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Some Dicarboxylic Acids and Esters Containing the Phosphine Oxide Group

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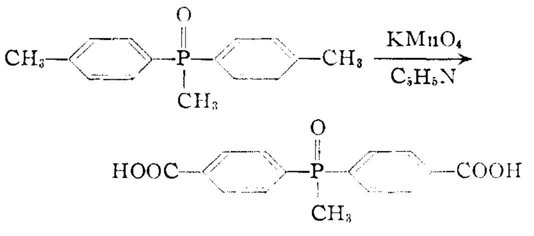
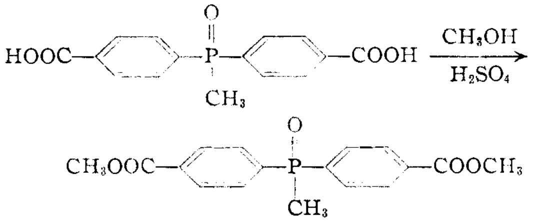
A series of bis-(*p*-carboxyphenyl)-phosphine oxides and their methyl esters have been prepared, which have as their third phosphorus substituents, methyl, ethyl and phenyl groups. The acids were obtained in high yield from the corresponding tolyl compounds by oxidation with potassium permanganate in a pyridine–water mixture. The synthesis of phenyl-di-*p*-tolylphosphine oxide and sulfide completes the series of mixed phenyl-*p*-tolylphosphines, phosphine oxides and phosphine sulfides. Oxidation of phenyldi-*p*-tolylphosphine sulfide with potassium permanganate produced bis-(*p*-carboxyphenyl)-phenylphosphine oxide.

A group of dibasic acids and a tribasic acid which contain the tertiary phosphine oxide unit were prepared and converted to their methyl esters. Only two such acids are recorded in the literature, bis-(*p*-carboxyphenyl)-*p*-chlorophenylphosphine oxide[1] and tris-(*p*-carboxyphenyl)-phosphine oxide.[2] Michaelis[3] also prepared mono-(carboxyphenyl)-dialkylphosphine oxides and Gilman and Brown[4] prepared diphenyl-3-carboxyphenylphosphine oxide. No esters of any of these acids have been described.

The methods of synthesis used in this work are not new but several improvements in techniques were made. Details, not previously recorded, concerning yields and properties of known intermediates are presented. One general route used to the bis-(carboxyphenyl)-phosphine oxides of the type $R_2R'PO$ was to treat phosphorus trichloride with tolylmagnesium bromide and then add alkyl iodide to the tritolylphosphine to form the phosphonium salt which was decomposed by heat and alkali to the ditolylalkylphosphine oxide. This was converted to the acid and ester as outlined in equations 1 and 2.

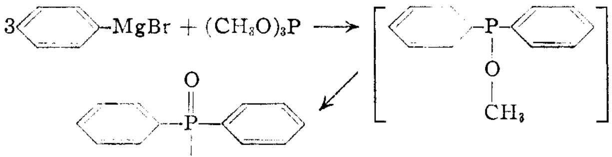


(1)



(2)

Tri-*p*-tolylphosphine was synthesized both by reaction of the tolyl Grignard reagent with phosphorus trichloride and with trimethyl or tributyl phosphite. In no case were the yields over 45%. Gilman and Robinson[5] reported that a 42% yield of methyldiphenylphosphine oxide was obtained by the action of phenylmagnesium bromide on trimethyl phosphite and that 10% of triphenylphosphine oxide was obtained with triethyl phosphite. They postulated a reaction according to equation 3 for the former preparation.



(3)

The intermediate methoxydiphenylphosphine was not isolated but the conversion of such compounds to phosphine oxides by Arbusov[6] was pointed out. Since this course of reaction would have been a short-cut to desired products in the present study, the alkyl phosphites were used with tolylmagnesium bromide, but no mixed or symmetrical phosphine oxide could be isolated regardless of the order of addition of reagents. Similar preparations were tried then with phenylmagnesium bromide and trimethyl phosphite. Only triphenylphosphine (54% yield of crude product; 26% yield of pure product, m.p. 82°) and some biphenyl were isolated. The former was identified by conversion to methyltriphenylphosphonium iodide with methyl iodide (m.p. 164–165°).[7] Methyldiphenylphosphine oxide melts at 111–112°[8] and does not react with methyl iodide. The only condition under which it appears possible that Gilman and Robinson could have obtained the mixed phosphine oxide with the proportion of reagents used is that their trimethyl phosphite had isomerized partially to dimethyl methanephosphonate in the presence of a trace of alkyl halide or hydrogen chloride, which would yield methyl chloride, during distillation or subsequent storage. Such rearrangements proceed readily at room temperature with trimethylphosphite.[9] In their second preparation triphenylphosphine oxide could result either from triethyl phosphate in the phosphite or air oxidation of the triphenylphosphine initially produced.[10]

Dörken[11] compiled a table of the melting points of the phenyl-*p*-tolylphosphines, phosphine oxides and phosphine sulfides, which is repeated here with references to the earliest preparations of each com-

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[1] A. Michaelis, *Ann.*, **315** 97 (1901).

[2] A. Michaelis, *ibid.*, **315**, 92 (1901).

[3] A. Michaelis, *ibid.*, **293**, 284, 290 (1896).

[4] H. Gilman and G. E. Brown, THIS JOURNAL, **67**, 824 (1945).

[5] H. Gilman and J. D. Robinson, *Rec. trav. chim.*, **48**, 328 (1929).

[6] A. E. Arbusov, *J. Russ. Phys. Chem. Soc.*, **42**, 395 (1910).

[7] A. Michaelis and L. Gleichmann, *Ber.*, **15**, 801 (1882).

[8] A. Michaelis and H. von Soden, *Ann.*, **229**, 311, 316 (1885).

[9] A. Arbusov, *J. Russ. Phys. Chem. Soc.*, **38**, 687 (1906).

[10] See also G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 108.

[11] C. Dörken, *Ber.*, **21**, 1505 (1888).

pound and the melting points of new compounds prepared in this work. General effects of structural changes are obvious from these data. The symmetrical derivatives form the highest melting groups. Conversion of the phosphine to its oxide or sulfide raises the melting point in most cases. The tritolylphosphine oxide is an exception. The sulfides are the highest melting derivatives. The selenides, where known, have still higher melting points.

TABLE I

Compound	M.p., °C.	Reference
$(C_6H_5)_3P$	75- 76	7
	80	13
	82	This article
$(C_6H_5)_3PO$	153.5	8, p. 306
$(C_6H_5)_3PS$	157.5	8, p. 307
	161	12
$(C_6H_5)_2C_7H_7P$	68	11
$(C_6H_5)_2C_7H_7PO$	129–130	11
$(C_6H_5)_2C_7H_7PS$	139	11
$C_6H_5(C_7H_7)_2P$	57	11
$C_6H_5(C_7H_7)_2PO$	79.5	This article
$C_6H_5(C_7H_7)_2PS$	154	This article
$(C_7H_7)_3P$	146	1, p. 78
$(C_7H_7)_3PO$	145	1, p. 80
$(C_7H_7)_3PS$	182	1, p. 82

Methylditolylphosphine oxide was prepared, as by Michaelis,[14] by decomposition of the quaternary phosphonium salt with silver oxide or alkali and heat and by the reaction of tolylmagnesium bromide on diphenyl methanephosphonate. The reaction of phosphonate esters with Grignard reagents has not been used previously for the preparation of phosphine oxides, although it is analogous to methods used for other phosphorus compounds. Neither procedure provides any great advantage over the other in yields but the latter is the shorter. Phenylditolylphosphine oxide and sulfide were prepared by a Grignard reaction on the corresponding dichlorophenylphosphine oxide or sulfide. The oxide was isolated with considerable difficulty because of its tendency to form an unstable low-melting hydrate and its poor crystallizability from most solvents.

Michaelis[1-3] found that the oxidation of tolyl groups on phosphine oxides and phosphinic and phosphonic acids would take place very slowly with alkaline permanganate or chromic acid and the yields of acid were very poor. We have found that the pyridine–permanganate procedure, applied by Bucher[15] to retene, is a mild, rapid method for achieving this end and that the yields of acid are 80 to 90%.

Experimental

Tri-*p*-tolylphosphine from Phosphorus Trichloride.—Phosphorus trichloride (137 g., 1 mole) in 400 ml. of dry ether was added over a period of six hours to 4 moles of *p*-tolylmagnesium bromide in 1700 ml. of dry ether. The mixture was cooled in an ice–salt-bath throughout the addition. Thereafter the mixture was stirred for an hour at reflux temperature.

The reaction mixture was cooled and excess Grignard reagent was destroyed by the careful addition of 600 ml. of saturated aqueous ammonium chloride solution. The ether layer was separated and the aqueous slurry was extracted twice with 500-ml. portions of ether. The combined ether solutions were evaporated partially and stood overnight to permit some further concentration and crystallization. The tri-*p*-tolylphosphine was obtained as transparent rhombs. It crystallized from acetone in the same form and from aqueous alcohol as silky needles. After recrystallization, the yield was 53.5 g., m.p. 146°[16] (Table I). The yield of crude product (m.p. 144–146°) never exceeded 35%. The crude product always possessed a strong "phosphine-like" odor, whereas the pure compound was odorless. This odor was probably due to the presence of primary or secondary phosphines or the corresponding trivalent phosphonous or phosphinous acids. From the mother liquors were isolated considerable bitolyl and an unidentified, phosphorus-containing oil.

An alternative method of purification of the phosphine was to evaporate the ether solution to dryness, repeatedly extract the product with petroleum ether to remove bitolyl, dissolve out the oil quickly with cold alcohol or acetone, and finally recrystallize the product from acetone or ether. The order of increasing solubility in several common solvents was petroleum ether, ethanol, acetone and ether.

Tri-*p*-tolylphosphine from Trialkyl Phosphites.—Trimethyl phosphite[17] (40 g., 0.32 mole) in 150 ml. of dry ether was added over a period of two hours to 1.2 moles of *p*-tolylmagnesium bromide in 450 ml. of dry ether. Heat was evolved during the addition. Additional trimethyl phosphite (10 g.) was introduced without the evolution of heat and the mixture therefore was heated one hour at reflux temperature. After decomposition of the Grignard reagent, the product was isolated from the ether extracts as a mixture of an oil and dense crystals. Forty-eight grams (37.4% based on trimethyl phosphite) of pure tri-*p*-tolylphosphine (m.p. 146°) was obtained by fractional crystallization from acetone and alcohol. The mixed melting point with methyldi-*p*-tolylphosphine oxide (m.p. 146°) was about 122°.

The reaction was repeated with addition in the reverse order. *p*-Tolylmagnesium bromide (0.62 mole) in 270 ml. of dry ether was transferred after preparation to a dropping funnel by nitrogen pressure. This solution was added dropwise to a solution of trimethyl phosphite (0.21 mole) in 80 ml. of dry ether. The yield of pure tri-*p*-tolylphosphine was 26 g. (41.7%). A mixed melting point with methyldi-*p*-tolylphosphine oxide was about 125°.

Tributyl phosphite (1.0 mole) and *p*-tolylmagnesium bromide (4.0 moles) were allowed to react as in the first preparation above and 49.5 g. (16%) of pure tri-*p*-tolylphosphine were obtained.

Methyltri-*p*-tolylphosphonium Iodide.—Tri-*p*-tolylphosphine (91.5 g., 0.31 mole) and methyl iodide (94 g., 1.5 moles) were mixed in 1 l. of dry ether and a white crystalline addition product began to form immediately. Sufficient heat was evolved to maintain refluxing for one hour. Thereafter the mixture was heated at reflux temperature for four hours. The salt was separated, washed with ether, and dried at 105°; yield 125 g. (94%), m.p. 220.5°.

When the salt was recrystallized from hot water, it formed a hydrate melting below 100°. It was this form for which Michaelis[18] reported a melting point of 108°. Upon heating in an Abderhalden drying pistol, the water of hydration was lost and the melting point rose to 220–220.5°.

Anal. Calcd. for $C_{22}H_{24}PI$: C, 59.20; H, 5.42; P, 6.94. Found: C, 59.48; H, 5.54; P, 6.96.

Methyldi-*p*-tolylphosphine Oxide.—To a suspension of 129 g. of methyltri-*p*-tolylphosphonium iodide in 385 ml. of water in a flask equipped with still-head and condenser was added 60 ml. of 40% KOH. The flask was heated and water

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[12] W. Strecker and C. Grossman, *Ber.*, **49**, 74 (1916).

[13] P. Walden and R. Swinne, *Z. physik. Chem.*, **79**, 714 (1912).

[14] Reference 1, p. 84.

[15] J. E. Bucher, THIS JOURNAL, **32**, 374 (1910).

[16] All melting points below 230° were determined in glass capillaries with thermometers calibrated against National Bureau of Standards standard thermometers, but are otherwise uncorrected. Higher melting points were determined on a Maquenne type block without corrections.

[17] T. Milobendzki and A. Sachnowski, *Chem. Polski*, **15**, 34–37 (1917).

[18] Reference 1, p. 84.

and toluene, formed from decomposition of the phosphonium hydroxide, distilled off until evolution of toluene was complete. The residue was extracted with benzene and the product obtained in these extracts was recrystallized from benzene–petroleum ether; yield 56 g. (80%), m.p. 146–147°. Michaelis[18] reported a melting point of 143°.

Bis-(*p*-carboxyphenyl)-methylphosphine Oxide.—Methyldi-*p*-tolylphosphine oxide (53.5 g.) was dissolved in 265 ml. of pyridine and 140 ml. of water was added. To this mixture, which was heated on a steam-bath, was added finely powdered potassium permanganate (251 g.) portionwise at a rate to maintain refluxing. Water, to bring the total volume to 480 ml., was added as required to keep the mixture from becoming pasty. The addition required five hours and the heating was continued two hours longer. The mixture was steam distilled until the odor of pyridine was no longer evident. During this process the color of unreacted permanganate also disappeared. The residue was filtered to remove manganese dioxide and the filtrate taken almost to *p*H 7 with dilute sulfuric acid. It was concentrated on a hot-plate and the precipitated potassium sulfate filtered off. On acidification of the filtrate with dilute sulfuric acid, the bis-(*p*-carboxyphenyl)-methylphosphine oxide was precipitated as a thick oil, which slowly solidified to a hard mass. This was ground and dried at 105°; yield 58.5 g. (88%), m.p. 285°.

In an alternative procedure for isolation of the acid the steam distillation and separation of the potassium sulfate were omitted. The pyridine was neutralized and the product precipitated directly with hydrochloric acid. The isolated acid was then reprecipitated from sodium bicarbonate solution. In this case it was necessary to remove any unreacted potassium permanganate before acidification by reaction with methanol. The acid, which was precipitated as a monohydrate, was soluble in methanol and insoluble in ether and water.

Anal. Calcd. for $C_{15}H_{13}O_5P{\cdot}H_2O$: neut. equiv., 161.1; Found: neut. equiv., 169.0.

Bis-(*p*-carbomethoxyphenyl)-methylphosphine Oxide.—Bis-(*p*-carboxyphenyl)-methylphosphine oxide (59 g.) was dissolved in 400 ml. of absolute methanol with 4.5 ml. of concentrated sulfuric acid and the solution refluxed 16 hours. The product crystallized from the cooled reaction mixture. After recrystallization from benzene and methanol, 30 g. of pure ester melting at 225.5° was obtained.

Anal. Calcd. for $C_{17}H_{17}O_5P$: C, 61.44; H, 5.16; P, 9.32; CH_3O, 18.68; sapn. equiv., 166.1. Found: C, 61.19; H, 5.01; P, 9.26; CH_3O (Zeisel), 17.93; sapn. equiv., 167.7.

Diphenyl Methanephosphonate.—Triphenyl phosphite (124 g., 0.4 mole) and methyl iodide (25 ml., 0.4 mole) were refluxed together 16 hours. The cooled mixture crystallized and was washed several times with dry ether.

The phosphonium iodide was decomposed by reaction with 800 ml. of 5% sodium hydroxide, which caused the separation of an oil accompanied by the evolution of considerable heat. The oil was collected by ether extraction and the extract dried over potassium carbonate and distilled. Some phenol was obtained and liquid diphenyl methanephosphonate; yield 65.5 g. (66%), b.p. 151° (0.8 mm.), m.p. 35°. Michaelis[19] reported a melting point of 36–37°.

Methyl-*p*-tolylphosphine Oxide from Diphenyl Methanephosphonate.—Diphenyl methanephosphonate (62 g., 0.25 mole) in 200 ml. of absolute ether was added dropwise to a cooled solution of 0.75 mole *p*-tolylmagnesium bromide in 320 ml. of dry ether. During the reaction an oil separated which solidified upon hydrolysis of the excess Grignard reagent. The mixture was filtered through glass wool and the ether layer separated and combined with ether washings of the solid residue. After removal of the ether, the crude product (84 g.) was distilled twice under vacuum and yielded 23 g. of bitolyl, 10.5 g. of phenol, 35 g. of methyldi-*p*-tolylphosphine oxide and a carbonaceous residue.

Ethyltri-*p*-tolylphosphonium Iodide.—Tri-*p*-tolylphosphine (104 g.) and ethyl iodide (140 ml.) reacted to give a 73% yield of the phosphonium iodide (m.p. 187–187.5°) by a procedure similar to that used for the methyl analog.[20]

Anal. Calcd. for $C_{23}H_{26}PI$: C, 59.99; H, 5.69; P, 6.73. Found: C, 60.56; H, 5.77; P, 6.48.

Ethyldi-*p*-tolylphosphine Oxide.—Ethyltri-*p*-tolylphosphonium iodide (108 g.), 320 ml. of water and 64 ml. of 40% potassium hydroxide were heated at reflux temperature for four hours and then the by-product toluene was distilled out with water. The hot residue was extracted with hot benzene and the extract concentrated. Starting material (20 g.) was recovered by the addition of ether, leaving crude phosphine oxide in the mixed solvents (49 g., 100% yield based on phosphonium salt consumed). The ethyldi-*p*-tolylphosphine oxide was purified by crystallization from hot *n*-heptane, in which it was only slightly soluble, m.p. 77.5°. It was readily soluble in ether, ethanol and benzene.

Anal. Calcd. for $C_{16}H_{19}OP$: C, 74.40; H, 7.41. Found: C, 74.30; H, 7.16.

Bis-(*p*-carboxyphenyl)-ethylphosphine Oxide.—Ethyldi-*p*-tolylphosphine oxide (49 g.) was oxidized by the alternate procedure for the methyl analog and 50 g. (82% yield) of crude acid was obtained. Reprecipitation from sodium bicarbonate solution with hydrochloric acid gave 39 g. of purer acid, m.p. 265°.

Anal. Calcd. for $C_{16}H_{15}O_5P$: neut. equiv., 159.1. Found: neut. equiv., 169.0.

Bis-(*p*-carbomethoxyphenyl)-ethylphosphine Oxide.—This ester was prepared by a procedure similar to that for the methyl analog and was crystallized initially by addition of water to the reaction mixture; yield 82%, m.p. 151.5°. Recrystallization from benzene–petroleum ether raised the melting point to 162°.

Anal. Calcd. for $C_{18}H_{19}O_5P$: C, 62.43; H, 5.53. Found: C, 62.31; H, 5.80.

Phenyldi-*p*-tolylphosphine Oxide.—Dichlorophenylphosphine oxide (164 g.) in 600 ml. of dry ether was added with stirring to a solution of *p*-tolylmagnesium bromide (made from 460 g. of *p*-bromotoluene and 60 g. of magnesium in 1200 ml. of dry ether) during a period of one hour. The mixture was hydrolyzed with 10% H_2SO_4 and the ether extract collected, washed with 10% sodium bicarbonate solution, and distilled. There was obtained 20 g. of toluene, 22 g. of bromotoluene, 90 g. of bitolyl and 211.5 g. of a thick, fluorescent oil, b.p. 245–250° (1.3 mm.). The latter compound was very soluble in acetone, ether, chloroform and ethanol and insoluble in petroleum ether and water. It was crystallized with considerable difficulty from the melt or from dry *n*-heptane, m.p. 79.5°. Crystallization from *n*-heptane after precipitation from alcohol–water yielded a hydrate, m.p. 91°, which was converted to the anhydrous form by drying at 100° and cooling. A mixed melting point was broad and intermediate. Several other arylphosphine oxides have been reported to form hydrates.[1,7]

Anal. Calcd. for $C_{20}H_{19}OP{\cdot}{}^1/_2H_2O$: C, 76.18; H, 6.39; water of hydration, 2.84. Found for compound melting at 91°: C, 76.26; H, 6.48; weight loss at 100°, 2.92. Calcd. for $C_{20}H_{19}OP$: C, 78.43; H, 6.25; P, 10.12. Found for compound melting at 79.5°: C, 78.20; H, 5.90; P, 10.40; no weight loss at 100°.

Phenyldi-*p*-tolylphosphine Oxide–Zinc Chloride Complex.—Undistilled phenyl-*p*-tolylphosphine oxide (145 g.) was dissolved in 300 ml. of hot absolute ethanol and 100 g. of anhydrous zinc chloride was added. The solution was allowed to stand overnight and a fine crystalline powder separated which was collected and washed with water and ether; yield 66.5 g., m.p. 227–229°. Fifty-nine grams of a less pure product was obtained from the filtrate. This complex could not be crystallized from aqueous alcohol, but decomposed to the oily phosphine oxide, which, when crystallized, was identical with the distilled product.

Anal. Calcd. for $2(C_{20}H_{19}OP){\cdot}ZnCl_2$: Cl, 9.47; P, 8.24. Found: Cl, 10.0; P, 8.0.

Although satisfactory carbon and hydrogen values were not obtained, they did indicate the correctness of the above formula. Zinc chloride has been found to combine with other phosphine oxides in this ratio by Pickard and Kenyon.[21]

Bis-(*p*-carboxyphenyl)-phenylphosphine Oxide.—Phenyldi-*p*-tolylphosphine oxide was oxidized by the procedure set forth for the methyl analog; yield 13.9 g. of dibasic acid (m.p. 307–310°) and 1.5 g. of unchanged oxide from 14.5 g. of oxide. The acid had a neutral equivalent of 209 (calcd., 183) which was not improved by reoxidation.

Twenty-one grams of the methyl ester (m.p. 165.5°) was

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(19) A. Michaelis and R. Kähne, *Ber.*, **31**, 1050 (1898).

(20) Reference 1, p. 85.

(21) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **89**, 262 (1906).

heated on a steam-bath with 300 ml. of 1.7% NaOH for one hour. The pure acid, precipitated with HCl, melted at 335° and had a neutral equivalent of 180.

Bis-(*p*-carbomethoxyphenyl)-phenylphosphine Oxide.—The crude acid such as described above (37 g.) was esterified as for the methyl analog. Several crystallizations of the product from benzene–petroleum ether yielded 18 g. of pure ester, m.p. 165–166°.

Anal. Calcd. for $C_{22}H_{19}O_5P$: C, 67.00; H, 4.86; P, 7.86. Found: C, 67.00; H, 5.11; P, 7.80.

Tris-(*p*-carboxyphenyl)-phosphine Oxide.—Tri-*p*-tolylphosphine (15 g.) was oxidized in pyridine solution with potassium permanganate and 10 g. of a white, powdery acid was obtained, m.p. 323–330°. Michaelis[2] reported a melting point of 247°.

Anal. Calcd. for $C_{21}H_{15}O_7P$: neut. equiv., 136.8. Found: neut. equiv., 136.0.

Tris-(*p*-carbomethoxyphenyl)-phosphine Oxide.—The above acid (8 g.) was esterified in methanol with sulfuric acid as the catalyst. The crude product was crystallized by cooling the solution to Dry Ice temperature and melted at 106–112°. Recrystallization from benzene–petroleum ether yielded 6 g. of ester, m.p. 123–125°.

Anal. Calcd. for $C_{24}H_{21}O_7P$: C, 63.8; H, 4.68; sapn. equiv., 150.8. Found: C, 63.4; H, 4.90; sapn. equiv., 153.4.

Phenyldi-*p*-tolylphosphine Sulfide.—This compound was prepared from phenyldichlorophosphine sulfide in a manner analogous to that used for the oxide. The major portion of the by-product bitolyl was separated by solution in low boiling petroleum ether. The phenyldi-*p*-tolylphosphine sulfide was purified by repeated crystallization from acetone. It formed clusters of glassy prisms, melting at 153.5–154°; yield 62%.

Anal. Calcd. for $C_{20}H_{19}PS$: C, 74.53; H, 5.94; P, 9.61; S, 9.96. Found: C, 74.46; H, 5.99; P, 9.21; S, 10.00.

When this compound was oxidized with potassium permanganate, as in preceding experiments, the sulfur was replaced by oxygen and bis-(*p*-carboxyphenyl)-phenylphosphine oxide was obtained.

Stability of Phosphine Oxides.—Phosphine oxides possess great thermal and chemical stability. They withstand strong oxidizing or reducing treatments, normal hydrolytic reactions, and nitrations. They may be distilled at high temperatures under reduced pressure without sign of decomposition. However, when a small sample (0.7 g.) of ethyldi-*p*-tolyphosphine oxide was heated with water at 245° for two hours, in a sealed tube, the aqueous washings from the tube were distinctly more acid than cold washings of a similar quantity of phosphine oxide. The contents of the tube possessed a phosphine-like odor.

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[CONTRIBUTION FROM THE WALKER LABORATORY, DEPARTMENT OF CHEMISTRY, RENSSELAER POLYTECHNIC INSTITUTE, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY COLLEGE, LONDON]

The Direct Cyanogenation of Benzene

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The reaction of cyanogen with benzene in the gas phase at atmospheric pressure and 740° is reported. When cyanogen is used in excess, biphenyl and para-cyanogen formation reactions are suppressed. Benzonitrile is the primary product formed (42% yields) although even at short contact times, dinitriles are obtained (8% yields). The reaction of cyanogen with benzonitrile under similar conditions gives only dinitriles as the product. The dinitrile product is found to be a mixture of 1,4- and 1,3-isomers only, and the 1,4-dinitrile isomer (terephthalonitrile) is formed in larger amounts. Thermodynamic calculations for reactions of interest with reference to the direct cyanogenation of benzene are reported.

The only reference to a reaction of cyanogen with benzene is a report by Merz and Weith[1] that when the reactants were passed through a hot tube (glowing faintly red) benzonitrile and terephthalonitrile were formed in small amounts, as well as biphenyl. This communication reports on a reinvestigation of this reaction which may be considered as a direct cyanogenation of an aromatic compound. The interest lay primarily in establishing the conditions of temperature and ratio of reactants favorable for this reaction, and in the nature and composition of the products obtained.

Experimental

Apparatus and Chemicals.—The reaction vessel was a silica tube (outside diameter, 1.3 cm.). This was mounted in a vertical position in the furnace which had been constructed with a 2.5 cm. diameter steel pipe suitably insulated and wound with nichrome resistance wire. Temperatures were measured with a chromel–alumel thermocouple. The benzene and cyanogen, metered into the system at controlled rates, were mixed in a preheater before passing into the reaction zone. A receiver cooled with an ice–water mixture was connected to the exit of the reactor to trap the liquid products. A series of traps at −80° were used to condense the more volatile products.

The cyanogen was prepared by the reaction of aqueous sodium cyanide with copper sulfate. A modification of the apparatus of Hahn and Leopold[2] was used for the cyanogen generator and the cyanogen was stored in small steel cylinders after it had been dried and redistilled.[3] The benzene was the thiophene free grade from Eastman Kodak Co. Organic Chemicals. All experiments were at atmospheric pressure.

Benzene and Cyanogen.—The reaction was first attempted at 500° using an equimolar ratio of reactants and flow rates to give a 20-second contact time. Only traces of benzonitrile were found in the product. At about 640°, similar reaction times, the yields of benzonitrile were still quite small, but at about 750°, the yields were considerably greater. A short reaction time was chosen to minimize side reactions. Using the reactants in equimolar ratio at these temperatures, it was found that biphenyl was also formed. This side reaction was suppressed when cyanogen was used in excess. At 745° and 2–3 seconds contact time, using a twofold excess of cyanogen in the feed, the yield of benzonitrile was as high as 42%, calculated on the benzene conversion per pass. Even at these short reaction times, some phthalonitriles (1 to 5%) were also obtained in the reaction product. The benzene conversion per pass calculated from the input and the benzene recovered unreacted, was about 46%. With silica chips packing in the reactor, the yields were lower, probably indicating that side reactions are being promoted by this packing. As well as silica, tests were made using steel chips, a cobalt oxide on alumina, and pumice chips. With the exception of the latter, in each case side reactions (*e.g.*, polymerization of cyanogen, decomposition) were promoted rather than the direct cyanogenation reaction. The pumice did not appreciably affect the rate or course of reaction and may thus be of interest as a catalyst support in evaluating the activity of various catalysts in this reaction.

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[1] V. Merz and W. Weith, *Ber.*, **10**, 753 (1877).

[2] G. Hahn and W. Leopold, *ibid.*, **68**, 1974 (1935).

[3] G. J. Janz, R. G. Ascah and A. G. Keenan, *Can. J. Research*, **B25**, 272 (1947).