picrate melted at 122.3°, the hydrochloride at 157–158°, and the chloroferrate[6] at 82.5°.

3-Aminopyridine-2-carboxylic acid. 3-Nitro-2-methylpyridine (III) (25 g.) was oxidized by 57 g. of potassium permanganate as previously described. There was obtained 3 g. of acid which was recrystallized from alcohol-water and melted at 122–123°. The yield of purified product was 12% based on starting material not recovered.

This acid (2 g.) was reduced by heating in a mixture of powdered iron, hydrochloric acid, and alcohol for 2 hrs. The amino acid was purified thru the copper salt and there was obtained 1 g. (62%) melting at 217°. Mixed melting point with a sample of this acid prepared by the method of Sucharda[3b] showed no depression.

3-Nitro-2,4,6-collidine. 2,4,6-Collidine (180 g.) was nitrated according to Plazek.[2] There was obtained 226 g. (93%) boiling at 120° (19 mm.) and melting at 38°.

Acid mixture by oxidation of 3-nitro-2,4,6-collidine. 3-Nitrocollidine (IV) (200 g.) was oxidized with 400 g. of solid potassium permanganate as previously described. The crude acid obtained was recrystallized from alcohol-water (1:1) to give 25 g. (13% based on starting material unrecovered) of 3-nitro-2,4-dimethylpyridine-6-carboxylic acid (IV) melting at 138°.

Anal. Calcd. for $C_8O_2N_2$: C, 48.98; H, 4.11. Found: C, 49.20; H, 3.89.

On standing the filtrate gradually deposited 0.5 g. of 3-nitro-2,6-dimethylpyridine-4-carboxylic acid (V) melting at 238°.

Neut. equiv. Calcd. for $C_8H_8O_2N_2$: 196. Found: 194.

3-Nitro-2,4-dimethylpyridine. 3-Nitro-2,4-dimethylpyridine-6-carboxylic acid (VI) (30 g.) was decarboxylated at a bath temperature of 180–220° in a nitrogen atmosphere at 260 mm. There was obtained 20 g. (86%) of 3-nitro-2,4-dimethylpyridine (VII) boiling at 113° (20 mm.). The material had a freezing point of 9.5°, formed a picrate melting at 151°, and a hydrochloride melting at 144°.

Anal. Calcd. for $C_7H_8O_2N_2$; C, 55.26; H, 5.30. Found: C, 54.93; H, 5.36.

Reduction in a Parr low pressure hydrogenation apparatus using palladum on charcoal gave a quantitative yield of amine melting at 74–75°.

Decarboxylation of 3-nitro-2,6-dimethylpyridine-4-carboxylic acid (V). One gram of this acid was decarboxylated in the above manner to give 3-nitro-2,6-dimethylpyridine (I) melting at 38°. The picrate melted at 141° and a mixed melting point with authentic material showed no depression.

Acid mixture from the oxidation of 3-nitro-2,4-dimethylpyridine. Ten grams of nitro compound (VII) was oxidized by 20 g. of potassium permanganate as previously described. The crude acid mixture so obtained was recrystallized from alcohol-water (1:1). The first crop obtained by cooling a short time was 0.5 g. of 3-nitro-4-methylpyridine-2-carboxylic acid (IX) melting at 138°.

Anal. Calcd. for $C_7H_6O_4N_2.H_2O$: C, 42.03; H, 4.03. Found: C, 41.56; H, 3.73.

On standing overnight the mother liquor from the above product precipitated 1.5 g. of 3-nitro-2-methylpyridine-4-carboxylic acid (VIII) melting at 250--252° (sealed tube).

Anal. Calcd. for $C_7H_6O_4N_2$: C, 46.16; H, 3.32. Neut. equiv., 182 Found: C, 46.44; H, 3.45. Neut. equiv., 185.

3-Amino-4-methylpyridine. 3-Nitro-4-methylpyridine-2-carboxylic (IX) acid (0.5 g.) was decarboxylated with a bath temperature of 145°. The decarboxylated material was then reduced by refluxing for 1 hr. in a mixture of ethyl alcohol, iron powder, and hydrochloric acid. After making the mixture basic, extracting with ether and evaporating, there was obtained white crystals of 3-amino-4-methylpyridine (X) melting at 105° and giving no melting point depression with an authentic sample.[3a,7]

3-Nitro-2-methylpyridine. 3-Nitro-2-methylpyridine-4-carboxylic (VIII) acid (1.5 g.) was decarboxylated at a bath temperature of 280° to yield 0.8 g. of 3-nitro-2-methylpyridine[3a] (III) melting at 28.5°. The picrate melted 122–123° and the hydrochloride 157–158°.

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(6) A. H. Blatt and N. Gross, *J. Am. Chem. Soc.*, **77**, 6424 (1955).

(7) E. Koenigs and Fulde, *Ber.*, **60**, 2106 (1927).

Dichlorophosphination

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Although the reaction of aromatic compounds with phosphorus trichloride and anhydrous aluminum chloride, dichlorophosphination, has long been known[1] and improved upon[2,3] the orientation of the entering group has generally been assumed and has been determined in only a few cases. For example, Kosolapoff[4,5] used an extended fractional crystallization of the mixed tolylphosphonic acids to determine the isomer distribution. He found an *ortho:meta:para* ratio of 1.0 : 2.7 : 6.3 for the tolylphosphonic acids with an approximate 15% loss of the acids during the crystallizations. Ethylbenzene yielded mainly the *para* isomer with a small amount of an ethylphenylphosphonic acid which was thought to be the *meta* isomer (*meta:para* = *ca.* 1.0 : 8.8). Other workers have generally assumed that dichlorophosphination gives only the *para* isomer[2b,6–8] or a mixture of *ortho* and *para* isomers.[4]

We have examined the dichlorophosphination of ethylbenzene, *p*-xylene, and chlorobenzene, utilizing a combination of infrared and vapor phase chromatographic techniques to establish the isomer distribution. Ethylbenzene formed only the *meta* and *para* isomers in a ratio of 1.00/1.63,[9] and *p*-xylene yielded only the 1,2,4- isomer. On the other

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(1) A. Michaelis, *Ber.*, **12**, 1009 (1879); *Ann.*, **293**, 193 (1896); **294**, 1 (1896).

(2)(a) B. Buchner and L. B. Lockhart, Jr., *J. Am. Chem. Soc.*, **73**, 755 (1951); (b) *Org. Syntheses*, **31**, 88 (1951).

(3) W. T. Dye, Jr., *J. Am. Chem. Soc.*, **70**, 2595 (1948).

(4) G. M. Kosolapoff and W. F. Huber, *J. Am. Chem. Soc.*, **69**, 2020 (1947).

(5) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **74**, 4119 (1952).

(6) R. H. Wiley and C. H. Jarboe, *J. Am Chem. Soc.*, **73**, 4996 (1951).

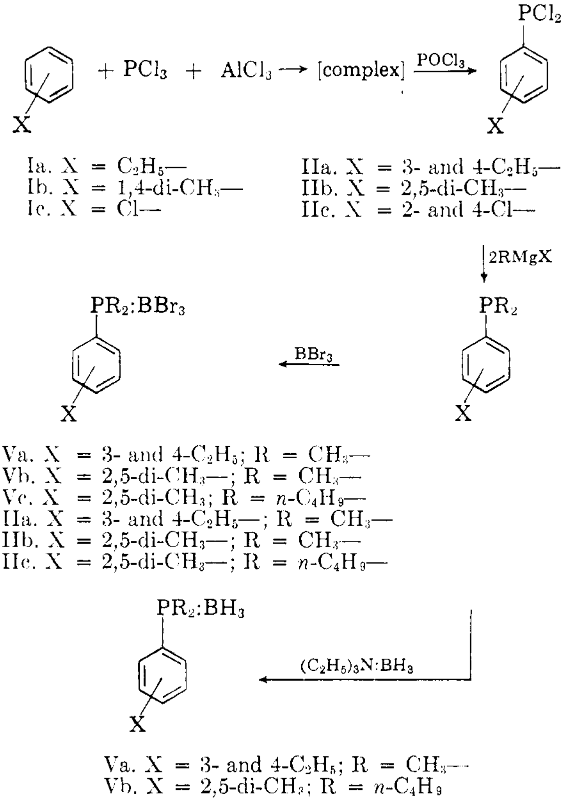
(7) I. K. Jackson, W. C. Davis, and W. J. Jones, *J. Chem. Soc.*, 2298 (1930); W. C. Davis and W. P. Walters, *J. Chem. Soc.*, 1786 (1935).

(8) W. J. Jones, W. C. Davis, S. T. Bowden, C. Edwards, V. E. Davis, and L. H. Thomas, *J. Chem. Soc.*, 1446 (1947).

(9) A small quantity of phenyldichlorophosphine was identified presumably arising from a dealkylation of ethylbenzene. A similar phenomenon has been observed during the dichlorophosphination of *sec*-amylbenzene.[2] We thank Dr. D. R. Stern for helpful discussions concerning alkyl group migration reactions. See D. R. Stern, Ph.D. thesis, University of Southern California, 1951

hand, chlorobenzene yielded predominately the *ortho* and *para* isomers with some *meta* indicated.

The mixtures of aryldichlorophosphines were converted into aryldialkylphosphines by reaction with methyl- and butylmagnesium bromide. The borane[10] and boron tribromide addition compounds of the tertiary phosphines were prepared and used for analysis.



Ia. X = C_2H_5—
Ib. X = 1,4-di-CH_3—
Ic. X = Cl—

IIa. X = 3- and 4-C_2H_5—
IIb. X = 2,5-di-CH_3—
IIc. X = 2- and 4-Cl—

IVa. X = 3- and 4-C_2H_5; R = CH_3—
IVb. X = 2,5-di-CH_3—; R = CH_3—
IVc. X = 2,5-di-CH_3; R = n-C_4H_9—
IIIa. X = 3- and 4-C_2H_5—; R = CH_3—
IIIb. X = 2,5-di-CH_3—; R = CH_3—
IIIc. X = 2,5-di-CH_3—; R = n-C_4H_9—

Va. X = 3- and 4-C_2H_5; R = CH_3—
Vb. X = 2,5-di-CH_3; R = n-C_4H_9

In view of these observations on the isomeric purity of the products obtained from the dichlorophosphination of aromatics and of derivatives, the data in the literature concerning these compounds must be viewed cautiously.

EXPERIMENTAL

The infrared spectra were determined on a Perkin-Elmer Model 21 Spectrophotometer. The vapor phase chromatographic work was done on a Perkin-Elmer Model 154B Vapor Fractometer equipped with a Model 194 integrator.

m- and p-Ethylphenyldichlorophosphine (IIa). A mixture of 128 g. (1.2 moles) of ethylbenzene, 213 g. (1.6 moles) aluminum chloride, and 658 g. (4.8 moles) of phosphorus trichloride was refluxed for 2.5 hr. and worked up as previously described.[2] Distillation at about 1 mm. gave 111 g. (0.537 mole, 44.7% yield) of a colorless liquid boiling at 91–93°. The infrared spectrum of this material indicated a mixture of *meta-* and *para-*isomers (absorptions at 12.2 and 12.61μ) with an absence of *ortho-*isomer. The mixture was partially resolved using a 2-m. silicone oil/Celite column (Perkin-Elmer Column C) at 210° with a helium flow rate of 33 cc./min. (20 p.s.i.g.). A broad minor peak at 4.2–6.0 min. and two slightly tailed, incompletely resolved major peaks at 6.3 and 6.9 min. were obtained with apparently some decomposition of the sample.

m- and p-Ethylphenyldimethylphosphine (IIIa). A 207.4-g. (1 mole) quantity of m- and p-ethylphenyldichlorophosphine dissolved in enough ether to give 500 ml. total volume was slowly added to 2.2 moles of methylmagnesium bromide (Arapahoe) to which an additional 800 ml. of ether had been added. Distillation of the liquid remaining after the usual work-up with ammonium chloride,[8] yielded three fractions:

	B.P.	Mm.	Wt., g.	VPC Analysis, % (Wt.)			
				C_8H_{10}	$C_6H_5P(CH_3)_2$	m-C_2H_5	p-C_2H_5
1.	to 100	18	[a]	0.3	3.6	51.5	44.6
2.	100–102	18	29.6[b]	—	—	49.8	50.2
3.	101–105	18	118.3	0.04	—	35.	64.9

[a] Small quantity, not weighed. [b] n_D^{21} = 1.5494.

The infrared spectra (absorptions at 12.2 and 12.65μ) of these three fractions supported the gas chromatographic analysis which indicated only *meta-* and *para-*isomers. Fractions 2 and 3 (147.9 g.) represent a yield of 89% m- and p-ethylphenyldimethylphosphine. Chromatography of the samples was carried out using a 2-m. Apiezon "L"/Celite high temperature column (Perkin-Elmer Column Q-HT) at 225°C. with a flow rate of 50 cc./min. (20 p.s.i.g.). Well resolved peaks with complete resolution and almost no observable tailing were observed at 1.4, 4.6, 8.6, and 9.8 min. Comparison of the peak heights of the two major components with the 12.65 and 12.2μ aromatic substitution bands in the infrared spectra showed that the first peak (8.6 min.) was m-ethylphenyldimethylphosphine and the second peak (9.8 min.) was p-ethylphenyldimethylphosphine. Comparison with retention times for ethylbenzene and phenyldimethylphosphine showed that the two minor peaks were these materials.

m- and p-Ethylphenyldimethylphosphine tribromoborane (IVa). A 4.47-g. (0.0178 mole) quantity of boron tribromide was slowly added with stirring to 2.96 g. (0.0178 mole) of a mixture of m- and p-ethylphenyldimethylphosphine dissolved in 25 ml. of dry petroleum ether (b.p. 30–60°) which was cooled by means of a Dry Ice–acetone bath. Filtration of the reaction mixture gave 6.63 g. (89%) of crude product, m.p. 58–69°. Recrystallization from methanol (Norite A) yielded 5.38 g. (0.0129 mole, 72.4%) of m- and p-ethylphenyldimethylphosphine tribromoborane (absorptions at 12.2 and 12.65μ) as a white, crystalline powder melting at 68–78°C.

Anal. Calcd. for $C_{10}H_{15}BBr_3P$: B, 2.60; Br, 57.52; P, 7.43. Found: B, 2.60; Br, 57.3; P 7.38.

When a portion of the powder was recrystallized slowly from a dilute solution, individual needles formed on the top of the main body of precipitate. Several of these larger crystals were separated by use of small tweezers and were found to have a melting point of 78–81°. An infrared spectrum of a single crystal and of several crystals indicated the presence of mostly the *para-*isomer (sharp absorption at 12.1 μ).

m- and p-Ethylphenyldimethylphosphine borane (Va). The interaction of 25.8 g. (0.155 mole) of a mixture of m- and p-ethylphenyldimethylphosphine and 20 g. (0.174 mole) of

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(10) R. A. Baldwin and R. M. Washburn, *J. Org. Chem.*, **26**, 3549 (1961).

triethylamineborane gave an almost quantitative yield, 27.9 g. (0.155 mole, 99.6%) of a mixture of *m*- and *p*-ethylphenyldimethylphosphine borane as a colorless liquid, b.p. 89–92° at 0.3 mm.[10] (infrared absorptions at 12.2 and 12.65 μ).

2,5-Dimethylphenyldichlorophosphine (IIb). Dichlorophosphination of *p*-xylene, carried out as described above for ethylbenzene, gave varying yields (19.9–32.8%) of 2,5-dimethylphenyldichlorophosphine as a colorless liquid, b.p. 134–136° at 18–20 mm.[8] An infrared absorption at 12.30 μ indicated only 1,2,4-trisubstitution.

2,5-Dimethylphenyldimethylphosphine (IIIb) *and 2,5-dimethylphenyldi-n-butylphosphine* (IIIc). 2,5-Dimethylphenyldichlorophosphine was converted *via* the appropriate Grignard to the dimethyl derivative, b.p. 110–112° at 18 mm.[7] in 71% yield and to the di-*n*-butyl derivative, b.p. 105–108° at 0.2 mm.[7] in 75.5% yield. Each of these tertiary phosphines had a single sharp absorption at 12.34 μ in the infrared indicative of 1,2,4-trisubstitution.

Gas chromatography of the di-*n*-butyl derivative gave a single slightly tailed peak (Perkin-Elmer Column C). Similarly, analysis of the dimethyl derivative showed it to be 98.5% pure (Perkin-Elmer Column Q-HT).

2,5-Dimethylphenyldi-n-butylphosphine borane (Vb). Triethylamine borane (11.5 g., 0.1 mole) exchanged with 25 g. (0.1 mole) of 2,5-dimethylphenyldi-*n*-butylphosphine to yield 23 g. (0.0833 mole, 83.3%) of 2,5-dimethylphenyldi-*n*-butylphosphine borane as a rather viscous, colorless liquid, b.p. 140–141° at 0.5 mm.[10] An absorption supporting 1,2,4-trisubstitution was observed at 12.17 μ for the borane and also for the tribromoboranes IVb and c.

2,5-Dimethylphenyldimethylphosphine tribromoborane (IVb). This adduct was prepared in 86.3% yield from 7.0 g. (0.0449 mole) of 2,5-dimethylphenyldimethylphosphine and 13.3 g. (0.053 mole) of boron tribromide in petroleum ether at −78°. The product, after recrystallization from isopropyl alcohol (Norite), was obtained as white needles, m.p. 162.5–165°.

Anal. Calcd. for $C_{10}H_{15}BBr_3P$: B, 2.60; Br, 57.52; P, 7.43. Found: B, 2.63; Br, 57.52; P, 7.47.

2,5-Dimethylphenyldi-n-butylphosphine tribromoborane (IVc). A yield of 88.5% was obtained from 6.84 g. (0.0274 mole) of the 2,5-dimethylphenyldi-*n*-butylphosphine and 9.3 g. (0.0372 mole) of boron tribromide using petroleum ether as the reaction solvent and under an inert atmosphere. Recrystallization from methyl alcohol gave white platelets melting at 107–109°.

Anal. Calcd. for $C_{16}H_{27}BBr_3P$: B, 2.16; Br, 47.86; P, 6.18. Found: B, 2.21; Br, 47.72; P, 5.99.

o-, m-, and p-Chlorophenyldichlorophosphine (IIc). Dichlorophosphination of chlorobenzene as described above for ethylbenzene gave 64.8% yield of mixed chlorophenyldichlorophosphines, b.p. 129–130° at 17 mm.[11] The infrared spectrum indicated that the product was a mixture of about equal quantities of the *ortho*- and *para*-isomers, absorptions at 13.45 and 12.25 μ respectively, with a trace of *meta*- indicated by a small absorption at 12.76 μ.

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[11] D. R. Nijk, *Rec. trav. chim.*, 41, 461 (1922).

Borane Exchange Reactions

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In view of the recent interest in amine boranes,[1–5] we wish to report a convenient laboratory synthesis of amine and phosphine boranes. Amine boranes have previously been prepared by the direct interaction of diborane and amine,[6] by borane exchange from pyridine to trimethylamine[6] by the reaction of an amine hydrochloride with lithium borohydride[7] and by the reduction of trialkylboranes in the presence of a tertiary amine.[8] The only trialkylphosphine borane known with certainty[9a] is trimethylphosphine borane.[9b] It was shown that with borane (BH_3) as the reference acid, the base strength of trimethylphosphine was greater than the base strength of trimethylamine[10] and, also, that the base strength of trimethylamine was greater than that of pyridine,[6]—*i.e.*, $(CH_3)_3P > (CH_3)_3N > C_5H_5N$. The apparent equilibrium nature of these reactions suggested that the equilibrium might be shifted in favor of a desired product by removal of a volatile amine (Equation 1).

$$R_3N{:}BH_3 + R'_3X\ (X = N \text{ or } P) \rightleftharpoons R'_3X{:}BH_3 + R_3N \quad (1)$$

This indeed has been found to be the case. Removal of a volatile amine, such as triethylamine, therefore provides a convenient method for the essentially quantitative preparation of a variety of phosphine and amine boranes by borane exchange. In a typical experiment, equal molar amounts of triethylamine borane and tri-*n*-butylphosphine were mixed, under argon, and the mixture slowly distilled through a Vigreux column to remove triethylamine. After approximately two-thirds of the amine had been removed, the mixture was aspirated to remove the remaining amine. Distillation of the residue gave a 79% yield of tri-*n*-butylphosphine borane. In a similar manner, triethylamine borane or trimethylamine borane was caused to react with other phosphines and amines. Table I reports the pertinent data for some new compounds prepared by borane

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(1) E. C. Ashby, *J. Am. Chem. Soc.*, **81**, 4791 (1959).

(2) M. F. Hawthorne, *J. Org. Chem.*, **23**, 1788 (1958).

(3) R. Köster, *Angew. Chem.*, **69**, 684 (1957).

(4) N. N. Greenwood and J. H. Morris, *Proc. Chem. Soc.*, 25 (1960).

(5) R. P. Barnes, J. H. Graham, and M. D. Taylor, *J. Org. Chem.*, **23**, 1561 (1958).

(6) H. C. Brown, H. I. Schlesinger, and S. Z. Cardon, *J. Am. Chem. Soc.*, **64**, 325 (1942).

(7) G. W. Schaeffer and E. R. Anderson, *J. Am. Chem. Soc.*, **71**, 2143 (1949).

(8) R. Köster, *Angew. Chem.*, **69**, 94 (1957).

(9)(a) F. Hewitt and A. K. Holliday, *J. Chem. Soc.*, 530 (1953). (b) A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **75**, 3872 (1953).

(10) W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **3**, 164 (1957).