m.p. 178–179° dec. The acid was insoluble in hot benzene, methanol, acetone, ethyl acetate, and dimethylformamide, but could be recrystallized from hot water or glacial acetic acid to give white plates melting at 179° dec. It was soluble in dilute alkali and appreciably soluble in 10% hydrochloric acid.

Anal. Calcd. for $C_6H_{13}N_2O_2PS_2$: C, 29.99; H, 5.45; N, 11.66; P, 12.89. Found: C, 30.03; H, 5.57; N, 11.40; P, 12.76.

Bis(2-thiocarbamoylethyl)phosphinic acid from bis(2-cyanoethyl)phosphinic acid and hydrogen sulfide. A solution of 5.16 g. (0.03 mole) of bis(2-cyanoethyl)phosphinic acid in 9.1 g. (0.09 mole) of triethylamine and 15 ml. of pyridine[2] was shaken for a short time in a conventional Parr low-pressure hydrogenation system charged to 2.2 atm. with dry hydrogen sulfide and then allowed to stand for about 60 hr. The dark green reaction mixture was poured into 50 ml. of water, and the solution was treated with 20 ml. of 10% sodium hydroxide solution. The solution was extracted five times with 25-ml. portions of chloroform. The extracts were discarded, and the pale green aqueous solution was filtered and acidified. After standing for several hours, the solution deposited 5.2 g. (72%) of white plates, m.p. 178–179° dec. A mixed melting point with the product obtained from bis(2-cyanoethyl)phosphine and sulfur was not depressed, and the infrared spectra of the two products were identical.

2-Cyanoethyl-2-thiocarbamoylethylphosphinic acid. A mixture of 10.0 g. (0.064 mole) of bis(2-cyanoethyl)phosphine oxide, 2.0 g. (0.063 g.-atom) of sulfur, and 30 ml. of moist isopropyl alcohol was refluxed under a nitrogen atmosphere for 1.5 hr. White crystals (6.0 g., 50%) separated on cooling. Recrystallization from a mixture of acetone and isopropyl alcohol gave an analytically pure sample, m.p. 142°.

Anal. Calcd. for $C_6H_{11}N_2O_2PS$: C, 34.94; H, 5.38; N, 13.58; P, 15.02. Found: C, 35.09; H, 5.52; N, 13.93; P, 15.31.

Cyclohexyl-2-thiocarbamoylethylthiophosphinic acid. Cyclohexyl-2-cyanoethylphosphine (5.1 g., 0.03 mole) was added gradually to a stirred mixture of 2.5 g. (0.078 g.-atom) of sulfur, 30 ml. of concd. aqueous ammonium hydroxide, and 50 ml. of water, under nitrogen. The mixture became warm and most of the sulfur dissolved. The reaction mixture was stirred for two additional hours at room temperature. The excess sulfur was filtered, and the filtrate was acidified with dilute hydrochloric acid. After cooling at −10° overnight, the white crystalline thiophosphinic acid separated. Two recrystallizations from a benzene-methanol mixture provided 5.7 g. (75%) of an analytically pure sample, m.p. 115–116° dec.

Anal. Calcd. for $C_9H_{18}NOPS_2$: C, 43.01; H, 7.22; P, 12.32. Found: C, 43.22; H, 7.12; P, 12.23.

Pyridinium bis(2-cyanoethyl)dithiophosphinate. A slurry of 10.8 g. (0.336 g.-atom) of sulfur in 75 ml. of pyridine was treated with 23.6 g. (0.168 mole) of bis(2-cyanoethyl)phosphine added dropwise so as to maintain a temperature below 60°. A clear yellow solution was obtained which deposited 45 g. (95%) of product on cooling.

Recrystallization from benzene containing a little pyridine provided an analytically pure sample, m.p. 95–96°.

Anal. Calcd. for $C_{11}H_{14}N_3PS_2$: N, 14.83; P, 10.93; S, 22.63. Found: N, 14.54; P, 10.90; S, 22.33.

Benzyl bis(2-cyanoethyl)dithiophosphinate. A mixture of 5.7 g. (0.02 mole) of pyridinium bis(2-cyanoethyl)dithiophosphinate, 2.6 g. (0.02 mole) of benzyl chloride, and 25 ml. of acetone was refluxed under nitrogen for 3 hr. The reaction mixture was cooled and poured into 75 ml. of cold water. An oil separated which crystallized on standing. The solid was collected to obtain 5.9 g. (100%) of the benzyl ester, m.p. 75–79°. Recrystallization from a mixture of benzene and petroleum ether (b.p. 30–60°) provided an analytical sample, m.p. 80–82°.

Anal. Calcd. for $C_{13}H_{15}N_2PS_2$: P, 10.52; N, 9.51; S, 21.78. Found: P, 10.62; N, 9.76; S, 22.27.

The properties and infrared spectrum of the product were in complete accord with the assigned structure.

Ureidocarbonylmethyl bis(2-cyanoethyl)dithiophosphinate. A mixture of 2.72 g. (0.02 mole) of chloroacetylurea, 5.66 g. (0.02 mole) of pyridinium bis(2-cyanoethyl)dithiophosphinate, and 25 ml. of acetone was refluxed under nitrogen for 3 hr. The reaction mixture was poured into 75 ml. of water to obtain 4.8 g. (79%) of the ester, m.p. 131–133°. Recrystallization from water gave needles, m.p. 132–134°.

Anal. Calcd. for $C_9H_{13}N_4O_2PS_2$: N, 18.41; P, 10.18; S, 21.07. Found: N, 17.92; P, 10.23; S, 20.88.

Acknowledgment. The authors are indebted to Mrs. E. C. Grim and Dr. J. A. Kuck for microanalyses and to N. B. Colthup for assistance in interpreting infrared spectra.

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[CONTRIBUTION FROM THE STAMFORD LABORATORIES, CHEMICAL RESEARCH DEPARTMENT, AMERICAN CYANAMID CO.]

The Free Radical Addition of Phosphines to Unsaturated Compounds

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The free radical–initiated addition of phosphine and several primary and secondary phosphines to carbon-carbon double bonds was investigated with the aim of improving reaction conditions and expanding the reaction scope. The reaction was found to be an excellent synthetic method for the preparation of primary and tertiary organophosphines and certain secondary phosphines. The addition of phosphines to acetylenic compounds was studied briefly.

Phosphine adds to olefinic double bonds under the influence of strong, nonoxidizing acids,[1] strong bases,[2] or free radical initiation[3] to give organophosphines. Of these three methods, the latter approach appeared most promising as a general synthetic method. Stiles, Rust, and Vaughan,[3] using ultraviolet light or di-*t*-butyl peroxide, found that with six olefinic compounds, primary, second-

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(1) M. C. Hoff and P. Hill, *J. Org. Chem.*, 24, 356 (1959); H. C. Brown, U. S. Patent 2,584,112 (Feb. 5, 1952).

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(3) A. R. Stiles, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **74**, 3282 (1952); U. S. Patent **2,803,597** (Aug. 20, 1959).

TABLE I. FREE RADICAL ADDITION OF PHOSPHINE TO OLEFINS

$PH_3 + CH_2{=}CH{-} \longrightarrow RPH_2 + R_2PH + R_3P$

Exp. No.	Olefin	Moles	Phosphine, Moles	Mole Ratio Phosphine/ Olefin	Initiator	Moles	Heptane, Ml.	Temp.	Time, Hr.	Pressure at 70° (p.s.i.g.)	Yield,[a] %			Total Conversion, %
											RPH_2	R_2PH	R_3P	
1	1-Octene (95%)	1.0	1.1	1.1	DTBP	0.05	0	128–130	21[b]	490	23	28	22	73
2	1-Octene (95%)	1.0	0.33	0.33	ABN	0.05	0	80–100[c]	6	<50	0	0	83	83
3	1-Octene (95%)	1.0	1.5	1.5	ABN	0.05	0	70–120[c]	0.5	540	36	32	14	82
4	1-Octene (95)[d]	0.50	0.61	1.2	ABN	0.05	75	79–84	4	[e]	30	28	17	75
5	1-Octene (95%)	0.50	1.8	3.6	ABN	0.05	75	78–80	4	500	65	18	4	87
6	1-Dodecene	0.60	0.71	1.2	ABN	0.05	0	84–87	4	[e]	23	20	26[f]	69
7	Cyclohexene	1.0	1.5	1.5	ABN	0.05	0	78–80	3.5	600	49	29	0	78
8	Cyclohexene	1.5	0.68	0.45	ABN	0.07	0	80–84	6	250	19	22	0	41[g]
9	Styrene	0.75	1.1	1.5	ABN	0.04	75	79–80	4	410	36	29	6	71
10	Isobutylene	1.0	1.0	1.0	ABN	0.05	50	80–81	4	330	18	52	21	91
11	Isobutylene	1.5	1.7	1.1	ABN	0.05	0	80–82	4	600	34	34	10	78
12	Isobutylene	1.0	1.4	1.4	ABN	0.05	0	78–82	4	450	30	35	7	72
13	Vinyl butyl ether	0.75	1.4	1.9	ABN	0.04	50	80–81	4	450	45	30	10	85
14	Ethyl acrylate	1.00	1.4	1.4	ABN	0.03	50	67–102[c]	0.5	400	21	20	23	83[h]
15	Ethyl acrylate	0.75	1.1	1.5	ABN	0.01	100	80–90	4	200	21	15	24	69[i]

[a] Yields are based on the olefin. [b] The reaction was incomplete after 5 hours. [c] The reaction was exothermic. [d] The olefin was added gradually during 1 hour. [e] Not recorded. [f] Crude product obtained from distillation residue. The actual yield was probably higher. [g] 48% of the cyclohexene was recovered. [h] 24.0 g. (19%) of bis(2-carbethoxyethyl)-2,4-dicarbethoxybutylphosphine was also obtained. [i] 7.3 g. (9%) of bis(2-carbethoxyethyl)-2,4-dicarbethoxybutylphosphine was also obtained.

ary, and tertiary phosphines were obtained in yields varying from 2 to 67%.

$$PH_3 + RCH{=}CH_2 \longrightarrow H_2PCH_2CH_2R + HP(CH_2CH_2R)_2 + P(CH_2CH_2R)_3$$

Because of our need for a variety of organophosphines, we investigated this reaction with the object of finding improved reaction conditions and expanding the reaction scope. The free radical addition of several primary and secondary phosphines to olefinic compounds was also studied, and the free radical addition of primary and secondary phosphines to alkyl acetylenes was investigated briefly.

Results obtained from reactions of phosphine with unsaturated compounds are shown in Table I. α,α′-Azobisisobutyronitrile (ABN) initiated the reactions more effectively than di-*t*-butyl peroxide (DTBP) under the conditions studied and was used in most experiments.

The effect of varying the mole ratio of phosphine to olefin in the reaction with 1-octene is illustrated in Table II. It is clear that either octylphosphine or trioctylphosphine can be the predominant product, but that the yield of dioctylphosphine has a relatively low maximum value.

TABLE II

EFFECT OF CHANGING REACTANT RATIOS IN REACTION OF 1-OCTENE WITH PHOSPHINE

Mole Ratio PH_3/Octene	Product Distribution, Relative %[a]		
	RPH_2	R_2PH	R_3P
0.33	0	0	100
1.1	32	38	30
1.2[b]	40	37	23
1.5	44	39	17
3.6	75	21	4

[a] Based on yield data from TableI. [b] See note *d*, Table I.

The effect of phosphine pressure at nearly constant reactant ratio is shown in the first two experiments with isobutylene in Table I. Increasing phosphine pressure increases the solubility of phosphine in the liquid phase and results in an increased yield of the primary phosphine.

The effect of olefin structure on the product ratio is illustrated in Table III. As the shielding of the olefinic double bond becomes greater, the product ratio shifts in favor of less substituted products. Moreover, the reactions with isobutylene and cyclohexene were not considerably exothermic while corresponding reactions with 1-octene were strongly exothermic. With isobutylene this steric effect seems appreciable only in the last step of the reaction sequence, *i.e.*, the reaction of diisobutylphosphine with isobutylene. In the reaction with cyclohexene, however, even the addition of phosphine appears inhibited with the magnitude of the effect increasing as the number of cyclohexyl groups on the phosphorus atom increases. Indeed

TABLE III

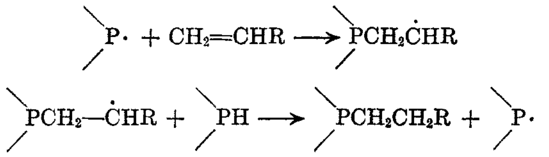
EFFECT OF OLEFIN STRUCTURE ON PRODUCT RATIOS

Olefin	Mole Ratio PH_3/Olefin	Product Distribution[a] RPH_2	R_2PH	R_3P
1-Octene	1.5	44	39	17
Isobutylene	1.4	42	49	9
Cyclohexene	1.5	63	37	0

[a] Based on yield data from Table I.

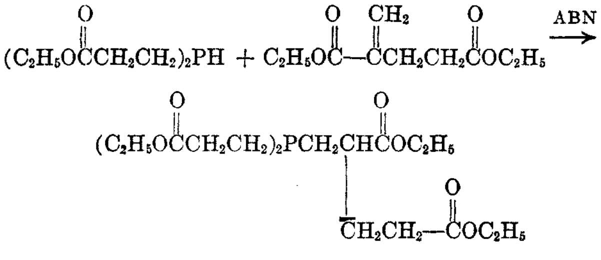
we were unable to obtain tricyclohexylphosphine even when a relatively large proportion of cyclohexene was used.

The free radical addition reaction has a wide scope. Even styrene and ethyl acrylate reacted to give good yields of organophosphines, although, in the absence of phosphine, they would have polymerized under the conditions employed. Evidently in the reaction mechanism



the second step occurs with considerable ease.

The reaction of phosphine with ethyl acrylate, however, did give a 4:1 acrylate-phosphine adduct in addition to the three expected organophosphine products. The 4:1 adduct appeared to be identical (boiling point, infrared spectrum, NMR spectrum, index of refraction, and elemental analysis) with bis(2-carbethoxyethyl)-2,4-dicarbethoxybutylphosphine, prepared unambiguously by the reaction of bis(2-carbethoxyethyl)phosphine with diethyl α-methyleneglutarate.



$$(C_2H_5OCCH_2CH_2)_2PH + C_2H_5OC{-}CCH_2CH_2COC_2H_5 \xrightarrow{ABN} (C_2H_5OCCH_2CH_2)_2PCH_2CHCOC_2H_5 (CH_2CH_2{-}COC_2H_5)$$

Unsymmetrical secondary and tertiary phosphines were obtained in good yields by the addition of 2-cyanoethylphosphine to a variety of unsaturated compounds as described in Table IV. Both di-*t*-butyl peroxide and α,α'-azobisisobutyronitrile effectively initiated the reactions, and initiation by x-radiation also gave good results.

The effect of steric inhibition is evident in the reactions with cyclohexene and 2,4,4-trimethylpentene-1. While 2-cyanoethylphosphine reacted with 1-octene to give 2-cyanoethyldioctylphosphine in 93% yield, similar reactions with cyclohexene and 2,4,4-trimethylpentene-1 gave predominantly secondary phosphines. Even under forcing conditions only a small amount of disubstitution oc-

TABLE IV

FREE RADICAL ADDITION OF MONO(2-CYANOETHYL)PHOSPHINE (MCEP) TO OLEFINS

$RPH_2 + CH_2{=}CH_2{-} \longrightarrow RR'PH + RR'_2P$

Exp. No.	Olefin	Moles	MCEP, Moles	Initiator	Moles	Temp.	Time, Min.	Yields[a] RR'PH Product, %	RR'$_2$P Product, %	MCEP Recovered, %
1	1-Octene (95%)	0.20	0.20	DTBP	0.01	125–127[b]	45	39	25	34
2	1-Octene (95%)	0.66	0.30	ABN	0.006	80–85[b]	120	0	93	0
3	Cyclohexene	0.10	0.05	X-ray	—	26–29	40	46	0	37
4	Cyclohexene	0.20	0.20	DTBP	0.02	95–125[c]	420	65	0	16
5	Cyclohexene	0.20	0.10	ABN[d]	0.01	80–85	240	74	9	0
6	2,4,4-Trimethylpentene-1	0.44	0.20	ABN	0.01	80–85	150	70	15	0
7	Allyl alcohol	0.10	0.10	X-ray	—	24–44[b]	8	31	17	12
8	Allyl alcohol	0.10	0.05	X-ray	—	25–43[b]	10	0	50	0
9	Allyl alcohol[e]	0.44	0.20	ABN	0.01	70–75[b]	80	0	76[f]	0
10	Allyl amine	0.10	0.05	X-ray	—	25–41[b]	34	18	56	0
11	Mesityl oxide	0.40	0.20	ABN	0.01	80–82	120	8	0	52[g]

[a] Yields are conversions based on the MCEP. [b] The reaction was strongly exothermic. [c] The reaction mixture was refluxed for 4 hr. while the temperature rose from 95–125°; then the temperature was held at 125° for 3 hr. [d] One half of the initiator was added at the start. The remaining half was added after 120 min. [e] The allyl alcohol was added during 20 min. to a solution of the mono(2-cyanoethyl)phosphine and α,α'-azobisisobutyronitrile in 20 ml. of benzene. This procedure was necessary to control the reaction. [f] This is the crude yield. The product decomposed appreciably during distillation. [g] 72% of unchanged mesityl oxide was recovered.

TABLE V

FREE RADICAL ADDITION OF BIS(2-CYANOETHYL)PHOSPHINE (BCEP) TO OLEFINS

$$(NCCH_2CH_2)_2PH + CH_2{=}CH{-} \longrightarrow (NCCH_2CH_2)_2PR$$

Exp. No.	Olefin	Moles	BCEP, Moles	Initiator	Moles	Temp.	Time, Min.	Yield, %[a]	BCEP Recovered, %
1	1-Octene (95%)[b]	0.05	0.05	X-ray	—	25-30	60	66	0
2	1-Octene (95%)[b]	0.22	0.20	DTBP	0.02	120-125[c]	60	86	0
3	1-Octene (95%)[b]	0.22	0.20	ABN	0.01	75-140[d]	15	74	11
4	Cyclohexene[b]	0.05	0.05	X-ray	—	25	60	Nil[e]	—
5	Cyclohexene[b]	0.22	0.20	ABN	0.01	83-84	90	55	37
6	2,4,4-Trimethylpentene-1[b]	0.05	0.05	X-ray	—	25	60	Nil[e]	—
7	2,4,4-Trimethylpentene-1[b]	0.22	0.20	ABN	0.03	80-85	180	13	46
8	Styrene	0.22	0.20	DTBP	0.02	120-133[d]	45	47	16
9	Allyl alcohol	0.05	0.05	X-ray	—	25-60[d]	5	78	0
10	Allyl alcohol	0.22	0.20	DTBP	0.01	120[c]	45	52[f]	18
11	Vinyl 2-ethylhexyl ether	0.10	0.10	ABN	0.005	80-85[c]	60	90	0
12	Acrylonitrile[g]	0.20	0.20	ABN	0.01	80-85[d]	25	92[h]	0

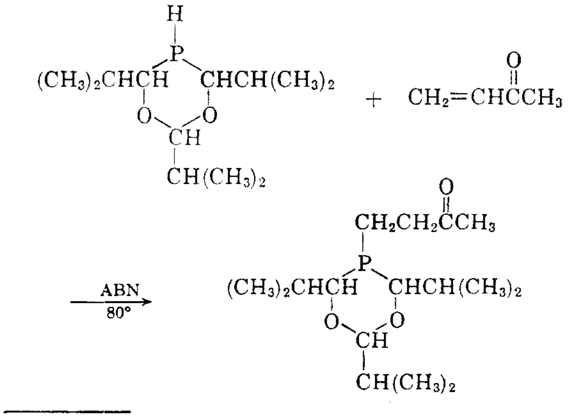
[a] Yields are conversions based on the BCEP. [b] Bis(2-cyanoethyl)phosphine was substantially insoluble in the olefin. [c] The reaction was moderately exothermic. [d] The reaction was strongly exothermic. [e] Infrared examination of the reaction mixture indicated that no reaction had taken place. [f] Considerable decomposition occurred during distillation. The actual yield was undoubtedly higher. [g] A solution of the acrylonitrile and initiator in 10 ml. of acetonitrile was added dropwise to the bis(2-cyanoethyl)phosphine which had been preheated to 75° under nitrogen. [h] The reaction mixture was poured into water and the solid product was collected, washed with ice-cold methanol, and air dried; m.p., 85-92° (lit.,[2] m.p. 98-99°).

curred. It is clear that advantage can be taken of this effect to prepare certain secondary phosphines in high yield.

2-Carbethoxyethylphosphine reacted with an equimolar quantity of 1-octene in the presence of di-*t*-butyl peroxide to give 2-carbethoxyethyloctylphosphine in 32% yield and 2-carbethoxyethyldioctylphosphine in 60% yield.

Unsymmetrical tertiary phosphines were obtained in good yields by the addition of bis(2-cyanoethyl)phosphine to a variety of unsaturated compounds as shown in Table V. Steric inhibition was again evident in additions to cyclohexene and 2,4,4-trimethylpentene-1.

Several experiments were carried out with other secondary phosphines. 2,4,6-Triisopropyl-1,3,5-dioxaphosphorinane[4] reacted with methyl vinyl ketone in the presence of α,α'-azobisisobutyronitrile to give 2,4,6-triisopropyl-5-(3-oxobutyl)-1,3,5-dioxaphosphorinane in 55% yield.



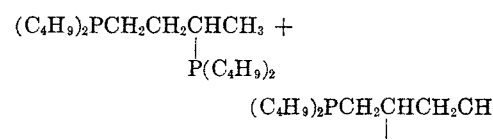
Reaction of 1,3-butadiene with excess dibutylphosphine in the presence of α,α'-azobisisobutyronitrile provided a 51% yield of dibutyl-2-*trans*-butenylphosphine along with a 7% yield of a 2:1 dibutylphosphine-butadiene adduct. The dibutyl-2-*trans*-butenylphosphine results from 1,4-addition and like other sterically hindered unsaturates is not readily attacked by phosphorus free radicals.

$$(C_4H_9)_2P\cdot + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow (C_4H_9)_2PCH_2{-}CH{=}CHCH_2\cdot$$

$$(C_4H_9)_2PCH_2{-}CH{=}CHCH_2\cdot + (C_4H_9)_2PH \longrightarrow (C_4H_9)_2PCH_2{-}CH{=}CHCH_3 + (C_4H_9)_2P.$$

The 2:1 adduct obtained could result from either the reaction of dibutylphosphine with dibutyl-3-butenyl phosphine (formed by 1,2-addition)(Equation 1) or by the reaction of dibutylphosphine with some of the dibutyl-2-butenylphosphine obtained as the main product (Equation 2).

$$(C_4H_9)_2PCH_2CH_2CH{=}CH_2 + (C_4H_9)_2PH \longrightarrow (C_4H_9)_2PCH_2CH_2CH_2CH_2P(C_4H_9)_2 \quad (1)$$



$$(C_4H_9)_2PCH_2CH{=}CHCH_3 + (C_4H_9)_2PH \longrightarrow (C_4H_9)_2PCH_2CH_2\underset{\underset{P(C_4H_9)_2}{|}}{C}HCH_3 + (C_4H_9)_2PCH_2\underset{\underset{P(C_4H_9)_2}{|}}{C}HCH_2CH_3 \quad (2)$$

To explore the second possibility dibutyl-2-butenylphosphine was combined with dibutylphosphine and α,α'-azobisisobutyronitrile, and the solution was heated at 80°. None of the 2:1 adduct was found. It seems likely therefore that the 2:1 adduct is formed according to Equation (1) and that it is 1,4-butylene bis(dibutylphosphine).

Several experiments were carried out with acetylenic compounds. Bis(2-cyanoethyl)phosphine

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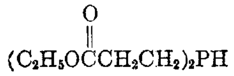
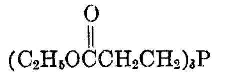
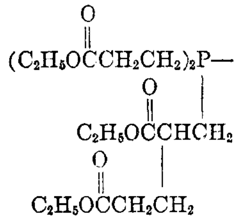
(4) S. A. Buckler and V. P. Wystrach, *J. Am. Chem. Soc.*, 80, 6454 (1958).

TABLE VI

PRODUCTS FROM REACTIONS OF PHOSPHINE WITH UNSATURATED COMPOUNDS

Compound	B.P. (Mm.)	n_D^{25}	Carbon, %		Hydrogen, %		Phosphorus, %	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
$(CH_3)_2CHCH_2PH_2$	77[a]	1.4308	53.31	53.34	12.31	12.72	34.38	33.25
$[(CH_3)_2CHCH_2]_2PH$	47–48 (8)[b]	1.4487	65.72	65.49	13.10	13.32	21.18	20.96
$[(CH_3)_2CHCH_2]_3P$	85 (7)[c]	1.4530	71.24	71.18	13.45	13.68	15.31	15.13
$CH_3(CH_2)_6CH_2PH_2$	66–68 (7)[d]	1.4539	65.72	66.06	13.10	13.27	—	—
$[CH_3(CH_2)_6CH_2]_2PH$	137 (0.25)	[e]	74.36	74.25	13.65	13.67	11.99	11.88
$[CH_3(CH_2)_6CH_2]_3P$	173–178 (0.3)[f]	1.4666	77.77	77.27	13.87	13.96	8.36	8.44
n-$C_{12}H_{25}PH_2$	80 (0.1)	1.4585	71.24	71.08	13.45	13.46	15.31	15.13
$(n$-$C_{12}H_{25})_2PH$	197–199 (0.35)	[g]	77.82	76.40	13.85	13.58	8.33	8.65
$C_6H_{11}PH_2$	145[h]	1.4822	—	—	—	—	—	—
$(C_6H_{11})_2PH$	129 (8)	1.5142	72.69	71.93	11.69	11.45	15.62	15.59
$C_6H_5CH_2CH_2PH_2$	75 (8)	1.5494	69.55	69.19	8.03	8.21	22.42	21.85
$(C_6H_5CH_2CH_2)_2PH$	158 (0.5)	1.5815	79.31	79.23	7.90	7.99	12.78	12.99
$(C_6H_5CH_2CH_2)_3P$	218–224 (0.35)	1.5950	83.20	82.82	7.86	8.02	8.94	8.76
n-$C_4H_9OCH_2CH_2PH_2$	47 (9)	1.4478	53.72	53.72	11.27	11.39	23.09	21.59
$(n$-$C_4H_9OCH_2CH_2)_2PH$	139 (9)	1.4570	61.51	61.87	11.61	11.57	13.22	13.49
$(n$-$C_4H_9OCH_2CH_2)_3P$	148–152 (0.25)	1.4617	64.64	64.81	11.75	11.67	9.26	9.40
 $C_2H_5O\overset{\overset{O}{\Vert}}{C}CH_2CH_2PH_2$	52–53 (9)	1.4552	44.77	44.85	8.26	8.38	23.09	23.00
 $(C_2H_5O\overset{\overset{O}{\Vert}}{C}CH_2CH_2)_2PH$	109–110 (0.2)	1.4668	51.27	51.46	8.18	8.41	13.23	13.33
 $(C_2H_5O\overset{\overset{O}{\Vert}}{C}CH_2CH_2)_3P$	193–194 (1)[i]	1.4748[i]	—	—	—	—	—	—
 $(C_2H_5O\overset{\overset{O}{\Vert}}{C}CH_2CH_2)_2P{-}CH_2CH(\overset{\overset{O}{\Vert}}{C}OC_2H_5)CH_2CH_2\overset{\overset{O}{\Vert}}{C}OC_2H_5$	195–198 (0.2)	1.4730	55.28	55.35	8.12	8.18	7.13	7.19

[a] Lit.,[3] b.p. 78.0–79.6°. [b] Lit.,[3] b.p. 169.6–171.8°. [c] Lit.,[5] b.p. 215°. [d] Lit.,[6] b.p. 184–187°. [e] Not recorded. [f] Lit.,[7] b.p. 291° (50 mm.). [g] Solid at room temperature. [h] Lit.,[3] b.p. 146.8–149.4°. [i] Lit.,[2] b.p. 193–194° (1 mm.); n_D^{25} 1.4748.

reacted with heptyne-1 and with octyne-1 in the presence of α,α'-azobisisobutyronitrile to give unsaturated tertiary phosphines in 27–30% yields.

$$(NCCH_2CH_2)_2PH + HC{\equiv}C(CH_2)_nCH_3 \xrightarrow{ABN} (NCCH_2CH_2)_2PCH{=}CH(CH_2)_nCH_3$$

$$n = 4 \text{ and } 5$$

The reaction mixtures were complex and contained substantial amounts of high-boiling materials. In an effort to determine the origin of these by-products, experiments were run in which bis(2-cyanoethyl)-1-octenylphosphine was heated with bis(2-cyanoethyl)phosphine and with 1-octyne in the presence of α,α'-azobisisobutyronitrile. No reaction took place in either case, and most of the starting materials were recovered unchanged. The high-boiling by-products, therefore, do not arise from attack on the olefinic tertiary phosphine product but evidently result from side reactions involving the intermediate, $(NCCH_2CH_2)_2PCH{=}\dot{C}R$.

Heptyne-1 combined with an equimolar quantity of 2-cyanoethylphosphine gave a 26% yield of 2-cyanoethylbis(1-heptenyl)phosphine. Forty-seven per cent of the 2-cyanoethylphosphine was recovered unchanged. Only a trace of the intermediate secondary phosphine, $NCCH_2CH_2\overset{H}{P}CH{=}CH(CH_2)_4CH_3$, was obtained, which suggests either that it is more reactive than the starting phosphine or that it is very susceptible to side reactions.

$$NCCH_2CH_2PH_2 + 2\,HC{\equiv}C(CH_2)_4CH_3 \longrightarrow NCCH_2CH_2P[CH{=}CH(CH_2)_4CH_3]_2$$

An experiment in which bis(2-cyanoethyl)phosphine was treated with acetylene in the presence of α,α'-azobisisobutyronitrile was not successful. Although a reaction took place, we were unable to isolate a product from the reaction mixture.

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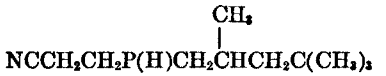
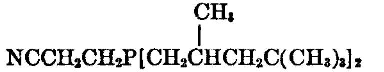
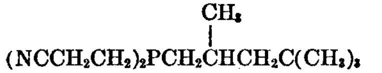
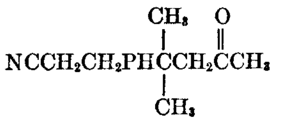
(5) A. W. Hofmann, *Ber.*, **6**, 292 (1873).

(6) W. Moslinger, *Ann.*, **185**, 49 (1877).

(7) I. K. Jackson, W. C. Davies, and W. J. Jones, *J. Chem. Soc.*, 2109 (1931).

TABLE VII

PRODUCTS FROM REACTIONS OF 2-CYANOETHYLPHOSPHINE AND BIS(2-CYANOETHYL)PHOSPHINE WITH UNSATURATED COMPOUNDS

Compound	B.P. (Mm.)	n_D^{25}	Carbon, %		Hydrogen, %		Phosphorus, %	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
$NCCH_2CH_2P(H)CH_2(CH_2)_6CH_3$	118 (0.4)	1.4745	66.29	66.19	11.13	11.17	15.55	15.69
$NCCH_2CH_2P[CH_2(CH_2)_6CH_3]_2$	165–167 (0.15)	1.4735	73.26	73.14	12.30	12.29	9.95	10.07
$(NCCH_2CH_2)_2PCH_2(CH_2)_6CH_3$	183–186 (0.2)	1.4885	66.64	64.85	9.99	9.86	12.28	12.00
 $NCCH_2CH_2P(H)CH_2\overset{CH_3}{\overset{\mid}{C}}HCH_2C(CH_3)_3$	102 (0.3)	1.4735	66.30	65.74	11.13	10.88	15.55	15.56
 $NCCH_2CH_2P[CH_2\overset{CH_3}{\overset{\mid}{C}}HCH_2C(CH_3)_3]_2$	156 (0.8)	1.4712	73.26	73.00	12.30	12.40	9.95	9.84
 $(NCCH_2CH_2)_2PCH_2\overset{CH_3}{\overset{\mid}{C}}HCH_2C(CH_3)_3$	157 (0.15)	1.4920	66.63	65.60	9.99	9.90	12.28	12.08
$NCCH_2CH_2P(H)C_6H_{11}$	97 (0.3)	1.5088	63.88	64.17	9.53	9.79	18.31	18.39
$NCCH_2CH_2P(C_6H_{11})_2$	149 (0.4)	1.5235	71.67	70.85	10.43	9.53	12.33	12.32
$(NCCH_2CH_2)_2PC_6H_{11}$	185–186 (0.4)	1.5241	64.84	64.60	8.62	8.90	13.94	13.48
$NCCH_2CH_2P(H)CH_2CH_2CH_2OH$	131–135 (0.2)	1.5090	49.65	49.38	8.33	8.13	21.34	21.11
$NCCH_2CH_2P(CH_2CH_2CH_2OH)_2$	190–196 (0.7)	1.5230	53.19	53.13	8.93	9.07	15.24	15.10
$(NCCH_2CH_2)_2PCH_2CH_2CH_2OH$	227–229 (0.5)	1.5202	54.54	54.38	7.63	7.75	—	—
$NCCH_2CH_2P(H)CH_2CH_2CH_2NH_2$	86–96 (0.4)	[a]	49.99	51.03	9.09	9.55	21.49	20.63
$NCCH_2CH_2P(CH_2CH_2CH_2NH_2)_2$	163–167 (0.5)	1.5250	53.71	53.42	10.02	10.32	15.39	15.33
$(NCCH_2CH_2)_2PCH_2CH_2C_6H_5$	212 (0.6)	1.5580	68.83	68.80	7.02	6.83	12.68	12.78
 $(NCCH_2CH_2)_2P\underset{CH_2CO_2C_2H_5}{\underset{\mid}{C}}HCO_2C_2H_5$	225–228 (0.9)	1.4922	53.84	54.01	6.78	6.88	9.92	10.25
 $NCCH_2CH_2PH\overset{CH_3}{\underset{CH_3}{C}}CH_2\overset{O}{\overset{\Vert}{C}}CH_3$	127 (0.8)	[a]	58.36	58.11	8.53	8.81	16.72	16.05[b]
 $(NCCH_2CH_2)_2PCH_2CH_2OCH_2\overset{C_4H_9}{\overset{\mid}{C}}HC_2H_5$	204–207 (0.2)	1.4860	64.83	64.61	9.86	10.00	10.45	10.41[c]

[a] Not recorded. [b] Nitrogen analysis: Calcd., 7.56; Found, 7.73. [c] Nitrogen analysis: Calcd., 9.45; Found, 9.68.

EXPERIMENTAL[8]

Materials. Liquid phosphine was obtained from Rocky Mountain Research, Inc., and was used without additional purification. 2-Cyanoethylphosphine and bis(2-cyanoethyl)-phosphine were obtained by the base-catalyzed addition of phosphine to acrylonitrile.[2] 2,4,6-Triisopropyl-5-(3-oxobutyl) 1,3,5-dioxaphosphorinane was obtained by the acid-catalyzed reaction of phosphine with isobutyraldehyde.[4] Dibutylphosphine was obtained by fractionation of a 10% solution supplied by the Westvaco Mineral Products Division, Food Machinery and Chemical Corp. Diethyl α-methyleneglutarate was obtained by the tris(2-cyanoethyl)-phosphine-catalyzed dimerization of ethyl acrylate, an investigation which we will report separately.

Procedure for treating phosphine with unsaturated compounds. The olefinic compound, heptane (when desired), and initiator were combined in a 300-ml. stainless steel autoclave, and the autoclave was closed, weighed, and thoroughly cooled in a Dry Ice–acetone mixture. The autoclave was evacuated and charged with phosphine from a transfer bomb. The desired amount of phosphine was approximated by the pressure drop in the transfer bomb, and after the addition the autoclave was weighed to determine the exact amount of phosphine added. The autoclave was rocked and heated for the desired length of time, allowed to cool to room temperature, and the excess phosphine was vented slowly into the exhaust of an efficient hood. The autoclave was evacuated, and the vacuum was broken with nitrogen. The reaction mixture was transferred into a nitrogen filled flask, cooled to 0°, and filtered under nitrogen. The filtrate was distilled under nitrogen or under vacuum to obtain the products. The results are shown in Table I and the products are described in Table VI.

Procedure for the addition of mono(2-cyanoethyl)phosphine and bis(2-cyanoethyl)phosphine to unsaturated compounds. The chemically initiated reactions in Tables II and III were carried out, with the exceptions noted, by combining the reactants with the initiator (α,α′-azobisisobutyronitrile or di-*t*-butyl peroxide) and heating the stirred mixture to the indicated temperature. In many cases the reaction was exothermic, and an ice bath was applied to maintain the desired temperature. The products were obtained by distillation under nitrogen or reduced pressure and are described in Table VII.

In the x-ray-initiated reactions the reactants were combined in a small Pyrex glass ampoule having a wall thickness of approximately 0.075 in. The mixture was subjected to three freeze-thaw cycles under vacuum to eliminate dissolved gases, and the evacuated ampoule was sealed. The ampoule was positioned 4.2 cm. from the tungsten target of a General Electric Maxitron x-ray tube having a beryllium target and was irradiated for the indicated length of time. The tube was operated at 250 k.v.p. and 30 m.a. The products were obtained by distillation and are described in Table VII.

Reaction of 2-carbethoxyethylphosphine and octene-1. A solution of 3.0 g. (0.02 mole) of di-*t*-butyl peroxide in 32.2 g. (0.275 mole) of 95% octene-1 was added dropwise during 75 min. with stirring to 37.0 g. (0.275 mole) of the phosphine preheated to 120° under nitrogen. The reaction mixture was stirred at 120° for an additional hour and then distilled to obtain 6.7 g. (18.1%) of unchanged 2-carbethoxyethylphosphine, b.p. 65–70° (23 mm.), 21.3 g. (31.4%) of 2-carbethoxyethyloctylphosphine, b.p. 90–110° (0.3 mm.), and 29.8 g. (60%) of 2-carbethoxyethyldioctylphosphine, b.p. 160–175° (0.35 mm.)

A sample of 2-carbethoxyethyloctylphosphine, b.p. 106° (0.25 mm.), n_D^{25} 1.4620, was analyzed.

Anal. Calcd. for $PO_2C_{13}H_{27}$: C, 63.38; H, 11.05; P, 12.58. Found: C, 63.68; H, 10.95; P, 12.67.

A sample of 2-carbethoxyethyldioctylphosphine b.p. 165° (0.2 mm.), n_D^{25} 1.4655, was analyzed.

Anal. Calcd. for $PO_2C_{21}H_{43}$: C, 70.35; H, 12.09; P, 8.64. Found: C, 70.02; H, 12.13; P, 8.69.

Bis(2-carbethoxyethyl)-2,4-dicarbethoxybutylphosphine. A solution of 9.35 g. (0.04 mole) of bis(2-carbethoxyethyl)-phosphine, 8.0 g. (0.04 mole) of diethyl 2-methyleneglutarate, 10 ml. of heptane, and 0.33 g. (0.002 mole) of α,α′-azobisisobutyronitrile was heated at 80–85° for 1 hr. while stirring under nitrogen. The solvent was removed under reduced pressure, and the residue was distilled to obtain 13.2 g. (76%) of bis(2-carbethoxyethyl)-2,4-dicarbethoxybutylphosphine, b.p. 190–205° (0.2 mm.). Redistillation provided material, b.p. 196–201° (0.2 mm.), n_D^{25} 1.4730. The infrared and NMR spectra were identical to the spectra of the 4:1 ethyl acrylate–phosphine adduct.

2,4,6-Triisopropyl-5-(3-oxybutyl)-1,3,5-dioxaphosphorinane. A solution of 36.3 g. (0.15 mole) of 2,4,6-triisopropyl-1,3,5-dioxaphosphorinane, 11.6 g. (0.17 mole) of methyl vinyl ketone, and 0.8 g. (0.005 mole) of α,α′-azobisisobutyronitrile was stirred under nitrogen at 80–83° for 2 hr. The reaction mixture was distilled to obtain 5.1 g. (14%) of unchanged starting phosphine and 25.1 g. (55%) of the product, b.p. 120–124° (0.4 mm.). A center cut, b.p. 122° (0.4 mm.), n_D^{25} 1.4749 was analyzed.

Anal. Calcd. for $C_{16}H_{31}O_3P$: C, 63.54; H, 10.35; P, 10.25. Found: C, 63.84; H, 10.55; P, 10.60.

Reaction of dibutylphosphine with 1,3-butadiene. Into a stainless steel autoclave filled with nitrogen were placed 102 g. (0.7 mole) of dibutylphosphine, 19.0 g. (0.35 mole) of butadiene, 5.74 g. (0.035 mole) of α,α′-azobisisobutyronitrile, and 50 ml. of heptane. The autoclave was closed and rocked at 79–84° for 4 hr. The reaction mixture was distilled to obtain 49.1 g. (48%) of unchanged dibutylphosphine and 35.7 g. (51% based on butadiene) of dibutyl-2-butenylphosphine, b.p. 118–124° (11 mm.). Redistillation of the latter provided an analytical sample, b.p. 118° (13 mm.), n_D^{25} 1.4725.

Anal. Calcd. for $C_{12}H_{25}P$: C, 71.95; H, 12.58; P, 15.47. Found: C, 71.47; H, 12.60; P, 15.44.

The infrared spectrum indicated that the product had the *trans* configuration.

Further distillation of the reaction mixture provided 9.0 g. (7%) of a 2:1 dibutylphosphine-butadiene adduct, b.p. 134–159° (0.25 mm.). Redistillation gave an analytical sample, b.p. 144° (0.07 mm.); n_D^{25} 1.4895.

Anal. Calcd. for $C_{20}H_{44}P_2$: C, 69.30; H, 12.81; P, 17.87. Found: C, 68.39; H, 12.53; P, 17.56.

Attempted reaction of dibutylphosphine and dibutyl-2-butenylphosphine. A solution of 7.3 g. (0.05 mole) of dibutylphosphine, 10.0 g. (0.05 mole) of dibutyl-2-butenylphosphine, 3.6 ml. of heptane, and 0.41 g. (0.0025 mole) of α,α′-azobisisobutyronitrile was heated at 80–85° for 4 hr. with stirring under nitrogen, and was then distilled to recover 5.3 g. (72.6%) of dibutylphosphine, b.p. 65° (8 mm.) and 9.3 g. (93.0%) of dibutyl-2-butenylphosphine b.p. 100–101° (5 mm.). About 1 g. of a yellow oily residue remained. The infrared spectrum of the residue was unlike that of the 2:1 dibutylphosphine-butadiene adduct.

Reaction of heptyne-1 with bis(2-cyanoethyl)phosphine. A mixture of 28.0 g. (0.2 mole) of the phosphine, 19.2 g. (0.2 mole) of heptyne-1, and 1.5 g. (0.01 mole) of α,α′-azobisisobutyronitrile was heated under nitrogen with stirring to 75°. A mild exotherm occurred, and the mixture became homogeneous. The solution was heated at 80–85° for 60 min. and distilled to obtain 2.1 g. (7%) of unchanged starting phosphine and 12.7 g. (27%) of bis(2-cyanoethyl)-1-heptenylphosphine, b.p. 170–175° (0.4 mm.). A center cut, b.p. 170–171° (0.4 mm.), n_D^{25} 1.5008, was analyzed.

Anal. Calcd. for $C_{13}H_{21}N_2P$: C, 66.07; H, 8.96; P, 13.11. Found: C, 65.76; H, 8.84; P, 13.12.

The presence of a double bond was clearly indicated by the infrared spectrum.

Further distillation of the reaction mixture was accom-

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(8) Boiling points are not corrected.

panied by decomposition, and additional products could not be isolated.

Reaction of octyne-1 with bis(2-cyanoethyl)phosphine. A mixture of 28.0 g. (0.2 mole) of the phosphine, 22.0 g. (0.2 mole) of octyne-1, 1.5 g. (0.01 mole) of α,α'-azobisisobutyronitrile, and 25 ml. of dry benzene was heated under nitrogen with stirring to 68°. A mild exotherm occurred, and the mixture became homogeneous. The solution was heated at 80–85° for 45 min. and distilled to obtain 3.0 g. (11%) of unchanged starting phosphine and 15.0 g. (30%) of bis(2-cyanoethyl)-1-octenyl-phosphine, b.p. 176–190° (0.6 mm.). A center cut, b.p. 187–190° (0.6 mm.), n_D^{25} 1.5000, was analyzed.

Anal. Calcd. for $C_{14}H_{23}PN_2$: C, 67.17; H, 9.26, N, 11.20; P, 12.37. Found: C, 66.97; 9.35; N, 11.20; P, 12.58.

The infrared spectrum was identical to that of the heptenyl analog.

Reaction of heptyne-1 with 2-cyanoethylphosphine. A solution of 8.7 g. (0.1 mole) of the phosphine, 9.6 g. (0.1 mole) of heptyne-1, and 0.75 g. (0.005 mole) of α,α'-azobisisobutyronitrile was heated under nitrogen at 80–85° for 2 hr. The orange reaction mixture was distilled to obtain 4.1 g. (47%) of unchanged starting phosphine and 3.6 g. (26%) of 2-cyanoethylbis(1-heptenyl)phosphine, b.p. 130–145° (0.2 mm.). Redistillation of the latter provided an analytical sample b.p. 140° (0.25 mm.), n_D^{25} 1.4930.

Anal. Calcd. for $C_{17}H_{30}NP$: C, 73.07; H, 10.82; P, 11.09. Found: C, 73.34; H, 11.10; P, 11.19.

The infrared spectrum showed the presence of a double bond and the absence of a P—H bond.

Further distillation of the reaction mixture resulted in decomposition.

Reaction of acetylene with bis(2-cyanoethyl)phosphine. Into a 300-ml. stainless steel autoclave were placed 50.0 g. (0.36 mole) of the phosphine 5.9 g. (0.07 mole) of α,α'-azobisisobutyronitrile, and 75 ml. of tetrahydrofuran. The autoclave was closed, evacuated, and charged to 4.4 atm. with dry nitrogen. The autoclave was then rocked while acetylene was added to a pressure of 13.6 atm. The autoclave was heated with rocking at 80° for 4 hr. The reaction mixture was stripped of solvent to obtain a yellow oil. The infrared spectrum indicated only a trace of olefinic unsaturation. An attempt made to distil one half of the product was unsuccessful because of extensive decomposition. Also unsuccessful were attempts to induce crystallization of the product or to prepare crystalline derivatives by oxidation with hydrogen peroxide or quaternization with methyl iodide.

Acknowledgment. The authors are indebted to D. J. Wilson and M. Sabia for assistance with the pressure experiments and to R. L. Webb for the x-radiation experiments. The authors also wish to express their sincere appreciation to Mrs. E. C. Grim, Dr. J. A. Kuck, and associates for microanalyses, to N. Colthup for infrared spectra, and to Dr. J. E. Lancaster for NMR spectra.

STAMFORD, CONN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

Further Studies of the Synthesis of *N*-Substituted Aminodiphenylphosphines

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The chlorodiphenylphosphination reaction has been extended to nine additional aliphatic and aromatic amines and resulted in the preparation of 2-pyridylaminodiphenylphosphine, *N*-methylbutylaminodiphenylphosphine, morpholinodiphenylphosphine, ethyleniminodiphenylphosphine, hexamethyleniminodiphenylphosphine, and *P*-3(3-azabicyclo[3.2.2]-nonyl)diphenylphosphine. Under other than anhydrous conditions, the chlorodiphenylphosphination of dibenzylamine and 1,1,3,3-tetramethylbutylamine yielded dibenzylaminodiphenylphosphine oxide dihydrate and 1,1,3,3-tetramethylbutylaminodiphenylphosphine oxide hydrate. The aminodiphenylphosphines were converted to the corresponding oxides and/or sulfides.

In a recent communication[1] we reported the synthesis of some *N*-substituted aminodiphenylphosphines by the direct chlorodiphenylphosphination of aliphatic and aromatic amines. Further work in our laboratory has resulted in the synthesis of several new compounds which extends significantly the range of these chlorophosphination reactions. The additional aminophosphines are 2-pyridylaminodiphenylphosphine, *N*-methylbutylaminodiphenylphosphine, morpholinodiphenylphosphine, ethyleniminodiphenylphosphine, hexamethyleniminodiphenylphosphine, and *p*-3(3-azabicyclo[3.2.2]nonyl)diphenylphosphine.

The *N*-substituted aminodiphenylphosphines derived from chlorophosphination reactions are viscous liquids or crystalline solids which are very reactive toward water, alkylation reagents, and certain metal salts. Some of the syntheses involve reactions that are best conducted under an anhydrous, inert atmosphere. Under other than anhydrous conditions, the chlorodiphenylphosphination of dibenzylamine and 1,1,3,3-tetramethylbutylamine results in the formation of dibenzylaminodiphenylphosphine oxide dihydrate and 1,1,-3,3 - tetramethylbutylaminodiphenylphosphine oxide hydrate.[2]

The aminodiphenylphosphines were converted

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(1) H. H. Sisler and N. L. Smith, *J. Org. Chem.*, **26**, 611 (1961).

(2) The oxide hydrates of these aminophosphines might be considered quasiphosphonium type compounds since their infrared spectra show a phosphonium type structure with principal bands at 1120 cm.$^{-1}$ and in the region 940–820 cm.$^{-1}$ See J. C. Sheldon and S. Y. Tyree, Jr., *J. Am. Chem. Soc.*, **80**, 2117 (1958).