ 1.48–1.50). Then 50 ml. of xylene was added and distilled through the column to remove residual ethanol. After standing overnight, the solution deposited cetyl alcohol. Combining the filtrates and distilling to dryness gave a solid which was recrystallized from acetic acid three times to give 13.5 g. (0.015 mole, 77.5%) of white product, m.p. 130–131°.

*Anal.* Calc'd for $C_{64}H_{86}O_4$: C, 83.61; H, 9.43; Found: C, 83.66; H, 9.67.

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