Reactions of Phosphorus Compounds.[1] 29. Preparation and Reactions of Pyrazolinyltriphenylphosphonium Salts

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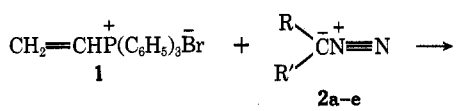
Unsubstituted and substituted pyrazolinyltriphenylphosphonium salts are prepared by 1,3-dipolar cycloaddition of diazoalkanes to vinyltriphenylphosphonium bromide. Thermal decomposition, aqueous basic hydrolysis, alkylation, and Wittig olefination reactions are examined.

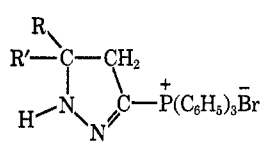
Synthetic methods for the preparation of heterocyclic compounds by 1,3-dipolar cycloadditions have been reviewed recently by Huisgen.[2] Pyrazolinylphosphonates,[3-9] pyrazoylphosphonates,[10,11] and pyrazolinyldialkylphosphine oxides and sulfides[12] have been prepared by 1,3-dipolar cycloadditions. Zbiral[13] investigated the preparation of triazoles from 1,3-dipolar cycloaddition reactions of acyl-substituted vinyltriphenylphosphonium chlorides and sodium azide.

We wish to report the preparations and reactions of unsubstituted and 5-substituted 2-pyrazolin-3-yltriphenylphosphonium salts.[14] The uniqueness of these salts over the products mentioned above,[3-12] which retain the phosphorus moiety, is that they provide an intermediate of great synthetic utility which may undergo a number of interesting conversions as depicted generally in Scheme I.

Vinyltriphenylphosphonium bromide (**1**), on reaction with diazoalkanes **2a–e** at room temperature for 1–2 hr, gave only the corresponding 2-pyrazolin-3-yltriphenylphosphonium bromides, **3a–e**, in excellent yields (84–100%). None of the corresponding 4-substituted salts



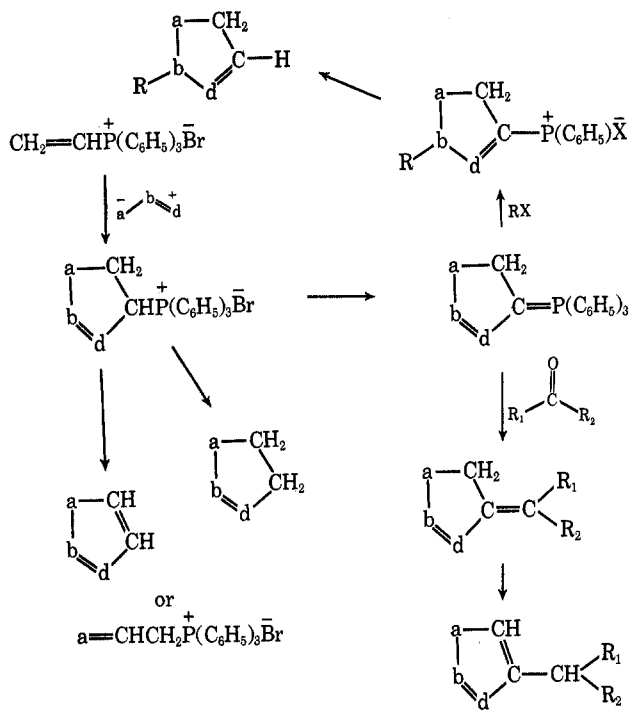
1 **2a–e**



3a, R = R′ = H
b, R = H; R′ = CH_3
c, R = R′ = CH_3
d, R = H; R′ = C_6H_5
e, R = R′ = C_6H_5

were obtained. Undoubtedly steric factors inhibit the formation of 4-substituted salts which would require the phosphonium moiety of the vinyl salt **1** to be adjacent to the substituted diazoalkane carbon moiety. Allylphenylphosphonium or β-substituted vinyltriphenylphosphonium salts did not react with diazoalkanes to give 1,3-dipolar cycloaddition products. Only starting salts were recovered even under more vigorous reaction conditions.

SCHEME I



Only species with the 2-pyrazoline structures were isolated, from the reaction of **1** and **2**, even when mild conditions were employed similar to those which were used by Pudovik[9] to obtain 1-pyrazolin-3-yldialkylphosphonates instead of the 2-pyrazolin-3-yldialkylphosphonates, on reaction of diphenyldiazomethane with vinylphosphonates. The rapid isomerization of the 1- into the 2-pyrazoline structure during the reaction is due to the greater stability of the 2-pyrazoline structure engendered by overlapping between the π electrons of the C=N bond and a vacant d orbital of the positive phosphorus atom.[8]

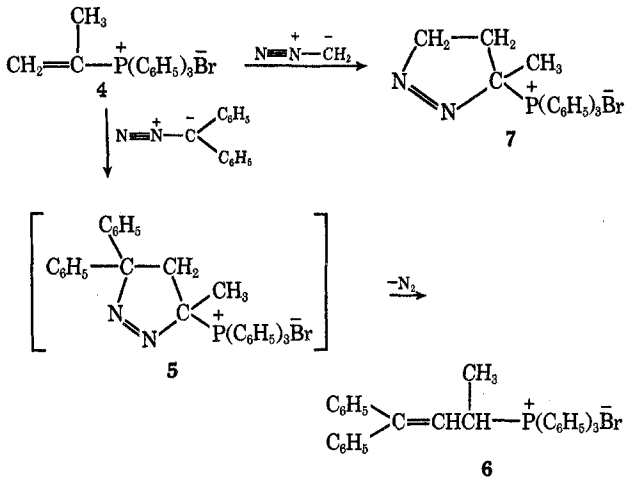
If the diazoalkane was not added in excess, or all at once, phosphonioethylated compounds[15] were also formed, and the separation of the mixed salts was very difficult. The reaction, however, was readily controlled by rapid addition of diazoalkanes **2a–e** in excess to **1** in order to obtain pure pyrazolinyl salts, **3a–e**.

(1) Part 28: E. E. Schweizer, T. Minami, and D. M. Crouse, *J. Org. Chem.*, **37**, 4028 (1972).
(2) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 563, 633 (1963).
(3) D. Seyferth, P. Hilbert, and R. S. Marmor, *J. Amer. Chem. Soc.*, **89**, 4811 (1967).
(4) N. Kreutzkamp, E. Schmidt-Samoa, and K. Herberg, *Angew. Chem.*, **77**, 1138 (1965).
(5) M. Regitz, W. Anscheutz, and A. Liedhegener, *Chem. Ber.*, **101**, 3734 (1968).
(6) A. N. Pudovik, *et al.*, *Zh. Obshch. Khim.*, **40**, 1189 (1970).
(7) A. N. Pudovik, *et al.*, *ibid.*, **40**, 1025 (1970).
(8) A. N. Pudovik, *et al.*, *ibid.*, **39**, 1536 (1969).
(9) A. N. Pudovik, *et al.*, *ibid.*, **34**, 3942 (1964).
(10) B. C. Saunders and P. Simpson, *J. Chem. Soc.*, 3351 (1963).
(11) A. N. Pudovik and N. G. Khusaimova, *Zh. Obshch. Khim.*, **40**, 697 (1970).
(12) I. G. Kolokol, *et al.*, *ibid.*, **40**, 667 (1970).
(13) von E. Zbiral, *et al.*, *Justus Liebigs Ann. Chem.*, **725**, 22 (1969).
(14) E. E. Schweizer, C. S. Kim, and R. A. Jones, *Chem. Commun.*, **39**, 1584 (1970).
(15) Part 30: E. E. Schweizer and C. S. Kim, *J. Org. Chem.*, **36**, 4041 (1972).

The ir spectra of **3a–e** show a strong, broad band at 3050–3150 cm^{-1} which indicates a strong intermolecular interaction between amine proton and bromine anion (N—H···$\bar{B}r$). This type of interaction is supported[16] by the observation that the N–H stretching vibration band shifted into higher frequencies (3200–3250 cm^{-1}) when the bromine anion was replaced by tetraphenylborate anion in compound **3a**. The nmr data for **3a–e** are consistent with the structures assigned.[12,17–22]

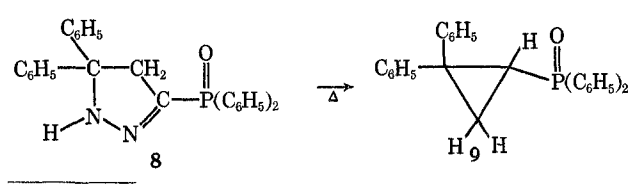
When the isopropenyl salt **4** was allowed to react with diphenyldiazomethane (**2e**) for 1 week at room temperature, a decomposition product, **6**, of the initially formed adduct, **5**, was obtained in 45% yield. On the other hand, a 1-pyrazoline adduct, **7**, was isolated from the reaction of **4** and diazomethane, **2a** (Scheme II). This

SCHEME II



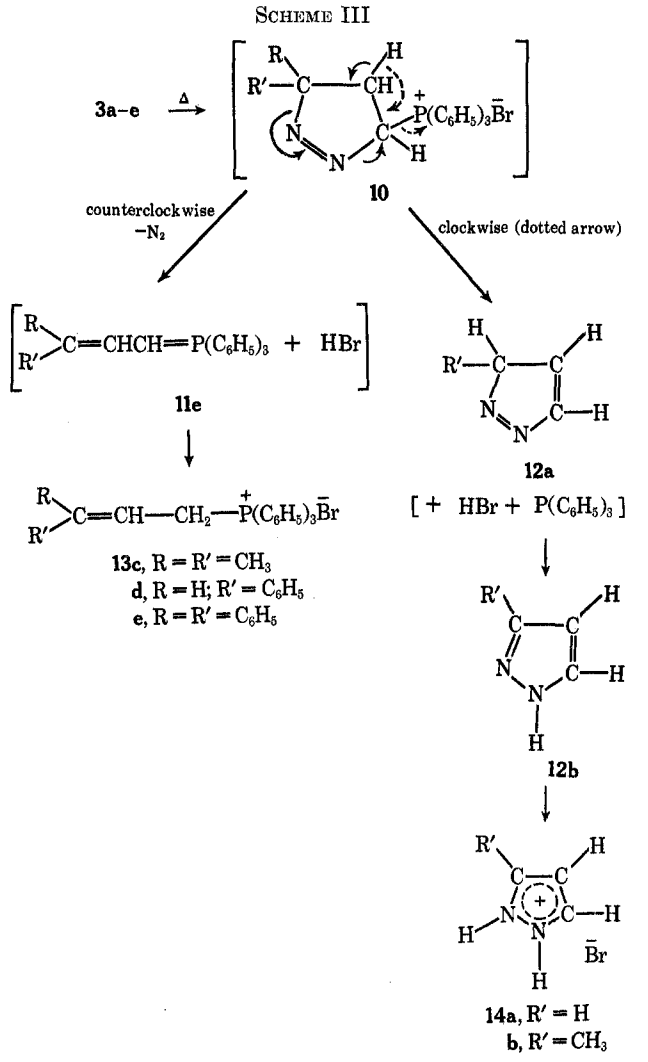
latter adduct slowly decomposed on standing at room temperature into 3-methylpyrazole hydrobromide (**14a**) and triphenylphosphine. Attempts to purify **7** without decomposition proved unsuccessful. Only in CD_3OD solution could an acceptable nmr spectrum be obtained before the salt would undergo spontaneous decomposition. Immediate decomposition was observed in deuterated chloroform or in trifluoroacetic acid.

Thermal Decomposition of 3a–e.—It has been known[2] that 2-pyrazolines decompose thermally to give cyclopropanes and olefins with varying product distributions. In most cases, the corresponding cyclopropanes were observed, either as a major product or as a contaminant. Pudovik reported[8] that he only isolated the corresponding cyclopropane product **9** in 92% yield by heating **8** to 160–170°. The catalyzing effect



of the bromine anion in the present system was suggested by the fact that the corresponding cyclopropane compounds were not observed as thermal decomposition products of the salts **3a–e** and **7**. The salts **3a**, **3b**, and **7** eliminated triphenylphosphine to form the corresponding pyrazole hydrobromides (**14a,b**) while **3c–e** resulted in the formation of the corresponding allyltriphenylphosphonium bromides, **13c–e**, by loss of nitrogen (Scheme III).

SCHEME III



In the mechanism of the thermal decomposition of 2-pyrazolines, the isomerization of 2- into 1-pyrazoline before losing nitrogen has been generally accepted as a first step.[23] The isomerized 1-pyrazoline, **10**, will decompose by two unique pathways (see Scheme III). In **3c–e** the allylphosphonium salts, **13c,e**, are expected since the intermediate, **12a**, formed by clockwise electron transfer would not be able to isomerize into a stable pyrzole, **12b**, due to the absence of a proton at C-5. Isomerization (to **12a**) is possible if one of the C-5 substituents is a hydrogen, as in **3a,b**, *via* a 1,3-hydrogen shift. The formation of **13d**, rather than the alternate pyrazole salt, **14** (from **3d**), may be due to the electron-withdrawing effect of the phenyl ring at C-5. This effect would result in the formation of the double bond in conjugation with the phenyl giving **11**, rather than the

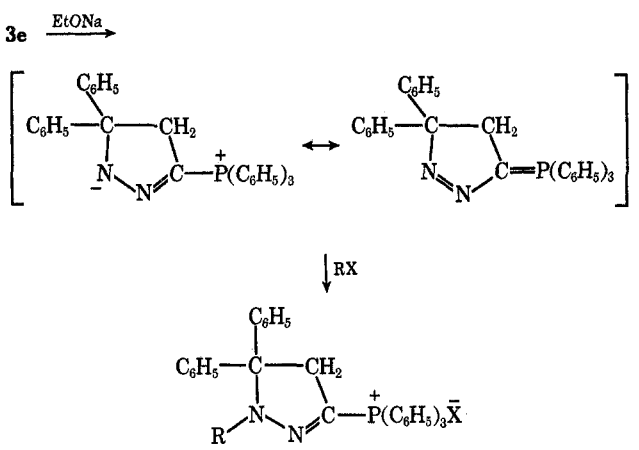
(16) L. B. Senyavina, *et al.*, *Zh. Obshch. Khim.*, **37**, 499 (1967).
(17) K. B. Sloan and N. Rabjohn, *J. Heterocycl. Chem.*, **7**, 1273 (1970).
(18) R. Sustmann, R. Huisgen, and H. Huber, *Chem. Ber.*, **100**, 1802 (1967).
(19) A. Hassner and M. J. Michelson, *J. Org. Chem.*, **27**, 3974 (1962).
(20) R. C. Cookson, *et al.*, *Tetrahedron Suppl.*, No. 7, 355 (1967).
(21) J. R. Dyer, "Application of the Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Englewood Cliffs, N. J., 1965, p 108.
(22) G. L. Vecchio, M. Crisafulli, and M. C. Aversa, *Tetrahedron Lett.*, 1909 (1966).
(23) R. H. Wiley, "Chemistry of Heterocyclic Compounds (Pyrazolines)," Interscience, New York, N. Y., 1967, p 209.

intermediate **12a** where the double bond formed is not in conjugation with the phenyl.

The structure of **13e** was supported by allowing the phosphorane produced from **13e** to react with benzophenone. This resulted in the known 1,1,4,4-tetraphenylbutadiene (62%).

Attempted Alkylation of 3a–e.—Only N-alkylated compounds, **15a–c**, were obtained upon treatment of reactive alkyl halides by the ylide formed from the salt **3e** in the presence of ethanolic sodium ethoxide (Scheme IV). Only the corresponding pyrazoles were

SCHEME IV

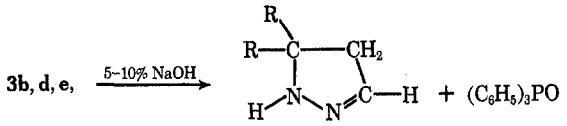


15a, R = CH_3; X = I (84%)
b, R = CH_2-COOEt, X = Br (69%)
c, R = COOEt, X = Cl (43%)

observed on attempting to alkylate salts **3a,b,d**, under basic conditions, *i.e.*, when **3** contained one or more protons in the C-5 position.

In addition to the spectra data, which supported the structures assigned, hydrolysis of **15a–c** gave the corresponding N-alkylated 2-pyrazolines, **16a,b**. Where the intermediate anion **17** is stabilized (in **15c**), the cyanourethane, **18**, was obtained by N–N bond cleavage as well as **16c** (Scheme V) in a ratio of 7 to 3, respectively (overall yield 67%). The saponified acid, **16b**, was thermally decarboxylated into **16a** (100%).

Hydrolysis of 3a–e.—When compounds **3b,d,e** were treated with 5–10% aqueous NaOH, the corresponding 2-pyrazolines, **19b,d,e**, and triphenylphosphine oxide were isolated.

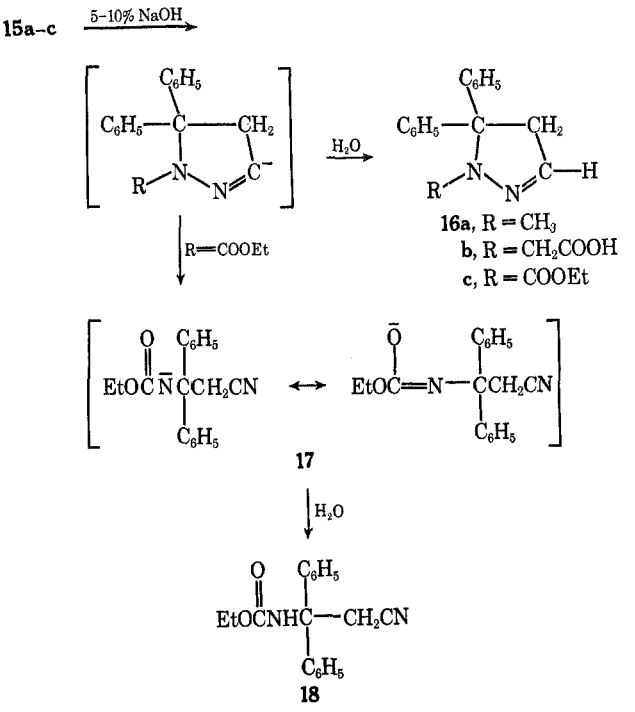


19b, R = H; R′ = CH_3
d, R = H; R′ = C_6H_5
e, R = R′ = C_6H_5

Triphenylphosphine oxide was similarly isolated, in 90–95% yield, on basic hydrolysis of **3a** and **3c**; the corresponding 2-pyrazolines were not isolated.

Wittig Olefination Reaction of 3a–e.—The salts **3a–e** undergo the Wittig olefination reaction. Reactions of **3a–e** with ethanolic sodium ethoxide and benzaldehyde gave different types of products, and the yields depend on the order of mixing the starting materials (Scheme VI).

SCHEME V



Three orders of mixing were employed for these reactions: (a) benzaldehyde was added to a mixture of the salt and ethanolic sodium ethoxide, (b) the salt was added to a mixture of benzaldehyde and ethanolic sodium ethoxide, and (c) ethanolic sodium ethoxide was added to an ethanolic solution of the salt and benzaldehyde.

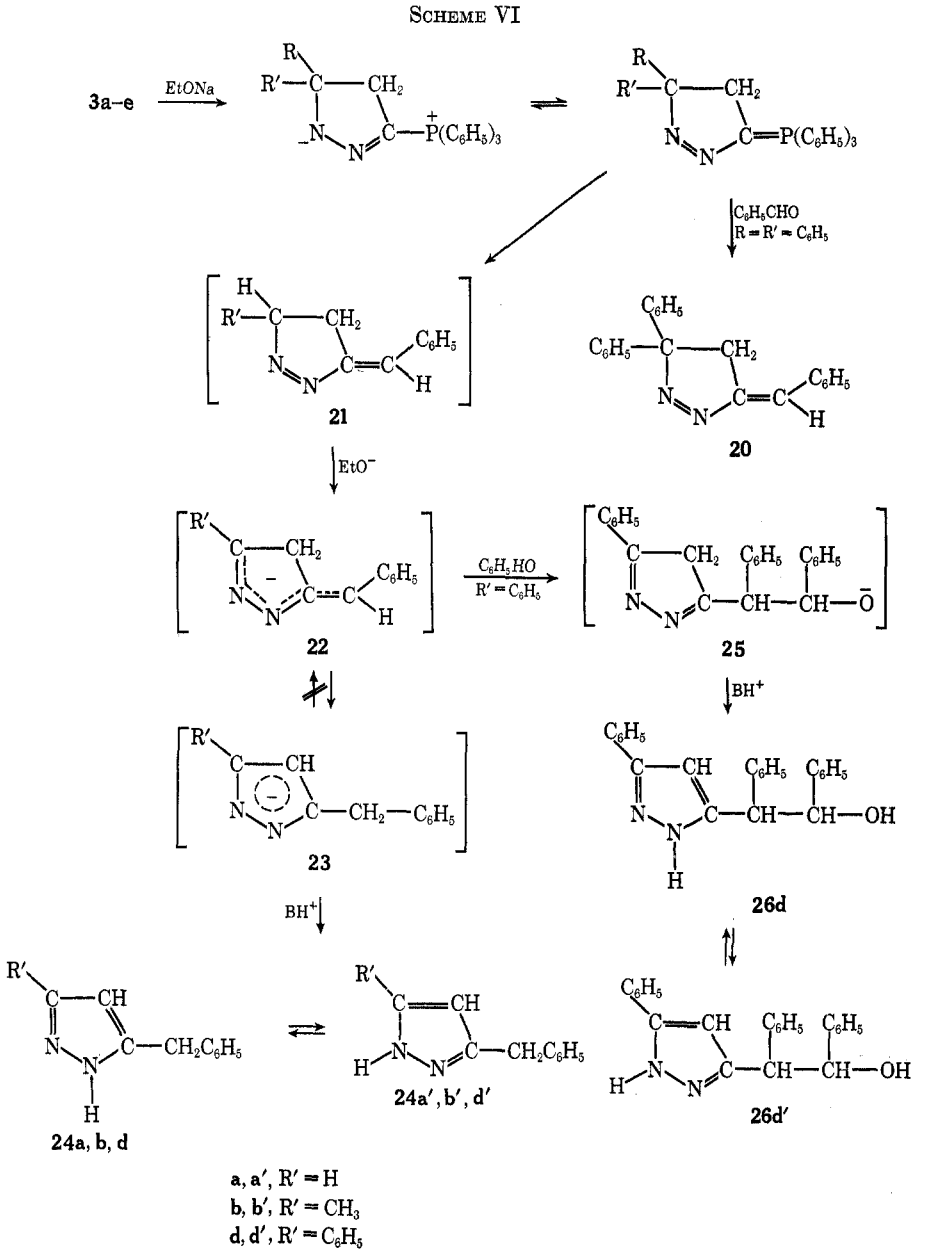
Only **3e** furnished the expected benzilidene product, **20**, regardless of the order of mixing (78% by method c). The structure of **20** was supported by its spectral data.[21,24,25]

When **3a,b,d** were treated in manner "a," no Wittig olefination products were observed. The corresponding pyrazoles were isolated as observed previously on attempting the alkylation reactions. If, however, **3a,b,d** were allowed to react under method b or c, Wittig olefination products, **24a,b** and **26**, were obtained in good yields. Generally method c gives the best yields. Further isomerization or addition of benzaldehyde to the initial product, **21**, is undoubtedly caused by the relative stability of the anion intermediate, **22**. Thus, if R′ = H or CH_3, **22** will isomerize rapidly to the more stable anion, **23**, which has aromatic character. On the other hand, if R′ is phenyl, **22** has a long enough lifetime to be able to react with another mole of benzaldehyde and give adduct **26**. In both cases the alternate products were observed in trace amounts. The reversibility of **23** to **22** was ruled out by experiments in which 3(5)-methyl- (**24b**) or phenyl-5(3)-benzylpyrazoles (**24d**) were observed to give unchanged starting materials and none of adducts of type **26** upon treatment with benzaldehyde in the presence of ethanolic sodium ethoxide.

Several reactions were carried out in order to support structure **26**. Thermal decomposition of **26** by heating

(24) von P. Bosshard, *et al.*, *Helv. Chim. Acta*, **47**, 769 (1964).
(25) R. J. Crawford, A. Mishra, and R. J. Dummel, *J. Amer. Chem. Soc.*, **88**, 3959 (1966).

SCHEME VI



to 260–290° gave 1 mol of 3(5)-benzyl-5(3)-phenylpyrazole [**24d(d′)**] and benzaldehyde (Scheme VII).

Treatment of **26** with 48% aqueous hydrogen bromide furnished an unstable bromine-substituted salt, **27**, whose analysis was not consistent with the structure. When **27** was recrystallized from methanol, it underwent a solvolysis reaction to give **28** (**29** was obtained in ethanol.)

The ir spectrum of **26** in KBr indicates that **26d** is in equilibrium with **26d′**, since a sharp and strong band appears at 3365 ± 5 cm^{-1} due to free NH and a strong broad band at 3310–3325 cm^{-1} due to hydrogen-bonding hydroxy group. The nmr spectrum also suggests the existence of the hydrogen-bonded structure of type **26d**, since a free NH shows at δ 5.30 with one of the benzal hydrogens and a hydrogen-bonded OH as part of the phenyl proton region.

The salt **3c** gave benzaldehyde diethyl acetal in 80% yield (isolated) when it was treated under condition c and worked up in the standard manner. The mechanism of acetal formation is not clear at present. A similar result was observed during an intramolecular Wittig olefination reaction by Minami and Schweizer.[26]

Experimental Section

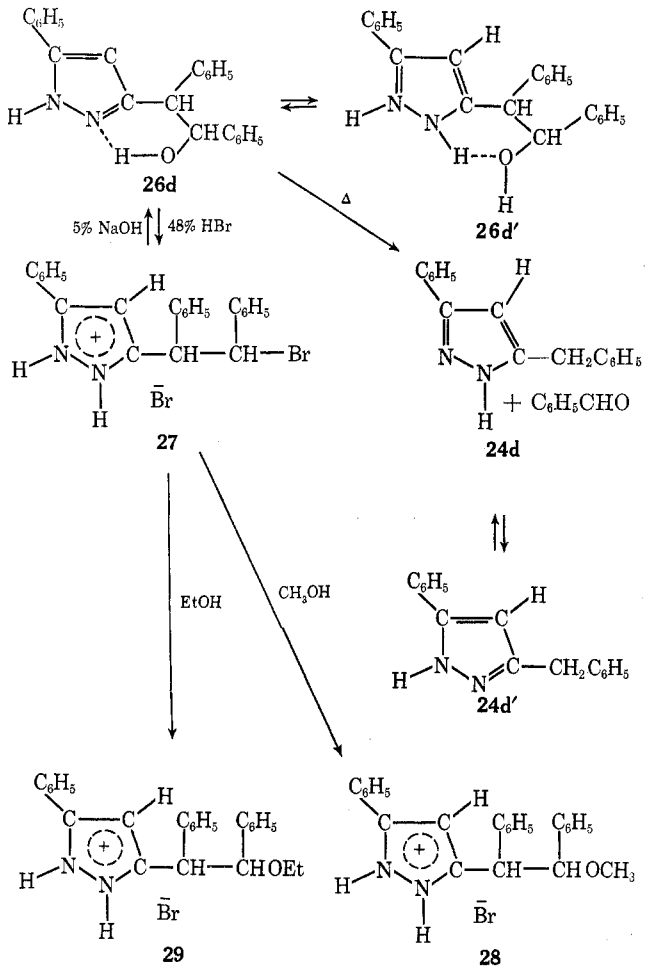
Indices of refraction were obtained on a Bausch and Lomb refractometer, ultraviolet spectra on a Perkin-Elmer Model 202 spectrometer, infrared spectra on a Perkin-Elmer 137 spectrophotometer or a Perkin-Elmer Model 421 grating spectrophotometer, and nmr spectra on a Varian A-60A spectrometer using tetramethylsilane as internal standard. All melting points were uncorrected and obtained on a Thomas–Hoover capillary melting point apparatus. Elemental analyses are by Micro-Analysis Inc., Wilmington, Del., and MHW Laboratories, Garden City, Mich. 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. All solvents used were anhydrous.

Warning. Diazoalkanes are skin irritants and reactions for their preparation and use should be done in a hood, wearing gloves.

2-Diazopropane (2c).—Reagent grade acetone (52 g, 1.0 mol) was added to 32 g (1.0 mol) of 95% hydrazine in the course of

(26) T. Minami and E. E. Schweizer, unpublished results.

SCHEME VII



2 hr with cooling. After all the acetone was added, the mixture was allowed to stir for an additional 1 hr at room temperature. The resultant mixture was extracted with 300 ml of ether and filtered through anhydrous magnesium sulfate into a 500-ml flask equipped with a magnetic stirrer. The extract was cooled to −5° in an ice–salt mixture, and yellow mercuric oxide (50 g) was added portionwise while keeping the temperature below 0°. After all of the mercuric oxide had been added, the reaction mixture was stirred until a deep pink color developed. The ethereal solution was filtered immediately through a cotton plug. The filtrate was used immediately for a further reaction and the yield was not determined.

Phenyldiazomethane (2d).[27]—Benzaldehyde (110 g, 1.03 mol) was added dropwise over a period of 1 hr with vigorous stirring to a mixture of 100 ml of ether and 95% hydrazine (32 g, 1.0 mol). The reaction was cooled with cold water in order to prevent the ether from boiling. The solution was diluted with 100 ml of ether, and cooled to below 5° in an ice–salt mixture. Yellow mercuric oxide (113 g) was added slowly, making sure that no nitrogen was evolved. Bubbling indicates a too rapid rate of oxide addition. The deep red mixture was allowed to stir vigorously for 2 hr at room temperature, filtered through a cotton plug, and dried ($MgSO_4$). The dried ethereal solution was allowed to react immediately with vinyl salts.

2-Pyrazolin-3-yltriphenylphosphonium Bromide (3a).—A freshly distilled ethereal solution of diazomethane[28] was added as rapidly as possible, at room temperature, to a solution of vinyltriphenylphosphonium bromide[29] (1) (56 g, 0.15 mol) dissolved in 400 ml of methylene chloride. Addition was continued until the orange color persisted. The mixture was allowed to stir for an additional 2 hr at room temperature. Ether was added to the solution in order to precipitate white crystals which were collected (61.0 g, 97%) by filtration. The crystals were dissolved in methylene chloride and precipitated with ethyl acetate to give an analytically pure sample: mp 162–164° dec; ir (KBr) 3100 (hydrogen bonded NH), 2850 (CH), 1580 (C=N, phenyl), 1115 (CP), 725, 690 cm^{-1} (phenyl); uv (MeOH) λ_{max} 231 mμ (ε 26,000), 301 (9800); nmr ($CDCl_3$) δ 2.88–3.30 (m, 2, C_4), 3.70–4.30 (m, 2, C_5), 7.45–8.20 (m, 15, C_6H_5), 9.90 ppm (s, 1, NH). The NH proton chemical shift depends on concentration and its exchangeable with D_2O for all **3a–e** species.

Anal. Calcd for $C_{21}H_{20}BrN_2P$: C, 61.32; H, 4.90. Found: C, 61.17; H, 5.08.

2-Pyrazolin-3-yltriphenylphosphonium Tetraphenylborate.—Methylene chloride (10 ml) was added to a solution of **3a** (1 g) and sodium tetraphenylborate (0.7 g). The mixed solution was boiled for 5 min and filtered. The filtrate was concentrated while adding EtOAc to precipitate 1.0 g of needlelike crystals. Recrystallization from acetone–ether gave an analytically pure sample: mp 181–185°; ir (KBr) 3250 (NH), 2980 (CH), 1580 (C=N, phenyl), 1115 (CP), 735, 710 cm^{-1} (phenyl).

Anal. Calcd for $C_{45}H_{40}BN_2P$: C, 83.07; H, 6.19. Found: C, 83.15; H, 6.21.

5-Methyl-2-pyrazolin-3-yltriphenylphosphonium bromide (3b) was prepared by the above procedure using a freshly distilled ethereal solution of diazoethane,[30] 200 ml of methylene chloride, and 23.48 g (0.0635 mol) of vinyltriphenylphosphonium bromide (1). On filtration, 26.7 g (99%) of white crystals were collected. An analytical sample was obtained as in the previous experiment: mp 174–175° dec; ir (KBr) 3050 (hydrogen bonded NH, CH), 1115 (CP), 755, 730, 693 cm^{-1} (phenyl); nmr ($CDCl_3$) δ 1.42 (d, 3, CH_3, J = 6.5 Hz), 2.54 (dd, 1, C_4, $J_{vic\text{-}trans}$ = 10 Hz, J_{gem} = 16 Hz), 3.17 (dd, 1, C_4, $J_{vic\text{-}cis}$ = 11.5 Hz), 4.46 (m, 1, C_5, J = 6.5 Hz), 7.40–8.20 (m, 15, C_6H_5), 10.18 ppm (s, 1, NH).

Anal. Calcd for $C_{22}H_{22}BrN_2P$: C, 62.12; H, 5.21. Found: C, 62.28; H, 5.32.

5,5-Dimethyl-2-pyrazolin-3-yltriphenylphosphonium Bromide (3c).—A freshly prepared deep pink ethereal solution of 2-diazopropane was added to a solution of 1 (5 g, 0.0135 mol) in 100 ml of methylene chloride while keeping the temperature below 5° until the color persisted. The pink-colored mixture was stirred for 1 hr at room temperature, and precipitated 5.0 g (84%) of white crystals by adding ether. The product was recrystallized from CH_2Cl_2–EtOAc: mp 180–183° dec; ir (KBr) 3150, 3100 (hydrogen bonded NH), 1575 (C=N, phenyl), 1115 (CP), 760, 695 cm^{-1} (phenyl); nmr ($CDCl_3$) δ 1.53 (s, 6, CH_3), 2.80 (s, 2, C_4), 7.30–8.10 (m, 15, C_6H_5), 10.22 ppm (s, 1, NH).

Anal. Calcd for $C_{23}H_{24}BrN_2P$: C, 62.88; H, 5.50. Found: C, 62.99; H, 5.14.

5-Phenyl-2-pyrazolin-3-yltriphenylphosphonium Bromide (3d).—An ethereal solution of phenyldiazomethane was added to a solution of 1 (60.1 g, 0.16 mol) in 400 ml of methylene chloride with vigorous stirring at room temperature until the color persisted. After 30 min of stirring, ether was added slowly to precipitate white crystals (79 g, 100%). An analytical sample was recrystallized from CH_2Cl_2–MeOH–EtOAc: mp 202–203° dec; ir (KBr) 3050 (hydrogen bonded NH), 1608, 1580 (C=N, phenyl), 1115 (CP), 753, 530, 690 cm^{-1} (phenyl); nmr (CF_3CO_2H) δ 3.22 (dd, 1, C_4, $J_{vic\text{-}trans}$ = 9 Hz, J_{gem} = 18 Hz), 3.73 (1, C_4, $J_{vic\text{-}cis}$ = 10 Hz), 5.38 (dd, 1, C_5), 7.07 (s, 5, CC_6H_5), 7.20–7.83 ppm (m, 15, PC_6H_5).

Anal. Calcd for $C_{27}H_{24}BrN_2P$: C, 66.59; H, 4.97. Found: C, 66.54; H, 5.02.

5,5-Diphenyl-2-pyrazolin-3-yltriphenylphosphonium Bromide (3e).—To a solution of 1 (40 g, 0.108 mol) dissolved in 300 ml of methylene chloride was added crystalline diphenyldiazomethane[31] (23 g, 0.118 mol) in 50 ml of ether or a dark red petroleum ether (bp 30–60°) solution of diphenyldiazomethane[32] in excess. The mixture was vigorously stirred at room temperature for 1 hr. Ether (200 ml) was added slowly to complete the precipitation of the product (53.9 g, 97.5%). The crude salt was placed in boiling CH_2Cl_2 (250 ml) and methanol was added until it dissolved. The solution was filtered and ethyl acetate was added while concentrating to give analytically pure white crystals. An analytical sample had mp 213–216° dec: ir (KBr) 3050 (hydrogen bonded NH), 1580 (C=N, phenyl), 1110 (CP), 750, 720, 690 cm^{-1}

(27) This synthesis was a modification of C. G. Overberger, *J. Amer. Chem. Soc.*, **86**, 658 (1964).
(28) J. A. Moore and D. E. Reed, *Org. Syn.*, **41**, 16 (1961).
(29) E. E. Schweizer and R. D. Bach, *ibid.*, **48**, 129 (1969).
(30) A. L. Wilds and A. L. Meader, *J. Org. Chem.*, **13**, 763 (1948).
(31) J. B. Miller, *ibid.*, **24**, 560 (1959).
(32) L. I. Smith and K. L. Howard, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 351.

(phenyl); uv (EtOH) λ_{max} 216 mμ (ε 30,100), 302 (ε 10,050); nmr (CF_3CO_2H) δ 3.92 (s, 2, CH_2), 7.37 (s, 10, CC_6H_5), 7.5–8.1 ppm (m, 15, PC_6H_5).

Anal. Calcd for $C_{30}H_{28}BrN_2P$: C, 70.34; H, 5.01. Found: C, 70.24; H, 4.75.

3-Methyl-1-pyrazolin-3-yltriphenylphosphonium Bromide (7).—The reaction was run by the same manner as in **3a**, using 100 ml of methylene chloride, an ethereal solution of diazomethane, and isopropenyltriphenylphosphonium bromide[33] (**4**) while keeping the temperature below 20° during addition. White crystals (9 g, 81.5%) were obtained by filtration. This salt slowly decomposed even at room temperature. In a protonic solvent like chloroform or trifluoroacetic acid, the salt decomposed into 3-methylpyrazole hydrobromide and triphenylphosphine. No analytical sample was obtained by recrystallization. Nmr, ir, and uv spectra were taken immediately after reprecipitation from MeOH with EtOAc: mp 100–102°; ir (KBr) 3000, 2940 (CH), 1550 (C=N), 1115 (CP), 757, 730, 692 cm^{-1} (phenyl); uv (MeOH) λ_{max} 235, 332 mμ; nmr (CD_3OD) δ 1.85 (d, t, 2, protons at C-4, J_{gem} = 15, J_{vic} = 8 Hz), 4.85 (m, 2, protons at C-5), 7.65–8.25 ppm [m, 15, $P(C_6H_5)_3$].

Anal. Calcd for $C_{22}H_{22}BrN_2P$: C, 62.11; H, 5.21; N, 6.58. Found: C, 61.03; H, 5.34; N, 6.17.

3,3-Diphenyl-1-methylallyltriphenylphosphonium Bromide (6).—A mixture of **4** (2.0 g, 0.0053 mol) and an excess amount of diphenyldiazomethane (1.3 g, 0.0061 mol) in 10 ml of methylene chloride was allowed to stand for 1 week at room temperature (reaction is too slow at 5°) and precipitated into ether to obtain 1.3 g (45%) of **6**. An analytical sample was recrystallized from CH_2Cl_2–EtOAc: mp 194–196°; ir (KBr) 2950 (CH), 1480 (phenyl), 1430 ($-CH_3$), 1110 cm^{-1} (CP); nmr ($CDCl_3$) δ 1.80 (d d, 3, $-CH_3$, J_{HP} = 18.5, J = 7 Hz), 4.55 (m, 1, proton at C-1), 5.77 ppm (d d 1, vinyl proton at C-2, J = 7.5, J_{HP} = 10.5 Hz).

Anal. Calcd for $C_{34}H_{30}PBr$: C, 74.97; H, 5.50. Found: C, 74.83; H, 5.50.

Thermal Decomposition of 3a–e. Method A.—A sample of **3a–e** was heated to its melting point temperature for 15–30 min in an oil bath (temperature maintained 10° over melting point). After cooling, the solidified decomposition product was worked up by individual procedure.

Method B.—A sample of the salt was refluxed in mesitylene for 12–24 hr under dry nitrogen. After cooling the mixture, the solvent was removed by decantation and the solid material was purified.

Pyrazole Hydrobromide (14a).—Compound **3a** (4.2 g, 0.01 mol) was treated by method A. The solidified residue was washed with anhydrous ether several times under nitrogen atmosphere. The ether-insoluble solid was dissolved in methylene chloride and concentrated while adding EtOAc to precipitate 1.4 g (93.5%) of **14a**. The product was extremely hygroscopic. An analytical sample was prepared by sublimation at 60° under vacuum. Spectral data and melting point were the same as as those of an authentic sample prepared from pyrazole: mp 164–166°; nmr ($CDCl_3$) δ 6.82 (t, 1, proton at C-4, J = 2.5 Hz), 8.42 (d, 2, proton at C-3 and C-5), 13.04 ppm (broad s, 2, NH, chemical shift depends on concentration, exchangeable with D_2O).

3(5)-Methylpyrazole Hydrobromide (14b).—The residue resulting from the reaction of **3b** by method A or B was washed with EtOAc. Triphenylphosphine was obtained in quantitative yield by concentration of the EtOAc wash. The insoluble residue (2 g, 100%) was sublimed (50°) to obtain an extremely hygroscopic analytical sample: mp 98–101°; nmr ($CDCl_3$) δ 6.69 (d, 1, proton at C-4, J = 2.5 Hz), 2.66 (s, 3, $-CH_3$), 8.25 [d, 1, proton at C-3 (5)], 14.65 ppm (s, 2, NH, exchangeable with D_2O, and chemical shift depends on concentration).

Anal. Calcd for $C_4H_7BrN_2$: C, 29.46; H, 4.26; N, 17.18. Found: C, 29.52; H, 4.31; N, 16.92.

3,3-Dimethylallyltriphenylphosphonium Bromide (13c).—A sample of **3c** (2 g, 0.0045 mol) was treated by method B, refluxing for 12 hr. The solid residue (1.8 g, 98%) was recrystallized from CH_2Cl_2–EtOAc: mp 234–236° (lit.[34] mp 242°); ir (KBr) 1380, 1385 (geminal methyl), 1120 (CP) 895, 845 (vinyl), 755, 725, 695 cm^{-1} (phenyl); nmr ($CDCl_3$) δ 1.32 (d, 3, cis methyl to vinyl proton, J = 4.0 Hz), 1.70 (d, 3, trans methyl to vinyl proton, J = 6.0 Hz), 7.40–8.25 ppm [m, 15, $-P(C_6H_5)_3$].

3-Phenylallyltriphenylphosphonium Bromide (13d).—A 5-g (0.0102 mol) quantity of sample, **3d**, was heated by method A for 20 min. A pale yellow solid (4.6 g, 100%) was recrystallized from CH_2Cl_2–EtOAc: mp 249–250° (lit. mp 240°[35], 256–258°[36]); ir (KBr) 1125 (CP), 980 (trans vinyl), 760, 745, 695 cm^{-1} (phenyl); nmr ($CDCl_3$) δ 4.95 (d d, 2, $-CH_2-$, J = 7 Hz, J_{HP} = 15.5 Hz), 6.01 (d d, t, 1, vinyl proton at C-2 J_{trans} = 15.5, J_{HP} = 5 Hz, 687 ppm (d d, 1, vinyl proton at C-3, J_{HP} = 5.5 Hz). The nmr spectrum indicated a trans configuration between the phenyl at C-3 and the methylene group.

3,3-Diphenylallyltriphenylphosphonium Bromide (13e).—A quantitative yield of the crude salt was obtained by method A (15 min heating) or method B (refluxing 24 hr). An analytical sample was recrystallized from CH_2Cl_2–EtOAc: mp 248–250°; ir (KBr) 3000 (CH), 1110 cm^{-1} (CP); uv (MeOH) λ_{max} 212 mμ (ε 46,000), 270 (17,600); nmr ($CDCl_3$) δ 4.77 (d d, 2, $-CH_2-$, J_{HP} = 15.5 Hz), 6.00 (d d, 1, vinyl proton at C-2, J = 8 Hz), 6.67–7.50 (m, 10, phenyl protons at C-3), 7.50–8.18 ppm [m, 15, $-P(C_6H_{28})_3$].

Anal. Calcd for $C_{23}H_{28}BrP$: C, 73.80; H, 5.28; Br, 14.93. Found: C, 73.95; H, 5.36; Br, 14.88.

Thermal Decomposition of 7.—On heating **7** for 5 min (method A), **14b** and triphenylphosphine were obtained in a quantitative yield. The salt **7** was also decomposed completely during drying at 60° under vacuum for 1 day.

5,5-Diphenyl-1-methyl-2-pyrazolin-3-yltriphenylphosphonium Iodide (15a).—To a solution of 0.23 g (0.01 g-atom) of sodium dissolved in 150 ml of ethanol was added 5.63 g (0.01 mol) of **3e** under dry nitrogen. The solution was stirred at room temperature for 10 min. The resulting yellow mixture was allowed to stir with 4.2 g (0.03 mol) of methyl iodide at room temperature for 18 hr. The solution was precipitated by adding to ether (500 ml), filtered, and the residue dissolved in CH_2Cl_2. Insoluble sodium bromide was eliminated by filtration and the filtrate was concentrated and precipitated by adding EtOAc; 5.2 g (84%) of **15a** was obtained and recrystallized from methylene chloride–ethyl acetate: mp 249–254°; ir (KBr) 1580 (C=N, phenyl), 1080 (CP), 760, 730, 690 cm^{-1} (phenyl); uv (MeOH) λ_{max} 215 mμ (ε 37,200), 321 (11,600); nmr ($CDCl_3$) δ 3.15 (s, 3, $-CH_3$), 3.78 (s, 2, $-CH_2-$), 7.43 (s, 10, phenyl protons at C-5), 7.55–8.10 ppm [m, 15, $P(C_6H_5)_3$].

Anal. Calcd for $C_{34}H_{30}IN_2P$: C, 65.39; H, 4.85. Found: C, 65.26; H, 4.97.

5,5-Diphenyl-1-ethylaceto-2-pyrazolin-3-yltriphenylphosphonium bromide (15b) was prepared by the same procedure as **15a** using 0.23 g (0.01 mol) of sodium, 5.63 g (0.01 mol) of **3e**, and 3.7 g (0.02 mol) of ethyl bromoacetate. The precipitate was partially dissolved in boiling acetone, and the sodium bromide and unreacted starting salt were removed by filtration. The acetone solution was concentrated while adding ethyl acetate to precipitate 4.4 g (69%) of **15b**, recrystallized from acetone–ethyl acetate: mp 207–210°; ir (KBr) 1750 (C=O), 1210 (CO), 1115 (CP), 770, 730, 700 cm^{-1} (phenyl); nmr ($CDCl_3$) δ 1.08 (t, 3, $-CH_3$, J = 7.0 Hz), 3.88 (q, 2, $-OCH_2-$), 3.88 (s, 2, two protons at C-4), 4.32 (s, 2, $-NCH_2-$), 7.38 (s, 10, phenyl protons at C-5), 7.50–8.10 ppm [m, 15, $P(C_6H_5)_3$].

Anal. Calcd for $C_{37}H_{34}BrN_2O_2P$: C, 68.40; H, 5.28. Found: C, 68.58; H, 5.18.

1-Carbethoxy-5,5-diphenyl-2-pyrazolin-3-yltriphenylphosphonium Chloride (15c).—A mixture of 0.42 g (0.01 mol) of NaH (57% mineral oil dispersion) and 5.63 g (0.01 mol) of **3e** in 100 ml of acetonitrile was allowed to stir at room temperature for 3 hr. To the resulting yellow solution was added ethyl chloroformate (1.5 g, 0.015 mol) and the mixture was stirred at room temperature for 8 hr. After filtering the reaction mixture, the filtrate was precipitated by adding to ether; 2.5 g (43%) was collected of **15c**. An analytical sample was recrystallized from CH_2Cl_2–EtOAc: mp 179–180° dec; ir (KAr) 1750 (C=O), 1350 ($-CH_2-$, CN), 1200 (CO), 1115 (CP), 760, 730, 700 cm^{-1} (phenyl); nmr ($CDCl_3$) δ 1.00 (t, 3, $-CH_3$, J = 7.0 Hz), 4.06 (q, 2, $-CH_2O-$), 4.08 (s, 2, protons at C-4), 7.40 (s, 10, phenyl protons at C-5), 7.45–8.00 ppm [m, 15, $P(C_6H_5)_3$].

Anal. Calcd for $C_{36}H_{32}ClN_2OP$: C, 73.15; H, 5.46. Found: C, 73.35; H, 5.56.

Aqueous Basic Hydrolysis of 15a,b. General Methods.—A sample of the salt was allowed to stir with a volume of 10% aqueous sodium hydroxide by warming the mixture to *ca.* 80° for

(33) P. T. Keough and M. Grayson, *J. Org. Chem.*, **29**, 631 (1964).
(34) R. Rüegg, *et al.*, *Helv. Chim. Acta*, **44**, 994 (1961).
(35) K. Friedrich and H. G. Henning, *Chem. Ber.*, **92**, 2756 (1959).
(36) E. T. Shaffer, Ph.D. Thesis, University of Delaware, 1967, p 32.

1 hr. The resulting mixture was cooled to room temperature and worked up as described in the individual procedures.

5,5-Diphenyl-1-methyl-2-pyrazoline (16a).—The resultant heterogeneous reaction mixture from the treatment by the general method, using 6.3 g (0.01 mol) of **15a** and 50 ml of 10% aqueous sodium hydroxide, was diluted with an equal volume of water, and extracted with ether (300 ml). The ether extract was washed with water several times and dried ($MgSO_4$). The dried ether extract was concentrated to give an oily liquid which was chromatographed (silica gel–ether) to obtain 1.8 g (76%) of **16a**. An analytical sample was collected by a microscale distillation under vacuum: $n^{23}D$ 1.5998; ir (neat) 3050, 2950 (CH), 1600 (phenyl, C=N), 1230 (CN), 760, 700 cm^{-1} (phenyl); uv (MeOH) λ_{max} 217 mμ (ε 12,700), 273 (4700); nmr ($CDCl_3$) δ 2.55 (s, 3, $-CH_3$), 3.37 (d, 2, $-CH_2-$, J = 1.7 Hz), 6.68 (t, 1, vinyl proton at C-3), 7.25 ppm (s, 10, phenyl protons).

Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.30; H, 6.82. Found: C, 81.49; H, 6.82.

5,5-Diphenyl-2-pyrazolin-1-ylacetic Acid (16b).—Compound **15b** (4.5 g, 0.0069 mol) was treated with 20 ml of 10% aqueous sodium hydroxide by the general method. The cooled mixture was filtered to collect 1.4 g (73%) of triphenylphosphine oxide. The aqueous filtrate was washed with ether several times to eliminate dissolved phosphine oxide. The aqueous alkaline layer was neutralized with dilute hydrochloric acid to precipitate 1.6 g of a pale yellow crude product, which was recrystallized from ether–methanol–hexane to obtain 1.4 g (71.5%) of **16b**: mp 164–167°; ir (KBr) 3050–3100 (hydrogen bonded OH), 1720 (C=O), 1600 (C=N, phenyl), 1250 (CO), 760, 710 cm^{-1} (phenyl); nmr ($CDCl_3$) δ 3.37 (s, 2, $-NCH_2-$), 3.55 (d, 2, protons at C-4, J = 1.7 Hz), 7.06 (t, 1, vinyl proton at C-3), 7.36 (s, 10, phenyl protons), 11.37 ppm (m, 1, –OH, exchangeable with D_2O, chemical shift depends on concentration).

Anal. Calcd for $C_{17}H_{16}N_2O_2$: C, 72.83; H, 5.75. Found: C, 72.93; H, 5.98.

Thermal Decomposition of 16b.—A small amount of **16b**, in an nmr tube, was heated to 180° for 40 min in an oil bath (bath temperature 170–190°). After cooling, the orange solid was dissolved in deuterated chloroform and its nmr spectrum was shown to be identical with that of **16a**.

Aqueous Basic Hydrolysis of 15c.—The salt **15c** (4.0 g, 6.8 mmol) was stirred with 50 ml of 5% aqueous sodium hydroxide for 4 hr at room temperature. The cooled reaction mixture was extracted with ether (300 ml), dried ($MgSO_4$), and concentrated to furnish an oily liquid. The oily liquid was chromatographed (silica gel–ether) to obtain 0.96 g (47%) of **18** and 0.40 g (20%) of **16c**.

An analytically pure sample of each compound was furnished by recrystallization from ether–petroleum ether.

β-Cyano-α,α-diphenylethylurethane (18).—An analytically pure sample had mp 114–116°; ir (KBr) 3230 (NH), 2230 (CN), 1710 (C=O), 1245 (CO), 770, 703 cm^{-1} (phenyl); nmr ($CDCl_3$) δ 1.15 (t, 3, $-CH_3$, J = 7.0 Hz), 3.74 (s, 2, $-CH_2CN$), 3.98 (q, 2, $-OCH_2-$), 5.88 (s, 1, NH, exchangeable with D_2O slowly and chemical shift depends on concentration), 7.25 ppm (s, 10, phenyl protons).

Anal. Calcd for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.51. Found: C, 73.30; H, 6.21; N, 9.41.

1-Carbethoxy-5,5-diphenyl-2-pyrazoline (16c).—An analytically pure sample melted at 157–158°: ir (KBr) 1705 (C=O), 1608 (C=N phenyl), 1165 (CO), 850 (vinyl), 762, 700 cm^{-1} (phenyl); nmr ($CDCl_3$) δ 1.14 (t, 3, $-CH_3$, J = 7.0 Hz), 3.58 (d, 2, protons at C-4, J = 1.3 Hz), 3.96 (q, 2, $-OCH_2-$), 6.83 (t, 1, proton at C-3), 7.25 ppm (s, 10, phenyl protons).

Anal. Calcd for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16. Found: C, 73.93; H, 6.19.

Attempted Alkylation of 3a and 3d.—A 0.01-mol sample of the individual salt was treated under the same procedure as **15a**. The precipitated salt in ether was identified as methyltriphenylphosphonium iodide in 50–70% yield. No alkylated salt was observed in each case. From the ether solution the corresponding pyrazole was isolated in over 70% yield and identified by comparing its nmr spectrum with that of the reported nmr spectrum.[37]

Reaction of 3d,e with Ethanolic Sodium Ethoxide. 3(5)-Phenylpyrazole.—Compound **3d** (4.87 g, 0.01 mol) was added to a solution of 0.23 g (0.01 g-atom) of sodium in 150 ml of ethanol. The mixture was allowed to reflux for 10 hr. After cooling, the resultant mixture was concentrated to 20 ml, and 200 ml of ether was added. The resulting solution was washed with two 20-ml portions of ether. The ether layer was vigorously shaken with dilute hydrochloric acid (150 ml), and the acidic aqueous layer was separated and washed with ether–ethyl acetate (1:1) mixture which was combined with the former ether layer. The combined organic layers furnished triphenylphosphine (2.6 g, 97%). The acidic aqueous solution was basified with 10% aqueous sodium hydroxide. The heterogeneous resultant solution was extracted with ether (100 ml), dried ($MgSO_4$), and concentrated to obtain 1.5 g (80%) of an oil which crystallized on standing, mp 77–78° (lit.[38] mp 78°). The nmr spectrum is identical with that found in the literature.[39]

3(5)-Phenylpyrazole Picrate.—To a solution of 1.0 g (0.007 mol) of pyrazole in 10 ml of ether was added a saturated ether solution of picric acid (2.13 g, 0.01 mol). The solution was brought to a boil and then cooled immediately. Cooling overnight gave 2.2 g (91%) of yellow crystals: mp 170–172° (lit.[40] mp 168–170°); nmr ($CDCl_3$) δ 6.92 (d, 1, proton at C-4, J = 2.5 Hz), 8.09 [d, 1, proton at C-3(5)], 7.32–7.62 (m, 3, meta and para protons of phenyl ring), 7.62–7.96 (m, 2, ortho protons of phenyl ring), 8.71 (s, 2, protons of picric acid ring), 14.84 ppm (broad s, 2, NH, exchangeable with D_2O, chemical shift depends on concentration).

5,5-Diphenyl-2-pyrazoline, (19).—This reaction was run in the same manner as the reaction with **3d** using 0.23 g (0.01 g-atom) of sodium and 5.63 g (0.01 mol) of **3e**. Refluxing for 3 hr gave triphenylphosphine oxide instead of triphenylphosphine from the combined organic layers. After the usual work-up procedure, 1.4 g (72.5%) of an oily product was obtained. All spectral data and melting point were identical with those of **19e** obtained by basic hydrolysis of **3e**: ir (KBr) 3330 (NH), 1600 (C=N, phenyl), 780, 740, 700 (phenyl), 545 cm^{-1} (vinyl); nmr ($CDCl_3$) δ 3.23 (d, 2, $-CH_2-$, J = 1.6 Hz), 6.67 (t, 1, proton at C-3), 5.9 (broad s, 1, NH, exchangeable with D_2O, chemical shift depends on concentration), 7.21 ppm (s, 10, phenyl protons).

Aqueous Basic Hydrolysis of 3a–e. General Procedure.—A sample (0.01 mol) of **3a–e** was allowed to stir with a specified volume of 10% aqueous sodium hydroxide at room temperature or warmed and then immediately cooled to room temperature. The resultant reaction mixture was diluted with an equal volume of water and extracted with ether (200 ml). The ether extract was washed with dilute hydrochloric acid (two 100-ml portions). The separated acidic aqueous layer was washed with ether (50 ml), and the organic layers were combined, dried ($MgSO_4$), and concentrated to give triphenylphosphine oxide. The aqueous solution was basified and extracted with ether (200 ml). The dried ($MgSO_4$) ether extract was concentrated to obtain the individual 2-pyrazoline (see results in Table I).

TABLE I

AQUEOUS BASIC HYDROLYSIS OF COMPOUNDS **3a–e**

Salt	Base, ml	Time, min	Temp, °C	$(C_6H_5)_3PO$, %	2-Pyrazoline (**19**), %	Ref
3a	50	30	25	99	[a]	
3b	70	60	25	95	62.5[b]	43
3c	60[c]	120	25	100	[a]	
3d	50[c]	80	40	96	83[e]	44
3e	100	60	80	97	83.3[d]	44, 45

[a] 2-Pyrazoline was not observed. [b] Picrate was prepared, mp 124–126° [mp 126°, von K. Freudenberg and W. Stoll, *Justus Liebigs Ann. Chem.*, **440**, 44 (1924)]. [c] 5% aqueous sodium hydroxide. [d] Mp 70–73° [mp 72–78.5°, D. S. Matteson, *J. Org. Chem.*, **27**, 4293 (1962); 64.5–65.5°, M. Hamada, *et al.*, *Bull. Inst. Chem. Res., Kyoto Univ.*, **24**, 81 (1951)]; see the nmr and ir data in **19e**. [e] Nmr ($CDCl_3$) δ 2.38 (ddd, 1, cis proton at C-4 to phenyl, J_{gem} = 16.5 Hz, J_{trans} = 9.5 Hz), 2.90 (ddd, 1, trans proton at C-4 to phenyl, J_{cis} = 10 Hz), 4.52 (t, 1, proton at C-5), 6.56 (t, 1, proton at C-3, J = 1.5 Hz), 7.19 (s, 5, phenyl protons), 5.20 ppm (broad, s, 1, NH, exchangeable with D_2O, chemical shift depends on concentration).

(37) N. S. Bhacca, *et al.*, "NMR Spectra Catalog," Vol. II, Varian Associates, Palo Alto, Calif., 1963.

(38) K. Bowden and E. R. H. Jones, *J. Chem. Soc.*, 953 (1946).

(39) L. G. Tensmeyer and C. Ainsworth, *J. Org. Chem.*, **31**, 1878 (1966).

(40) I. I. Grandberg, *Zh. Obshch. Khim.*, **31**, 2793 (1961).

Attempted Wittig Olefination Reaction of 3a–e.[41] **General Method A.**—Sodium was dissolved in ethanol and the salt was added. After stirring the mixture for 10 min, freshly distilled carbonyl compound was added to the yellow ylide solution and allowed to stir at room temperature for 12 hr. The reaction mixture was worked up by the individual procedure cited.

General Method B.—To a solution of sodium dissolved in ethanol was added freshly distilled carbonyl compound and then the salt was added portionwise through a wide rubber tube which is connected to an erlenmeyer flask. The reaction mixture was allowed to stir at room temperature and worked up as described.

General Method C.—To a mixture of salt and carbonyl compound in ethanol was slowly added ethanolic sodium ethoxide through a dropping funnel. After stirring the reaction mixture for a defined time at room temperature, the mixture was worked up as described.

3(5)-Benzylpyrazole [24a(a′)].—The reaction was carried out by method B, using 250 ml of ethanol, 0.69 g (0.03 g-atom) of sodium, 3.67 g (0.035 mol) of benzaldehyde, and 12.3 g (0.03 mole) of **3a**. Reaction time was 8 hr. The resultant reaction mixture was concentrated to 50 ml, poured into water (100 ml), extracted with ether–ethyl acetate (3:2) mixture (150 ml), and dried ($MgSO_4$). After removing the solvent, the pale yellow oily liquid was distilled (short path) under vacuum. A colorless oil (3.0 g, 65%) was collected at 140–150° (0.05 mm Hg): $n^{20}D$ 1.5762; ir (neat) 3300 (free NH), 3100 (hydrogen bonded NH), 1608 (C=N, phenyl), 950 (vinyl), 765, 720 700 cm^{-1} (phenyl); nmr ($CDCl_3$) δ 3.95 (s, 2, $-CH_2-$), 5.96 (d, 1, proton at C-4, J = 2 Hz), 7.18 (s, 5, phenyl protons), 7.28 ppm [d, 1, proton at C-3(5)]. The chemical shift of the NH proton depends on concentration of sample and is exchangeable with D_2O.

Anal. Calcd for $C_{10}H_{10}N_2$: C, 75.91; H, 6.36; N, 17.71. Found: C, 75.96; H, 6.49; N, 17.67.

3(5)-Benzylpyrazole Picrate.—To a solution of 0.2 g (1.33 mmol) of **24a(a′)** in 5 ml of ethanol was added 0.458 g (2.0 mmol) of picric acid. The solution was boiled for 5 min. To the orange-colored mixture was added enough hexane to double the volume, and it was cooled in the refrigerator overnight. Yellow crystals (0.5 g, 99.5%) were collected and recrystallized from ethanol–petroleum ether: mp 125–127°; nmr (DMSO-d_6 + $CDCl_3$) δ 4.17 (s, 2, $-CH_2-$), 6.42 (d, 1, proton at C-4, J = 2.5 Hz), 7.30 (s, 5, phenyl protons), 8.01 [d, 1, proton at C-3(5)], 8.76 (s, 2, protons of picric acid ring), 15.54 ppm (s, 2, NH, chemical shift depends on concentration, exchangeable with D_2O).

Anal. Calcd for $C_{16}H_{13}N_5O_7$: C, 49.61; H, 3.38; N, 18.08. Found: C, 49.60; H, 3.24; N, 18.14.

3(5)-Benzyl-5(3)-methylpyrazole [24b(b′)].—The reaction was run according to method C using 150 ml of ethanol, 8.5 g (0.02 mol) of **3b**, 2.5 g (0.025 mol) of benzaldehyde, and 0.46 g (0.02 g-atom) of sodium. The ethanolic sodium ethoxide was added over the period of 2 hr and the reaction mixture was subsequently stirred for 10 hr. The resultant mixture was concentrated to 20 ml and ether (300 ml) was added. The solution was washed with water (two 200-ml portions). The ether layer was shaken with 10–20% hydrochloric acid (100 ml) for 10 min. The acidic aqueous layer was separated and washed with ether and ethyl acetate, basified with 20% aqueous sodium hydroxide, and extracted with two 200-ml portions of ether. The combined, dried ($MgSO_4$) ether extracts were concentrated to give 3.3 g (96%) of a pale yellow oil. An analytical sample of **24b(b′)** was obtained by distillation at 135–145° (0.05 mm). The distillate solidified on standing: mp 71–73° (lit. mp 72–73.5°,[42] 77–78° [43]); ir (KBr) 3370 (free NH), 3170–3070 (hydrogen bonded NH), 1600, 1580 (C=N, phenyl), 1030 (vinyl), 735, 700 cm^{-1} (phenyl); nmr ($CDCl_3$) δ 2.17 (s, 3, $-CH_3$), 3.91 (s, 2, $-CH_2-$), 5.75 (s, 1, vinyl proton at C-4), 7.20 (s, 5, phenyl protons), 12.40 ppm (s, 1, NH, exchangeable with D_2O and chemical shift depends on concentration). Compound **28b(b′)** was also obtained by method B (95%).

3-Benzyl-5-methylpyrazole Picrate.—To a solution of 1.0 g (5.9 mmol) of **24b(b′)** in 20 ml of ether and a few drops of EtOAc was added 2.0 g (8.7 mmol) of picric acid dissolved in EtOAc (3 ml). The mixture was boiled for 10 min and petroleum ether was added. After cooling in a refrigerator, one obtained 2.2 g (93%) of yellow crystals, recrystallized from ethanol: mp 119–121°; nmr (DMSO-d_6 + $CDCl_3$) δ 2.42 (s, 3, $-CH_3$), 4.11 (s, 2, $-CH_2-$), 6.17 (s, 1, proton at C-4), 7.30 (s, 5, phenyl protons), 8.88 ppm (s, 2, protons of picric acid ring). Two NH protons are exchangeable with D_2O and their chemical shifts depend on concentration.

Anal. Calcd for $C_{17}H_{15}N_5O_7$: C, 50.87; H, 3.77; N, 17.45. Found: C, 50.74; H, 3.69; N, 17.39.

3(5)-α,β-Diphenyl-β-hydroxyethyl-5(3)-phenylpyrazole [26d(d′)].—The reaction was carried out by method B using ethanol (200 ml), 0.69 g (0.03 g-atom) of sodium, 7.42 g (0.07 g-atom) of benzaldehyde, and 15 g (0.031 mol) of **3d**. The reaction was run for 11 hr. The resultant reaction mixture was concentrated to half its volume, poured into water, and extracted with 300 ml of ether. The dried ($MgSO_4$) ether extract was concentrated to furnish an oily liquid. The oily liquid was chromatographed on silica gel (hexane–ethyl acetate). Compound **26d(d′)**, was obtained (9.0 g, 88%), recrystallized from CH_2Cl_2–EtOAc: mp 183–185°; ir (KBr) 3360 (free NH), 3225–3125 (hydrogen bonded NH and OH), 1580, 1550 (C=N, phenyl), 1050 (CO), 770, 700 cm^{-1} (phenyl); nmr (DMSO-d_6) δ 4.35 [d, 1, $-CH(C_6H_5)$, J = 8.0 Hz], 5.30 [d, 2, NH and $-CH(C_6H_5)OH$], 6.59 (s, 1, proton at C-4), 7.00–7.58 [m, 14, OH phenyl protons at side chain and meta and para protons of the phenyl ring at C-5(3)], 7.58–7.90 ppm [m, 2, ortho protons of phenyl ring at C-5(3)]. After added D_2O, the integration of the phenyl proton region was 13 and 1 at 5.30.

Anal. Calcd for $C_{23}H_{20}N_2O$: C, 81.15; H, 5.92; N, 8.23. Found: C, 81.36; H, 5.63; N, 8.30.

3-(α,β-Diphenyl-β-hydroxyethyl)-5-phenylpyrazole Picrate.—To a solution of 0.5 g (1.45 mmol) of **26d(d′)** dissolved in EtOAc (10 ml) was added 0.6 g (2.00 mmol) of picric acid in EtOAc (5 ml). After boiling for 5 min, the resultant yellow solution was concentrated while adding hexane to precipitate 0.8 g (100%) of the picrate, recrystallized from EtOAc–hexane: mp 183–185°; nmr (DMSO-d_6 + $CDCl_3$) δ 4.52 [d, 1, $-CH(C_6H_5)-$, J = 6.0 Hz], 5.45 [d, 1, $-CH(C_6H_5)OH$], 6.84 (s, 1, proton at C-4), 7.19–7.35 (d, 10, phenyl protons at side chain), 7.35–7.60 (m, 3, meta and para protons of phenyl ring at C-5), 8.81 (s, 2, protons of picric acid ring), 10.39 ppm (s, 2, NH and OH, exchangeable with D_2O and chemical shift depends on concentration).

Anal. Calcd for $C_{29}H_{23}N_5O_8$: C, 61.15; H, 4.06; N, 12.02. Found: C, 61.03; H, 4.15; N, 12.13.

3(5)-Benzyl-5(3)-phenylpyrazole [24d(d′)] by Thermal Decomposition of 26d(d′).—A sample of **26d(d′)** (2 g, 5.8 mmol) was heated to 270–290° for 90 min in a microscale distillation apparatus. In the center section of the apparatus, 0.53 g (91.3%) of benzaldehyde was collected. The residue was dissolved in ether and concentrated while adding petroleum ether until crystals formed. The white crystalline **24d,d′** (1.3 g, 93.5%) was obtained: mp 89–90° (lit. mp 89–90°,[44] 90.5–91° [45]); ir (neat) 3250–3150 (NH), 1595, 1575 (phenyl, C=N), 1040, 1015 (vinyl), 970 (vinyl), 770, 720, 700 cm^{-1} (phenyl); nmr ($CDCl_3$) δ 3.75 (s, 2, $-CH_2-$), 6.15 (s, 1, proton at C-4), 7.0–7.4 (m, 8, para and meta proton of phenyl ring at C-5 and phenyl protons at side chain), 7.5–7.7 (m, 2, ortho protons of phenyl ring at C-5), 13.48 ppm (s, 1, NH, exchangeable with D_2O, chemical shift depends on concentration).

Attempted Reactions of 3(5)-Methyl- [24b(b′)] or Phenyl-5(3)-benzylpyrazole[46] **[24d(d′)] with Benzaldehyde.**—A sample (0.005 mol) of **24b(b′)** or **24d(d′)** was added to 30 ml of ethanol in which an equimolar amount of benzaldehyde and a catalytic amount of sodium had been dissolved. The resultant solution was allowed to stir at room temperature for 12 hr. The reaction mixture was poured into water, extracted with ether (100 ml), and dried ($MgSO_4$). The dried ether extract was concentrated to obtain an oily liquid which was shown by nmr to be only a mixture of starting materials in each case. No additional products were observed.

3-(α,β-Diphenyl-β-bromoethyl)-5-phenylpyrazole Hydrobromide (27).—A sample of **26d(d′)** (0.5 g, 1.47 mmol) was allowed to stir with 48% hydrogen bromide (20 ml) at room temperature for 1 hr. The mixture was filtered to furnish wet solids which were dissolved in chloroform. The chloroform solution was dried ($MgSO_4$) and concentrated while adding ether to pre-

(41) Attempted reactions with benzophenone, cyclohexanone, or cyclopentanone gave the same results as the reactions with refluxing ethanolic sodium ethoxide alone.

(42) J. B. Wright, *et al.*, *J. Med. Chem.*, **7**, 102 (1964).

(43) V. Y. Grinshtein, *et al.*, *ibid.*, **32**, 1077 (1962).

(44) D. G. Farnum and P. Yates, *J. Amer. Chem. Soc.*, **84**, 1399 (1962).

(45) C. Bürow and H. Grotowsky, *Chem. Ber.*, **34**, 1479 (1901).

(46) Prepared by a method reported by D. S. Matteson, *J. Org. Chem.*, **27**, 4293 (1962).

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.

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

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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).

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