Reactions of Phenylhydrazones with Electron-Deficient Alkenes

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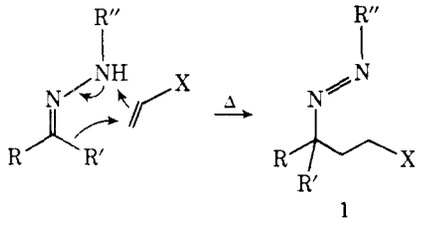
Reaction of aliphatic aldehyde phenylhydrazones with methyl acrylate or acrylonitrile gives phenylazoalkanes (**1**) by an ene reaction. With more electron-deficient alkenes such as methyl vinyl ketone or β-nitrostyrene, Michael reaction at nitrogen occurs followed by cyclization to give pyrazolidines. The reactions of phenylhydrazone monoanions with acrylonitrile take a variety of pathways depending on the counterion. The cuprous salt reacts from carbon to give **1**, the lithium salt initiates polymerization, and the diethylaluminum salt alkylates on nitrogen.

Hydrazones[1] are ambident nucleophiles and can react with electrophiles at either carbon or nitrogen. We hoped that monosubstituted hydrazones would undergo ene reactions[2] with electron-deficient alkenes (eq 1), which would force



(1)

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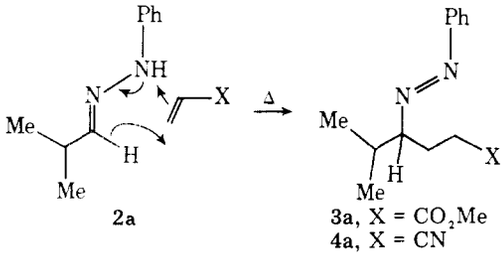
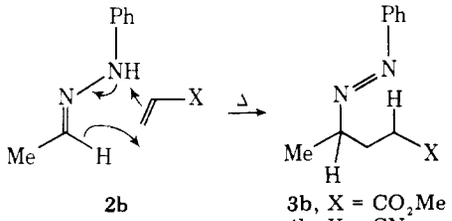
substitution to take place at carbon. Ene adduct **1** would be a useful intermediate since it could be converted to a ketone (if R′ = H) by isomerization and hydrolysis or to a primary amine by hydrogenolysis. Thus, hydrazones would constitute a class of carbonyl and amine anion equivalents which would undergo exclusively 1,4 addition in the absence of base. Ene-type products have been observed in the reaction of hydrazones with oxygen[3] and diethyl azodicarboxylate.[4] However, there are very few examples of reaction of carbon electrophiles at the carbon of hydrazones of simple carbonyl compounds.[5,6]

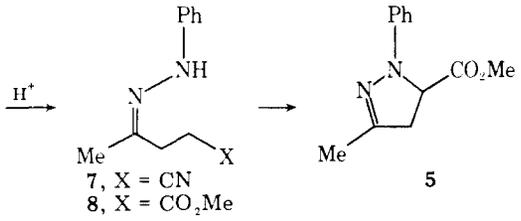
We chose to investigate phenylhydrazones. The more electron-deficient mono- and dinitrophenylhydrazones should be less reactive toward electrophilic species.[1,2] Replacement



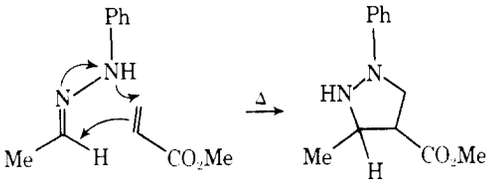
2a **3a**, X = CO_2Me; **4a**, X = CN

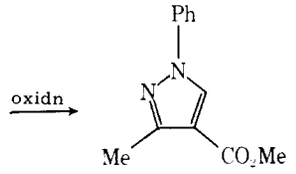


2b **3b**, X = CO_2Me; **4b**, X = CN



7, X = CN; **8**, X = CO_2Me **5**





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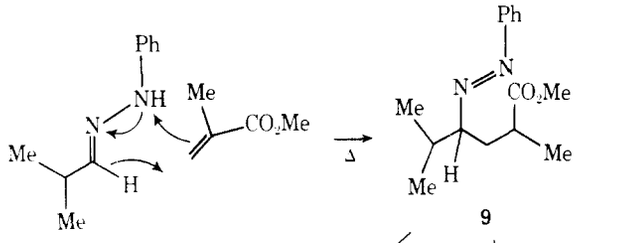

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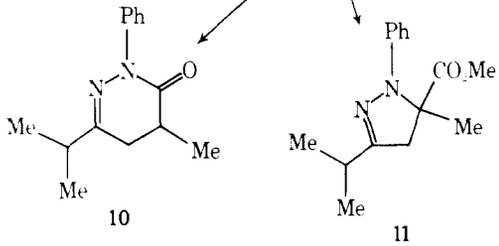

10 **11**

of the phenyl by an alkyl moiety is known to enhance reactivity at nitrogen more than at carbon.[7] Our initial experiments with methyl acrylate and acrylonitrile were encouraging. Treatment of isobutyraldehyde phenylhydrazone (**2a**) with methyl acrylate at 120 °C gives the ene adduct **3a** in 48% yield as a 93:7 mixture of trans/cis azo isomers.[8] Similarly, treatment of **2a** with acrylonitrile gives the phenylazoalkane **4a** in 71% yield as a 90:10 trans/cis mixture. Treatment of acetaldehyde phenylhydrazone (**2b**) with methyl acrylate gives 33% of the azo compound **3b** as a 66:34 trans/cis mixture. In addition, 21% of the pyrazoline **5**[9] and 5% of the pyrazole **6**[9] are obtained. Treatment of **2b** with acrylonitrile gives phenylazoalkane **4b** in 48% yield as an 85:15 trans/cis mixture and 19% of phenylhydrazone **7** derived from isomerization of **4b**. Phenylhydrazone **2a** reacts with excess methyl methacrylate at 120 °C, giving 20% of the *trans*-phenylazoalkane **9**, 21% of the dihydro-3-pyridazinone **10**, and 10% of the pyrazoline **11**. More hindered alkenes do not react with phenylhydrazones.[10]

The isolation of these novel azo compounds rather than the more stable isomeric hydrazones is of interest. It is known that

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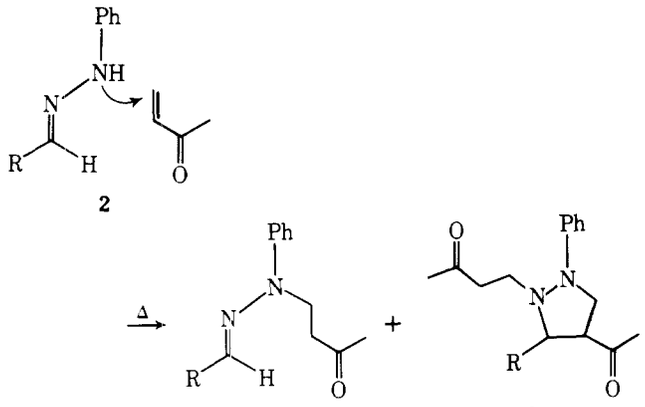
azo compounds isomerize to hydrazones in the presence of acid, base, or free radicals, or at elevated temperatures.[13] The temperatures used in our reactions are apparently low enough to permit isolation of the azo compounds. If deuteriochloroform probably containing traces of acid is used as solvent in the reaction of **2b** with methyl acrylate, the only product isolated is the phenylhydrazone **8**.[14] Pyrazolines **5** and **11** are probably derived from the azo compounds **3b** and **9**, respectively. Pyrazole **6** is probably derived from initial reaction at nitrogen (vide infra).

In contrast to the results with methyl acrylate and acrylonitrile, exclusive reaction at nitrogen occurs with methyl vinyl ketone. Treatment of **2a** with excess methyl vinyl ketone, neat, at 70 °C gives the Michael adduct **12a** in 40% yield along with



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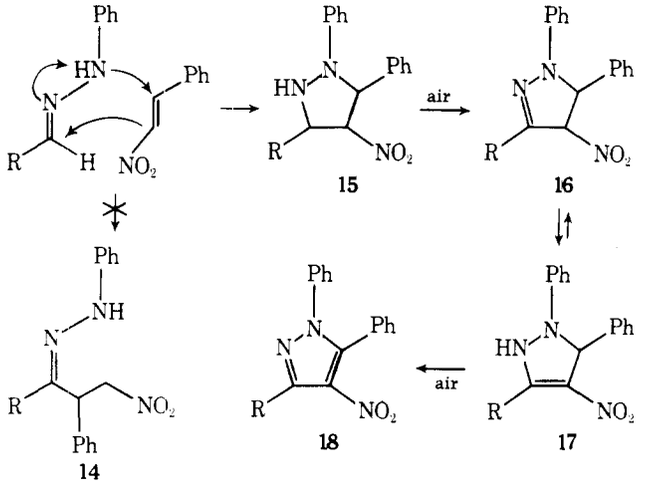
12 **13**

a, R = $CH(CH_3)_2$; b, R = CH_3

the 2:1 adduct pyrazolidine **13a** in 18% yield. In carbon tetrachloride **13a** is obtained as the only product in virtually quantitative yield. The reactions of **2b** with methyl vinyl ketone are completely analogous, giving **12b** and **13b** neat and only **13b** in carbon tetrachloride.

The reactions of phenylhydrazones with β-nitrostyrene at 30 °C were reported to give the alkylated phenylhydrazone **14**.[15] In light of our observation that either azo compounds or



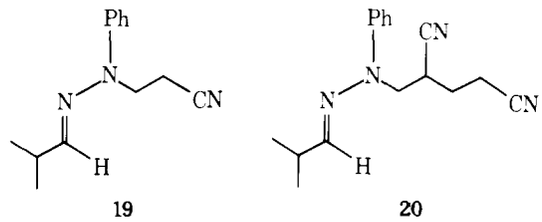
14 **15** **16** **17** **18**

a, R = $CH(CH_3)_2$; b, R = CH_2CH_3

N-functionalized compounds were obtained as initial products, this warranted reinvestigation. In our hands, treatment of **2a** with β-nitrostyrene, neat, at 25 °C gives the pyrazolidine **15a** in 77% yield.[16] Similarly, reaction of propionaldehyde phenylhydrazone with β-nitrostyrene gives the pyrazolidine **15b** in 57% yield. On standing in air, **15** oxidizes to the 2-pyrazoline **16**, which isomerizes rapidly to the apparently more stable 3-pyrazoline **17**.[17] On standing in air, **17** slowly oxidizes to the pyrazole **18**. The reactions of hydrazones with methyl vinyl ketone or β-nitrostyrene provide a simple route to a variety of unusual pyrazolidines.

The nature of the reaction of phenylhydrazones with electron-deficient alkenes varies with the substituent. While methyl acrylate and acrylonitrile give the desired ene reaction, better Michael acceptors such as methyl vinyl ketone or β-nitrostyrene react only at nitrogen. These differences suggest that reaction at carbon or nitrogen of the hydrazones might occur by different mechanisms. Reaction at carbon may proceed by a concerted ene reaction while reaction at nitrogen occurs by a Michael reaction. The relative reactivities of the alkenes used support this interpretation. While vinyl ketones are roughly four times as reactive as acrylonitriles or acrylates in the related Diels–Alder reactions,[18] they are 50–100 times as reactive in Michael reactions.[19] This suggests that increasing the strength of the electron-withdrawing group on the double bond will increase the rate of Michael reaction from nitrogen faster than the rate of the competing ene reaction.

To explore alternative approaches to C-functionalization of phenylhydrazones, we investigated the reactions of phenylhydrazone monoanions with acrylonitrile. The lithium salt of **2a** (obtained from **2a** and butyllithium in THF) initiated polymerization of acrylonitrile. On workup, polyacrylonitrile and recovered **2a** are obtained. Addition of 1 equiv of cuprous iodide to the lithium salt of **2a** presumably gives an organocopper species which reacts with acrylonitrile to give azo compound **3a** in 50% yield. On the other hand, addition of 1 equiv of diethylaluminum chloride to the lithium salt followed by addition of acrylonitrile gives the monoadduct **19** in 16%



19 **20**

yield and the diadduct **20** in 7% yield. Variation of the counterion of phenylhydrazone monoanions is a potentially valuable method for controlling the site of reaction of this ambident nucleophile.

Experimental Section

All reactions of phenylhydrazones were run under a nitrogen atmosphere in pyridine-washed glassware. Reactions at elevated temperatures were performed in sealed tubes that were degassed and sealed in vacuo. THF and benzene were distilled from sodium benzophenone ketyl. Acrylonitrile, methyl acrylate, methyl methacrylate, and methyl vinyl ketone were distilled before use. Phenylhydrazones were prepared by literature procedures[20] and purified by vacuum distillation. Phenylhydrazones are mixtures of syn and anti isomers. Azo compounds are inseparable mixtures of cis and trans isomers.

NMR spectra were obtained on a Varian A-60 or XL-100 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 283. Mass spectra were recorded on an AEI MS-9 and ultraviolet spectra on a Cary 14. Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected.

Reaction of Methyl Acrylate with 2a. Isobutyraldehyde phenylhydrazone (**2a**; 112 mg, 0.69 mmol), methyl acrylate (144 mg, 1.68 mmol), and hydroquinone (2.5 mg) were heated in 0.5 mL of benzene-d_6 for 63 h at 120 °C. The solvent was evaporated in vacuo, and the residue was chromatographed on alumina in 9:1 petroleum ether–ether, giving 82 mg (48%) of a 93:7 trans/cis mixture of **3a** as a yellow oil. The spectral data for the trans isomer are the following: NMR ($CDCl_3$) δ 0.98 (3 H, d, J = 7 Hz), 1.05 (3 H, d, J = 7 Hz), 2.1 (5 H, m), 3.35 (1 H, m), 3.65 (3 H, s), and 7.21–7.78 (5 H, m); IR (neat) 1741, 1591, 1581, and 1521 cm^{-1}; MS m/e (relative intensity) 249 (0.6), 248 (M^+, 2.8), 218 (0.9), 217 (9.1), 189 (22.2), 175 (3.3), 144 (5.2), 143 (62.4), 111 (89.4), 83 (69.4), and 77 (100.0); UV λ_{max} (heptane) (log ε) 255 (4.12) and 407 (2.13) nm; ^{13}C NMR ($CDCl_3$) δ 19.1, 19.3, 25.7, 30.9, 31.9, 51.4, 82.6, 122.1, 128.7, 130.2, and 173.4. The absorption due to the fully substituted phenyl carbon was too weak to be observed. The

cis isomer was detected by NMR: ($CDCl_3$) δ 6.75 (2 H, d of d, J = 8, 2 Hz). Anal. Calcd for $C_{14}H_{20}N_2O_2$: C, 67.71; H, 8.19; N, 11.28. Found: C, 67.63; H, 8.19; N, 11.46.

Reaction of Acrylonitrile with 2a. Isobutyraldehyde phenylhydrazone (**2a,** 188 mg, 1.15 mmol) and acrylonitrile (121 mg, 2.27 mmol) were heated in 0.5 mL of benzene-d_6 for 63 h at 120 °C. The solvent was evaporated in vacuo, and the residue was chromatographed on alumina in 9:1 petroleum ether–ether, giving 177 mg (71.4%) of a 90:10 trans/cis mixture of **4a** as a yellow oil. The spectral data for the trans isomer are the following: NMR ($CDCl_3$) δ 0.96 (3 H, d, J = 7 Hz), 1.02 (3 H, d, J = 6.5 Hz), 2.22 (5 H, m), 3.49 (1 H, m), 7.26–7.83 (5 H, m); IR (neat) 2252, 1601, 1521, and 1496 cm^{-1}; MS m/e (relative intensity) 216 (1.0), 215 (M^+, 17.3), 196 (2.4), 145 (1.5), 144 (3.5), 143 (2.4), 131 (2.7), 130 (1.2), 117 (31.8), 105 (94.3), 78 (51.1), and 77 (100.0). The cis isomer was detected by NMR: ($CDCl_3$) δ 6.75 (2 H, d of d, J = 8, 2 Hz). Anal. Calcd for $C_{13}H_{17}N_3$: m/e 215.1422. Found: m/e 215.1427.

Reaction of Methyl Acrylate with 2b. Acetaldehyde phenylhydrazone (**2b;** 93 mg, 0.625 mmol), methyl acrylate (360 mg, 4.18 mmol), and hydroquinone (5 mg) were heated for 12 h at 110 °C and for 20 h at 115 °C. Evaporation in vacuo followed by chromatography on alumina in 9:1 petroleum ether–ether gave 46 mg (33%) of **3b** as a 2:1 trans/cis mixture, 6.7 mg (5%) of pyrazone **6,** and 29.3 mg (21%) of pyrazoline **5.**

The spectral data for **3b** are as follows: trans isomer NMR ($CDCl_3$) δ 1.38 (3 H, d, J = 7 Hz), 2.0–2.5 (4 H, m), 3.65 (3 H, s), 3.6–3.9 (1 H, m), and 7.2–7.8 (5 H, m); cis isomer NMR ($CDCl_3$) δ 1.21 (3 H, d, J = 7 Hz), 2.0–2.5 (4 H, m), 3.61 (3 H, s), 3.6–3.9 (1 H, m), 6.67 (2 H, d of d, J = 8, 2 Hz), and 7.2–7.8 (3 H, m); IR (neat) 1740, 1600, 1520, and 1500 cm^{-1}; MS m/e (relative intensity) 220 (M^+, 6.2), 189 (26.4), 162 (8.4), 115 (90.1), 105 (100.0), and 77 (65.9). Anal. Calcd for $C_{12}H_{16}N_2O_2$: m/e 220.1212. Found: m/e 220.1217.

The spectral data for **6** are the following: NMR (CCl_4) δ 2.5 (3 H, s), 3.77 (3 H, s), 7.2–7.8 (5 H, m), and 8.25 (1 H, s); IR (neat) 1705, 1600, 1550, and 1510 cm^{-1}; MS m/e (relative intensity) 216 (M^+, 3.5), 79 (100.0), and 77 (63.8). This compound has spectral data identical with those previously reported.[5c]

The spectral data for **5** are as follows: NMR (CCl_4) δ 2.01 (3 H, t, J = 1 Hz), 2.99 (2 H, m), 3.67 (3 H, s), 4.45 (1 H, d of d, J = 8, 10.5 Hz), and 6.8–7.3 (5 H, m); IR (neat) 1740, 1600, and 1500 cm^{-1}; MS m/e (relative intensity) 218 (M^+, 6.1), 159 (29.6), 142 (15.2), 123 (33.3), 105 (35.4), 95 (51.9), 81 (100.0), and 77 (92.6). The NMR spectrum of **5** is identical with the previously reported spectrum.[5c]

Reaction of Acrylonitrile with 2b. Acetaldehyde phenylhydrazone (**2b;** 289 mg, 1.94 mmol), acrylonitrile (1 g), and hydroquinone (15 mg) were heated for 47 h at 115 °C. Evaporation in vacuo and chromatography on silica in 9:1 petroleum ether–ether gave 59 mg (17%) of an unidentified compound and 174 mg (48%) of **4b** as an 85:15 trans/cis mixture followed by 68.3 mg (19%) of **7.**

The spectral data for the trans isomer of **4b** are the following: NMR ($CDCl_3$) δ 1.38 (3 H, d, J = 7 Hz), 2.0–2.6 (4 H, m), 3.6–4.2 (1 H, m), and 7.2–7.9 (5 H, m); IR (neat) 2255, 1595, 1520, and 1485 cm^{-1}; MS m/e (relative intensity) 187 (M^+, 5.5), 117 (8.2), 105 (35.5), 91 (3.6), 82 (5.5), 78 (11.8), and 77 (100.0). The cis isomer was detected by NMR: ($CDCl_3$) δ 6.75 (2 H, d of d, J = 8, 2 Hz). Anal. Calcd for $C_{11}H_{13}N_3$: m/e 187.1109. Found: m/e 187.1113.

The spectral data for **7** are as follows: NMR ($CDCl_3$) δ 1.78, 2.10 (3 H, 2s, CH_3, syn + anti isomer), 2.4–2.7 (4 H, m), and 6.6–7.5 (6 H, m); IR (neat) 3340, 2255, 1600, and 1500 cm^{-1}.

Reaction of Methyl Methacrylate with 2a. Isobutyraldehyde phenylhydrazone (**2a;** 139 mg, 0.86 mmol), methyl methacrylate (403 mg, 4.03 mmol), and hydroquinone (5 mg) were heated for 69 h at 120 °C. Chromatography on alumina using 9:1 petroleum ether–ether gave 20% of **9,** 21% of **10,** and 10% of **11.**

The spectral data for **9:** NMR ($CDCl_3$) δ 0.95 (3 H, d, J = 6.5 Hz), 1.00 (3 H, d, J = 7 Hz), 1.20 (3 H, d, J = 7 Hz), 1.63–2.86 (4 H, m), 3.53 (3 H, s), 3.27–3.85 (1 H, m), and 7.30–7.87 (5 H, m); IR (neat) 1739, 1600, and 1520 cm^{-1}; MS m/e (relative intensity) 262 (M^+, 2.5), 230 (8.3), 203 (2.5), 187 (2.5), 156 (59.7), 125 (13.3), 105 (58.3), 97 (94.4), and 77 (100.0). Anal. Calcd for $C_{15}H_{22}N_2O_2$: m/e 262.1681. Found: m/e 262.1678.

The spectral data for **10:** NMR ($CDCl_3$) δ 1.13 (6 H, d, J = 6.5 Hz), 1.30 (3 H, d, J = 6.5 Hz), 2.15–3.06 (4 H, m), and 7.0–7.7 (5 H, m); IR (neat) 3350, 1671, 1596, and 1490 cm^{-1}; MS m/e (relative intensity) 230 (M^+, 53.2), 215 (2.9), 201 (5.4), 187 (8.8), 157 (33.7), 145 (9.8), 133 (22.0), 132 (27.3), 105 (40.5), and 77 (100.0). Anal. Calcd for $C_{14}H_{18}N_2O$: m/e 230.1419. Found: m/e 230.1422.

The spectral data for **11:** NMR ($CDCl_3$) δ 1.21 (6 H, d, J = 7 Hz), 1.49 (3 H, s), 2.71 (1 H, m), 2.82 (1 H, d, J = 17 Hz), 3.31 (1 H, d, J = 17 Hz), 3.76 (3 H, s), and 6.72–7.32 (5 H, m); IR (neat) 1740, 1600, 1577, and 1500 cm^{-1}; MS m/e (relative intensity) 260 (M^+, 18.6), 231 (7.2), 230 (7.2), 201 (99.1), 159 (41.2), 126 (22.4), 105 (48), and 77 (100.0). Anal. Calcd for $C_{15}H_{20}N_2O_2$: m/e 260.1525. Found: m/e 260.1524.

Reaction of 2b with Methyl Acrylate in Chloroform. Methyl acrylate (146 mg, 1.7 mmol) and **2b** (115 mg, 0.86 mmol) were heated overnight at 120 °C in deuteriochloroform. Chromatography on silica with 7:3 petroleum ether–ether as eluent gave 66 mg (35%) of **8** as an ca. 3:1 mixture of syn and anti isomers as the only identifiable product: mp 80–84 °C; NMR ($CDCl_3$) δ 1.68 (0.75 × 3 H, s), 1.95 (0.25 × 3 H, s), 2.4–3.1 (4 H, m), 3.48 (0.75 × 3 H, s), 3.51 (0.25 × 3 H, s), and 6.55–7.35 (6 H, m); IR (KBr) 3335, 1733, 1710, 1600, and 1502 cm^{-1}; MS m/e (relative intensity) 221 (9.0), 220 (M^+, 55.8), 189 (9.0), 161 (13.5), 160 (14.1), 159 (87.2), 92 (100.0), and 77 (94.2). Anal. Calcd for $C_{12}H_{16}N_2O_2$: m/e 220.1212. Found: m/e 220.1206.

Reaction of Methyl Vinyl Ketone with 2a Neat. Isobutyraldehyde phenylhydrazone (**2a;** 171 mg, 1.06 mmol), methyl vinyl ketone (347 mg, 4.91 mmol), and hydroquinone (13 mg) were heated for 48 h at 50 °C and 18 h at 70 °C. Purification was accomplished by chromatography on silica gel. Elution with 7:3 petroleum ether–ether gave 40% of **12a** as a yellow oil: NMR ($CDCl_3$) δ 1.14 (6 H, d, J = 7 Hz), 2.17 (3 H, s), 2.32–3.04 (1 H, m), 2.68 (2 H, t, J = 7 Hz), 4.08 (2 H, t, J = 7 Hz), 6.87 (1 H, d, J = 4.5 Hz), and 6.5–7.5 (5 H, m); IR (neat) 1713 cm^{-1}; MS m/e (relative intensity) 232 (M^+, 8.8), 217 (4.5), 175 (9.0), 160 (48.3), 159 (100.0), 105 (18.1), 91 (36.9), and 77 (59.5). Anal. Calcd for $C_{14}H_{20}N_2O$: m/e 232.1575. Found: m/e 232.1560.

Elution with 3:7 petroleum ether–ether gave 18% of the 2:1 adduct **13a:** NMR ($CDCl_3$) δ 0.65 (3 H, d, J = 6.5 Hz), 0.90 (3 H, d, J = 6 Hz), 1.27–1.86 (1 H, m), 2.04 (3 H, s), 2.28 (3 H, s), 2.10–4.16 (8 H, m), and 6.75–7.58 (5 H, m); IR (neat) 1707, 1595, and 1495 cm^{-1}; MS m/e (relative intensity) 302 (M^+, 8.0), 259 (9.0), 232 (67.4), 231 (27.9), 189 (15.1), 176 (10.1), 175 (73.3), and 77 (100.0). Anal. Calcd for $C_{18}H_{26}N_2O_2$: m/e 302.1994. Found: m/e 302.2000.

Reaction of Methyl Vinyl Ketone and 2a in Carbon Tetrachloride. Methyl vinyl ketone (137 mg, 1.96 mmol), **2a** (86 mg, 0.53 mmol), and hydroquinone (4 mg) were dissolved in 5 mL of carbon tetrachloride and heated for 7.5 h at 70 °C. Evaporation of the solvent and excess methyl vinyl ketone in vacuo gave a quantitative yield of **13a** which was pure as determined by NMR spectroscopy.

Reaction of Methyl Vinyl Ketone and 2b Neat. Methyl vinyl ketone (600 mg), hydroquinone (10 mg), and **2b** (238 mg, 1.78 mmol) were heated for 2.5 h at 70 °C. Evaporation of the excess methyl vinyl ketone gave an ca. 2:1 mixture of **12b** and **13b.** The spectral data for **12b** are the following: NMR ($CDCl_3$) δ 2.02 (3 H, d, J = 4.5 Hz), 2.10 (3 H, s), 2.68 (2 H, t, J = 7.5 Hz), 4.02 (2 H, t, J = 7.5 Hz), 6.8 (1 H, m), and 6.9–7.4 (5 H, m).

Reaction of 2b with Methyl Vinyl Ketone in Carbon Tetrachloride. Methyl vinyl ketone (200 mg, 2.86 mmol) and **2b** (200 mg, 1.49 mmol) were heated for 3 h at 70 °C in 1 mL of carbon tetrachloride. Evaporation of the solvent gave virtually pure **13b** which could be purified by chromatography on silica to give 250 mg (83%) of **13b:** NMR ($CDCl_3$) δ 0.61 (3 H, d, J = 6.5 Hz), 1.97 (3 H, s), 2.17 (3 H, s), 2.53 and 3.02 (4 H, A_2B_2), 3.3–3.9 (4 H, m), and 6.7–7.4 (5 H, m); IR (neat) 1710, 1595, and 1495 cm^{-1}.

Reaction of β-Nitrostyrene with 2a. A mixture of isobutyraldehyde phenylhydrazone (**2a;** 631 mg, 3.89 mmol) and β-nitrostyrene (580 mg, 3.39 mmol) was allowed to stand for 48 h under nitrogen. The orange solid which formed was triturated twice with ether and recrystallized from hexane, giving orange crystals: mp 153–155 °C in vacuo (lit.[16] mp 139–140 °C); NMR ($CDCl_3$) δ 1.00 (3 H, d, J = 5.5 Hz), 1.22 (3 H, d, J = 5 Hz), 1.61 (1 H, m), 3.39 (1 H, m), 4.43 (1 H, br d, J = 13 Hz, exchanges with D_2O), 4.97 (1 H, d, J = 1 Hz), 5.10 (1 H, d of d, J = 1, 4 Hz), and 6.6–7.5 (10 H, m); IR ($CHCl_3$) 3157, 3090, 3069, 3037, 2972, 2940, 2917, 2900, 2880, 1602, 1541, 1500, 1472, 1454, 1393, 1375, and 1362 cm^{-1}; MS m/e (relative intensity) 263 ($M^+ - (NO_2 + H_2)$, 9.7), 262 (50.7), 248 (13.8), 247 (69.5), 143 (20.7), 111 (15.6), 105 (31.2), and 77 (100.0).

Under a variety of conditions we have been unable to obtain any other products from this reaction. The orange color is probably due to a highly colored impurity not easily removed by recrystallization.

Reaction of Propionaldehyde Phenylhydrazone with β-Nitrostyrene. β-Nitrostyrene (754 mg, 5 mmol) and propionaldehyde phenylhydrazone (740 mg, 5 mmol) were dissolved in 1 mL of ether, giving a homogeneous solution. The ether was removed in vacuo, and the resulting mixture was allowed to stand for 48 h at 25 °C. On addition of ether, an orange precipitate formed. This was washed twice with 1 mL of ether and dried at 0.1 torr, giving 0.84 g (2.38 mmol, 56.7%) of **15b,** mp 125–127 °C in vacuo (lit.[16] mp 115–116 °C). Recrystallization from hexane under nitrogen did not change the melting point. The spectral data for **15b** are as follows: NMR ($CDCl_3$) δ 0.90–1.72 (5 H, m, A_3B_2), 3.40–4.00 (1 H, m), 4.34 (1 H, br d, J = 12 Hz, exchanges with D_2O), 5.05 (2 H, m), and 6.6–7.5 (10 H, m); MS

m/e (relative intensity) 298 (7.8), 297 (M^+, 32.1), 248 (20.0), 148 (20.0), 145 (100.0), 117 (12.2), 105 (7.8), 93 (14.8), 92 (17.4), 91 (19.1), and 77 (32.2). Anal. Calcd for $C_{17}H_{19}N_3O_2$: *m/e* 297.1477. Found: *m/e* 297.1486.

Oxidation of 15a. Pyrazolidine **15a** (135 mg) was dissolved in 0.5 mL of $CHCl_3$ and stirred at 25 °C for 48 h, giving **17a** in quantitative yield as an orange oil: NMR ($CDCl_3$) δ 1.34 (6 H, d, J = 7 Hz), 3.13 (1 H, hept, J = 7 Hz), 6.35 (1 H, s), and 7.23–7.25 (10 H, 2s); IR (neat) 1600, 1552, 1508, and 1375 cm^{-1}; MS *m/e* (relative intensity) 263 ($M^+ - NO_2$, 98.2), 261 (26.1), 248 (35.6), 247 (98.2), 143 (81.2), and 77 (100).

At shorter reaction times the presence of **16a** was detected spectroscopically: NMR ($CDCl_3$) δ 5.45 (1 H, d, J = 4.5 Hz) and 5.68 (1 H, d, J = 4.5 Hz).

Oxidation of 17a. On standing in air, **17a** oxidized to form **18a** as a yellow solid: mp 133–138 °C; NMR ($CDCl_3$) δ 1.42 (6 H, d, J = 7 Hz), 3.74 (1 H, hept, J = 7 Hz), and 7.08–7.53 (10 H, m); IR (KBr) 1596, 1552, 1502, and 1359 cm^{-1}; MS *m/e* (relative intensity) 307 (M^+, 68.2), 292 (12.0), 291 (21.2), 290 (100.0), 262 (31.1), 247 (37.1), 180 (61.2), and 77 (75.9). Anal. Calcd for $C_{18}H_{17}N_3O_2$: *m/e* 307.1321. Found: *m/e* 307.1322.

Oxidation of 15b. A solution of **15b** (64 mg) was allowed to stand for 72 h in 0.5 mL of deuteriochloroform with exposure to the air. Examination of the NMR spectrum indicated that an ca. 3:1 mixture of **17b** and **18b** was present. On further standing the proportion of **18b** in the mixture increased. The spectral data for **17b** are the following: NMR ($CDCl_3$) δ 1.33 (3 H, t, J = 7.5 Hz), 2.70 (2 H, q, J = 7.5 Hz), 4.72 (1 H, br s), 6.38 (1 H, s), and 7.23–7.28 (10 H, 2s). The spectral data for **18b** are as follows: NMR ($CDCl_3$) δ 1.47 (3 H, t, J = 7.5 Hz), 3.13 (2 H, q, J = 7.5 Hz), and 7.23–7.28 (10 H, m).

Reaction of the Lithium Salt of 2a with Acrylonitrile. To a solution of butyllithium (0.73 mL, 1.17 mmol, 1.6 M in hexane) in 10 mL of THF at −78 °C was added a solution of **2a** (190 mg, 1.17 mmol) in 2 mL of THF. The resulting yellow solution was stirred at −78 °C for 1 h followed by addition of acrylonitrile (80.6 mg, 1.52 mmol). The solution was then stirred for 3 h at −78 °C, allowed to warm slowly to 25 °C, and stirred for 6 h. Quenching with water (5 mL) and addition of ether (5 mL) gave an orange precipitate, which was filtered, washed with water, and dried in vacuo. The resulting solid had IR spectral and solubility properties characteristic of polyacrylonitrile.

The aqueous layer was washed with ether, and the combined organic layers were dried over magnesium sulfate and evaporated, giving 167 mg (88%) of recovered **2a.**

Reaction of the Copper Salt of 2a with Acrylonitrile. Cuprous iodide (215 mg, 1.12 mmol) was transferred from a Schlenk tube to a Schlenk flask containing the lithium salt of **2a** prepared as previously described from 169 mg (1.04 mmol) of **2a.** The resulting solution was allowed to stir for 2 h at −30 °C, giving a homogeneous green solution. Acrylonitrile (67.3 mg, 1.27 mmol) was added in 2 mL of THF, and the solution was stirred for 1.5 h at −25 °C and quenched with 15 mL of water. The organic layer was separated, and the aqueous layer was washed twice with ether. The combined organic layers were washed with water, dried over magnesium sulfate, and evaporated, giving 196 mg (97% recovery) of yellow oil which was shown by NMR to be 60% **4a** and 40% recovered **2a.** Purification by chromatography on alumina gave pure **4a** in 50% yield.

Reaction of the Aluminum Salt of 2a with Acrylonitrile. To a solution of the lithium salt of **2a** prepared as previously described from 180 mg of **2a** (1.11 mmol) was added diethylaluminum chloride (0.618 mL, 1.106 mmol, 25% in toluene). The mixture was stirred for 1 h at −78 °C, and acrylonitrile (198 mg, 3.73 mmol) was added. The solution was stirred for 3 h at −78 °C and overnight at 25 °C. The reaction was quenched with 10 mL of saturated ammonium chloride solution and extracted with three 5-mL portions of ether. The combined organic layers were filtered through Celite, washed with water, and dried over sodium sulfate. Evaporation in vacuo gave 148 mg of yellow oil which was chromatographed on silica gel. Elution with 20% ethyl acetate in hexane gave 34 mg (16%) of **19** and 18.5 mg (7%) of **20.**

The spectral data for **19:** NMR ($CDCl_3$) δ 1.04 (6 H, d, J = 6.5 Hz), 2.51 (2 H, t, J = 7.5 Hz), 2.4–2.6 (1 H, m), 3.93 (2 H, t, J = 7 Hz), 6.82 (1 H, d, J = 5 Hz), and 6.91–7.50 (5 H, m); MS *m/e* (relative intensity) 216 (11.0), 215 (M^+, 79.0), 176 (13.0), 175 (99.0), 146 (10.0), 106 (85.0), 105 (71.0), 104 (62.0), 91 (10.0), and 77 (100.0). Anal. Calcd for $C_{17}H_{13}N_3$: *m/e* 215.1422. Found: *m/e* 215.1427.

The spectral data for **20:** NMR ($CDCl_3$) δ 0.99 (6 H, d, J = 6.5 Hz), 1.20–2.75 (5 H, m), 3.20 (1 H, m), 3.75 (2 H, m), 6.75 (1 H, d, J = 5 Hz), and 7.0–7.5 (5 H, m); MS *m/e* (relative intensity) 269 (5.7), 268 (M^+, 27.6), 176 (13.6), 175 (100.0), 106 (41.2), 105 (32.0), 104 (32.6), 91 (8.8), and 77 (39.5). Anal. Calcd for $C_{16}H_{20}N_4$: *m/e* 268.1688. Found: *m/e* 268.1690.

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Registry No.—(*E*)-**2a,** 68184-48-5; (*Z*)-**2a,** 68184-49-6; **2a**·lithium, 68184-81-6; **2a**·copper, 68184-82-7; **2a**·aluminum, 68184-83-8; (*E*)-**2b,** 20488-38-4; (*Z*)-**2b,** 27935-60-0; *cis*-**3a,** 68184-50-9; *trans*-**3a,** 68184-51-0; *cis*-**3b,** 68184-52-1; *trans*-**3b,** 68184-53-2; *cis*-**4a,** 68184-54-3; *trans*-**4a,** 68184-55-4; *cis*-**4b,** 68184-56-5; *trans*-**4b,** 68184-57-6; **5,** 55115-02-1; **6,** 18093-95-3; (*E*)-**7,** 68184-58-7; (*Z*)-**7,** 68184-59-8; (*E*)-**8,** 68184-60-1; (*Z*)-**8,** 68184-61-2; **9,** 68184-62-3; **10,** 68184-63-4; **11,** 68184-64-5; (*E*)-**12a,** 68184-65-6; (*Z*)-**12a,** 68184-66-7; (*E*)-**12b,** 68184-67-8; (*Z*)-**12b,** 68184-68-9; **13a,** 68184-69-0; **13b,** 68184-70-3; **15a,** 68184-71-4; **15b,** 68184-72-5; **16a,** 68184-73-6; **17a,** 68184-74-7; **17b,** 68184-75-8; **18a,** 68184-76-9; **18b,** 68184-77-0; (*E*)-**19,** 68184-78-1; (*Z*)-**19,** 68212-37-3; (*E*)-**20,** 68184-79-2; (*Z*)-**20,** 68184-80-5; methyl methacrylate, 80-62-6; β-nitrostyrene, 102-96-5; methyl vinyl ketone, 78-94-4; propionaldehyde phenylhydrazone, 5311-88-6; methyl acrylate, 96-33-3; acrylonitrile, 107-13-1; polyacrylonitrile, 25014-41-9.

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