cipitate 0.4 g (56.5%) of white crystals. Even after numerous attempts at recrystallization, an analytical sample could not be obtained. The best sample we could obtain had mp 210–212°; ir (KBr) 3250 (NH), 2650, 2900 (amine salt); nmr (DMSO-d_6) δ 4.50 [d, 1, $-CH(C_6H_5)-$, J = 8.0 Hz], 5.43 [d, 1, $-CH(C_6H_5)$-Br], 7.10 (s, 1, proton at C-4), 7.10–8.00 (m, 15, phenyl protons), 9.6 ppm (s, 2, NH, exchangeable with D_2O, chemical shift depends on concentration).

3-(α,β-Diphenyl-β-methoxyethyl)-5-phenylpyrazole Hydrobromide (28).—Reagent grade methanol (5 ml) was added to a boiling solution of 0.4 g (0.83 mmol) of **27** dissolved in 10 ml of CH_2Cl_2. The clear solution was concentrated while adding hexane to precipitate 0.35 g (98%) of **28**. Recrystallization from methanol–hexane gave an analytical sample: mp 150–153°; ir (KBr) 3200 (NH), 2700 (amine salt), 1070 (CO), 750, 705, 695 cm^{-1} (phenyl); nmr (DMSO-d_6) δ 3.35 (s, 3, $-OCH_3$), 4.61 [d, 1, $-CH(C_6H_5)-$, J = 6.5 Hz], 5.58 [d, 1, $-CH(C_6H_5)O-$), 6.99 (s, 1, proton at C-4), 7.08–7.66 (m, 13, meta and para protons of phenyl ring at C-5, protons of phenyl ring at side chain), 7.66–8.00 (m, 2, ortho protons of phenyl ring at C-5), 9.00 ppm (s, 2, NH, exchangeable with D_2O and chemical shift depends on concentration).

Anal. Calcd for $C_{24}H_{23}BrN_2O$: N, 6.43. Found: N, 6.29.

3-(α,β-Diphenyl-β-ethoxyethyl)-5-phenylpyrazole hydrobromide (29) was prepared in the same manner as described above but using reagent grade ethanol instead of methanol. A 0.36-g (94%) sample of **29** was obtained. Recrystallization from ethanol–hexane gave an analytically pure sample: mp 154–156°; ir (KBr) 3200 (NH), 2700 (amine salt), 1630 (C=N, phenyl), 1040 (CO), 1005 ($-CH_2CH_3$), 745, 700 cm^{-1} (phenyl); nmr (DMSO-d_6 + $CDCl_3$) δ 1.18 (t, 3, $-CH_3$, J = 6.0 Hz), 3.62 (q, 2, $-OCH_2-$), 4.60 [d, 1, $-CH(C_6H_5)-$, J = 6.2 Hz], 5.57 [d, 1, $-CH(C_6H_5)O-$], 6.92 (s, 1, proton at C-4), 7.00–7.58 (m, 13, meta and para protons of phenyl ring at C-5 and phenyl protons at side chain), 7.58–8.00 (m, 2, ortho protons of phenyl ring at C-4), 8.33 ppm (s, 2, NH, exchangeable with D_2O and chemical shift depends on concentration).

Anal. Calcd for $C_{25}H_{25}NrN_2O$: N, 6.23. Found: N, 6.25.

3-Benzilidene-5,5-diphenyl-1-pyrazoline (20) was prepared by following method C using 13.8 g (0.025 mol) of **3e**, 200 ml of ethanol, 2.75 g (0.026 mol) of benzaldehyde, and 0.57 g (0.025 g-atom) of sodium. The reaction mixture was allowed to stir 15 hr. The resultant mixture was concentrated to 50 ml, poured into water (100 ml), and extracted with ether (300 ml). The dried $Mg(SO_4)$ ether extract furnished a pale yellow, oily liquid on concentration. To the oily liquid was added methanol (20 ml) and water (5 ml), and the mixture was allowed to stand in a refrigerator overnight. Needlelike crystals (6 g, 78%) were obtained. Recrystallization from ether–methanol gave an analytically pure sample of **20**: mp 123–124°; ir (KBr) 1575 (-N=N-), 1100 (CN, vinyl), 780–700 cm^{-1} (phenyl); uv (MeOH) λ_{max} 212 mμ (ϵ 21,800), 316 (19,400); nmr ($CDCl_3$) δ 3.23 (d, 2, $-CH_2-$, J = 2.5 Hz), 7.00–7.55 (m, 15, phenyl protons), 7.64 ppm (t, 1, benzilidene proton).

Anal. Calcd for $C_{21}H_{18}N_2$: C, 84.80; H, 6.15. Found: C, 84.78; H, 5.98.

From the mother liquor, 5,5-diphenyl-2-pyrazoline (**19e**) was identified in trace amount by nmr spectrum. By method A **24** was also prepared in 65% yield.

1,1,4,4-Tetraphenyl-1,3-butadiene.—The reaction was carried out by method A using 50 ml of ethanol, 0.23 g (0.01 g-atom) of sodium, 5.4 g (0.01 mol) of **13e** and 1.8 g (0.01 mol) of benzophenone in the course of 7 hr. The resultant reaction mixture was diluted with 10 ml of water and cooled in a refrigerator overnight. Collected was 2.2 g (61.5%) of white crystals of the product: mp 195–196°; ir (KBr) 2950 (CH), 910 (vinyl), 765, 703 cm^{-1} (phenyl). The nmr spectrum was identical with that reported in the literature.[37]

Registry No.—**3a**, 32251-61-9; **3a** tetraphenylborate, 32237-61-9; **3b**, 32251-62-0; **3c**, 32251-63-1; **3d**, 32251-64-2; **3e**, 32251-65-3; **6**, 32251-66-4; **7**, 32251-67-5; **13c**, 1530-34-3; **13d**, 7310-74-9; **13e**, 25201-67-6; **14a**, 27981-65-3; **14b**, 32251-72-2; **15a**, 32251-73-3; **15b**, 32251-74-4; **15c**, 32251-75-5; **16a**, 32251-76-6; **16b**, 32251-77-7; **16c**, 32251-78-8; **18**, 32251-79-9; **19e**, 25201-66-5; **20**, 25201-65-4; **24a(a′)**, 32251-82-4; **24a(a′)** picrate, 32251-83-5; **24b(b′)**, 32251-84-6; **24b(b′)** picrate, 32251-85-7; **24d(d′)**, 21917-99-7; **26d(d′)**, 32251-87-9; **26d(d′)** picrate, 32304-10-2; **27**, 32251-88-0; **28**, 32251-89-1; **29**, 32251-90-4; 3(5)-phenylpyrazole picrate, 6456-07-1; 1,1,4,4-tetraphenyl-1,3-butadiene, 1450-63-1.

Acknowledgment.—This work was supported by a U. S. Public Health Service Grant (CA 11000) for which we are most grateful.

Reactions of Phosphorus Compounds.[1,2] 30. Preparation and Basic Hydrolysis of 1-(β-Triphenylphosphonioethyl)-2-pyrazolin-3-yltriphenylphosphonium Dibromides

EDWARD E. SCHWEIZER* AND CHOONG S. KIM

Department of Chemistry, University of Delaware, Newark, Delaware 19711

Received May 24, 1971

Unsubstituted or 5-substituted 1-(β-triphenylphosphonioethyl)-2-pyrazolin-3-yltriphenylphosphonium dibromides were prepared by the phosphonioethylation reaction of vinyltriphenylphosphonium bromide and unsubstituted or 5-substituted 2-pyrazolinyltriphenylphosphonium bromides. Their basic hydrolysis was investigated and unusual phenyl migration and N–N bond cleavage were observed on the hydrolysis of phosphonium moiety attached at C-3.

During investigations of the preparations and reactions of pyrazolinyltriphenylphosphonium salts,[2] we found that vinyltriphenylphosphonium bromide easily undergoes Michael-type additions[3] (phosphonioethylation) with 2-pyrazolinyltriphenylphosphonium salts. In the preparation of pyrazolinyltriphenylphosphonium salts, when diazoalkanes were added slowly (not in excess) to vinyltriphenylphosphonium bromide, the phosphonioethylated salts were observed as contaminants. On the other hand, the phosphonioethylated salts, **3a–d** were prepared (>95% yield) by treatment of equal molar amounts of vinyltriphenylphosphonium bromide (**1**) and 2-pyrazolin-3-yltriphenylphosphonium bromides (**2a–d**) in the presence of a catalytic amount of base (potassium *tert*-butoxide) (Scheme I).

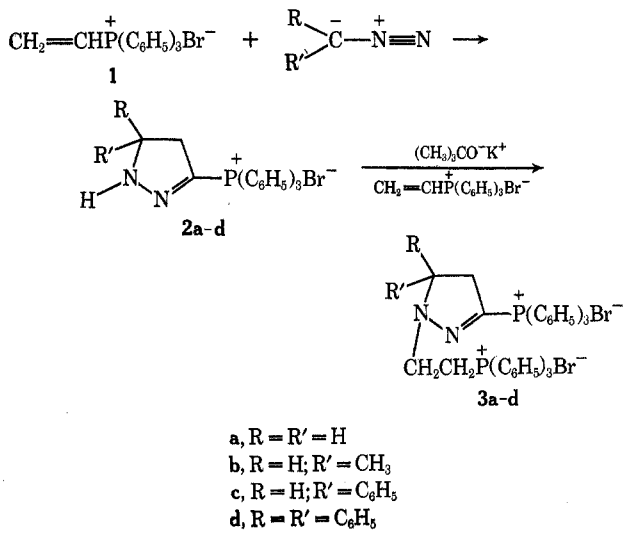
The phosphonioethylation reactions of 5-substituted salts of **2a** necessitated more vigorous reaction conditions in order to achieve comparable yields to that of the unsubstituted salt. This sluggishness is postulated as being due to the steric hindrance of substituents next to the reaction site.

(1) Part 28: E. E. Schweizer, T. Minami, and D. M. Crouse, *J. Org. Chem.*, **36**, 4028 (1971).

(2) Part 29: E. E. Schweizer and C. S. Kim, *ibid.*, **36**, 4033 (1971).

(3) E. E. Schweizer and R. D. Bach, *ibid.*, **29**, 1746 (1964).

SCHEME I



a, R = R′ = H
b, R = H; R′ = CH_3
c, R = H; R′ = C_6H_5
d, R = R′ = C_6H_5

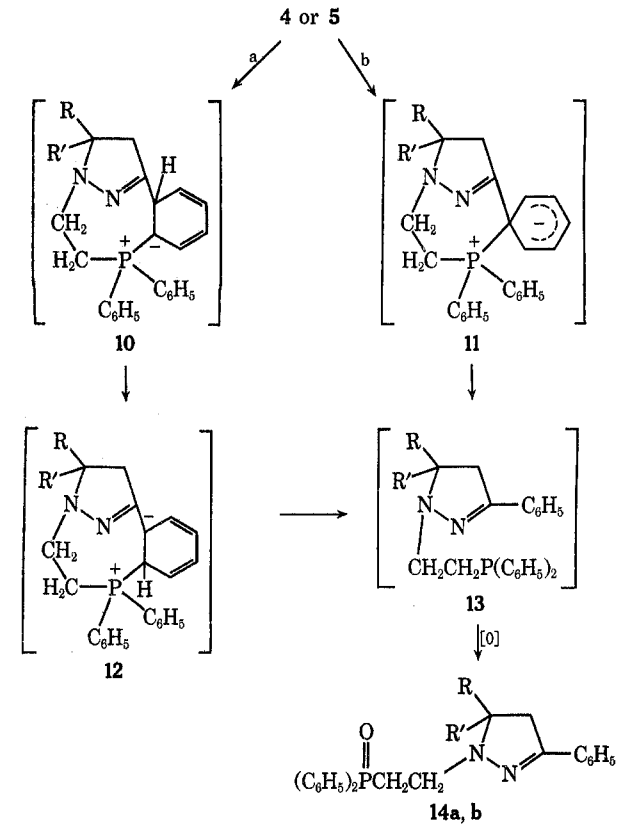
In the nmr spectrum the chemical shifts for protons at C-4, C-5, and the ethyl group attached to nitrogen could not be assigned individually, except for the single proton at C-5 in **3d**.

The basic hydrolysis of **3a–d** gave a series of unique products whose relative abundance could be varied by changing the acidity of the solvent used (Scheme II).

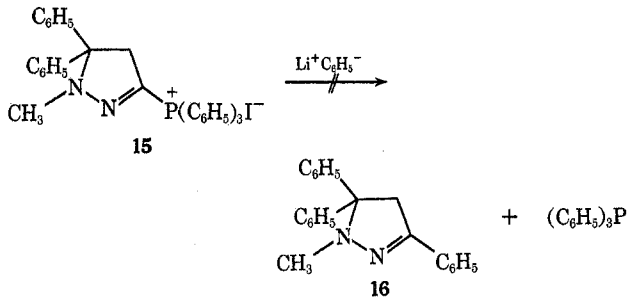
Hydrolysis in anhydrous methanolic sodium hydroxide gave relatively greater amounts of phenyl migrated product **14** (60%) over protonated compound **7** (40%). Hydrolysis in aqueous sodium hydroxide gave **14** (40%) and **7** (60%). If the carbanion **5** is assumed to be an intermediate during the hydrolysis reaction, the carbanion **5** will be protonated less readily in methanol than in the more acidic aqueous medium, as shown by the above ratio. The carbanion **5** attacks the phenyl moiety (attached to the phosphorus atom at the β-ethyl position) more readily in methanol (where it is longer lived) than in water. We have, however, no data which would allow us to say that the free carbanion **5** is indeed an intermediate in this reaction or that a concerted reaction, similar to that postulated by Trippett,[4] takes place. Similarly, the yield of **9** was also increased on hydrolysis of **3d** in methanol (47%) in comparison to the yield of **9** observed in water (<10%).

The phosphorus atom attached to C-3 was expected to be more electrophilic than the phosphonium group attached at the β-ethyl position. This expectation was borne out by the fact that at no time could it be shown that basic hydrolysis would form a diphenylphosphine oxide moiety at the β-ethyl position prior to the cleavage of the phosphonium moiety attached at C-3. The phosphonium salts, **8b** and **6c**, were, however, isolated, thus clearly showing precedence of hydrolysis. This difference is attributed to the greater electrophilicity imparted by the –N=C< group attached to the former (C-3) phosphonium moiety in contrast to the $-CH_2CH_2-$ group attached to the latter (β-ethyl).

The phenyl migration in this system is quite unusual, comparable only to 1,2-phenyl migrations reported by earlier workers.[5,6] The migrated (to C-3) phenyl moiety is one of the phenyl substituents attached to the phosphorus atom at the β-ethyl position. The two migrating pathways (a and b) are possible from the



intermediate **4** or the free carbanion **5** described in Scheme II. Attempts to isolate the assumed intermediate **13** were fruitless. This intermediate was presumably easily oxidized to give **14** under the hydrolysis condition, similar to the oxidation of ethyldiphenylphosphine.[7] The possibility of the nucleophilic attack (SN2) on C-3 by the phenyl anion formed by the hydrolysis of the phosphonium moiety attached to the β-ethyl position was ruled out by two facts: (a) no triphenylphosphine was observed; (b) 1-methyl-5,5-diphenyl-2-pyrazolin-3-yltriphenylphosphonium iodide (**15**) did not give the phenyl-substituted compound (**16**) at C-3, when it was allowed to react with phenyllithium. No reaction is observed.



The phenyl migrated structure, **14** (where R = R′ = H), was characterized by its comparison with an authentic sample prepared by aqueous basic hydrolysis of

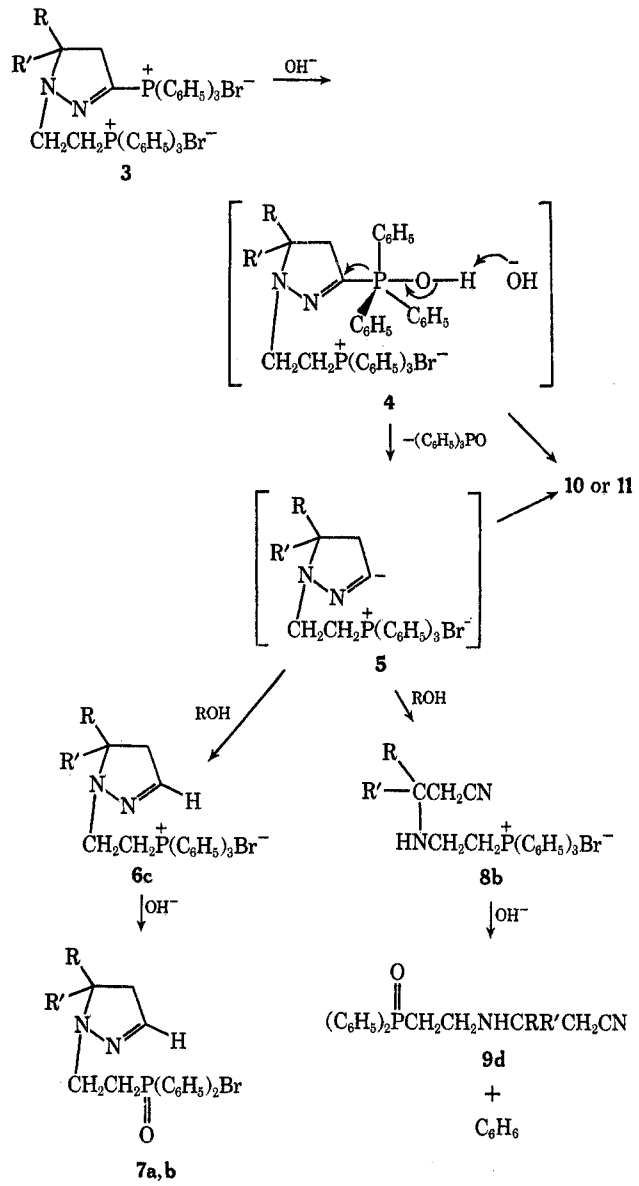
(4) J. R. Corfield and S. Trippett, *Chem. Commun.*, 1267 (1970).

(5) J. J. Brophy, K. L. Freeman, and M. J. Gallagher, *J. Chem. Soc.*, 2260 (1968).

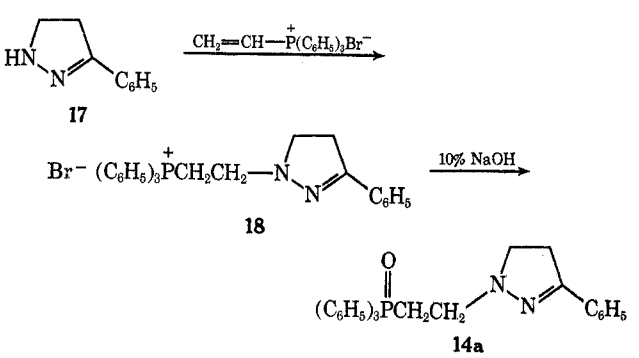
(6) E. Zbiral and L. Werner, *Justus Liebigs Ann. Chem.*, **707**, 130 (1967).

(7) von A. Michaelis and A. Link, *ibid.*, **207**, 214 (1881).

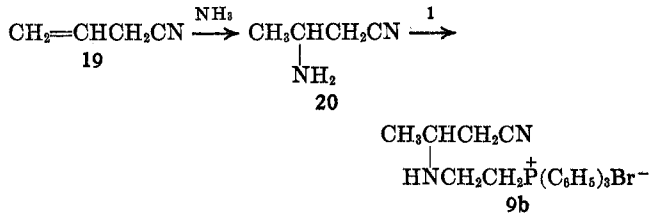
SCHEME II



3-phenyl-2-pyrazolin-1-ylethyltriphenylphosphonium bromide (**18**), which was synthesized from 3-phenyl-2-pyrazoline (**17**) and **1**.



The formation of nitrile compounds by N–N bond cleavage of 3-unsubstituted 2-pyrazolines under basic conditions was reported in the literature.[8-10] This cleavage during basic hydrolysis of **3** may be considered to take place *via* intermediate **4** or **5** by β elimination. Kost[10] reported that 3-alkyl substituted 2-pyrazoline did not give any N–N bond cleavage product (nitrile compound) under conditions which gave nitrile products from the 3-H species. The alkyl substituent at C-3 obviously blocked the formation of the anion at C-3. The structure of **9b** was shown to be identical with that of an authentic sample prepared by the phosphonioethylation of **1** and 2-aminobutyronitrile (**20**), which was synthesized by the ammonolysis of allyl cyanide (**19**).



Experimental Section

Infrared spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer or a Perkin-Elmer Model 421 grating spectrophotometer, and nmr spectra were obtained on a Varian A-60A spectrometer using tetramethylsilane as internal standard. All melting points were uncorrected and obtained on a Thomas–Hoover capillary melting point apparatus. Elemental analyses are by M. H. W. Laboratories, Garden City, Mich., and Micro-Analysis Inc., Wilmington, Del.

Any analytical and spectral data not included in the text may be found in the tables. All reactions were run under dry nitrogen except for aqueous reactions, and solvents used were anhydrous.

Preparation of Phosphonioethylated Salts. General Method A.—A catalytic amount of potassium *tert*-butoxide was added to a mixture of the salt (0.01 mol) and vinyltriphenylphosphonium bromide (3.7 g, 0.01 mol) in acetonitrile (50 ml) and allowed to stir at room temperature for 6 hr. To the resultant reaction mixture was added EtOAc (100 ml) slowly to precipitate the phosphonioethylated salt. An analytically pure sample was obtained by recrystallization from CH_2Cl_2–EtOAc.

General Method B.—The reaction was carried out in the same manner as method A using 0.03 mol of the starting materials, and refluxed for 12 hr. The reaction mixture was worked up by the general procedure of method A.

1-(β-Triphenylphosphonioethyl)-2-pyrazolin-3-yltriphenylphosphonium dibromide (3a) was prepared by method A in 95% yield: mp 251–253°; ir (KBr) 1570 (C=N, phenyl), 1340 (-CH_2-), 1115, 1100 (CP), 730, 695 cm^{-1} (phenyl); nmr ($CDCl_3$) δ 2.85–3.35 (m, 2, protons at C-4), 3.75–4.68 (m, 6, protons at C-5 and ethyl group), 7.45–8.19 (m, 30, phenyl protons).

Anal. Calcd for $C_{41}H_{38}Br_2N_2P_2$: C, 63.09; H, 4.89; P, 7.93. Found: C, 63.11; H, 4.90; P, 8.06.

5-Methyl-1-(β-triphenylphosphonioethyl)-2-pyrazolin-3-yltriphenylphosphonium Dibromide (3b).—The salt prepared by method A in quantitative yield had mp 251–252°: ir (KBr) 1590 (C=N, phenyl), 1150, 1100 (CP), 725, 690 cm^{-1} (phenyl); nmr ($CDCl_3$) δ 1.32 (d, 2, -CH_3, J = 6.0 Hz), 2.35–5.15 (m, 7, protons at C-4, C-5, and ethyl group), 7.40–8.20 (m, 30 phenyl protons).

Anal. Calcd for $C_{42}H_{40}Br_2N_2P_2$: P, 7.79. Found: P, 7.72.

5-Phenyl-1-(β-triphenylphosphonioethyl)-2-pyrazolin-3-yltriphenylphosphonium Dibromide (3c).—The salt prepared by method B (94%) had mp 262–264° dec: ir (KBr) 3000 (CH), 1580 (C=N, phenyl), 1440 (-CH_2), 1115–1105 (CP), 730, 695 cm^{-1} (phenyl); nmr ($CDCl_3$) δ 2.50–5.25 (m, 6, protons at C-4 and ethyl group), 6.19 (d, d, 1, protons at C-5, J_{cis} = 13, J_{trans} = 12 Hz), 7.25–8.20 (m, 35, phenyl protons).

Anal. Calcd for $C_{47}H_{42}Br_2N_2P_2$: C, 65.89; H, 4.94; N, 3.27. Found: C, 65.92; H, 5.01; N, 3.18.

5,5-Diphenyl-1-(β-triphenylphosphonioethyl)-2-pyrazolin-3-yltriphenylphosphonium dibromide (3d) was prepared by method B in 94% yield. Recrystallized salt by the general method had mp 182–185°: ir (KBr) 1580 (C=N, phenyl), 1340 (-CH_2-), 1115–

(8) N. Rabjohn, H. R. Havens, and J. L. Rutter, *J. Heterocycl. Chem.*, **3**, 413 (1966).

(9) J. J. Grandberg and A. V. Potanova, *Zh. Obshch. Khim.*, **32**, 651 (1962).

(10) A. N. Kost, *et al.*, *Dokl Akad. Nauk SSSR*, **144**, 359 (1962).

1105 (CP), 727, 695 cm^{-1} (phenyl); nmr ($CDCl_3$) δ 3.50–4.30 (broad s, 6, protons at C-4 and ethyl group), 7.45 (s, 10, phenyl protons at C-5), 7.50–8.20 (m, 30, protons attached to phenyl on phosphorus atoms).

Anal. Calcd for $C_{53}H_{46}Br_2N_2P_2$: C, 68.24; H, 4.97; P, 6.53. Found: C, 68.07; H, 5.11; P, 6.34.

Basic Hydrolysis of 3a–d. General Method A.—A sample of the salt (0.01 mol) was allowed to stir with 10% aqueous sodium hydroxide (100 ml) at 60° for 2 hr. The resultant heterogeneous solution was diluted with water to double its volume and extracted with EtOAc–ether (3:1) mixed solvent (300 ml). The dried ($MgSO_4$) extract was concentrated to obtain a white solid which was chromatographed (silica gel–EtOAc) to give compounds **7**, **14**, and ring-opened products.

General Method B.—A mixture of the salt (0.01 mol) and NaOH (1.2 g, 0.03 mol) in methanol (100 ml) was allowed to reflux for 1 day. The cooled reaction mixture was poured into water (200 ml) and extracted with EtOAc–ether (3:1) mixed solvent (300 ml). The dried ($MgSO_4$) extract was worked up by the same procedure as the above.

β-(2-Pyrazolin-1-yl)ethyldiphenylphosphine oxide (7a) was prepared by method A (25% yield) or by method B (16%): mp 114–116°; ir (KBr) 2800 (CH), 1580 (C=N, phenyl), 1180 (PO), 1125 (CP), 810 (vinyl), 720, 700 cm^{-1} (phenyl); nmr ($CDCl_3$) δ 2.30–3.50 (m, 8, protons at C-4, C-5, and ethyl group), 6.77 (t, 1, vinyl proton at C-3, J = 1.5 Hz), 7.25–8.10 (m, 10, phenyl protons).

Anal. Calcd for $C_{17}H_{19}N_2OP$: C, 68.79; H, 6.43; P, 10.82. Found: C, 68.59; H, 6.53; P, 10.88.

β-(3-Phenyl-2-pyrazolin-1-yl)ethyldiphenylphosphine oxide (14a) was prepared by method A (17%) or by method B (26%), mp 153–155°.

Preparation of Authentic Sample of 14a.—The salt **18** (1.5 g, 2.9 mmol) was allowed to warm with 10% aqueous sodium hydroxide (30 ml) for 1 hr. The cooled reaction mixture was filtered and washed with water and gave 1 g (92%) of pale yellow crystals. An analytically pure sample was obtained by recrystallization from EtOAc–ether: mp 152–154°; mmp with **14a**, 151–154°; ir (KBr) 2800 (CH), 1580 (C=N, phenyl), 1180 (PO), 1125 (CP), 765, 700 cm^{-1} (phenyl); nmr ($CDCl_3$) δ 2.35–3.70 (m, 8, protons at C-4, C-5, and ethyl group), 7.00–8.10 (m, 15, phenyl protons).

Anal. Calcd for $C_{23}H_{23}N_2OP$: C, 73.78; H, 6.46; N, 7.48. Found: C, 73.85; H, 6.48; N, 7.50.

β-(3-Phenyl-2-pyrazolin-1-yl)ethyltriphenylphosphonium Bromide (18).—A mixture of **1** (7.2 g, 0.02 mol) and 3-phenyl-2-pyrazoline[11] (3.0 g, 0.0206 mol) was allowed to stir in acetonitrile (60 ml) and a catalytic amount of potassium *tert*-butoxide at room temperature for 7 hr. The resulting reaction mixture was precipitated by pouring into ether to collect pale yellow solids (6.2 g, 60%). An analytically pure sample was recrystallized from CH_2Cl_2–acetone: mp 192–196°; ir (KBr) 1553 (C=N), 1120 (CP), 760, 740, 695 cm^{-1} (phenyl); nmr ($CDCl_3$) δ 2.50–4.52 (m, 8, protons at C-4, C-5, and ethyl group), 7.10–8.20 (m, 20, phenyl protons).

Anal. Calcd for $C_{29}H_{28}BrN_2P$: C, 67.57; H, 5.47; N, 5.43. Found: C, 67.80; H, 5.37; N, 5.32.

β-(5-Methyl-2-pyrazolin-1-yl)ethyldiphenylphosphine oxide (7b) was prepared by method A (26%) or by method b (23%): mp 98–100°; nmr ($CDCl_3$) δ 1.15 (d, 3, $-CH_3$, J = 5.5 Hz), 1.95–3.75 (m, 7, protons at C-4, C-5, and ethyl group), 6.70 (t, 1, proton at C-3, J = 1.5 Hz), 7.20–8.00 (m, 10, phenyl protons).

Anal. Calcd for $C_{18}H_{21}N_2OP$: C, 69.21; H, 6.77. Found: C, 69.45; H, 6.83.

β-(5-Methyl-3-phenyl-2-pyrazolin-1-yl)ethyldiphenylphosphine oxide (14b) was prepared by method A (18%) or method B (30%): mp 144–147°; ir (KBr) 3000, 2900, 2800 (C–H), 1555 (C=N), 1180 (PO), 1120 (CP), 760, 690 cm^{-1} (phenyl); nmr ($CDCl_3$) δ 1.25 (d, 3, $-CH_3$ J = 5.5 Hz), 2.35–3.90 (m, 7, protons at C-4, C-5, and ethyl group), 7.00–8.00 (m, 15, phenyl protons).

(11) von K. Auwers and P. Heimke, *Justus Liebigs Ann. Chem.*, **458**, 211 (1927).

Anal. Calcd for $C_{24}H_{25}N_2OP$: C, 74.26; H, 6.48. Found: C, 74.31; H, 6.25.

β-[N-(β-Cyano-α-methyl)ethyl]aminoethyltriphenylphosphonium Bromide (8b).—The salt **3b** (16.0 g, 0.02 mol) was allowed to stir with 5% aqueous NaOH at room temperature for 5 hr. The heterogeneous reaction mixture was diluted with water (100 ml), neutralized with dilute HCl, and extracted with EtOAc (500 ml). The dried ($MgSO_4$) extract was concentrated to 10 ml and ether was added to precipitate white crystals (1.2 g, 13%). A pure sample was recrystallized from CH_2Cl_2–EtOAc, mp 175–177°. This sample was identical in all respects with an authentic sample.

Preparation of 8b from 1 and β-Aminobutyronitrile.—A mixture of **1** (16.8 g, 0.045 mol) and β-aminobutyronitrile[12] (3.8 g, 0.045 mol) was allowed to stir in acetonitrile (50 ml) at room temperature for 10 hr. Ethyl acetate (20 ml) was added to the solution and the mixture was stirred for 30 min. White crystals (19.5 g, 85%) were collected. A recrystallized sample from CH_2Cl_2–EtOAc gave analytically pure **8b**: mp 175–176°; ir (KBr) 3200 (NH), 2230 (C≡N), 1120 (CP), 760, 755, 730, 680 cm^{-1} (phenyl); nmr ($CDCl_3$) obtained after adding D_2O, δ 1.01 (d, 3, $-CH_3$, J = 6.0 Hz), 2.37 (d, 2, $-CH_2CN$, J = 5.5 Hz), 3.03 (d, t, 2, NCH_2-, J_{HP} = 17.5, J = 6.0 Hz), 3.93 (d, t, 2, $-CH_2P$; J_{HP} = 11.5 Hz), 2.55–3.35 (m, 1, >CHCH$_3$), 7.50–8.15 (m, 15, phenyl protons).

Anal. Calcd for $C_{24}H_{26}BrN_2P$: C, 63.57; H, 5.78; P, 6.83. Found: C, 63.55; H, 5.90; P, 6.71.

β-(5-Phenyl-2-pyrazolin-1-yl)ethyltriphenylphosphonium Bromide (6c).—The salt **3c** (4.2 g, 5.0 mmol) was allowed to react with 0.2 g (5.0 mmol) of NaOH in refluxing water (20 ml) for 12 hr. The reaction mixture was extracted with EtOAc (300 ml), dried ($MgSO_4$), and concentrated to obtain an oily liquid. The oily liquid was partly dissolved in EtOAc–ether (1:1) mixed solvent (100 ml) and filtered to collect crystals (1.0 g, 40%). Recrystallization from CH_2Cl_2–EtOAc gave an analytically pure sample: mp 194–196°; ir (KBr) 2950, 2800 (CH), 1580 (C=N, phenyl), 1115 (CP), 755, 725, 690 cm^{-1} (phenyl); nmr ($CDCl_3$) δ 2.25–4.85 (m, 7, protons at C-4, C-5, and ethyl group), 6.85 (t, 1, protons at C-3, J = 1.5 Hz), 6.95–7.45 (m, 5, phenyl protons at C-5), 7.45–8.00 (m, 15, protons attached to phenyl on phosphorus atom).

Anal. Calcd for $C_{29}H_{28}BrN_2P$: C, 67.57; H, 5.47; N, 5.43; P, 6.00. Found: C, 67.73; H, 5.62; N, 5.38; P, 6.17.

β-[N-(β-Cyano-α,α-diphenyl)ethyl]aminoethyldiphenylphosphine oxide (9d).—The salt **3d** (3 g, 3.12 mmol) was allowed to reflux in 10% aqueous NaOH (50 ml) for 2 hr. The cooled mixture was extracted with EtOAc (100 ml); the extract was dried ($MgSO_4$) and concentrated to 5 ml. Ether (100 ml) was added to the concentrated solution, and the solution was allowed to stand overnight in a refrigerator. Collected were white crystals of **9d** (0.65 g, 47%). Recrystallization from EtOAc gave an analytically pure sample: mp 176–178°; ir (KBr) 3250 (NH), 2250 (C≡N), 1200 (PO), 1130 (CP), 730, 725, 700 cm^{-1} (phenyl); nmr ($CDCl_3$) δ 2.18–3.00 (m, 5, $-CH_2CH_2-$ and NH, after adding D_2O integration decreased to four protons), 3.17 (s, 2, $-CH_2CN$), 7.26 (s, 10, protons attached to phenyl on carbon), 7.30–7.95 (m, 10, protons attached to phenyl on phosphorus).

Anal. Calcd for $C_{29}H_{27}N_2OP$: N, 6.22; P, 6.87. Found: N, 6.23; P, 6.71.

Registry No.—**3a**, 32247-17-9; **3b**, 32247-18-0; **3c**, 32247-19-1; **3d**, 32304-09-9; **6c**, 32247-20-4; **7a**, 32247-21-5; **7b**, 32247-22-6; **8b**, 32247-23-7; **9d**, 32247-24-8; **14a**, 32247-25-9; **14b**, 32247-26-0; **18**, 32247-27-1.

Acknowledgment.—The authors gratefully acknowledge a grant (CA 11000) from the U. S. Public Health Service.

(12) T. Kurihara and K. Ro, *J. Pharm. Soc. Jap.*, **75**, 1267 (1955).