S, 18.5; mol. wt., 346. Found: C, 54.8; H, 9.1; N, 7.5; S, 18.4; mol. wt., 334 (Rast method), 311 (Mechrolab osmometer in acetonitrile).

A solution of 5.0 g. (0.029 mole) of above product and 8.3 g. (0.031 mole) of triphenylphosphine in 50 ml. of chloroform was heated to reflux for 7 hr. Chloroform was removed; the residue was stirred with 130 ml. of hexane vigorously at room temperature. The hexane-insoluble material was collected and recrystallized from hexane. The crystalline solid, m.p. 161–162°, identified as triphenylphosphine sulfide (no depression in melting point with authentic sample) was obtained in 1.3-g. (0.0044 mole, 15%) yield. There was also isolated 0.7 g. (0.004 mole, 15.2%) of VIIIb from the hexane mother liquors. The very viscous oil was not distillable at 320° (0.15 mm.).

Infrared and elemental analysis of the sample, $n^{25}\text{D}$ 1.5131, after standing at room temperature for several months, did not change. However, its refractive index increased: $n^{25}\text{D}$ 1.5164. The compound after purification through silica gel gave a light yellow oil, $n^{25}\text{D}$ 1.5166, with no change in its infrared spectrum. Elemental analysis and molecular weight of the chromatogrammed sample remained essentially the same.

N,N-Diethyl-2,3-dithioacetylpropionamide (Xc).—N,N-Diethylacrylylamide (VIIIc) was prepared from diethylamine and acrylyl chloride in ether solution, b.p. 39–40° (0.2 mm.), $n^{25}\text{D}$ 1.4645, 97% yield.

Anal. Calcd. for $C_7H_{13}NO$: C, 66.2; H, 10.2; N, 11.0. Found: C, 66.1; H, 10.1; N, 11.2.

Bromination of VIIIc in chloroform solution gave N,N-diethyl-2,3-dibromopropionamide (IXc) as a light yellow oil in quantitative yield, b.p. 124–125° (3 mm.), $n^{25}\text{D}$ 1.5270, 57% yield.

Anal. Calcd. for $C_7H_{13}Br_2NO$: C, 29.3; H, 4.5; N, 4.9; Br, 55.8. Found: C, 29.6; H, 4.4; N, 4.7; Br, 55.8.

The procedure as described for the preparation of Xa, b was used. The pyridine hydrobromide was obtained in 89.0% yield (based upon 2 mole equiv. of salt for 1 mole equiv. of IXc). The desired product, Xc, $n^{25}\text{D}$ 1.5194, was obtained in 94% yield.

Anal. Calcd. for $C_{11}H_{19}NO_3S_2$: C, 47.7; H, 6.9; N, 5.1; S, 23.1. Found: C, 47.3; H, 6.9; N, 5.0; S, 23.3.

2,5-[Bis(diethylaminocarbamoyl)]-1,4-dithiane (XIIc or XIIIc).—The procedure for the preparation of XIIb or XIIIb was used. The product, a light yellow oil, $n^{25}\text{D}$ 1.5110, was obtained in 48% yield.

Anal. Calcd. for $C_{14}H_{26}N_2O_2S_2$: C, 52.7; H, 8.2; N, 8.8; S, 20.1; mol. wt., 318. Found: C, 52.7; H, 8.4; N, 8.0; S, 19.2; mol. wt., 313 (Rast method), 291 (Mechrolab osmometer in acetonitrile).

The compound, after standing at room temperature for several days, did not react with triphenylphosphine.

Synthesis and Some Reactions of Triphenylphosphinamino- and (β-N-Disubstituted amino)imines

HANS ZIMMER AND GURDIAL SINGH

Department of Chemistry, University of Cincinnati, Cincinnati 21, Ohio

Received December 5, 1963

Triphenylphosphinamino- and (β-N-disubstituted amino)imines have been prepared by dehydrobromination of hydrazino- and (β-N-disubstituted hydrazino)triphenylphosphonium bromides, respectively. The aminophosphinimines have been treated further with methyl and ethyl iodides, and the structures of the resulting α-N-alkyl hydrazino- and (α-N-alkyl β-N-disubstituted hydrazino)triphenylphosphonium iodides have been confirmed through elemental analyses, hydrolysis to triphenylphosphine oxide and substituted hydrazines, and nuclear magnetic resonance studies. The hydrolysis of (α-N-alkyl β-N-disubstituted hydrazino)triphenylphosphonium iodides represents a new way for the synthesis of 1,1,2-trisubstituted hydrazines.

Recently we reported the preparation of some triphenylphosphinalkyl imines (I, R = alkyl)[1] and their successful utilization for the synthesis of sterically hindered dialkyl amines, such as *t*-butylmethylamine and *t*-butylethylamine, which are not easily available through conventional methods. It was also discovered that triphenylphosphine-*t*-butylamine (I, R = *t*-Bu)

$$\underset{\text{I}}{Ph_2P{=}NR}$$

was a very stable compound at ambient conditions. Triphenylphosphinisopropylimine (I, R = *i*-Pr) was less stable but sufficiently resistant towards moisture that an analytical sample could be prepared. All other triphenylphosphinalkyl imines decomposed rapidly to triphenylphosphine oxide and the corresponding alkyl amines when exposed to the atmosphere. Until then, the only stable triphenylphosphinimines known were resonance-stabilized ones,[2–8] such as $Ph_3P{=}NPh$.

A plausible explanation for the stability of triphenylphosphine-*t*-butylimine is that the *t*-butyl group, due to its bulk, exercises an effective shielding on the P=N bond.

These results made it appear desirable to study type I compounds further. It was of particular interest to investigate the effects of groups of different electronic and steric requirements on the reactivity of the phosphorus nitrogen double bond, and to investigate whether these phosphinimines could be used as tools in organic and inorganic syntheses. In this paper the synthesis and some properties of triphenylphosphinamino- and (β-N-disubstituted amino)imines (I, R = NH_2 or NXY), as well as their utilization for the preparation of trisubstituted hydrazines, are communicated.

Results and Discussion

Triphenylphosphine dibromide reacted with anhydrous hydrazine or 1,1-disubstituted hydrazines in the presence of triethylamine to give the hydrazino- or (β-N-disubstituted hydrazino)triphenylphosphonium bromides (eq. 1 and Table I).

Under the conditions employed, the free amino group of the hydrazinotriphenylphosphonium bromide (**1**) failed to react further with triphenylphosphine dibromide to give the diphosphonium bromide (eq. 2).

---

(1) H. Zimmer and G. Singh, *J. Org. Chem.*, **28**, 483 (1963).

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

(3) H. Staudinger and E. Hauser, *ibid.*, **4**, 861 (1921).

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

(5) A. V. Kirsanov and G. I. Derkach, *Zh. Obshch. Khim.*, **26**, 2631 (1956); *Chem. Abstr.*, **51**, 1821 (1927).

(6) L. Horner and H. Oediger, *Ann.*, **627**, 142 (1959).

(7) V. I. Shevchenko and V. T. Stratienko, *Zh. Obshch. Khim.*, **30**, 1958 (1960); *Chem. Abstr.*, **55**, 6425 (1961).

(8) G. I. Derkach, E. S. Gubnitskaya, and A. V. Kirsanov, *ibid.*, **31**, 3679 (1961).

TABLE I

HYDRAZINO- AND (β-N-DISUBSTITUTED HYDRAZINO)TRIPHENYLPHOSPHONIUM BROMIDES

$[Ph_3PNHNXY]^+Br^-$

Compd. no.	X	Y	Formula	Color	M.p., °C.	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
1	H	H	$C_{18}H_{18}BrN_2P$	White	215[a]	83.5	57.91	58.31	4.82	4.90	7.51	7.28
2	CH_3	CH_3	$C_{20}H_{22}BrN_2P$	White	190–191 dec.	90.0	59.85	59.84	5.49	5.43	6.98	6.88
3	CH_3	C_6H_5	$C_{25}H_{24}BrN_2P$	White	213	87.3	64.79	64.38	5.22	5.05	6.04	6.18
4	C_6H_5	C_6H_5	$C_{30}H_{26}BrN_2P$[b]	Light yellow	249–250	98.5	68.57	68.57	4.98	4.92	5.33	5.33

[a] Ref. 6, m.p. 210–212°. [b] Calcd. for $C_{30}H_{26}BrN_2P$: Br, 15.21. Found: Br, 15.39.

$$Ph_3PBr_2 + H_2NNXY \xrightarrow{Et_3N} [Ph_3PNHNXY]^+Br^- + [Et_3NH]^+Br^- \quad (1)$$

1, X = Y = H
2, X = Y = CH_3
3, X = CH_3; Y = C_6H_5
4, X = Y = C_6H_5

$$[Ph_3PNHNH_2]^+Br^- + Ph_3PBr_2 \xrightarrow{Et_3N} [Ph_3PNHNHPPh_3]^{+2}2Br^- + [EtNH]^+Br^- \quad (2)$$

Hydrazino- and (β-N-disubstituted hydrazino)triphenylphosphonium bromides, obtained according to eq. 1, could be easily dehydrobrominated with sodamide in liquid ammonia to the corresponding triphenylphosphinamino- and (β-N-disubstituted amino)imines (eq. 3 and Table II).

TABLE II

TRIPHENYLPHOSPHINAMINO- AND (β-N-DISUBSTITUTED AMINO)IMINES

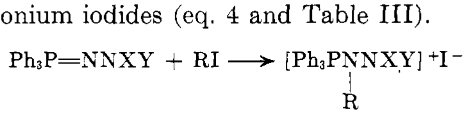
$Ph_3P{=}NNXY$[a]

Compd. no.	X	Y	M.p., °C.	Yield,[b] %	Color
5	H	H	115–116	90.0	Yellow
6	CH_3	CH_3	121–123	86.0	Light yellow
7	CH_3	C_6H_5	106–108	90.1	Light yellow
8	C_6H_5	C_6H_5	114–145 dec.	68.3	Light green

[a] Owing to their instability, no attempt was made to get analytically pure samples. [b] The yields were calculated on the assumption that no decomposition of the aminophosphinimines occurred.

$$[Ph_3PNHNXY]^+Br^- \xrightarrow[\text{liq. } NH_3]{NaNH_2} Ph_3P{=}NNXY + NaBr + NH_3 \quad (3)$$

Like triphenylphosphinalkyl imines,[1,9] the triphenylphosphinamino- and (β-N-disubstituted amino)imines described in this paper were bases and decomposed rapidly in air to give triphenylphosphine oxide and the corresponding hydrazines. The structures of the triphenylphosphinaminoimines and their nucleophilicity were confirmed by treating them with methyl and ethyl iodides and isolating the stable α-N-methylhydrazino- and (α-N-alkyl β-N-disubstituted hydrazino)triphenylphosphonium iodides (eq. 4 and Table III).

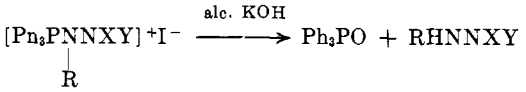


$$Ph_3P{=}NNXY + RI \longrightarrow [Ph_3P\underset{\displaystyle R}{\underset{|}{N}}NXY]^+I^- \quad (4)$$

II

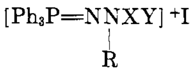
R = CH_3 or C_2H_5

The structures of these α-N-methylhydrazino- and (α-N-alkyl β-N-disubstituted hydrazino)triphenylphosphonium iodides (eq. 4 and Table III) were verified through elemental analyses, hydrolysis with alcoholic potassium hydroxide to triphenylphosphine oxide and the corresponding hydrazines (eq. 5), and nuclear magnetic resonance studies.



$$[Pn_3P\underset{\displaystyle R}{\underset{|}{N}}NXY]^+I^- \xrightarrow{\text{alc. KOH}} Ph_3PO + RHNNXY \quad (5)$$

Hydrolysis of compounds **10**, **11**, **12**, and **13** gave 1,1,-2-trimethylhydrazine, 1,2-dimethyl-1-phenylhydrazine, 1-methyl-2,2-diphenylhydrazine, and 1-ethyl-2,2-diphenylhydrazine, respectively, thus establishing that during the reactions of aminophosphinimines with alkyl iodides (eq. 4) the alkylation occurred at the α-nitrogen atom in agreement with structure II and not at the β-nitrogen atom as indicated in structure III.



$$[Ph_3P{=}N\underset{\displaystyle R}{\underset{|}{N}}XY]^+I^-$$

III

This sequence of reactions (1 → 3 → 4 → 5) represents a new and very convenient method for the preparation of 1,1,2-trisubstituted hydrazines in excellent yields and great purity (see Experimental).

N.m.r. data (see Table IV) obtained from **9**, **10**, **11**, and **12** furnished further evidence supporting structure II rather than III. In a recent paper[10] the occurrence of long-range P^{31}–H^1 coupling in systems such as PNCH and PNCCH was reported. The long-range coupling was not detectable in compounds containing the PNNCH system. Thus, if one considers the reaction between methyl iodide and triphenylphosphinaminoimines, two possible modes of addition might be discussed, namely, addition to the α-nitrogen atom to yield structure II-type compounds, or addition to the β-nitrogen atom to give structure of type III. As is evident from Table IV, **9**, **10**, **11**, and **12** showed the long-range coupling between phosphorus atom and the protons of the methyl group. This spin–spin coupling is only possible if the compounds in question possess structure II, since only it contains the PNCH system, which is capable of exhibiting the long-range coupling effect. Thus, structure II is supported by both physical evidence and chemical behavior.

Experimental[11]

Hydrazino- and (β-N-Disubstituted hydrazino)triphenylphosphonium Bromides (Table I).—A solution of anhydrous hydrazine or 1,1-disubstituted hydrazines (0.1 mole) in triethylamine (10.1 g., 0.1 mole) was added simultaneously, with stirring, to freshly prepared triphenylphosphine dibromide (42.2 g., 0.1 mole) in dry benzene (200 ml.) over a period of 0.5 hr. The stirring

---

[9] H. Zimmer and G. Singh, *Angew. Chem.*, **75**, 574 (1963).

[10] F. Kaplan, G. Singh, and H. Zimmer, *J. Phys. Chem.*, **67**, 2509 (1963).

[11] Melting points are uncorrected. Microanalyses were by A. Berhnardt, Mikroanalytisches Laboratorium im Max-Planck-Institut, Mülheim/Ruhr, Germany, and by Galbraith Laboratories, Knoxville, Tenn.

TABLE III

α-N-METHYLHYDRAZINO- AND (α-N-ALKYL β-N-DISUBSTITUTED HYDRAZINO)TRIPHENYLPHOSPHONIUM IODIDES

Compd. no.	X	Y	R	Formula	Color	M.p., °C.	Yield, %	Carbon, %		Hydrogen, %		Nitrogen, %	
								Calcd.	Found	Calcd.	Found	Calcd.	Found
9	H	H	CH_3	$C_{19}H_{20}IN_2P$	White	181–182 dec.	100	52.53	52.07	4.61	4.51	6.45	6.70
10	CH_3	CH_3	CH_3	$C_{21}H_{24}IN_2P$	White	143 dec.	98.0	54.54	53.92	5.20	5.12	6.06	6.01
11	CH_3	C_6H_5	CH_3	$C_{26}H_{26}IN_2P$	Light yellow	177 dec.	95.5	59.54	59.80	4.96	4.93	5.34	5.23
12	C_6H_5	C_6H_5	CH_3	$C_{31}H_{28}IN_2P$	Light yellow	179 dec.	80.0	63.51	63.72	4.78	4.99	4.78	4.96
13	C_6H_5	C_6H_5	C_2H_5	$C_{32}H_{30}IN_2P$	Light yellow	162 dec.	53.3	64.02	63.71	5.00	4.97	4.66	4.96

TABLE IV

N.M.R. DATA[a]

Compd. no.	Compound	δ_{CH_3}[b] PN-CH_3	PN-NCH_3	$J_{P,H}$ PN-CH_3	PN-NCH_3
2	$[Ph_3P-NH-N(CH_3)_2]^+Br^-$[c]		166.5		*d*
3	$[Ph_3P-NH-NCH_3Ph]^+Br^-$		190.2		*d*
6	$Ph_3P=N-N(CH_3)_2$[c]		192.5		*d*
9	$[Ph_3P-NCH_3-NH_2]^+I^-$[e]	199.9		9.0	
10	$[Ph_3P-NCH_3-N(CH_3)_2]^+I^-$[c]	187.0	150.9	8.8	*d*
11	$[Ph_3P-NCH_3-NCH_3Ph]^+I^-$[c]	193.6	187.8	7.8	*d*
12	$[Ph_3P-NCH_3-NPh_2]^+I^-$	202.0		7.1	

[a] Spectra were obtained in deuteriochloroform on a Varian A-60 spectrometer. [b] Chemical shifts were measured in c.p.s. from an internal reference of tetramethylsilane. [c] Data taken from ref. 10. [d] Coupling between phosphorus and the protons of the methyl group were not observed. [e] The doublet of the NH_2 group appeared at 296.8 c.p.s. (J = 9.0 c.p.s.).

was continued for an additional hour and dry ether was added to precipitate completely the phosphonium bromide. After a little more stirring, the solid was collected by filtration, washed first with ice-cold water (50 ml.) to remove triethylammonium bromide and then with ether. Analytical samples were prepared by recrystallization from chloroform–ethyl acetate mixture.

Triphenylphosphinamino- and (β-N-Disubstituted amino)imines (Table II).—The appropriate phosphonium bromide (see Table I, 0.05 mole) and sodamide (2.05 g., 0.055 mole) were stirred in liquid ammonia (about 300 ml.) under anhydrous conditions. The ammonia then was allowed to evaporate, and the residue was extracted with ether which had been dried over sodium. After distilling the ether, the respective aminophosphinimine was left behind.

α-N-Alkyl Hydrazino- and (α-N-Alkyl β-N-Disubstituted hydrazino)triphenylphosphonium Iodides (Table III).—The appropriate aminophosphinimine (see Table II, 0.005 mole) was refluxed with 5 ml. of methyl or ethyl iodide for 2–3 hr. The reaction mixture was then cooled and an excess of dry ether or ethyl acetate was added to precipitate the phosphonium iodides. In the case of triphenylphosphinaminoimine and triphenylphosphine-β-N-dimethylaminoimine, the crude mixture containing sodium bromide was employed for reaction with methyl or ethyl iodide. The reaction mixture was diluted with chloroform (5 ml.) and filtered. The phosphonium iodides were precipitated from the filtrate by adding on excess of ether or ethyl acetate. Analytical samples were recrystallized from a mixture of chloroform and ethyl acetate.

1,1,2-Trimethylhydrazine.—α-N-Methyl-β-N-dimethyltriphenylphosphonium iodide (**10**, 4.62 g., 0.01 mole) and 50 ml. of 2% alcoholic potassium hydroxide solution were refluxed for 2 hr. The ethanol and 1,1,2-trimethylhydrazine were distilled. To the distillate was added an excess of a saturated solution of oxalic acid in dry ether. The oxalic acid salt, which separated as white precipitate, was collected by filtration; yield was 87.5%. An analytical sample, prepared by recrystallization from anhydrous ethanol and dry ether mixture, melted at 96–98°.

Anal. Calcd. for $C_3H_{10}N_2 \cdot C_2H_2O_4$: C, 36.59; H, 7.32; N, 17.08. Found: C, 36.60; H, 7.49; N, 16.96.

1,2-Dimethyl-1-phenylhydrazine.—A mixture of 5.24 g. (0.01 mole) of α-N-methyl-β-N-methyl-β-N-phenylhydrazinotriphenylphosphonium iodide (**11**) and 50 ml. of 2% alcoholic potassium hydroxide was refluxed for 2 hr. The ethanol was removed by distillation and the residue was extracted with ether. After drying the ether extract over anhydrous sodium sulfate, the ether was removed by distillation and 1,2-dimethyl-1-phenylhydrazine, which was left behind as a yellow liquid, distilled at 92 ± 1° (2 mm.)[12] as a colorless liquid,[13] $n^{23.5}_{D}$ 1.5600; yield was 1.14 g. (88.0%).

Anal. Calcd. for $C_8H_{12}N_2$: C, 70.59; H, 8.83; N, 20.59. Found: C, 70.91; H, 8.68; N, 20.51.

1-Methyl-2,2-diphenylhydrazine and 1-Ethyl-2,2-diphenylhydrazine.—They were prepared by hydrolysis of α-N-methyl-β-N-diphenylhydrazinotriphenylphosphonium iodide (**12**, 5.86 g., 0.01 mole) and α-N-ethyl-β-N-diphenylhydrazinotriphenylphosphonium iodide (**13**, 6.00 g., 0.01 mole), respectively, with 2% alcoholic potassium hydroxide (50 ml.) in a similar way as described above. 1-Methyl-2,2-diphenylhydrazine distilled at 150 ± 2° (3 mm.), yielding 1.79 g. (90.0%) of colorless liquid,[13] n^{23}_{D} 1.6284.

Anal. Calcd. for $C_{13}H_{14}N_2$: C, 78.79; H, 7.07; N, 14.14. Found: C, 79.35; H, 6.98; N, 13.46.

1-Ethyl-2,2-diphenylhydrazine distilled at 155 ± 2° (2 mm.), also as colorless liquid,[13] n^{23}_{D} 1.6284; yield was 1.74 g. (82.0%).

Anal. Calcd. for $C_{14}H_{16}N_2$: C, 79.24; H, 7.54. Found: C, 78.98; H, 7.15.

Acknowledgment.—Financial support by the U. S. Army Research Office, Durham, North Carolina, and the National Institutes of Health, Bethesda, Maryland, is gratefully acknowledged. The Varian A-60 spectrometer was purchased with grants provided by the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation.

---

(12) C. D. Harries [*Ber.*, **27**, 696 (1894)] reports b.p. 93–94° (7 mm.).

(13) This turned yellow on standing.