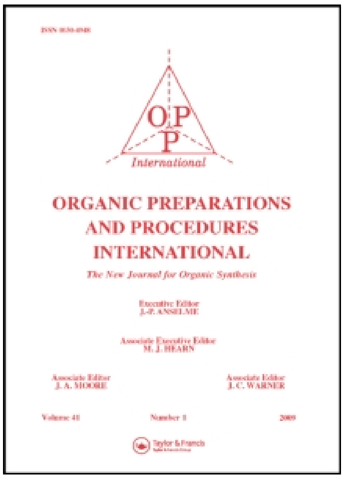

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

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To cite this Article Levy, Louis A.(1974) 'A CONVENIENT PREPARATION OF HOMOGENEOUS 2,3,6-TRICHLOROBENZOIC ACID AND ITS CONVERSION TO 2,2',3,3',6,6'-HEXACHLOROBIPHENYL', Organic Preparations and Procedures International, 6: 6, 275 — 280

To link to this Article: DOI: 10.1080/00304947409355120

URL: http://dx.doi.org/10.1080/00304947409355120

ORGANIC PREPARATIONS AND PROCEDURES INT. 6(6), 275-280 (1974)

A CONVENIENT PREPARATION OF HOMOGENEOUS 2,3,6-TRICHLOROBENZOIC ACID AND ITS CONVERSION TO 2,2',3,3',6,6'-HEXACHLOROBIPHENYL

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As part of a continuing investigation into the chemistry of chlorinated hydrocarbons and especially polychlorinated biphenyls,[1] a need arose for a considerable quantity of 2,3,6 trichlorobenzoic acid in order to unambiguously synthesize 2,2',3,3',6,6'-hexachlorobiphenyl. From the large number and nature of the citations to this compound in Chemical Abstracts, this material appears to be of some commercial importance as an intermediate in herbicide and pesticide formulations.

Commercially available material[2] labeled as 2,3,6 trichlorobenzoic acid was clearly not homogeneous as evidenced by its melting point range of approximately 50°. Some of the claims[3] in the patent literature on the synthesis of this compound recognize the formation of isomeric mixtures and it seems likely that other preparations also yield mixtures although this fact is not always made explicit in the claim. In all of these processes, the desired level of chlorination is achieved by what is surely a non-specific chlorination of a lower homolog. In one detailed investigation of the chlorination of toluene and of chlorotoluene and subsequent oxidation, a mixture of trichlorobenzoic acids was obtained consisting mainly of the 2,3,6 and 2,4,5 trichlorobenzoic acids along with a small amount of the 2,3,4 isomer.[4] In the same investigation, a rational but cumbersome synthesis of 2,3,6 trichlorobenzoic acid allowed the unambiguous assignment of the melting point to this isomer as 124-125° thereby correcting an earlier erroneous value of 163-164°.[5]

Esterification of the commercially available mixture with diazomethane and analysis of the resultant mixture of esters by gas-liquid chromatography showed it to consist of three components, eluting closely together, in the ratio 3:7:1. Esterification with diazomethane is known not to be subject to steric effects in contrast to the well known effects of steric hindrance due to ortho substituents in the Fisher method of esterification.[6] Since it appears that the desired 2,3,6 trichloro isomer is the only isomer present with both ortho positions substituted it was felt that the intruding isomers could be selectively esterified leaving the desired acid to be extracted from the reaction mixture.

Treatment of the acid mixture in the usual way with methanolic HCl produced a mixture of two of the three esters obtained from esterification of the acid mixture with diazomethane. Recovery of the unreacted acid by extraction with base and reacidification gave in 42% yield pure 2,3,6 trichlorobenzoic acid, mp. 124-127°.[7] Esterification of this acid with diazomethane and glc analysis showed it to be uncontaminated with any isomeric material and identical to the major component present in the mixture esterified with diazomethane. The acid could be conveniently transformed to the corresponding 2,3,6 trichloroaniline by use of diphenyl phosphoric azide to effect the Curtius reaction.[8] The conventional treatment of the acid with sulfuric acid and sodium azide resulted only in recovery of starting material. By straightforward methods, the aniline could be converted to the 2,3,6 trichloroiodobenzene and thence to 2,2',3,3',6,6' hexachlorobiphenyl, a component of commercial polychlorinated biphenyl mixtures. This biphenyl has recently been prepared by another route which provides additional confirmation as to the identity of 2,3,6 trichlorobenzoic acid.[9]

EXPERIMENTAL SECTION

Infrared spectra were measured in KBr discs on a Perkin Elmer 621 instrument. NMR spectra were determined with a Varian T-60 instrument in $CDCl_3$ solution. Elemental analysis was performed by Galbraith Laboratories. GLC analysis were carried out on a Varian model 2800 instrument using a 6' x 1/8" column packed with 3% SE-30 on 80/100 mesh Supelcoport. Each run was programmed from 100° to 250° at 10°/min. then held at that temperature. Carrier gas was helium with a flow rate of 35 ml/min.

2,3,6-Trichlorobenzoic Acid. - A rapid stream of HCl was passed into 500 ml of chilled anhydrous methanol for five minutes. To this solution was added, all at once, 100 g of a commercial mixture of trichlorobenzoic acids. An additional 150 ml of methanol was then added. The solution was refluxed gently overnight. The cooled solution was adjusted to pH 11 with solid sodium carbonate and the major portion of the solvent was removed at reduced pressure. The addition of 500 ml of water caused the separation of an organic layer which quickly solidified. The aqueous portion was extracted twice with ether and combined with the solid phase. The aqueous solution was acidified with sulfuric acid and extracted three times with ether. The combined ethereal extracts were washed well with water and finally with saturated sodium chloride solution. After drying and removal of the ether, 44.2 g of crystalline 2,3,6 trichlorobenzoic acid was obtained, mp. 124-127°. I.R. νmax: 2900, 1725, 1650, 1570, 1445, 1410, 1365, 1265, 1245, 1180, 1170, 1085, 875, 860, 810, 760, 745, 685 cm^{-1}. NMR: An AB system, δ: 7.30, 7.41 J=9.1 Hz.

N-(2,3,6-Trichlorophenyl) *t*-butyl carbamate. - A mixture of 20.25 g (0.1 mole) of 2,3,6 trichlorobenzoic acid, 10.1 g (0.1 mole) of triethylamine and 24.75 g (0.1 mole) of diphenylphosphonic azide in 100 of *t*-butyl alcohol was boiled gently for 22.5 hours. The bulk of the solvent was removed using a rotary evaporator. The residue was poured into water and extracted three times with ether. The combined ethereal extracts were washed with three portions of aqueous HCl, 10% sodium carbonate solution and finally saturated sodium chloride solution. After drying and removal of the ether, there was obtained 22.3 g (76%) of clear oil which crystallized on standing, mp. 103-105°. A sample for analysis was recrystallized from ethanol, mp. 111-112°. Anal. Calcd. for $C_{11}H_{12}Cl_3NO_2$: C, 44.54; H, 4.07; Cl, 35.86. Found: C, 44.53; H, 4.00; Cl, 35.98. I.R. νmax: 3250, 3030, 2975, 1680, 1560, 1510, 1440, 1405, 1365, 1270, 1240, 1160, 1140, 1060, 940, 860, 820, 770 cm^{-1}.

2,3,6-Trichloroaniline Hydrochloride. - A solution of HCl in ether was made up by passing a current of anhydrous HCl gas into 100 ml of cold, dry ether for 5 minutes. To this solution was added 5.0 g (0.017 mole) of the carbamate obtained above. After standing overnight, the originally homogeneous solution had deposited crystals. The volume of solvent was reduced by more than half and the precipitate filtered to yield 4.1 g (100%) of product. A sample of the 2,3,6 trichloraniline, mp. 60-61°, lit. mp. 63-64°[10] was prepared by treating the hydrochloride with aqueous sodium hydroxide.

2,3,6-Trichloroiodobenzene. - A solution of 2.5 g (0.032 mole) of sodium nitrite in 10 ml of water was added slowly, with stirring to a suspension of 7.2 g (0.031 mole) of 2,3,6 trichloroaniline hydrochloride in 10 ml of hydrochloric acid. The temperature was not allowed to rise above 5° during the diazotization. The resulting solution was added to a solution of 8.5 g of potassium iodide in 50 ml of water. The precipitated solid was filtered, dissolved in benzene and washed with aqueous sodium sulfite. The organic phase was dried and the solvent removed to yield 6.2 g (85%) of 2,3,6 trichloroiodobenzene, mp. 30-35°, lit. mp. 35-36°.[8]

2,2',3,3',6,6'-Hexachlorobiphenyl. - A mixture of 6.6 g (0.028 mole) of 2,3,6 trichloroiodobenzene and 2.1 g of copper dust was heated for three hours at 210°. The cooled reaction mixture was extracted three times with a total of 125 mole of hot benzene. The combined extracts were concentrated and chromatographed on a short column of alumina. Elution with hexane yielded 2.9 g (58%) of a white solid which after crystallization from hexane had mp. 112-114°, lit. mp. 114-115°.[8] I.R. νmax: 1425, 1400, 1355, 1175, 1045, 810, 795, 680 cm^{-1}. NMR: An AB system, δ=7.47, 7.36 J=8.8 Hz.

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(Received October 29, 1974; in revised form December 19, 1974)