

was washed with dilute sodium carbonate solution, then with dilute sodium sulfate solution, dried over sodium sulfate, and fractionated.

Method B.—Monoisobutyrate, monostearate, diacetate, diisobutyrate, dicaproate, distearate, and dibenzoate: The reaction vessel was a three-necked flask fitted with a thermometer, dropping funnel, and mercury-sealed stirrer. For monoester formation, 0.50 mole of the acid chloride was added dropwise, over a period of one hour at a reaction temperature of 25–35°, to a stirred, cooled mixture of 0.50 mole of 2-methyl-2,4-pentanediol (10% excess for the monoisobutyrate, and 100% excess for the monostearate) and 0.50 mole of pyridine. For diester formation the quantities of reactants, in the same procedure, were 0.50 mole of 2-methyl-2,4-pentanediol and 1.05–1.10 moles of both the acid chloride and pyridine. After the acid chloride addition, the mixture was allowed to react further for either eighteen hours at room-temperature or one hour at 60–70°. The final reaction mixture was treated with 100 ml. of water, and the two layers were separated. The ester layer was washed with dilute sodium carbonate or sodium hydroxide solution, then with dilute sodium sulfate solution, dried over sodium sulfate, and fractionated.

With the mono- and distearate, ether and some alcohol were added to the ester layer to facilitate the difficult phase-separation after washing. The ether was evaporated from the dried solution, and the ester was heated up to 110° at 2 mm. before analysis. In attempted distillations of the mono- and distearate, a portion was heated in a Claisen flask to 200° at 2 mm. Decomposition was evident with both esters; it then was found that the acid no. of the samples had risen to about 54.

Unsuccessful Esterification Reactions with 2-Methyl-2,4-pentanediol.—In several unsuccessful attempts at esterification, evidence was obtained of preferential dehydration of the 2-methyl-2,4-pentanediol, which presumably was catalyzed by the acidic nature of the reaction mixtures. Thus a mixture of 0.75 mole of the diol and 0.50 mole of stearic acid, which was heated for four hours at an increasing temperature of 180–245° under a fractionating column fitted for azeotropic removal of water with benzene, gave 23 ml. of water layer instead of the 9 ml. calculated for esterification. A mixture of 0.50 mole of the diol and 1.00 mole of benzoyl chloride was heated for four hours at an increasing temperature of 30–90°. The crystalline product which separated on cooling the reaction mixture was identified as benzoic acid; the crude acid amounted to an 80% yield. In attempted esterifications with anhydrides of dibasic acids, mixtures of 0.25 mole of the diol and 0.50 mole of either phthalic, succinic, or maleic anhydride were heated at 100–120° for about an hour. The respective dibasic acids were isolated from the reaction mixtures in yields of 30–40%; the other products were not examined.

RESEARCH AND DEVELOPMENT DEPARTMENT
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The Preparation of *p*-Amino-tetraphenylmethane

BY BENJAMIN WITTEN AND E. EMMET REID

A systematic investigation of the preparation of *p*-aminotetraphenylmethane by the method of Ullmann and Munzhuber¹ has shown that the best method is to reflux for three hours triphenylcarbinol in two times its weight of glacial acetic acid with two equivalents of aniline hydrochloride. The yield is 70–80%, about the same as was obtained by Ullmann and Munzhuber with four equivalents of aniline hydrochloride and five hours

(1) Ullmann and Munzhuber, *Ber.*, **36**, 407 (1903).

of refluxing. In one hour the yield is only 48%. The aniline hydrochloride must be thoroughly dry. If triphenylmethyl chloride is substituted for the carbinol, the time of reflux can be cut to one hour without detriment to the yield. The product obtained in any case is the hydrochloride, from which the base is liberated by boiling with water containing alkali.

It has been reported² that triphenylmethyl chloride and aniline, refluxed in a mixture of alcohol and benzene, give *N*-triphenylmethylaniline, $(C_6H_5)_3CNHC_6H_5$. We have confirmed this, but have found, however, that, if acetic acid is used as the reaction medium, para substitution takes place and the product is *p*-triphenylmethylacetanilide, $(C_6H_5)_3CC_6H_4NHC(=O)CH_3$. This has been compared with compound obtained from action of acetyl chloride on 4-aminotetraphenylmethane and found to be identical.

Thus three different compounds can be obtained from triphenylmethyl chloride and aniline, depending on the solvent and the presence or absence of hydrochloric acid.

Experimental

***p*-Triphenylmethyl Acetanilide.**—A solution of 2 g. of *p*-aminotetraphenylmethane and 10 g. of acetyl chloride in 100 ml. of benzene was refluxed for one hour. The benzene was boiled off at reduced pressure and the residue recrystallized from benzene. The yield was 2.5 g. (93%) of colorless needles of *p*-triphenylmethylacetanilide melting at 229°.

A mixture of 14 g. of triphenylmethyl chloride, 10 g. of aniline and 50 ml. of acetic acid was refluxed for three hours and poured into 200 ml. of water. The precipitate was filtered off, washed with water, dried at 110°, and recrystallized from toluene. The yield was 16 g. (84%) of colorless crystals melting at 229°.

Anal. Calcd. for $C_{27}H_{27}NO$: C, 85.9; H, 6.1; N, 3.72. Found: C, 86.2; H, 6.1; N, 3.69.

A mixture of this preparation and the former melted at the same temperature.

Acknowledgment.—We wish to thank Mrs. V. Beatrice Jones for her assistance in several of the preparations reported in this paper.

(2) Elbs, *Ber.*, **17**, 704 (1884); Hemilian, *ibid.*, **17**, 746 (1884); Gomberg, *ibid.*, **35**, 1829 (1902); Van Alphen, *Rec. trav. chim.*, **46**, 500 (1927).

CHEMICAL CORPS TECHNICAL COMMAND
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NEW COMPOUNDS

Esters of *p*-Cyclohexylphenol¹

p-Cyclohexylphenyl propionate (m. p. 48–50°) was prepared in 53% yield as follows: 20 g. of *p*-cyclohexylphenol, 44 ml. of propionic anhydride and 2 ml. of anhydrous pyridine were refluxed for sixty-five minutes. The volatile portion was distilled off, and the residue was

(1) Abstracted from the thesis presented by Albert J. Byer to DePaul University in partial fulfillment of the requirements for the M.S. degree in 1943.

washed in dilute, aqueous sodium carbonate solution and recrystallized twice from cold 30% ethanol and twice from cold 95% ethanol to give a white crystalline product.

In this and in the following syntheses in which the preliminary purifications are described as recrystallizations from solvents diluted with water, the product was first dissolved in a minimum of hot, concentrated solvent and then precipitated by addition of water after the solution had cooled.

Anal. Calcd. for $C_{15}H_{20}O_2$: sapon. equiv., 232.2. Found: sapon. equiv., 232.2.

p-Cyclohexylphenyl *n*-butyrate (m. p. 30–31°) was prepared in 78% yield by the reaction of 17.6 g. of *p*-cyclohexylphenol with 10.3 ml. of *n*-butyryl chloride at 100° for fifteen minutes. The crude product was washed like the propionate and recrystallized twice from slightly diluted propanol. The crystals were handled in chilled apparatus to prevent fusion. To dry the product, it was dissolved in chloroform and the solvent evaporated. The colorless, odorless oil that remained solidified to white crystals in the refrigerator.

Anal. Calcd. for $C_{18}H_{24}O_2$: sapon. equiv., 246.2. Found: sapon. equiv., 245.7.

p-Cyclohexylphenyl *n*-valerate (m. p. 19–20°) was prepared in 84% yield as follows: 5 ml. of valeric acid and 5 ml. of thionyl chloride were warmed together, and 8 g. of *p*-cyclohexylphenol was added. The mixture was warmed for fifteen minutes, 5 ml. more of thionyl chloride was added and the heating continued another thirty minutes. The product was washed like the propionate, cooled to a semisolid state, and recrystallized once from 18% ethanol and twice from ligroin, the crystals being handled in chilled apparatus. The excess ligroin was evaporated, and the product was distilled at 185–189° at 9 mm. to give an oil that yielded waxy crystals when cooled.

Anal. Calcd. for $C_{17}H_{24}O_2$: sapon. equiv., 260.2. Found: sapon. equiv., 267.5.

p-Cyclohexylphenyl *p*-methoxybenzoate (m. p. 97–98°) was obtained in 86% yield as follows: 10 g. of *p*-cyclohexylphenol and 14 ml. of *p*-methoxybenzoyl chloride were warmed together for an hour. The product was stirred into hot, dilute, aqueous sodium carbonate solution and cooled overnight. The white crystals of crude product were recrystallized from propanol and washed with cold ethanol.

Anal. Calcd. for $C_{20}H_{22}O_3$: sapon. equiv., 310.2. Found: sapon. equiv., 303.7.

p-Cyclohexylphenyl *o*-bromobenzoate (m. p. 90.5–92°) was prepared in 48% yield as follows: 16 g. of *o*-bromobenzoic acid was kept at 100°, and 20 ml. of thionyl chloride was added in small portions. A clear melt was obtained, and to it was added 10 g. of *p*-cyclohexylphenol. The mixture was warmed for twenty minutes and washed like the *p*-methoxybenzoate. The white crystals of crude product were recrystallized once from 15% propanol and once from 95% ethanol.

Anal. Calcd. for $C_{19}H_{19}O_3Br$: sapon. equiv., 359.2. Found: sapon. equiv., 357.9.

p-Cyclohexyl *m*-bromobenzoate (m. p. 89–90°) was obtained in 74% yield by the reaction of 10 g. of *p*-cyclohexylphenol with 15 ml. of *m*-bromobenzoyl bromide at 100° for thirty minutes. The product was washed like the *p*-methoxybenzoate and recrystallized from propanol to yield white crystals.

Anal. Calcd. for $C_{19}H_{19}O_2Br$: sapon. equiv., 359.2. Found: sapon. equiv., 350.9.

p-Cyclohexyl *p*-bromobenzoate (m. p. 118–119°) was prepared in 20% yield as follows: To 18.5 g. of *p*-bromobenzoyl chloride that had evidently become partially hydrolyzed was added 20 ml. of thionyl chloride in small portions. The mixture was warmed for twenty minutes, 10 g. of *p*-cyclohexylphenol was added and the heating continued another twenty minutes. The product was washed like the *p*-methoxybenzoate, recrystallized once from 30% propanol and twice from pure propanol and then washed with cold 95% ethanol to give white crystals.

Anal. Calcd. for $C_{19}H_{19}O_2Br$: sapon. equiv., 359.2. Found: sapon. equiv., 350.2.

Saponification Procedure.—In the determination of the saponification equivalents, the esters were hydrolyzed under reflux in hot ethanol with excess standard aqueous sodium hydroxide solution. The excess alkali was then neutralized with standard acid, and the solution was back-titrated with alkali and phenolphthalein indicator, the final volume being controlled to give a maximum ethanol content of 25% and the temperature of the mixture being maintained below 5°. Under these conditions, satisfactory blanks and end-points were obtained in the presence of free *p*-cyclohexylphenol. These were not satisfactory with higher temperatures or greater ethanol concentrations or with propanol as solvent or when the saponification was carried out with potassium hydroxide in diethylene glycol.² Under those unsatisfactory conditions, the ionization of the phenol was probably encouraged.

After the titrations, each mixture contained a voluminous precipitate that was identified by its melting point in each case as *p*-cyclohexylphenol. This identification established that the hydrolyzed compound was the ester and not a product of a side reaction.

p-Cyclohexylphenyl acetate had been previously reported,^{3,4} but it had been purified only by vacuum distillation to give a product melting at 35°. This report was checked by the preparation of the ester from *p*-cyclohexylphenol and acetyl chloride with subsequent recrystallizations from ethanol. The white crystals obtained melted at 43–45°.

p-Cyclohexylphenyl benzoate had been previously reported⁵ as melting at 114–114.5°. To check this report *p*-cyclohexylphenol and benzoic anhydride were refluxed in anhydrous pyridine. The crude product was precipitated by addition of water to the pyridine and was recrystallized twice from propanol to give white crystals melting at 118.5°.

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(2) Ernst C. Redeman and Howard J. Lucas, *Ind. Eng. Chem., Anal. Ed.*, **9**, 521–522 (1937).

(3) J. V. Braun, E. Anton, W. Haensel and G. Werner, *Ann.*, **472**, 1–89 (1929).

(4) "Phenol, *p*-cyclohexyl-, acetate" is listed in *C. A.*, **33**, 10872 (1929); but the name should be *p*-cyclohexylphenoxyacetic acid. The mistake springs from an ambiguous listing of the unnamed compound VI Aa in the table by Martin E. McGreal, Victor Niederl and Joseph B. Niederl, *THIS JOURNAL*, **61**, 345 (1929). Their other unnamed aryloxyacetic acids—VII Aa, VIII Aa, IX Aa and X Aa—were similarly listed in the table and are also carried in *C. A.* as "acetates." Suitable names for these would be, respectively, *p*-cyclohexyl-*o*-methylphenoxyacetic acid, *p*-(3-methylcyclohexyl)-phenoxyacetic acid, *p*-(4-methylcyclohexyl)-phenoxyacetic acid and *p*-cyclopentylphenoxyacetic acid. Their unnamed compound VIIa is doubly ambiguous in that it is shown in the text both as a true "diacetate" and as an "aryloxyacetic acid," with two methods of preparation that could not give the same product. It would seem to be *p,p'*-(1,1-cyclohexyl)-bis-(3-methylphenoxyacetic acid).

(5) J. F. Bartlett with C. E. Garland, *THIS JOURNAL*, **49**, 2098–2101 (1927).

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Hexadecyl Trisulfide and Hexadecyl Tetrasulfide

Several low molecular weight tetrasulfides were prepared by Chakravarti¹ by the action of sulfur monochloride on mercaptans. This method has now been applied successfully to the preparation of hexadecyl tetrasulfide, and by an obvious extension of the method, hexadecyl trisulfide has been prepared by the reaction of hexadecyl mercaptan with sulfur dichloride.

(1) Chakravarti, *J. Chem. Soc.*, **123**, 964 (1923).