

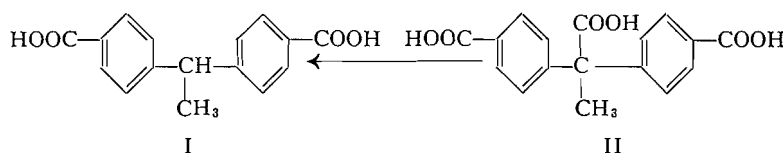
# SYNTHESIS OF 1,1-DI-(*p*-CARBOXYPHENYL)ETHANE AND ITS ESTERS<sup>1</sup>

BY HENRY BADER<sup>2</sup> AND W. A. EDMISTON

## ABSTRACT

The condensation of chlorobenzene with ethylidene diacetate in presence of fluosulphonic acid - hydrogen fluoride catalyst has been improved to give high yields of 1,1-di-(*p*-chlorophenyl)ethane, which was converted into the corresponding dinitrile by a modification of the cuprous cyanide method. Alkaline hydrolysis of the dinitrile gave 1,1-di-(*p*-carboxyphenyl)ethane. Its methyl and 2-ethylhexyl esters were prepared directly from the diacid or via the diacid chloride.

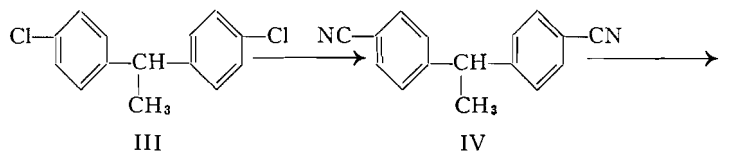
The interesting properties of the polyesters of terephthalic acid prompted us to prepare other aromatic *p*-diacids expected to possess similar properties, i.e. 1,1-di-(*p*-carboxyphenyl)ethane (I).



This compound was previously obtained by Haiss (4) by partial decarboxylation of 2,2-di-(*p*-carboxyphenyl)propionic acid (II), which was produced by oxidation of the condensation product of toluene and pyruvic acid.

The simplest approach to the synthesis of compound (I) would be to oxidize 1,1-di-(*p*-tolyl)ethane to the diacid or to the dialdehyde, as described by Perron and Barré (8, 9) for the 2,2,2-trichloro-1,1-di-(*p*-tolyl)ethane. However, the stability of the ethylidene bridge is much lower than that of the trichloroethylidene group and it is the first one attacked on oxidizing 1,1-di-(*p*-tolyl)ethane. Thus Anschütz (1) reported formation of di-*p*-tolyl ketone and of *p*-toluylbenzoic acid when hot chromic acid was used, and similarly in this laboratory (5) chromium trioxide in glacial acetic acid at 55° gave only di-*p*-tolyl ketone.

This synthesis was carried out successfully through the route outlined in the following scheme:



<sup>1</sup>Manuscript received November 14, 1955.

Contribution from the Research Laboratory, Dominion Tar and Chemical Company Limited, Ville LaSalle, Quebec.

<sup>2</sup>Present address: Ortho Research Foundation, Raritan, N.J., U.S.A.

The starting material, 1,1-di-(*p*-chlorophenyl)ethane, was prepared by an improvement of the method previously evolved in this laboratory (2). The original method gives a 48.6% yield of the isomeric mixture of 1,1-di-(chlorophenyl)ethane by reacting chlorobenzene with ethylidene diacetate in presence of a mixture of fluosulphonic acid and hydrogen fluoride. It has now been found that the presence of sulphuric acid in the reaction mixture lowers the yield of the product. When the fluosulphonic acid is redistilled immediately before use and thus freed from the sulphuric acid it contains, the yield of mixed isomers can be raised to 71.5%. The solid *p,p'* isomer can be easily isolated and purified by crystallization.

When the conversion of the dichloride (III) into the dicyanide (IV) was attempted with cuprous cyanide in pyridine or quinoline under the standard conditions described in the literature (cf. *inter alia* Newman (7)), there resulted an extensive charring of the product and the reaction was incomplete, the monochlorocyanide being the main product. By using, however, at least a three times higher molar ratio of the organic base to cuprous cyanide than is customary, a good yield of 1,1-di-(*p*-cyanophenyl)ethane (IV) was obtained. While our work was in progress Lorz and Baltzly (6) reported improved yields of 4-alkoxy-1-naphthonitriles by doubling the amount of pyridine used by Newman (7) thus confirming our findings.

The dinitrile was hydrolyzed to the corresponding diacid (I) in almost theoretical yield by alkaline hydrolysis in the presence of glycol. Ethanol, propanol, or glycerol can also be used, the time of the reaction depending on the boiling point of the alcoholic component.

Some attempts were made to synthesize the diacid (I) or its esters by a one stage process from benzoic acid or methyl benzoate using ethylidene chloride, ethylidene diacetate, or acetaldehyde in presence of sulphuric acid, aluminum chloride, fluosulphonic acid, hydrogen fluoride, or the fluosulphonic acid-hydrogen fluoride mixture. Also condensations of acetylene in presence of aluminum chloride or mercuric chloride were tried, but no reaction took place under any of these conditions.

The dimethyl ester of the diacid (I) was best prepared by converting the diacid to its dichloride with thionyl chloride and treating the dichloride with methanol. The di-2-ethylhexyl ester was prepared directly from the diacid and 2-ethylhexanol in presence of sulphuric acid and of xylene as an azeotropic component.

#### EXPERIMENTAL\*†

##### 1,1-Di-(*p*-chlorophenyl)ethane

Chlorobenzene (1410 gm.) was charged to a stainless steel reaction vessel and cooled to 0°. Under vigorous stirring 1000 gm. of liquid hydrogen fluoride were first added, followed by 1675 gm. of freshly redistilled fluosulphonic acid, and then a mixture of ethylidene diacetate (490 gm.) and of chlorobenzene (770 gm.) was introduced dropwise over a period of 40 min. while the tempera-

\*All melting points are uncorrected.

†The microanalyses were performed by Dr. Robert Dietrich of Zurich, Switzerland.

ture rose slowly from 0° to 20°. The temperature was maintained at about 10° while the reaction mixture was agitated for another 30 min. It was then poured into 6 liters of ice water, the organic layer separated after the addition of some ether, and then washed with dilute caustic and water. After removal of the solvent the residue was fractionally distilled, yielding recovered chlorobenzene (1650 gm.) and 1,1-di-(chlorophenyl)ethane (603 gm.; 71.5% yield based on ethylidene diacetate) as a pale yellow oil, boiling point 138–142° at 1.0 mm.; refractive index,  $n_D^{21}$  1.5920. The major portion of the product crystallized on standing a few hours at room temperature. The supernatant liquor was decanted and the solid crystallized from methanol yielding 1,1-di-(*p*-chlorophenyl)ethane (375 gm.; 56.8% over-all yield) as colorless prisms melting at 53–55° (Grummit *et al.* (3) give m.p. 54–55°).

*1,1-Di-(p-cyanophenyl)ethane*

A mixture of 1,1-di-(*p*-chlorophenyl)ethane (475 gm.), cuprous cyanide (415 gm.; dried before use for 36 hr. at 110°), and anhydrous quinoline (1200 ml.; distilled over potassium hydroxide) was refluxed for 70 hr., then poured while still hot into a solution of ammonium hydroxide (1800 ml.; d. = 0.88) and water (1800 ml.). Benzene (1600 ml.) was added, the mixture allowed to cool to room temperature, and then ether (1000 ml.) was added. A brown solid separated which was removed by filtration. The organic layer was washed with dilute ammonia solution (4 × 1200 ml.), with a hydrochloric acid solution (2 *N*; 2 × 1200 ml.; a precipitate which separated at this stage was removed by filtration), then with water (2 × 1200 ml.) and finally with saturated brine (2 × 1200 ml.). The solution was dried over anhydrous copper sulphate and the solvent removed by distillation yielding the crude dinitrile (312 gm.; 71% yield). Crystallization from ethanol gave 1,1-di-(*p*-cyanophenyl)ethane (249 gm.) as colorless prisms which had a melting point of 112–118°C. After one more crystallization, the melting point was increased to 120–122.5°. Calc. for  $C_{16}H_{12}N_2$ : C, 82.75; H, 5.2; N, 12.05. Found: C, 82.65; H, 5.05; N, 12.3.

*1,1-Di-(p-carboxyphenyl)ethane*

A mixture of 1,1-di-(*p*-cyanophenyl)ethane (216 gm.), sodium hydroxide (120 gm.), ethylene glycol (1200 ml.), and water (240 ml.) was refluxed for 10 hr. by which time evolution of ammonia ceased. After it was cooled to room temperature, the solution was separated from a small amount of solidified oily material, diluted with ice water, and acidified with dilute hydrochloric acid under vigorous stirring. The resulting precipitate was filtered under suction, washed several times with water, and brought to a consistency of a cake by applying suction for several hours. The latter was dried either in an oven at 110° or by azeotropic distillation with benzene or xylene. In this way 1,1-di-(*p*-carboxyphenyl)ethane (239 gm.; 95.1% yield) was obtained in microcrystals, which melted at 265–278°, and then, on crystallization from ethyl acetate, at 273–278°. Calc. for  $C_{16}H_{14}O_4$ : C, 71.1; H, 5.2. Found: C, 71.7; H, 5.2.

*1,1-Di-(p-carboxyphenyl)ethane Dimethyl Ester*

Thionyl chloride (150 ml.) was added slowly to the diacid (150 gm.) causing heat evolution and progressive dissolution of the solid. The mixture was refluxed for one hour, then the excess of thionyl chloride removed under reduced pressure. To the residue methanol (150 ml.) was slowly added and then the mixture refluxed for a period of one hour and the excess methanol distilled off. The residue was taken up in ether, washed twice with sodium carbonate solution and then with water, and finally dried over anhydrous magnesium carbonate. Evaporation of the solvent left 1,1-di-(*p*-carbomethoxyphenyl)-ethane (156.9 gm.; yield 94.3%) which crystallized on standing. Recrystallization from cyclohexane-ether mixture or from ether gave colorless plates which melted at 56.5–58.2°. Calc. for  $C_{18}H_{18}O_4$ : C, 72.5; H, 6.1. Found: C, 72.35; H, 5.95.

*1,1-Di-(p-carboxyphenyl)ethane Di-(2'-ethyl)hexyl Ester*

A mixture of 1,1-di-(*p*-carboxyphenyl)ethane (355.4 gm.), 2-ethylhexanol (2000 ml.), concentrated sulphuric acid (55 gm.), and dry xylene (500 ml.) was refluxed for 100 hr. while water was separated in a Dean and Stark trap. The resulting solution was then washed with sodium carbonate solution and the excess of xylene and alcohol was distilled. Fractionation of the residue under reduced pressure gave 1,1-di-(*p*-carboxyphenyl)ethane di-(2'-ethyl)-hexyl ester (496.0 gm.; yield 76%) which boiled at 220° at 0.05 mm.; refractive index,  $n_D^{25}$  1.5252. Calc. for  $C_{32}H_{46}O_4$ : C, 77.7; H, 9.4. Found: C, 77.45; H, 9.05.

## REFERENCES

1. ANSCHÜTZ, R. Ann. 235:313, 315. 1886.
2. Dominion Tar and Chemical Co. Brit. Patent No. 668,283. 1952.
3. GRUMMIT, O., BUCK, A. C., and BECKER, E. I. J. Am. Chem. Soc. 67:2265. 1945.
4. HAISS, A. Ber. 15:1481. 1882.
5. KRZESZ, Z., LEIB, J., and SCHULTZ, G. Private communication.
6. LORZ, E. and BALTZLY, R. J. Am. Chem. Soc. 73:93. 1951.
7. NEWMAN, M. S. Org. Syntheses, 21:89. 1941.
8. PERRON, Y. Can. J. Chem. 31:4. 1953.
9. PERRON, Y. and BARRÉ, R. Can. J. Chem. 30:203. 1952.