# Spontaneous dehydrogenation of 2-hydrazinoethyl- and 4-hydrazinobut-2-enylphosphonium salts

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2-Hydrazinoethyl- and 4-hydrazinobut-2-enylphosphonium salts undergo spontaneous dehydrogenation leading to the corresponding hydrazones or diazenes, depending on the structure of the starting compounds or the reaction conditions. A possible mechanism of the transformations is discussed.

**Key words:** hydrazines, phosphonium salts, hydrazones, diazenes, spontaneous dehydrogenation, dehydrogenation—hydrogenation, hydride ion.

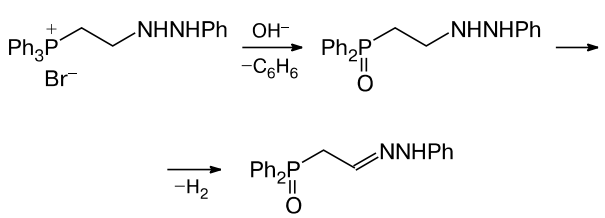
Ketone and aldehyde hydrazones find wide practical use.[1] They are structural parts of novel azapeptides, antibiotics, and many other compounds with valuable properties.[2—5] In addition, they are employed as building blocks in organic synthesis (specifically, as intermediates in the synthesis of heterocycles,[6] chiral amines,[7a,b] α-amino alcohols,[7c] ligands for asymmetric homogeneous catalysis,[7d] and pharmaceuticals of high enantiomeric purity[7e]). Carbanions generated by hydrazones can form carbon—carbon bonds.[8]

Phosphorus-containing substituents are known[9] to regulate essential biological functions. For this reason, hydrazones containing such substituents are of interest as useful substrates for the preparation of biologically active compounds.

In the last few years, we have discovered the tendency of hydrazinoethyl- and hydrazinobut-2-enylphosphonium salts and structurally related phosphine oxides to undergo spontaneous dehydrogenation under moderate heating, giving the corresponding hydrazone derivative or their prototropic azo isomers.

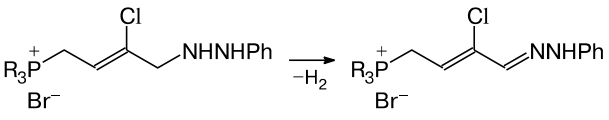
Earlier,[10] we have found that hydrolysis of (triphenyl)-(2-phenylhydrazinoethyl)phosphonium bromide in the presence of aqueous alkali yields a mixture of the *cis*- and *trans*-isomers of diphenylphosphorylacetaldehyde phenylhydrazones as major products. Since basic hydrolysis of phosphonium salts usually yields a reduction product of the more anion-sensitive substituent of the quaternary phosphonium salt and the corresponding tertiary phosphine oxide, a possible reaction pathway to the above compounds should involve initial dephenylation of the starting quaternary phosphonium salt, the formation of 1-(2-diphenylphosphorylethyl)-2-phenylhydrazine, and its *in situ* dehydrogenation (Scheme 1).

**Scheme 1**




Later,[11,12] it has been found that heating of (2-hydrazinoethyl)(triphenyl)(or tributyl)- and (3-chloro-4-hydrazinobut-2-enyl)(triphenyl)(or tributyl)phosphonium salts in ethanol or DMF in the absence of a base cause these salts themselves to undergo dehydrogenation leading to the corresponding hydrazone derivatives. In some cases, this process occurs even during the room-temperature synthesis of these phosphonium salts (Scheme 2).

**Scheme 2**




R = Bu, Ph

It has been also found[13] that hydrazine derivatives containing no phosphonium or phosphoryl group in the β-position undergo spontaneous dehydrogenation only at high temperatures, no matter whether strong oxidants are used or not.

Recently,[14] we have obtained structurally similar hydrazones **1** and **2** (except that they contain no Cl atom in the

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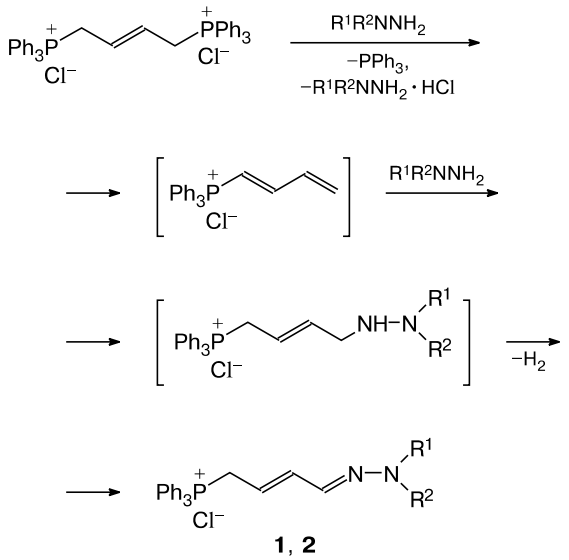
unsaturated substituent) by dehydrogenation of (4-hydrazinobut-2-enyl)phosphonium intermediates formed by reactions of 1,4-bis(triphenylphosphonio)but-2-ene dichloride with phenylhydrazine and *N*,*N*-dimethylhydrazine (Scheme 3).

**Scheme 3**

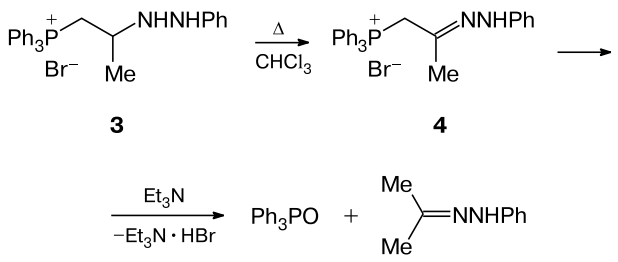


**1**, **2**

$R^1$ = H, $R^2$ = Ph (**1**); $R^1$ = $R^2$ = Me (**2**)

When continuing these investigations, we found that (triphenyl)[2-(2-phenylhydrazino)propyl]phosphonium bromide (**3**) prepared from (allyl)(triphenyl)phosphonium bromide and phenylhydrazine also undergoes dehydrogenation in boiling chloroform for 6 h to give (triphenyl)-[2-(phenylhydrazono)propyl]phosphonium bromide (**4**) in 90% yield (Scheme 4).

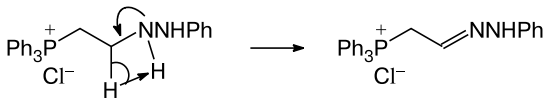
**Scheme 4**



**3** **4**

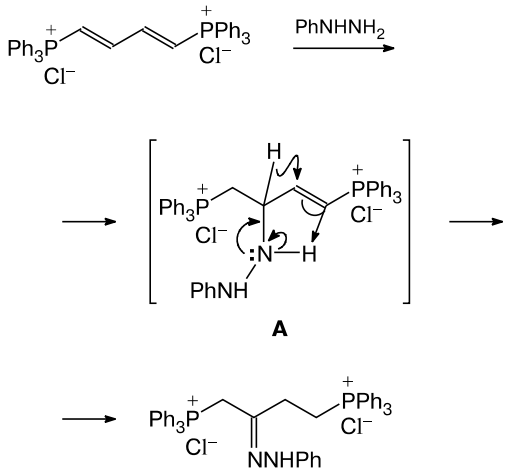
Based on the results obtained, we advanced a hypothesis of the cyclic character of this reaction involving the shift of the lone electron pair of the N atom toward the onium P atom and abstraction of the hydride ion from the adjacent methylene group at the N atom, with allowance for the tendency of the α-H atoms in alkylamines[15] and alkylhydrazines[16] to be detached as hydride ions (Scheme 5).

**Scheme 5**



The hydride-mediated mechanism is supported by our recent data[14] obtained in the study of a reaction of 1,4-bis-(triphenylphosphonio)buta-1,3-diene dichloride with phenylhydrazine. The reaction gives 2-phenylhydrazono-1,4-bis(triphenylphosphonio)butane dichloride in high yield, conceivably proceeding through the formation of intermediate **A** followed by its NH—CH dehydrogenation and C=C hydrogenation (Scheme 6).

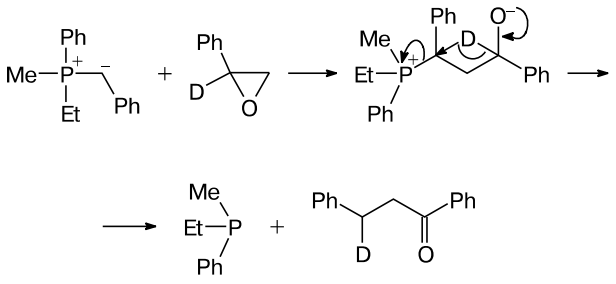
**Scheme 6**



**A**

The conjecture of a possible hydride shift in phosphonium compounds was first made by McEwen *et al.*,[17] who demonstrated that phosphobetaine prepared from (ethyl)-(methyl)(phenyl)phosphine and α-deuterated styrene oxide undergoes intramolecular nucleophilic substitution accompanied by 1,3-hydride shift (Scheme 7).

**Scheme 7**



Therefore, the presence of basic reagents that can generate a negative charge on the N atom of the hydrazine

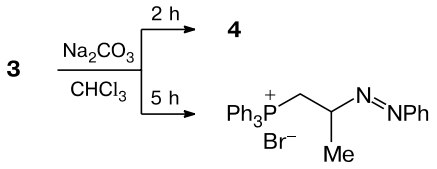
group in hydrazine-containing phosphonium salts could be expected to facilitate dehydrogenation noticeably.

For instance, we found that moderate heating of a suspension of salt **3** in benzene in the presence of $Et_3N$ even in 3 h gives dehydrogenation product **4** in a nearly equal ratio with the starting compound **3** ($^1$H NMR data). However, further heating upon the addition of more $Et_3N$ does not increase the yield of salt **4**; moreover, the fraction of salt **4** in the reaction mixture drops ($^1$H NMR data). At the same time, the $^{31}$P NMR spectrum exhibits a signal characteristic of triphenylphosphine oxide and the $^1$H NMR spectrum shows characteristic signals of triethylamine hydrobromide.

By carrying out a special experiment, we ascertained that $Et_3N \cdot HBr$ and $Ph_3PO$ are produced by an attack of triethylamine on the P atom of salt **4** followed by anionization of the azaallyl group, which is consistent with the literature data[18] (see Scheme 4).

Similar results were obtained in a room-temperature reaction of salt **3** with a slight excess of dry $Na_2CO_3$ in chloroform (Scheme 8). Salt **3** was half-converted into salt **4** in 2 h and this conversion of salt **3** remained the same upon the 5-h stirring of the reaction mixture, while phosphonium salt **4** underwent (conceivably base-catalyzed) isomerization into azo compound **5**.

**Scheme 8**




**5**

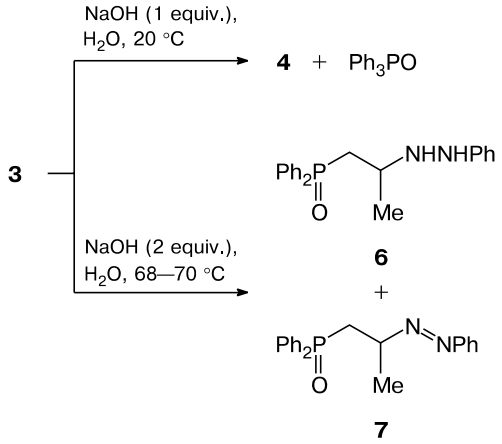
An attempt to increase the yield of salt **4** by a room-temperature reaction of salt **3** with an equimolar amount of MeONa, a stronger base, in methanol for 2 h resulted only in a 14% yield of salt **4**, the other reaction products being $Ph_3PO$ (65%) and acetone phenylhydrazone (60%) as a result of basic reduction of salt **4**.

As expected, the same reaction at 60 °C gave only basic hydrolysis products.

A room-temperature reaction of salt **3** with an equimolar amount of 25% aqueous NaOH afforded the same products: salt **4** (15%) and $Ph_3PO$ (36%). In the same reaction involving a double molar amount of NaOH at 68—70 °C, the dehydrogenation of salt **3** was suppressed. As a result, we obtained (diphenyl)[2-(2-phenylhydrazino)propyl]-phosphine oxide (**6**) and its dehydrogenation product (diphenyl)[2-(2-phenyldiazenyl)propyl]phosphine oxide (**7**) (Scheme 9).

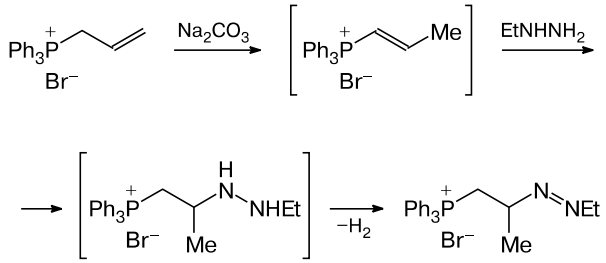
Therefore, an increase in both the reaction temperature and the molar amount of alkali prevents dehydrogenation of salt **3**, simultaneously favoring an attack of the $OH^-$ ions on the P atom. The resulting anionization of the phenyl group leads to tertiary phosphine oxide **6** and its dehydrogenation product **7**.

**Scheme 9**




Moderate heating of (triphenyl)(prop-1-enyl)phosphonium bromide (prepared by prototropic isomerization of (allyl)(triphenyl)phosphonium bromide in the presence of $Na_2CO_3$) with ethylhydrazine in acetonitrile exclusively afforded azo compound **8** *via* dehydrogenation of an ethylhydrazine intermediate (Scheme 10).

**Scheme 10**




**8**

It should be noted that we failed to obtain a dehydrogenation product from [2-(2-*N*,*N*-dimethylhydrazino)-propyl](triphenyl)phosphonium bromide[13] synthesized from (allyl)(triphenyl)phosphonium bromide and *N*,*N*-dimethylhydrazine. A reaction of the dimethylhydrazino phosphonium salt with $Na_2CO_3$ mainly involves 1,2-cleavage leading to (triphenyl)(prop-1-enyl)phosphonium bromide (Scheme 11).

When generalizing our experimental data on spontaneous dehydrogenation of 2-hydrazinoethyl- and 4-hydrazinobut-2-enylphosphonium salts, as well as data on the behavior of salt **3** in basic media, we can conclude that the abstraction of the NH proton is decisive for the reaction. This provides additional evidence for the reaction mechanism we have proposed earlier.

It should be emphasized that hydrazine-containing unsaturated phosphonium salts have been obtained earlier[19] from (triphenyl)(propargyl)phosphonium bromide and various hydrazines, including phenylhydrazine. The corresponding phosphonium salt is thus a prototropic isomer of salt **4**. However, we detected no traces of this isomer among the reaction products.

## Experimental

(Allyl)(triphenyl)phosphonium bromide and 1,4-bis(triphenylphosphonio)but-2-ene dichloride were prepared according to known procedures.[20,21] All reactions were carried out under dry nitrogen in a 50-mL three-necked flask equipped with a magnetic stirring bar, a reflux condenser, and a gas inlet tube. $^1$H and $^{31}$P NMR spectra were recorded on a Mercury-300 Varian spectrometer (300.077 ($^1$H) and 121.47 MHz ($^{31}$P)) at 303 K in DMSO-$d_6$. Chemical shifts are referenced to $Me_4Si$ ($^1$H) and 85% $H_3PO_4$ ($^{31}$P) as the internal standards.

**[4-(*N*,*N*-Dimethylhydrazono)but-2-enyl](triphenyl)phosphonium chloride (2).** A solution of *N*,*N*-dimethylhydrazine (0.4 g, 7 mmol) in anhydrous acetonitrile (5 mL) was added to a suspension of 1,4-bis(triphenylphosphonio)but-2-ene dichloride (1.6 g, 2.5 mmol) in anhydrous acetonitrile (20 mL). The reaction mixture was heated at 50—51 °C for 5 h and concentrated. The products were extracted with water and chloroform. The organic extract was dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was washed with benzene and anhydrous diethyl ether and dried *in vacuo*. The yield of salt **2** was 0.42 g (40%). Found (%): C, 69.24; H, 8.44; Cl, 9.13; N, 6.33; P, 7.01. $C_{24}H_{36}ClN_2P$. Calculated (%): C, 68.82; H, 8.60; Cl, 8.48; N, 6.69; P, 7.41. $^1$H NMR, δ: 1.80 (s, 6 H, $NMe_2$); 4.80 (dd, 2 H, $P^+CH_2$, $^2J_{P,H}$ = 16.8 Hz, $^3J_{H,H}$ = 7.5 Hz); 5.45 (dtd, 1 H, $CH_2C\underline{H}$, $^3J_{H,H}$ = 15.4 Hz, $^3J_{H,H}$ = 7.5 Hz, $^3J_{P,H}$ = 6.6 Hz); 6.39 (ddd, 1 H, $CH_2CH{=}C\underline{H}$, $^3J_{H,H}$ = 15.4 Hz, $^3J_{H,H}$ = 9.1 Hz, $^4J_{P,H}$ = 5.2 Hz); 6.82 (d, 1 H, N=CH, $^3J_{H,H}$ = 9.1 Hz); 7.55—7.90 (m, 15 H, $P^+Ph_3$). $^{31}$P NMR, δ: 26.18 (s).

Triphenylphosphine oxide (0.35 g, 50%), m.p. 156 °C, was isolated from the benzene extract.

**(Triphenyl)[2-(2-phenylhydrazino)propyl]phosphonium bromide (3).** A solution of phenylhydrazine (1.4 g, 13 mmol) in anhydrous acetonitrile (5 mL) was added to a suspension of (allyl)(triphenyl)phosphonium bromide (5 g, 13 mmol) in anhydrous acetonitrile (15 mL). The reaction mixture was heated at 77—78 °C for 8 h. The precipitate that formed was filtered off, washed with anhydrous diethyl ether, and dried *in vacuo*. The yield of salt **3** was 4.9 g (77%), light yellow crystals, m.p. 232—234 °C. Found (%): C, 66.02; H, 5.52; Br, 16.04; N, 5.41; P, 6.49. $C_{27}H_{28}BrN_2P$. Calculated (%): C, 65.99; H, 5.70; Br, 16.29; N, 5.70; P, 6.31. $^1$H NMR, δ: 1.21 (d, 3 H, Me, $^3J_{H,H}$ = = 6.3 Hz); 3.25 (dqt, 1 H, C$\underline{H}$(Me)N, $^3J_{H,H}$ = 6.3 Hz, $^3J_{H,H}$ = 6.2 Hz, $^3J_{P,H}$ = 9.5 Hz); 3.46 (ddd, 1 H, $P^+C(H_a)H_b$, $^2J_{H,H}$ = 15.6 Hz, $^2J_{P,H}$ = 11.6 Hz, $^3J_{H,H}$ = 6.2 Hz); 4.20 (ddd, 1 H, $P^+CH_a(H_b)$, $^2J_{H,H}$ = 15.6 Hz, $^2J_{P,H}$ = 13.5 Hz, $^3J_{H,H}$ = = 6.2 Hz); 4.40 (d, 1 H, N$\underline{H}$NHPh, $^2J_{H,H}$ = 7.2 Hz); 6.60—7.10 (m, 5 H, NPh); 7.55—7.90 (m, 15 H, $P^+Ph_3$). $^{31}$P NMR, δ: 27.8 (s).

**(Triphenyl)[2-(phenylhydrazono)propyl]phosphonium bromide (4).** A solution of salt **3** (1 g, 2 mmol) in chloroform (15 mL) was heated at 60 °C for 6 h. The solvent was removed and the residue was washed with anhydrous diethyl ether and dried *in vacuo*. The yield of salt **4** was 0.9 g (92%), yellow crystals, m.p. 217—218 °C. Found (%): C, 66.10; H, 5.54; Br, 16.00; N, 5.82; P, 6.21. $C_{27}H_{26}BrN_2P$. Calculated (%): C, 66.26; H, 5.32; Br, 16.36; N, 5.73; P, 6.34. $^1$H NMR, δ: 2.00 (s, 3 H, Me); 5.15 (d, 2 H, $P^+CH_2$, $^2J_{P,H}$ = 13.56 Hz); 6.25 (d, 2 H, $H(2)_{Ph}$, $H(6)_{Ph}$, $^3J_{H,H}$ = 11.11 Hz); 6.60 (t, 1 H, $H(4)_{Ph}$); 6.90 (t, 2 H, $H(3)_{Ph}$, $H(5)_{Ph}$); 7.55—8.00 (m, 15 H, $P^+Ph_3$); 8.95 (s, 1 H, NHPh). $^{31}$P NMR, δ: 27.3 (s).

**Reaction of salt 3 with triethylamine.** ***A.*** A mixture of salt **3** (1 g, 2 mmol) and triethylamine (0.2 g, 2 mmol) in anhydrous benzene (15 mL) was heated at 70—75 °C for 3 h. The solvent was removed and the products were extracted with water and chloroform. The organic extract was dried with $MgSO_4$, filtered, and concentrated. The residue was washed with anhydrous diethyl ether and dried *in vacuo*. The yield of a mixture of salts **3** and **4** was 0.9 g (**3** : **4** = ~53 : 47, $^1$H NMR data).

***B.*** A 53 : 47 mixture of salts **3** and **4** (0.9 g, see above) and triethylamine (0.2 g, 2 mmol) were suspended in anhydrous benzene (15 mL). The resulting suspension was heated at 70—75 °C for 9 h. The precipitate that formed was filtered off and the products were extracted with water and chloroform. Triethylamine hydrobromide was isolated from the aqueous extract. Yield 0.07 g, m.p. 246—248 °C (decomp.). The organic extract was dried with $MgSO_4$, filtered, and concentrated. The residue was washed with anhydrous diethyl ether and dried *in vacuo*. The yield of a mixture of salts **3** and **4** was 0.65 g (**3** : **4** = ~77 : 23, $^1$H NMR data). The benzene filtrate was concentrated and fractional recrystallization of the residue from AcOEt—$Pr^iOH$ gave triphenylphosphine oxide (0.1 g; m.p. 156 °C) and acetone phenylhydrazone (0.07 g; m.p. 42 °C).

**Reaction of salt 4 with triethylamine.** A mixture of salt **4** (0.5 g, 1 mmol) and triethylamine (0.2 g, 2 mmol) in anhydrous benzene (10 mL) was heated at 70 °C for 6 h. The precipitate that formed was filtered off and the products were extracted with water and chloroform. Triethylamine hydrobromide was isolated from the aqueous extract. Yield 0.1 g, m.p. 246—248 °C (decomp.). The organic extract was dried with $MgSO_4$, filtered, and concentrated. The residue was washed with anhydrous diethyl ether and dried *in vacuo*. Salt **4** (0.2 g, 40%) was recovered, m.p. 217—218 °C; the $^1$H and $^{31}$P NMR spectra are identical with those of an authentic sample. The benzene filtrate was concentrated and fractional recrystallization of the residue from AcOEt—$Pr^iOH$ gave triphenylphosphine oxide (0.1 g; m.p. 156 °C) and acetone phenylhydrazone (0.05 g; m.p. 42 °C).

**Reaction of salt 3 with sodium carbonate.** ***A.*** A mixture of salt **3** (1 g, 2 mmol) and anhydrous $Na_2CO_3$ (0.25 g, 2.35 mmol) in chloroform (15 mL) was stirred at room temperature for 2 h. The reaction mixture was filtered and concentrated. The residue was washed with anhydrous diethyl ether. The yield of a mixture of salts **3** and **4** was 0.95 g (**3** : **4** = ~50 : 50, $^1$H NMR data).

***B.*** The synthesis was performed as described under entry ***A*** with the exception that the mixture was stirred for 5 h. The reaction gave a mixture of salts **3** and **5** (0.98 g, **3** : **5** = ~44 : 56, $^1$H NMR data).

**(Triphenyl)[2-(2-phenyldiazenyl)propyl]phosphonium bromide (5).** $^1$H NMR, δ: 1.50 (dd, 3 H, Me, $^3J_{H,H}$ = 6.4 Hz, $^4J_{P,H}$ = 2.3 Hz); 4.20—4.35 (m, 1 H, C$\underline{H}$(Me)N=NPh); 4.40—4.65 (m, 2 H, $P^+CH_2$); 7.20—7.40 (m, 5 H, NPh); 7.60—7.80 (m, 15 H, $P^+Ph_3$). $^{31}$P NMR, δ: 28.3 (s).

**Reaction of salt 3 with sodium methoxide.** ***A.*** A solution of salt **3** (1 g, 2 mmol) in methanol (10 mL) was added to a solution

of MeONa (0.1 g, 1.85 mmol) in methanol (10 mL). The reaction mixture was stirred at room temperature for 2 h. The solvent was removed, the products were extracted with water and chloroform, and the chloroform extract was concentrated. Fractional recrystallization of the residue from AcOEt—Pr$^i$OH gave salt **3** (0.14 g, 14%), triphenylphosphine oxide (0.36 g, 65%; m.p. 156 °C), and acetone phenylhydrazone (0.18 g, 60%; m.p. 42 °C). The $^1$H and $^{31}$P NMR spectra of salt **3** are identical with those of the sample obtained from (allyl)(triphenyl)phosphonium bromide and phenylhydrazine.

***B.*** A reaction of salt **3** (1 g, 2 mmol) with MeONa (0.1 g, 1.85 mmol) at 58—60 °C followed by the workup described above yielded triphenylphosphine oxide (0.5 g, 90%; m.p. 156 °C) and acetone phenylhydrazone (0.25 g, 84%; m.p. 42 °C).

**Reaction of salt 3 with aqueous NaOH.** ***A.*** A mixture of salt **3** (1 g, 2 mmol) and 25% aqueous NaOH (0.32 g) in benzene (15 mL) was stirred at room temperature for 4 h. The organic layer was separated and the residue was diluted with water and chloroform. Triphenylphosphine oxide was isolated from the organic (benzene) layer. Yield 0.2 g (36%), m.p. 156 °C. The chloroform extract was dried with $MgSO_4$, filtered, and concentrated. The residue was washed with anhydrous diethyl ether and dried *in vacuo*. Fractional recrystallization of the residue from AcOEt—Pr$^i$OH gave salt **4** (0.15 g, 15%), acetone phenylhydrazone (0.09 g, 30%; m.p. 42 °C), and the starting salt **3** (0.35 g).

***B.*** A mixture of salt **3** (1 g, 2 mmol) and 25% aqueous NaOH (0.6 g) in benzene (15 mL) was stirred at 68—70 °C for 4 h. The organic layer was separated, dried with $MgSO_4$, filtered, and concentrated. The residue was dissolved in anhydrous diethyl ether. The undissolved substance was dried *in vacuo* to give phosphine oxide **6** (0.1 g, 14%). $^1$H NMR, δ: 1.21 (dd, 3 H, Me, $^3J_{H,H}$ = 6.4 Hz, $^4J_{H,H}$ = 1.0 Hz); 2.29 (ddd, 1 H, $P^+C(H_a)H_b$, $^2J_{H,H}$ = 15.2 Hz, $^2J_{P,H}$ = 9.1 Hz, $^3J_{H,H}$ = 5.0 Hz); 2.67 (ddd, 1 H, $P^+CH_a(H_b)$, $^2J_{H,H}$ = 15.2 Hz, $^2J_{P,H}$ = 12.2 Hz, $^3J_{H,H}$ = = 7.7 Hz); 3.36 (m, 1 H, CH); 5.51 (br, 1 H, NH); 6.68 (tt, 1 H, $H(4)_{Ph}$); 6.79 (m, 2 H, $H(2)_{Ph}$, $H(6)_{Ph}$); 7.10 (m, 2 H, $H(3)_{Ph}$, $H(5)_{Ph}$); 7.69—7.80 (m, 10 H, $PPh_2$). $^{31}$P NMR, δ: 36.02 (s).

The ethereal extract was concentrated and dried *in vacuo* to give phosphine oxide **7** (0.3 g, 43%). $^1$H NMR, δ: 1.48 (d, 3 H, Me, $^3J_{H,H}$ = 6.6 Hz); 2.65 (ddd, 1 H, $P^+C(H_a)H_b$, $^2J_{H,H}$ = 15.0 Hz, $^2J_{P,H}$ = 13.3 Hz, $^3J_{H,H}$ = 7.3 Hz); 3.01 (ddd, 1 H, $P^+CH_a(H_b)$, $^2J_{H,H}$ = 15.0 Hz, $^2J_{P,H}$ = 9.0 Hz, $^3J_{H,H}$ = 5.6 Hz); 4.40 (m, 1 H, CH); 7.34—7.52 (m, 5 H, NPh); 7.34—7.52 (m, 10 H, $PPh_2$). $^{31}$P NMR, δ: 34.02 (s).

The product from the aqueous layer was extracted with chloroform. The organic extract was dried with $MgSO_4$, filtered, and concentrated. The residue was washed with anhydrous diethyl ether and dried *in vacuo* to give the starting salt **3** (0.4 g).

**[2-(2-Ethyldiazenyl)propyl](triphenyl)phosphonium bromide (8).** A mixture of (allyl)(triphenyl)phosphonium bromide (1 g, 2.6 mmol) and dry $Na_2CO_3$ (0.55 g, 5.2 mmol) in anhydrous acetonitrile (15 mL) was stirred at room temperature for 2 h. The reaction mixture was filtered and ethylhydrazine (0.16 g, 2.7 mmol) was added. The resulting mixture was heated at 45—50 °C for 4 h. The solvent was removed *in vacuo*. The residue was recrystallized from AcOEt—Pr$^i$OH. The yield of salt **8** was 0.9 g (78%). Found (%): C, 62.24; H, 5.53; Br, 18.52; N, 6.21; P, 7.42. $C_{23}H_{26}BrN_2P$. Calculated (%): C, 62.59; H, 5.89; Br, 18.14; N, 6.35; P, 7.03. $^1$H NMR, δ: 1.19 (t, 3 H, $CH_2C\underline{H}_3$, $^3J_{H,H}$ = 7.1 Hz); 1.40 (dd, 3 H, Me, $^3J_{H,H}$ = 6.4 Hz, $^4J_{P,H}$ = 2.3 Hz); 3.30 (q, 2 H, $C\underline{H}_2Me$, $^3J_{H,H}$ = 7.1 Hz); 3.95—4.15 (m, 1 H, $C\underline{H}$(Me)N=NEt); 4.20—4.45 (m, 2 H, $P^+CH_2$); 7.60—7.80 (m, 15 H, $P^+Ph_3$). $^{31}$P NMR, δ: 28.32 (s).

**Reaction of [2-(2-*N*,*N*-dimethylhydrazino)propyl](triphenyl)-phosphonium bromide with $Na_2CO_3$.** A mixture of [2-(2-*N*,*N*-dimethylhydrazino)propyl](triphenyl)phosphonium bromide (1.2 g, 2.7 mmol) and dry $Na_2CO_3$ (0.3 g, 2.8 mmol) in chloroform (15 mL) was stirred at room temperature for 5 h. The reaction mixture was filtered and concentrated. The residue was washed with anhydrous diethyl ether and dried *in vacuo* to give (triphenyl)(prop-1-enyl)phosphonium bromide[20] (1 g, 97%), m.p. 213—214 °C. The $^1$H and $^{31}$P NMR spectra are identical with those of an authentic sample.

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