triethyl phosphite (1.66 g., 0.01 mole) with anhydrous *n*-propyl alcohol (50 ml.) *via* the same procedure as in the case of the above reaction. The reaction of bromomalonamide (1.81 g., 0.01 mole) and triethyl phosphite (1.66 g., 0.01 mole) with anhydrous *n*-propyl alcohol (50 ml.) also gave *n*-propyl diethyl phosphate in 77% yield (1.50 g.) by the same procedure.

Reaction of Benzyl Alcohol with Dibromomalonamide (1 mole) and Tribenzyl Phosphite (2 moles).—Dibromomalonamide (1.30 g., 0.005 mole) was added to a solution of tribenzyl phosphite (3.52 g., 0.01 mole) in freshly distilled benzyl alcohol (20 ml.). The mixture was stirred for 3 hr. at 5° and allowed to stand at room temperature overnight. The precipitate of malonamide was removed by filtration and 0.76 g. of thiourea[8] was added to the filtrate. The mixture was stirred for 15 min. at room temperature, after which the precipitate which formed was removed by filtration. Then the filtrate was washed with three 35-ml. portions of water. After the addition of a 35-ml. portion of ether, the solution was washed with one more 35-ml. portion of water. The ether solution was dried over anhydrous sodium sulfate after which the ether and excess benzyl alcohol were removed under reduced pressure (0.5 mm.) at 90° until a thick sirup remained. The sirup was dissolved in 30 ml. of anhydrous acetone containing 1.65 g. of sodium iodide. The solution was refluxed for 20 min. and the solvent was removed. After the addition of ether (40 ml.), the ether solution was extracted with two 40-ml. portions of water. The combined water extracts were acidified with hydrochloric acid; a colorless oil separated and was crystallized. The crystals, dibenzyl hydrogen phosphate (0.58 g., 20%), m.p. 79–80°, were recrystallized from ether.

Reaction of Phenol with Dibromomalonamide (1 mole) and Triethyl Phosphite (2 moles).—To a solution of triethyl phosphite (3.32 g., 0.02 mole) and phenol (1.88 g., 0.02 mole) in 50 ml. of anhydrous acetonitrile, thoroughly pulverized dibromomalonamide (2.60 g., 0.01 mole) was added at one time with vigorous stirring at room temperature. The solution was allowed to stand overnight at room temperature and the precipitate of malonamide was separated by filtration. Ethyl bromide and acetonitrile were removed under reduced pressure and the residual material was fractionated; 4.24 g. (86%) of phenyl diethyl phosphate, b.p. 90–103°/1.0 mm., was obtained and 0.10 g. of phenol was recovered.

Similarly, *p*-nitrophenyl and cyclohexyl diethyl phosphate were obtained by the reaction of the corresponding alcohols with dibromomalonamide and triethyl phosphite. The properties of these compounds together with the yields obtained are listed in Table I.

Reaction of Diethyl Hydrogen Phosphate (2 moles) with Dibromomalonamide (1 mole) and Trimethyl Phosphite (2 moles).—A solution of trimethyl phosphite (1.24 g., 0.01 mole) in 10 ml. of anhydrous acetonitrile was added slowly with stirring to a solution of diethyl hydrogen phosphate (1.54 g., 0.01 mole) and dibromomalonamide (1.30 g., 0.005 mole) in 40 ml. of anhydrous acetonitrile. The temperature was controlled by cooling in an ice bath. A white precipitate, malonamide, separated soon. After addition was completed, the mixture was stirred at 0° for 4 hr. and it was kept at room temperature overnight. Malonamide was removed by filtration. The filtrate was concentrated under reduced pressure and the resulting oil was treated with dry ether (50 ml.) to remove the residual malonamide. After concentration, the solution was distilled under high vacuum. *unsym*-Dimethyl diethyl pyrophosphate, 125–128°/0.06 mm., was obtained in 68% yield (1.78 g.).

In similar fashion, *unsym*-di-*n*-butyl diethyl pyrophosphate was prepared by the reaction of tri-*n*-butyl phosphite with diethyl hydrogen phosphate and dibromomalanamide. The results are summarized in Table II.

Reaction of Diethyl Hydrogen Phosphate (1 mole) with Dibromomalonamide (1 mole) and Triethyl Phosphite (1 mole).—When a mixture of triethyl phosphite (1.66 g., 0.01 mole), diethyl hydrogen phosphate (1.54 g., 0.01 mole) and dibromomalonamide (2.60 g., 0.01 mole) in acetonitrile was treated in the same manner as above, 2.27 g. (78%) of tetraethyl pyrophosphate, b.p. 108–110°/0.16 mm., and 1.64 g. of bromomalonamide were obtained.

Reaction of Diethyl Hydrogen Phosphate with Bromomalonamide and Triethyl Phosphite.—To a solution of bromomalonamide (0.90 g., 0.005 mole) in 30 ml. of anhydrous acetonitrile a solution of triethyl phosphite (0.83 g., 0.005 mole) in 10 ml. of anhydrous acetonitrile was added dropwise (in 5–10 min.) with stirring. The temperature was controlled by cooling in an ice bath. After the crystal of bromomalonamide was dissolved completely, a solution of diethyl hydrogen phosphate in 10 ml. of anhydrous acetonitrile was immediately dropped into the above mixture, and a white precipitate appeared. Then the mixture was treated in the usual manner and 1.01 g. (70%) of tetraethyl pyrophosphate, b.p. 112–116°/0.35 mm., was obtained.

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[8] Thiourea smoothly reacts with benzyl bromide forming a water soluble salt.[9]

[9] A. Bernthsen and H. Klinger, *Chem. Ber.*, **12**, 574 (1879).

Synthesis of Some Triphenylphosphinalkylimines and Mono- and Dialkylaminotriphenylphosphonium Halides

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The syntheses of some triphenylphosphinalkylimines and their addition reactions with alkyl halides to yield mono- and dialkylaminotriphenylphosphonium halides are reported. The limitation of alkyl halide addition reactions has been described. Sterically hindered *t*-butylmethylamine and *t*-butylethylamine have been prepared through the hydrolysis of the corresponding dialkylaminotriphenylphosphonium halides.

For other investigations in the field of nitrogen chemistry[1] a method for the preparation of di-*tert*-butylamine (I) in rather large quantities was needed. Though the synthesis of I has been reported previously,[2,3] the duplication of these results was not obtained. I could only be prepared in an impure state and in exceedingly small yields. Consequently, other methods of preparation were examined.

A possible route for the preparation of I was through the use of triphenylphosphinimines as intermediates. Staudinger[4] several decades ago found that triphenylphosphinimines added alkyl halides to yield dialkylaminotriphenylphosphonium halides. These compounds could be hydrolyzed to give triphenylphosphinoxide and dialkylamines.

$$[\mathrm{Ph_3\overset{\oplus}{P}{-}\overset{\ominus}{N}{-}R} \longleftrightarrow \mathrm{Ph_3P{=}N{-}R}] + \mathrm{R'X} \longrightarrow$$
$$[\mathrm{Ph_3P{-}NRR'}]^{\oplus}\mathrm{X}^{\ominus} \xrightarrow{\mathrm{H_2O}} \mathrm{Ph_3P{=}O} + \mathrm{HNRR'} \quad (1)$$

Horner[5a,b,c] recently increased the usefulness of this synthesis tremendously by introducing a simple method for the preparation of phosphinimines, according to

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[1] H. Zimmer, L. F. Audrieth, R. A. Rowe, and Marlies Zimmer, *J. Am. Chem. Soc.*, **77**, 790 (1955).

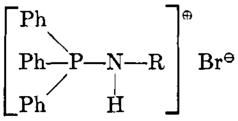
[2] F. Klages, G. Nober, F. Kircher, and M. Bock, *Ann.*, **547**, 1 (1941).

[3] F. Klages and H. Sitz, *Ber.*, **92**, 2606 (1959).

[4] H. Staudinger and E. Hauser, *Helv. Chim. Acta*, **4**, 861 (1921).

TABLE I

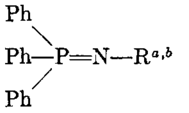
ALKYLAMINOTRIPHENYLPHOSPHONIUM BROMIDES



No.	R	Formula	M.p.	Yield, %	Analytical values C Calcd.	C Found	H Calcd.	H Found	N Calcd.	N Found
1	CH_3	$C_{19}H_{19}BrNP$	197–199	77.0	61.29	60.95	5.1	5.51	3.76	3.87
2	C_2H_5	$C_{20}H_{21}BrNP$	246–247	78.4	62.18	62.22	5.44	5.80	3.63	3.69
3	n-C_3H_7	$C_{21}H_{23}BrNP$	190–192	80.5	63.00	62.96	5.75	5.85	3.50	3.78
4	$CH(CH_3)_2$	$C_{21}H_{23}BrNP$	242–243	70.0	63.00	62.42	5.75	5.45	3.50	3.67
5	$CH_2CH(CH_3)_2$	$C_{22}H_{25}BrNP$	136–137	82.5	63.63	63.55	6.08	6.06	3.38	3.38
6	$C(CH_3)_3$	$C_{22}H_{25}BrNP$	223	92.8	63.73	63.29	6.08	6.06	3.38	3.10

TABLE II

TRIPHENYLPHOSPHONALKYLIMINES



No.	R	Formula	M.p.	Yield, %	Analytical values C Calcd.	C Found	H Calcd.	H Found	N Calcd.	N Found
7	CH_3	$C_{19}H_{18}NP$	67[c]	96.0	—	—	—	—	—	—
8	C_2H_5	$C_{20}H_{20}NP$	96[d]	98.3	—	—	—	—	—	—
9	n-C_3H_7	$C_{21}H_{22}NP$	112–114	98.0	—	—	—	—	—	—
10	$CH(CH_3)_2$	$C_{21}H_{22}NP$	126–127	98.8	78.91	78.56	6.89	6.77	4.39	3.87
11	$CH_2CH(CH_3)_2$	$C_{22}H_{24}NP$	79–81	93.0	—	—	—	—	—	—
12	$C(CH_3)_3$	$C_{22}H_{24}NP$	146–148	99.6	79.28	79.59	7.20	7.06	4.20	4.04

[a] Crystallized from ethylcyclohexane. [b] Analytically pure samples were obtained only when R = $CH(CH_3)_2$ and $C(CH_3)_3$; [c] Ref. 4, m.p. 62–65°. [d] Ref. 4, m.p. 96°.

equation 2. Other, but less convenient, syntheses have been reported during the years for this class of compounds.[6–12] Since examples for this synthesis in which R = alkyl in equation 1 are rare,[5c] it was decided to investigate systematically the following sequence of reactions, especially trying to apply it to the preparation of I.

$$Ph_3PBr_2 + H_2NR \xrightarrow{B} [Ph_2PHNR]^{\oplus}Br^{\ominus} + BH^{\oplus}Br^{\ominus} \quad (2)$$

$$[Ph_3P\text{—}HNR]^{\oplus}Br^{\ominus} \xrightarrow[\text{liqu. } NH_3]{NaNH_2} [Ph_3\overset{\oplus}{P}\text{—}\overset{\ominus}{N}R \longleftrightarrow Ph_3{=}NR] \quad (3)$$

$$[Ph_3\overset{\oplus}{P}\text{—}\overset{\ominus}{N}R \longleftrightarrow Ph_3P{=}NR] + R'I \longrightarrow [Ph_3P\text{—}NRR')^{\oplus}I^{\ominus} \quad (4)$$

$$[Ph_3P\text{—}NRR']^{\oplus}I^{\ominus} \xrightarrow{H_2O} Ph_3P{=}O + HNRR' \quad (5)$$

R = R′ = Me, Et, *n*-Pr, *i*-Pr, *i*-Bu, *t*-Bu

Initial condensations (equation 2) were run in benzene. Triethylamine was used as auxilliary base. Yields of alkylaminotriphenylphosphonium compounds were good to excellent and are reported in Table I.

Deprotonation (equation 3) was readily achieved by using sodamide in liquid ammonia (Table II). The resulting triphenylphosphinalkylimines showed great differences in behavior. Triphenylphosphinmethylimine (**7**) and triphenylphosphinethylmine (**8**) were extremely hygroscopic and air sensitive. When exposed to air for a few seconds they became wet and after a short period of time triphenylphosphinoxide could be found. However, triphenylphosphine-*t*-butylimine is a stable compound which can be exposed to air without suffering decomposition. Samples of it were kept for several years without a change in appearance and without decomposition.

The ultraviolet spectra of II and triphenylphosphinoxide (Fig. 1) are almost identical, indicating that both compounds are of a very similar structure.

The infrared spectra of the prepared compounds showed absorption peaks which were in agreement with the observations of other investigators. All of the triphenylalkylaminophosphonium salts shared a very strong peak at 1100–1110 cm.^{-1}.[5–12] and one of a much more modest intensity at 1155–1160 cm.^{-1}.[5] These two peaks were also present in the spectrum of compound **12**.

Addition of alkyl halides to the corresponding phosphinimines (equation 4) was accomplished by treating these compounds with excess of the alkyl iodides and refluxing the mixture for a short period of time (Table III).

As expected, the compounds obtained by addition of methyl iodide to compound **8** (Table II) and of ethyl iodide to compound **7** (Table II) are identical (see compounds **14** and **15** in Table III). The outcome

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(5) (a) L. Horner and H. Hoffmann, *Angew. Chem.*, **68**, 473 (1956); (b) L. Horner and H. Oediger, *Ber.*, **91**, 437 (1958); (c) L. Horner and H. Oediger, *Ann.*, **627**, 142 (1959).

(6) H. Stuadinger and J. Meyer, *Helv. Chim. Acta*, **2**, 635 (1919).

(7) F. G. Mann and E. J. Chaplin, *J. Chem. Soc.*, 527 (1937).

(8) A. V. Kirsanov and Z. D. Nekrasova, *Zh. Obsh. Khim.*, **26**, 903 (1956); *Chem. Abstr.*, **50**, 14631 (1956).

(9) A. V. Kirsanov and R. T. Makitra, *Zh. Obsh. Khim.*, **27**, 245 (1957); *Chem. Abstr.*, **51**, 245 (1957).

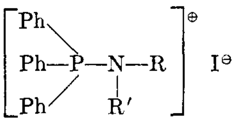
(10) A. N. McDonald and T. W. Campbell, *J. Am. Chem. Soc.*, **82**, 4669 (1960).

(11) H. H. Sisler, A. Sarkis, H. S. Ahuja, R. J. Drago, and N. L. Smith, *ibid.*, **81**, 2982 (1959).

(12) H. H. Sisler and N. L. Smith, *J. Org. Chem.*, **26**, 4733 (1961).

Table III

Dialkylaminotriphenylphosphonium Iodides

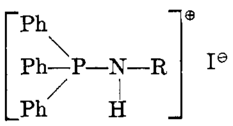


No.	R	R′	Formula	M.p.	Yield, %	Analytical values C Calcd.	C Found	H Calcd.	H Found	N Calcd.	N Found
13	CH_3	CH_3	$C_{20}H_{21}INP$	185	98.0	55.42	55.27	4.84	5.13	3.23	3.32
14	C_2H_5	CH_3[a]	$C_{21}H_{23}INP$	177	81.6	56.37	56.14	5.14	5.29	3.13	2.90
15	n-C_3H_7	CH_3	$C_{22}H_{25}INP$	205	78.7	57.27	57.02	5.42	5.49	3.04	3.07
16	$CH(CH_3)_2$	CH_3	$C_{22}H_{25}INP$	211	80.0	57.27	57.40	5.42	6.65	3.04	3.13
17	$CH_2CH(CH_3)_2$	CH_3	$C_{23}H_{27}INP$	206–207	76.8	58.10	58.43	5.69	5.65	2.95	3.09
18	$C(CH_3)_3$	CH_3	$C_{23}H_{27}INP$	214–215	94.0	58.10	57.81	5.62	5.82	2.95	2.94
19	CH_3	C_2H_5[a]	$C_{21}H_{23}INP$	177	90.0	—	—	—	—	—	—
20	C_2H_5	C_2H_5[b]	$C_{22}H_{25}INP$	174	71.0	57.27	57.31	5.42	5.75	3.04	2.97
21	$CH(CH_3)_2$	C_2H_5	$C_{23}H_{27}INP$	202	60.4	58.10	57.78	5.69	5.84	2.95	2.55
22	$CH_2CH(CH_3)_2$	C_2H_5	$C_{24}H_{29}INP$	184–186	68.0	58.89	59.01	5.93	6.14	2.86	3.00
23	$C(CH_3)_3$	C_2H_5	$C_{24}H_{29}INP$	220–221	84.4	58.89	58.75	5.97	5.87	2.86	3.01

[a] Identity of compounds 14 and 19 was confirmed by an undepressed mixed melting point. [b] Ref. 4, m.p. 164–165°; R. Appel and A. Hauss, *Z. anorg. allgem. Chem.*, **311**, 290 (1961), m.p. 162°.

Table IV

Alkylaminotriphenylphosphonium Iodides



No.	R	Formula	M.p.	Analytical values C Calcd.	C Found	H Calcd.	H Found	N Calcd.	N Found
24	CH_3	$C_{19}H_{19}INP$	184–185	54.41	54.24	4.53	4.55	3.34	3.10
25	C_2H_5	$C_{20}H_{21}INP$	170	55.43	56.15	4.85	5.31	3.23	3.04
26	n-C_3H_7	$C_{21}H_{23}INP$	154–155	56.37	56.84	5.14	5.20	3.13	3.03
27	$CH(CH_3)_2$	$C_{21}H_{23}INP$	224	56.37	56.74	5.14	5.12	3.13	3.23
28	$CH_2CH(CH_3)_2$	$C_{22}H_{25}INP$	154	57.26	57.17	5.42	5.33	3.03	2.95
29	$C(CH_3)_3$	$C_{22}H_{25}INP$	197–198	57.26	57.01	5.42	5.48	3.03	3.03

of these particular addition reactions can be taken as a proof for the structures of the reaction products. The order of reactivity of alkyl halides has been found to be R′I > R′Br >> R′Cl. Consequently, alkyl iodides were used predominantly in this study.

Unfortunately for our purposes and ultimate goal, methyl bromide, methyl iodide and, in most cases, ethyl iodide only could be added to the phosphonimines. Under all conditions tried, higher halides such as Pr, *i*-Pr, *i*-Bu and *t*-Bu reacted with all the mentioned phosphinimines with hydrogen iodide elimination to yield the corresponding monoalkylaminotriphenylphosphonium iodides as the only isolable products (Table IV). In this connection it was noted with surprise that triphenylphosphin-*n*-propylimine even with ethyl bromide or ethyl iodide yielded the corresponding hydrobromide or hydroiodide salts (compounds **3** and **26**) instead of the expected dialkylaminotriphenylphosphonium salts. The mechanisms of these elimination reactions are presently being investigated in this laboratory. It can, however, already be said that triphenylphosphinalkylimines are remarkably basic compounds.

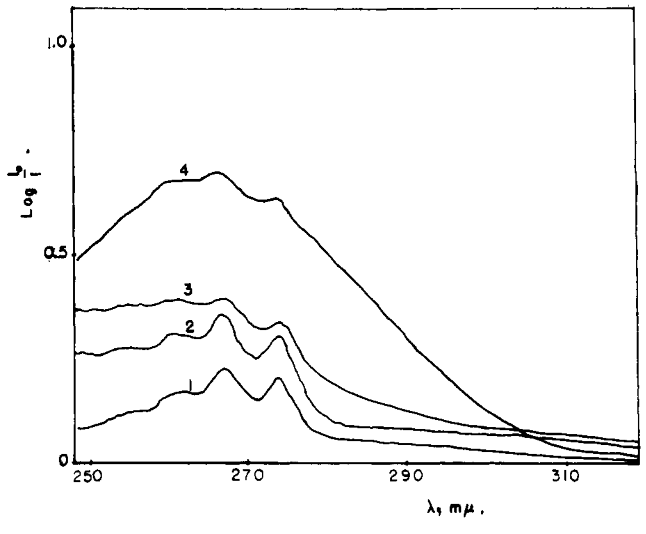
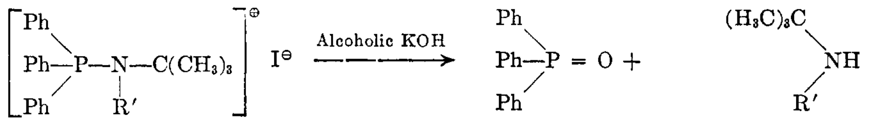


Fig. 1.—Ultraviolet spectra: 1 = $Ph_3P = O$; 2 = $Ph_3P = NCH_3$; 3 = $Ph_3P = NC(CH_3)_3$; 4 = Ph_3P. Concn.: 10^{-4} mole in chloroform.

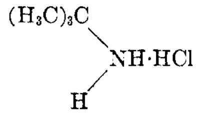
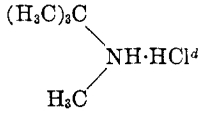
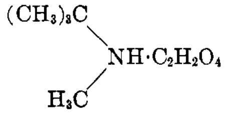
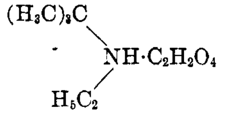
Since elimination was found to be competing with the desired addition reactions in the discussed syntheses, it was hoped to decrease the amount of elimination by carrying out the reactions at low temperatures and high dilutions. The results of attempted condensations of isopropyl iodide and butyl bromide with triphenyl-*N*-*t*-butylphosphinimine are summarized in Table VI. It was found that whenever reaction occurred the products were almost entirely **29** and **6**, thus, showing that eliminations were favored under all tested reaction conditions.

TABLE V

HYDROLYSIS OF PHOSPHONIUM SALTS



(R' = H, CH_3 or C_2H_5)

					Analytical value					
					C		H		N	
Compound	Refluxing period, hr.	Yield, %	Amine salt[a]	M.p.[b]	Calcd.	Found	Calcd.	Found	Calcd.	Found
29	3	59.5	 $(H_3C)_3C-\underset{H}{N}H\cdot HCl$	289–290[c]	43.83	43.62	10.96	10.95	11.87	11.90
22	3	66.4	 $(H_3C)_3C-\underset{H_3C}{N}H\cdot HCl$[d]	260	48.58	49.33	11.34	11.35	11.34	11.37
			 $(CH_3)_3C-\underset{H_3C}{N}H\cdot C_2H_2O_4$	116[e]	47.46	48.16	8.47	8.62	7.91	8.22
23	3	58.0	 $(H_3C)_3C-\underset{H_5C_2}{N}H\cdot C_2H_2O_4$	180–182	50.25	50.23	8.96	8.83	7.33	7.77

[a] Crystallized from anhydrous ethanol–ether mixture. [b] Uncorrected. [c] F. Klages, G. Nober, F. Kircher, and M. Bock, *Ann.*, **547**, 1 (1941); m.p. 291°. [d] Highly hygroscopic. [e] P. Sabatier and A. Mailhe, *Ann. Chim. Phys.*,[8] **16**, 96 (1909); m.p. 166°.

TABLE VI

REACTION OF TRIPHENYL-*N*-*t*-BUTYLPHOSPHINIMINE WITH EQUIMOLAR AMOUNT OF *i*-PrI AND *t*-BuBr[a] IN *t*-BuOH (10 MOLES)

Temp. range, °C.	Stirring period, hr.	Isopropyl iodide, product formed	*t*-Butyl bromide, product formed
30–35	24	No reaction	No reaction
35–40	24	Compound 29	No reaction
40–45	24	Compound 29	No reaction
45–50	24	Compound 29	No reaction
50–above	24	Compound 29	Compound 6

[a] *t*-BuBr was used instead of *t*-BuI because the latter decomposes slowly.

Thus, this method does not represent a way to obtain I. However, it provides a good route to obtain various mixed amines free from all impurities, since the hydrolysis of dialkylaminotriphenylphosphonium bromides (equation 5) proceeded essentially without side reaction.

Experimental[13]

Alkylaminotriphenylphosphonium Bromides (Table I).—To an ice-cooled solution of triphenylphosphine dibromide (44.2 g.; 0.1 mole) in benzene was added simultaneously triethylamine (0.1 mole) and the corresponding primary amine (0.1 mole) over a period of 30 min. The stirring was continued for an additional hour and the precipitate was collected and washed with ether followed by ice-cold water to remove triethylamine hydrobromide. The remaining solid was crystallized from a chloroform–ethyl acetate mixture.

Triphenylphosphinalkylimines (Table II).—To a stirred solution of the appropriate alkylaminotriphenylphosphonium bromide (0.05 mole) in 300 ml. of liquid ammonia was added sodamide (0.055 mole). The resulting mixture was stirred for another 30 min. and then the ammonia was evaporated. The remaining solid (which was a mixture of phosphinimine and sodium bromide) was extracted with anhydrous ether. Upon distilling the ether extract a crystalline solid was obtained which was recrystallized from ethylcyclohexane. Analytically pure samples were obtained only in the case of triphenylphosphineisopropylimine and triphenylphosphine-*t*-butylimine, while in other cases the phosphinimines underwent partial oxidation during recrystallization.

Alkylmethylaminotriphenylphosphonium Iodides (Table III; Compounds 13–18).—A mixture of triphenylphosphinalkylimine (0.01 mole) and 15 ml. of methyl iodide was refluxed for 3 hrs. In the case of unstable phosphinimines the crude mixture of the corresponding phosphinimine and sodium bromide was directly employed. The reaction mixture was filtered hot and the remaining solid was treated with 2 ml. of chloroform. The crystalline phosphonium iodides were isolated from the filtrate by adding an excess of ethylacetate. They were recrystallized from this solvent mixture.

Alkylethylaminotriphenylphosphonium Iodides (Table III; Compounds 19–23).—Same procedure was adopted as above except that equimolar quantities of the corresponding phosphinimine and ethyl iodide were refluxed in 10 ml. of *t*-butyl alcohol.

Alkylaminotriphenylphosphonium Iodides (Table IV).—In the above cases when *n*-propyl, isopropyl, isobutyl and *t*-butyl iodides were employed hydrogen iodide elimination took place from the alkyl iodides and it added to the phosphinimines to give the corresponding crystalline alkylaminotriphenylphosphonium iodides.

Hydrolysis of Compounds 18, 23, and 29 (Table V).—A mixture of 3 g. of the corresponding phosphonium iodide and 50 ml. of 2% alcoholic potassium hydroxide solution was refluxed for 3 hr. Ethanol and the resulting amine were distilled directly into a solution of anhydrous oxalic acid in dry ether or into dry ether saturated with hydrogen chloride to yield the corresponding salts.

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[13] Melting points are uncorrected. Microanalysis by A. Berhnardt, Mikroanalytisches Laboratorium im Max-Planck-Institut, Mulheim/Ruhr, Germany, and by Galbraith Laboratories, Knoxville, Tenn.