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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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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TABLE I

Tertiary Phosphine and Amine Boranes

Borane	M.P.[a]	B.P.	Mm.	Yield	n_D^t	Formula	Boron Calcd.	Boron Found	B/P Ratio	Phosphorus Calcd.	Phosphorus Found
Triethylphosphine	47–48	—	—	93.5	—	$C_6H_{18}BP$	8.20	8.24	1.03	23.47	22.9
Tri-*n*-propylphosphine	22.5–23[b]	116–118	1.5	92.0	1.4672^{25}	$C_9H_{24}BP$	6.22	6.36	1.02	17.80	17.8
Tri-*n*-butylphosphine	—	115–117	0.8	79.0	1.4691^{25}	$C_{12}H_{30}BP$	5.00	5.03	1.03	14.33	14.2
Phenyldimethylphosphine	—	84–87	0.5	86.6	1.5504^{21}	$C_8H_{14}BP$	7.12	7.07	0.99	20.38	20.3
m- and *p*-Ethylphenyldimethylphosphine[c]	—	89–92	0.3	100	1.5388^{25}	$C_{10}H_{18}BP$	6.01	5.81	0.966	17.21	17.22
2,5-Dimethylphenyldi-*n*-butylphosphine	—	140–141	0.5	83.3	$1.5267^{20.5}$	$C_{16}H_{30}BP$	4.10	4.08	0.99	11.72	11.7
Triphenylphosphine	182–184	—	—	83.4	—	$C_{18}H_{18}BP$	3.92	3.67	0.94	11.22	11.22
							Carbon			Hydrogen	
Triethylenediamine[d,e] (mono)	164–165	—	—	80	—	$C_6H_{15}BN_2$	57.18	57.30		12.00	11.42
Triethylenediamine[d,f] (bis)	390 dec.	—	—	100	—	$C_6H_{18}B_2N_2$	51.52	51.53		12.97	12.82

[a] All melting and boiling points are uncorrected. [b] Impure tri-*n*-propylphosphine borane reported to melt at about 10° (ref. 9a). [c] See Ref. 15. [d] First prepared in our laboratory by F. F. Caserio, Jr., and R. I. Wagner, unpublished results. [e] Recrystallized from benzene. [f] Insoluble in benzene.

exchange. Although triethylamine can be distilled from a mixture of pyridine and triethylamine borane, attempted distillation of the liquid residue at reduced pressures has resulted in sometimes violent decompositions.[11]

The necessary tertiary phosphine intermediates were prepared *via* the standard Friedel-Crafts and/or Grignard procedures.[12-15]

The phosphine boranes were found to be generally colorless, mobile liquids which were relatively stable to both water and air. In contrast to the amine boranes,[5] the phosphine boranes and the triethylenediamine boranes reacted very sluggishly with 2% alcoholic silver nitrate solution. All of the phosphine boranes gave strong infrared absorption near 4.2 μ with a weaker band at 4.35 μ.

EXPERIMENTAL

Phosphine boranes. In a typical experiment, 23 g. (0.2 mole) of triethylamine borane was mixed under argon with 40.4 g. (0.2 mole) of tri-*n*-butylphosphine and the mixture distilled slowly through a Vigreux column to remove triethylamine, b.p. 88–90° n_D^{21} 1.3990. When approximately two-thirds of the amine had been distilled, the mixture was attached to a water aspirator to remove the remaining amine. Distillation of the liquid residue yielded 34.1 g. of tri-*n*-butylphosphine borane (0.158 mole, 79%) as a clear liquid, b.p. 115–117° at 0.8 mm.

The analytical data for this and the other boranes are listed in Table I.

Phosphines. The necessary tertiary phosphines were prepared *via* standard Friedel-Crafts and/or Grignard techniques.[12-15]

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Complexes of Diols with Cuprammonium Reagent

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Experimental work was previously reported[1] in which the method of continuous variation was applied to the reaction between cuprammonium and diol-containing compounds. From this work, it was concluded that the cuprammonium-diol complex has a copper-diol ratio of 2:1. The lack of symmetry in the curves obtained for certain carbohydrates was assumed to be caused by hydroxyl groups not associated with the diol structure. Formation of a 2:1 copper-diol complex seemed conclusive from experiments with *cis*- and *trans*-

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