Anal. Calcd. for $C_{10}H_{12}N_2O_6S$: C, 41.7; H, 4.17; N, 9.73. Found: C, 41.99; H, 4.22; N, 9.48.

N-(Allylcarbamoyl)-4-allylureylenebenzenesulfonamide.—In a manner similar to that employed in the synthesis of the allyl alcohol derivative, 97 g. (1.7 moles) of allylamine in benzene was treated with 168 g. (0.75 mole) of III in benzene. The product obtained in 60% yield was recrystallized from ethanol, m.p. 203–204°.

Anal. Calcd. for $C_{14}H_{18}N_4O_4S$: C, 49.75; H, 5.36; N, 16.56. Found: C, 49.79; H, 5.67; N, 16.15.

N-(*n*-Butylcarbamoyl)-4-(*n*-butylureylene)benzenesulfonamide.—In a manner similar to that employed in the synthesis of the allyl alcohol derivative, 73.1 g. (1.0 mole) of *n*-butylamine in benzene was treated with 101 g. (0.45 mole) of III. The product, obtained in 85% yield, melted at 192–193.5°.

Anal. Calcd. for $C_{16}H_{26}N_4O_4S$: C, 51.90; H, 7.70; N, 15.10. Found: C, 52.0; H, 7.50; N, 14.80.

1,4-Butanedisulfonyl Isocyanate (IV).—Phosgene was sparged through a nitrobenzene (279 g.) solution of 31 g. (0.15 mole) of 1,4-butanedisulfonamide at a rate of 1.0 mole/hr. for 2 hr. at 100°, and then for 5 hr. at 160°. The resulting solution was sparged with nitrogen for 1 hr., filtered, and the nitrobenzene was removed under reduced pressure. The residual liquid solidified on cooling. The solid was washed with anhydrous ether and dried. The product (22.5 g., 57%) was isolated with a melting point of 60–63° and infrared maxima at 4.45 (NCO) and 7.5 and 8.60 μ (SO_2).

Anal. Calcd. for $C_6H_8N_2O_6S_2$: C, 26.9; H, 2.99; N, 10.45. Found: C, 26.66; H, 3.86; N, 10.78.

1,5-Pentanedisulfonyl Isocyanate (V).—The same general procedure was used as described for the synthesis of IV. Phosgene was sparged through a 10% nitrobenzene solution of 1,5-pentanedisulfonamide (23 g., 0.1 mole) for 5 hr. at 165°. The crude product (17 g.) was isolated in 60.2% yield which was subsequently flash distilled at 200° (0.1 mm.). Infrared absorption has the expected maxima at 4.45 (NCO) and 7.4 and 8.6 μ (SO_2).

Anal. Calcd. for $C_7H_{10}N_2O_6S_2$: C, 29.8; H, 3.55. Found: C, 29.45; H, 3.90.

1,5-Naphthalenedisulfonyl Isocyanate (VI).—A slurry of 143 g. (0.5 mole) of 1,5-naphthalenedisulfonamide in 2000 g. of Arochlor 1260 (chlorinated phenyl ether) was maintained at 250° as gaseous phosgene was added at a rate of 1.0 mole/hr. for 10 hr. The resulting solution was sparged with nitrogen for 1 hr. and then filtered. Anhydrous ether (500 ml.) was added to the filtrate and 91 g. (54%) of product was isolated which melted at 185–190°. The analytical sample was purified by sublimation at 240–260° and 0.1 mm.

Anal. Calcd. for $C_{12}H_6N_2O_6S_2$: C, 42.79; H, 1.77; N, 8.31; S, 18.36. Found: C, 42.84; H, 1.96; N, 7.92; S, 18.56.

Syntheses and Reactions of Some Hindered Organophosphorus Compounds[1]

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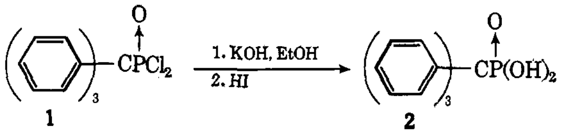
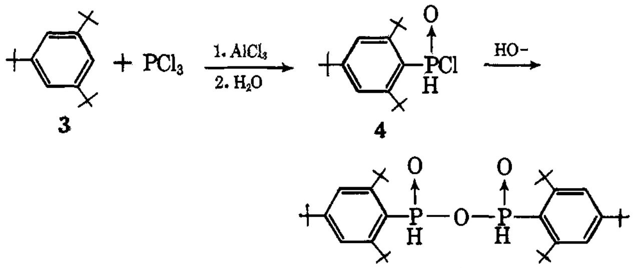
There has been little discussion in the literature of the effect of steric hindrance on the reactions of organophosphorus compounds. Triphenylmethylphosphonyl dichloride (1) can be hydrolyzed to the corresponding phosphonic acid 2 only with difficulty.[3-6] This is probably due to the steric shielding of the phosphorus atom by the three phenyl groups. Application of the synthetic procedure by which phenylphosphorus dichloride was obtained from benzene[7] (namely by the use of phosphorus trichloride and aluminum chloride with the aromatic hydrocarbon) to mesitylene, durene, and pentamethylbenzene primarily produced the corresponding diarylphosphinic chlorides.[8] Hydrolysis of these hindered phosphinic chlorides resulted in the formation of some surprisingly stable secondary diarylphosphine oxides which could not be oxidized to phosphinic acids by the normal procedure using alkaline hydrogen peroxide.[8] Resistance to oxidation by alkaline ferricyanide seemed to increase with increasing methyl substitution on the ring. These observed phenomena would appear to be due largely to steric effects.



1 2

Resistance to both hydrolysis and oxidation by organophosphorus chlorides which possess a substantial amount of steric hindrance, as illustrated by the examples mentioned above, has been found to an even greater extent in a more radically hindered organophosphorus chloride, namely 2,4,6-tri-*t*-butylphenylphosphinic chloride (**4**). This compound was readily synthesized in a 71% yield by treating 1,3,5-tri-*t*-butylbenzene[9] (**3**) with phosphorus trichloride and anhydrous aluminum chloride followed by hydrolysis.



3 4 5

The attempts to oxidize 2,4,6-tri-*t*-butylphenylphosphinic chloride with alkaline hydrogen peroxide or chlorine were not successful as shown by complete recovery of unchanged starting material. A substitution product, 2,4,6-tri-*t*-butylphenylphosphinic anhydride (**5**), was obtained in a small yield (15%) from the attempted oxidation of compound **4** with alkaline potassium ferricyanide.

Use of potassium permanganate in refluxing alkaline solution as an oxidizing agent for compound **4** strikingly illustrated the difficulty of oxidizing the phosphorus–hydrogen bond in this compound. It did oxidize one of the *t*-butyl groups to a carboxylic acid and hydrolyze the phosphorus chloride, thereby producing 2,6-di-*t*-butyl-4-carboxylphenylphosphinic acid (6) in a very small yield (7%); but the phosphorus–hydrogen bond in this product remained intact. It was shown to be a dibasic acid by the two breaks in its titration curve. The infrared spectrum of 6, when run

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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[3] D. R. Boyd and G. Chignell, *J. Chem. Soc.*, **123**, 813 (1923).

[4] H. H. Hatt, *ibid.*, 2412 (1929).

[5] G. M. Kosolapoff, *Org. Reactions*, **6**, 273 (1951).

[6] M. Halmann, L. Kugel, and S. Pinchas, *J. Chem. Soc.*, 3542 (1961).

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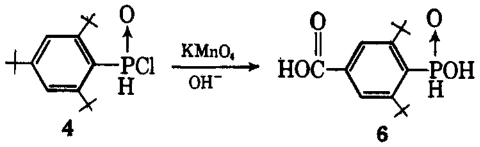
[8] A. W. Frank, *J. Org. Chem.*, **24**, 966 (1959).

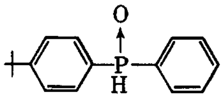
[9] L. R. C. Barclay and E. E. Betts, *Can. J. Chem.*, **33**, 672 (1955).



4 6

in a potassium bromide pellet, showed no bands in the 3500–3600-cm.$^{-1}$ region. It did exhibit several bands in the 2500–3000-cm.$^{-1}$ region and a band at 1705 cm.$^{-1}$. The infrared spectrum of **6** in dioxane solvent (in which carboxylic acids are usually monomeric[10]) showed a strong doublet appearing at 3550 and 3625 cm.$^{-1}$ along with a band at 1735 cm.$^{-1}$. This indicates that there is intermolecular rather than intramolecular hydrogen bonding present. Therefore the carboxylic acid group probably is *para* to the phosphinic acid group, assuming no rearrangement has taken place. There have been very few reports of a *t*-butyl group on an aromatic ring being oxidized to an aromatic carboxylic acid.[11]

The treatment of 1,3,5-tri-*t*-butylbenzene with phenylphosphonous dichloride and aluminum chloride resulted in the formation of *p*-*t*-butylphenylphenylphosphine oxide (**7**) in about a 4% yield as the only product isolated. The excess of phenylphosphonous dichloride in conjunction with the aluminum chloride caused the dealkylation of the 1,3,5-tri-*t*-butylbenzene.[12] The position of the *t*-butyl group was assigned as *para* on the basis of the infrared spectrum of **7** which exhibited strong maxima at 820 (due to *para* disubstitution), 755, and 725 cm.$^{-1}$, the latter two bands being due to a monosubstituted benzene ring.



7

Experimental

2,4,6-Tri-*t*-butylphenylphosphinic Chloride.—A stirred mixture of 42.23 g. (0.17 mole) of 1,3,5-tri-*t*-butylbenzene,[9] 60 ml. (0.68 mole) of phosphorus trichloride, and 33.3 g. (0.25 mole) of aluminum chloride was refluxed for 4 hr. After the reaction mixture was cooled to room temperature, 250 ml. of methylene chloride was added (when chlorine gas was added at this point no oxidation was found to take place) and the reaction mixture was poured into a water–ice mixture. The methylene chloride phase was separated, and the aqueous phase was extracted several times with fresh methylene chloride. The combined methylene chloride extracts were dried and filtered and the solvent was removed to yield a crystalline solid product. After one recrystallization from petroleum ether (b.p. 30–60°) a total of 38.0 g. (0.12 mole) of product was obtained representing a yield of 71%. It crystallized from petroleum ether as colorless needles, m.p. 133–134°, λ_{max}^{KBr} 2340 cm.$^{-1}$ (P–H).

Anal. Calcd. for $C_{18}H_{30}ClOP$: C, 65.74; H, 9.20; P, 9.42. Found: C, 65.62; H, 9.24; P, 9.76.

The product could not be oxidized with alkaline hydrogen peroxide.

Attempted Oxidation of 2,4,6-Tri-*t*-butylphenylphosphinic Chloride with Alkaline Potassium Ferricyanide.—A stirred mixture of 45.8 g. (0.14 mole) of 2,4,6-tri-*t*-butylphenylphosphinic chloride, 54.0 g. (0.16 mole) of potassium ferricyanide, 32.8 g. of sodium hydroxide, and 2 l. of water was heated at 80–100° for 22 hr. The solution was acidified with hydrochloric acid and extracted twice with benzene. The combined benzene extracts were dried and filtered and the solvent was removed. Some petroleum ether (b.p. 20–40°) was added to the residual oil to remove starting material and all but some colorless solid dissolved. Upon filtration, a total of 6.2 g. (0.01 mole) of 2,4,6-tri-*t*-butylphenylphosphinic anhydride was obtained representing a yield of 15%. It crystallized from ethyl acetate as colorless needles, m.p. 259.5–260.5°, λ_{max}^{KBr} 2340 cm.$^{-1}$ (P–H).

Anal. Calcd. for $C_{36}H_{60}O_3P_2$: C, 71.72; H, 10.03; P, 10.28. Found: C, 71.74; H, 10.40; P, 10.21.

Oxidation of 2,4,6-Tri-*t*-butylphenylphosphinic Chloride with Alkaline Potassium Permanganate.—A stirred mixture of 18.6 g. (0.06 mole) of 2,4,6-tri-*t*-butylphenylphosphinic chloride, 39.5 g. (0.25 mole) of potassium permanganate, and 250 ml. of 2 *N* aqueous sodium hydroxide was refluxed for 16 hr. All of the potassium permanganate had reacted by this time and the manganese dioxide precipitate was removed by filtration. The basic aqueous solution was washed with benzene, acidified with hydrochloric acid (at which time a gas was evolved from the solution), and extracted with benzene and 3-hexanone. The solvents were removed from the combined solutions and a thick oil remained. Addition of petroleum ether (b.p. 30–60°) to the oil caused a white insoluble precipitate to separate. A total of 1.2 g. (0.004 mole) of the white crystalline product, **2,6-di-*t*-butyl-4-carboxylphenylphosphinic acid**, was isolated by filtration representing a yield of 7%. It was dissolved in aqueous sodium hydroxide, washed with benzene, and reprecipitated with hydrochloric acid. It crystallized from *n*-heptane as colorless plates, m.p. 226–227°.

Anal. Calcd. for $C_{15}H_{23}O_4P$: C, 60.39; H, 7.77; P, 10.38; neut. equiv., 149. Found: C, 59.97; H, 7.59; P, 10.77; neut. equiv., 144.

The infrared spectrum (KBr pellet) exhibited a band at 1705 cm.$^{-1}$, and the spectrum using dioxane solvent showed bands at 3625, 3550, and 1735 cm.$^{-1}$. Likewise bands were found (KBr pellet) at 2360 (P–H) and 2650 cm.$^{-1}$ (P–OH).

Reaction of 1,3,5-Tri-*t*-butylbenzene with Phenylphosphonous Dichloride.—A stirred mixture of 45.4 g. (0.18 mole) of 1,3,5-tri-*t*-butylbenzene, 128.9 g. (0.72 mole) of phenylphosphonous dichloride, and 40 g. (0.3 mole) of anhydrous aluminum chloride was refluxed for 4 hr. Then, after adding 28 ml. (0.3 mole) of phosphorus oxychloride, refluxing for 0.5 hr., and washing with petroleum ether (b.p. 30–60°), the residue was added to a water–ice mixture. The aqueous solution was extracted with benzene, the combined benzene extracts were washed with aqueous sodium hydroxide and water, dried, and filtered, and the solvent was removed. Acetone was added to the residual oil and a colorless solid remained insoluble. A total of 2.02 g. (0.008 mole) of *p*-*t*-butylphenylphenylphosphine oxide was obtained which represents a yield of 4%. It separated from *n*-heptane as colorless needles: m.p. 130–131°; λ_{max}^{KBr} 2370 (P–H), 820, 755, and 725 cm.$^{-1}$. It can also be purified by sublimation.

Anal. Calcd. for $C_{16}H_{19}OP$: C, 74.40; H, 7.41; P, 11.99; mol. wt., 258. Found: C, 74.31; H, 7.39; P, 12.19; mol. wt. (ebulliscopic determination in benzene), 248.

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Problems of Orientation in Arylphosphonic Acids. I. 3-Chloro-4-tolylphosphonic Acid[1]

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3-Chloro-4-tolylphosphonic acid was first reported by Melchiker[2] and is listed in Kosolapoff's monograph[3]; it is also mentioned in the patent literature.[4] The synthetic procedure used by Melchiker involved a Friedel–

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[1] The work was supported in part by Research Grant GM-09479 from the National Institutes of Health, Public Health Service.

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