6-Acetamido-3-carboxy-5-oxo-4,5-dihydro-1,2-dithiolo-[4,3-*b*]pyrrole (11b). A solution of KOH (25 mg, 0.45 mmol) in methanol (0.5 mL) was added to the ester **11a** (8.7 mg, 0.032 mmol) in tetrahydrofuran (5 mL). After 7 h at room temperature crystals of the sodium salt of **11b** were separated by filtration and washed by tetrahydrofuran. A solution of this salt in water (0.3 mL) was acidified with excess 2 N HCl and the precipitated **11b** filtered and washed with water. Drying in vacuo and crystallization from tetrahydrofuran gave the acid **11b** as solvated orange crystals (4.1 mg, 50%): mp 201–202 °C (TLC of material recovered from the melting point determination showed the presence of holomycin formed by thermal decarboxylation); MS (70 eV) *m/e* (rel intensity) 214 ($M^+ - CO_2$, 40), 172 ($M^+ - CO_2 - CH_2CO$, 81), 44 (CO_2, 100).

Anal. Calcd for $C_8H_6N_2O_4S_2 \cdot \frac{2}{3}(C_4H_8O)$: C, 41.82; H, 3.73; N, 9.15. Found: C, 41.54; H, 3.87; N, 8.96.

6-Acetamido-5-oxo-4,5-dihydro-1,2-dithiolo[4,3-*b*]pyrrole (Holomycin, 11c). A mixture of the ester **11a** (10 mg, 0.037 mmol) and anhydrous LiI (70 mg, 0.52 mmol) in pyridine (2 mL) was heated on a steam bath for 35 h. Dilute HCl was added and the products extracted into ethyl acetate which was then washed with dilute HCl and brine. After drying ($MgSO_4$) the solvent was removed in vacuo and the residue purified by TLC (silica gel, ethyl acetate–hexane–acetic acid, 1:1:0.04) yielding holomycin (**11c**) as an orange powder (3.5 mg, 44%), mp 265–270 °C dec. A sample sublimed at 200 °C (0.4 mm) had mp 271–274 °C dec, not depressed by admixture with an authentic sample of mp 270–273 °C[6] (lit.[2,4b] 264–271 °C dec); UV max (CH_3OH) 230 (sh), 246 (sh), 299, 386 nm (log ϵ 3.48, 3.37, 3.11, 3.54); IR (KBr) 1660, 1635, 1595, 1545 cm^{-1}; MS (70 eV) *m/e* (rel intensity) 214 (M^+, 19), 172 (50), 43 (100). The physical data are consistent with the literature values.[2,4b]

Acknowledgments. We would like to thank A. Braemer and S. Hitt for the microbiological data and L. Tökés, M. Maddox, J. Nelson, and L. Kurz for the spectral data. We also thank E. J. Corey and G. Stork for very helpful suggestions. The authentic specimen of holomycin used for comparison with synthetic material was kindly supplied by G. H. Büchi.

Registry No.—**3**, 62698-38-8; **4**, 62698-39-9; 4 *p*-nitrobenzoyl derivative, 62698-37-7; **5**, 62698-40-2; **6**, 62698-41-3; **7**, 62698-42-4; **8**, 62698-43-5; **9**, 62698-44-6; **10a**, 62698-45-7; **10b**, 62698-46-8; **11a**, 62698-47-9; **11b** Na salt, 62698-48-0; **11b**, 62698-49-1; **11c**, 488-04-0; *p*-methoxyacetophenone, 100-06-1; methyl thioglycolate, 2365-48-2; methoxalyl chloride, 5781-53-3; methanesulfonyl chloride, 124-63-0; *p*-methoxybenzylamine, 2393-23-9; *N*-methanesulfonyl-*p*-methoxybenzylamine, 42060-31-1.

References and Notes

(1) Publication No. 480 from the Syntex Institute of Organic Chemistry.
(2) L. Ettlinger, E. Gäuemann, R. Hütter, W. Keller-Schierlein, F. Kradolfer, L. Neipp, V. Prelog, and H. Zähner, *Helv. Chim. Acta*, **42**, 563 (1959).
(3) Y. Kishi, T. Fukuyama, and S. Nakatsuka, *J. Am. Chem. Soc.*, **95**, 6490 (1973).
(4) (a) U. Schmidt and F. Geiger, *Justus Liebigs Ann. Chem.*, **664**, 168 (1963); (b) G. Büchi and G. Lukas, *J. Am. Chem. Soc.*, **86**, 5654 (1964); (c) K. Hagio and N. Yoneda, *Bull. Chem. Soc. Jpn.*, **47**, 1484 (1974).
(5) P. G. Pietta and G. R. Marshall, *Chem. Commun.*, 650 (1970).
(6) Kindly supplied by G. H. Büchi.

Nucleophilic Substitution Reactions on *N*-Nitropyrazoles[1]

Clarisse L. Habraken* and Eduard K. Poels

Gorlaeus Laboratory, The University, Leiden, The Netherlands

Received February 22, 1977

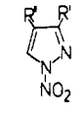
1,4-Dinitropyrazoles **1c–d** undergo "cine" substitution with secondary amines to give 3(5)-di-R-amino-4-nitropyrazoles. 1-Nitro-4-bromo- and 1,3-dinitropyrazoles **1a** and **1b** with cyclic secondary amines undergo displacement on the nitrogen of the *N*-nitro group to give the *N*-nitro amines.

The examples reported in the literature of aromatic nucleophilic substitution in azole rings[2] all follow, according to Miller,[3] an addition–elimination mechanism. In the case of halogeno pyrazoles the presence of strong electron-withdrawing groups appears to be required for the reaction to proceed as was recently confirmed by Alcalde et al.[4] Nevertheless, aromatic nucleophilic substitution in pyrazoles[2,5–7] has not been studied extensively and nothing systematic is known about the susceptibility or the point of attack in the ring and of its dependence on the activating effect of substituents in other positions in the ring.

To our knowledge, in all but one of the reported examples for pyrazoles, the activating group was at C-4 and the halogen displaced by nucleophiles was in either the 3(5) position for N-unsubstituted pyrazoles or C-5 for *N*-arylpyrazoles. The one exception reported by Coburn[8] is the reaction of 4-bromo-3,5-dinitro-1-methylpyrazole with amines to give the 4-amino derivatives, the nucleophilic substitution taking place in the 4 position and the two activating groups situated in positions 3 and 5.

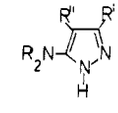
In continuation of our investigations of *N*-nitroazoles[1,9] we were interested in the reactivity toward nucleophiles of *N*-nitro-substituted pyrazoles. Therefore we investigated the reaction of some 3- and 4-substituted *N*-nitropyrazoles with secondary amines as nucleophiles.

Expecting nucleophilic substitution at the 4 position we refluxed 4-bromo-1-nitropyrazole (**1a**) with piperidine in



1a, R′ = H; R″ = Br
b, R′ = NO_2; R″ = H
c, R′ = H; R″ = NO_2
d, R′ = CH_3; R″ = NO_2

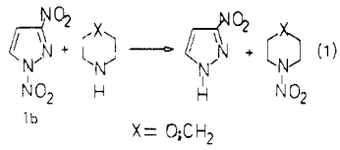
ethanol solution and in excess piperidine, respectively. However, the reaction products were a trace of 4-bromo-3(5)-piperidylpyrazole (**2a**), 4-bromopyrazole, and *N*-nitro-



2a, R′ = H; R″ = Br; R_2N = piperidyl
b, R′ = H; R″ = NO_2; R_2N = piperidyl
c, R′ = H; R″ = NO_2; R_2N = morpholyl
d, R′ = H; R″ = NO_2; R_2N = $(C_2H_5)_2N$
e, R′ = CH_3; R″ = NO_2; R_2N = piperidyl
f, R′ = CH_3; R″ = NO_2; R_2N = morpholyl

piperidine, the latter compound most likely originating from a nucleophilic displacement by piperidine on the nitrogen of the *N*-nitro group of **1a**. Assuming then that dinitropyrazoles might be even better molecules to undergo such a displacement reaction by considering that 3- or 4-nitropyrazole anions would be even better leaving groups than 4-bromopyrazole anion, we treated 1,3-dinitropyrazole (**1b**) and 1,4-dinitropyrazole (**1c**) with morpholine and with piperidine. The re-

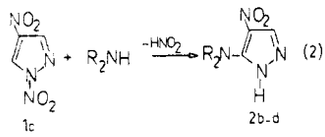
action of **1b** at reflux temperature either in ethanol or in acetonitrile solution indeed afforded respectively *N*-nitromorpholine and *N*-nitropiperidine besides 3(5)-nitropyrazole (see reaction 1). The only other product observed in both instances



(1)

was a nitroso amine, i.e., nitrosomorpholine and nitrosopiperidine, respectively.

On the other hand, the isomeric 1,4-dinitropyrazole (**1c**) when subjected to reaction with piperidine in ethanol solution at room temperature afforded chiefly 4-nitro-3(5)-piperidylpyrazole (**2b**) and no formation of *N*-nitropiperidine was observed (reaction 2). In the same way, from the reactions with

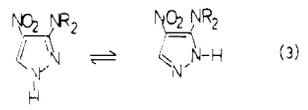


(2)

morpholine and with diethylamine 3(5)-morpholyl-4-nitropyrazole (**2c**) and 3(5)-diethylamino-4-nitropyrazole (**2d**) were obtained. Again, no nitro amines were formed, whereas just as in the reactions of **1b** *N*-nitroso amines were formed as minor products. In the reactions of **1c** these nitroso amines presumably are formed in a secondary reaction, a nitrosation of the amine by the nitrous acid produced along with the aromatic nucleophilic substitution in the ring (reaction 2). However, the question remains how to explain the occurrence of *N*-nitroso amines as by-products in the reactions of **1b** with secondary amines, i.e., how to explain the presence of a nitrosating agent when no products of a nucleophilic aromatic substitution are observed.

The results described above clearly indicate two modes of nucleophilic substitution on *N*-nitropyrazoles: an aromatic nucleophilic substitution in the pyrazole ring (reaction 2) and a nucleophilic displacement on the nitrogen of the *N*-nitro group as depicted in reaction 1.

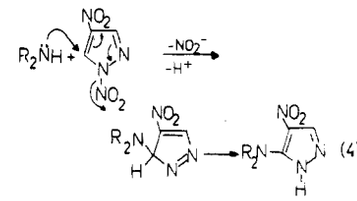
From the products of the aromatic substitution in **1c** no conclusion can be drawn about the point of attack in the ring. Attack on either the 3 or the 5 position affords 3(5)-substituted 4-nitropyrazoles **2b–d** because these actually consist of equilibrium mixtures of two tautomers.[2]



(3)

To determine whether the nucleophile attacks the 3 or the 5 position in the ring in **1c** we synthesized 1,4-dinitro-3-methylpyrazole (**1d**) and subjected it to the reaction with piperidine and with morpholine. The products isolated were 3(5)-methyl-4-nitro-5(3)-piperidylpyrazole (**2e**) and 3(5)-methyl-5(3)-morpholyl-4-nitropyrazole (**2f**) establishing unambiguously that **1d** and consequently also **1c** undergoes the aromatic nucleophilic substitution reaction in the 5 position of the ring and not in the 3 position.

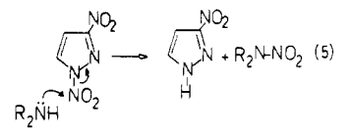
These examples of aromatic nucleophilic substitution in the pyrazole ring show that we are dealing here with a "cine" substitution reaction[10] of the 1,2-addition–elimination type as described by Miller.[3] In general the occurrence of a "cine" substitution, i.e., the entering group comes in ortho to the leaving group, is evidence for a 1,2-elimination–addition mechanism. In such a 1,2-elimination–addition sequence the elimination step gives the aryne intermediate and the following addition step commonly gives a mixture of two products, one of which is a "cine" substitution product. However, no aromatic nucleophilic substitution proceeding via a hetaryne intermediate has ever been established unambiguously for a five-membered heterocycle.[11] Therefore, we assume that we are dealing here with the less common "cine" substitution reaction of the 1,2-addition–elimination mechanism, the actual molecule initially formed being a 3*H*-pyrazole:



(4)

The ultimate product obtained is then formed in a subsequent fast hydrogen rearrangement reaction.

The other nucleophilic substitution reaction consists of a displacement on the *N*-nitro group by a nucleophile of a pyrazole anion (see reaction 1). Such nucleophilic substitution reactions on the nitrogen of a nitro group are well documented. For example, the use of nitrate esters for the preparation of *N*-nitro amines is considered to be a nucleophilic displacement on the nitro group of the ester.[12] Another example is the alkaline hydrolysis of tetranitromethane where the trinitromethane anion is the leaving group.[13]



(5)

In *N*-nitropyrazoles presumably a delicate balance operates between the capacities of a 3 or a 4 substituent for activating the 5 position in the ring for nucleophilic attack and for making the pyrazole anion a better leaving group. Apparently a nitro group in the 4 position activates primarily for nucleophilic attack in the ring whereas for a 3-nitro group no such activation is found and nucleophilic displacement takes place on the *N*-nitro group. The fact that the reactions of **1c**, contrary to those of **1a** and **1b**, occur at room temperature almost instantaneously supports this assumption.

Finally, 3(5)-(*N*,*N*-dialkylamino)pyrazoles cannot be synthesized by alkylation of the 3(5)-amino group because that would also result in alkylation of the pyrazole nitrogen giving a mixture of 1,3 and 1,5 isomers. In fact no 3(5)-(*N*,*N*-dialkylamino)pyrazoles are described in the literature.[7] Consequently, this "cine" substitution reaction of 1,4-dinitropyrazoles, in addition to its mechanistic merits, provides a convenient way for the synthesis of 3(5)-[*N*,*N*-dialkylamino]pyrazoles.

Experimental Section

General. NMR spectra (δ expressed in parts per million) were recorded on a JEOL 60-MHz Minimar or on a JEOL PS-100 instrument; IR spectra (KBr) were recorded on a Beckman IR-10 instrument; mass spectra were recorded on a AE MS-902 spectrometer. Elemental analyses were performed by Mr. W. J. Buis, TNO Laboratory of Organic Chemistry, Utrecht, The Netherlands. For the separation of products the short-column chromatography technique of Hunt and Rigby[14] was used on silica gel H according to Stahl (Merck). Spraying with Rhodamine B solution (0.05% in ethanol) was used for detection of nitropyrazoles on TLC.

N-Nitropyrazoles **1a–c** were prepared as has been previously described;[9] these compounds must be stored under exclusion of moisture to prevent slow hydrolysis to nitric acid and the original N-unsubstituted pyrazole.

N-Nitropiperidine and *N*-nitromorpholine were identified by comparison with an independently synthesized specimen.[12] The identification of *N*-nitrosopiperidine and *N*-nitrosomorpholine was based on comparison of NMR and mass spectral data reported in the

literature.[15,16] The structure assignments of compounds **2a–f** were primarily based on NMR and IR spectra. In particular the NMR spectra recorded in acetone-d_6 of **2b–d** showed two signals for the 3(5) proton. This, according to Elguero and Jacquir et al.,[17] is typical for NMR spectra of 3(5)-substituted 4-nitropyrazoles taken in acetone-d_6 only and not in other solvents.

Reactions of 1a–b. TLC analysis showed that after refluxing for 10 min of 1 g of **1a** in 4 mL of piperidine all **1a** had reacted, whereas after refluxing for 5 days in ethanol (15 mL) solution of 0.6 g of **1a** and 0.3 g of piperidine some unreacted **1a** was still present. Column chromatography (heptane–acetone, 7:1) of the first reaction mixture afforded 0.2 g of N-nitropiperidine (30% based on **1a**), 0.42 g of 4-bromopyrazole (53%), and 0.14 g of a mixture of **2a** and 4-bromopyrazole according to the NMR spectrum. By sublimation enough of **2a** was isolated to obtain a mass spectrum, mol wt 231.01890 and 229.02045 (calcd for $C_8H_{12}BrN_3$, 231.01954 and 229.02151).

1b was reacted with piperidine and morpholine in a number of ways and the reactions were followed by TLC (chloroform–ethyl acetate, 9:1). The reaction with piperidine in acetonitrile was very slow at room temperature (5 days); after refluxing, however, for 0.75 h all **1b** had reacted. Also **1b** reacted very slowly with morpholine in ethanol solution at room temperature; on the other hand, the reaction in refluxing ethanol was completed in 16 h. No difference was observed on addition of urea, K_2CO_3, or $MgCO_3$ to the reaction mixture in an attempt to suppress the formation of nitroso amines. Column chromatography (chloroform–ethyl acetate, 9:1) afforded pure samples of N-nitro- and N-nitrosopiperidine, N-nitro- and N-nitrosomorpholine, and 3(5)-nitropyrazole. No other products were obtained. In one case the reaction of **1b** with morpholine in refluxing ethanol afforded after column chromatography 84% of N-nitromorpholine, 14% of N-nitrosomorpholine, and 84% of 3(5)-nitropyrazole.

General Procedure for the Synthesis of 2b–f. To a solution of 3 mmol of the N-nitropyrazole in 10–15 mL of ethanol, under stirring and while maintaining the temperature under 30 °C, a solution of 1.1–2.0 equiv of the secondary amine in 5 mL of ethanol was added slowly. Completion of the reaction was determined by TLC (chloroform–ethyl acetate, 9:1). Workup, i.e., separation from the nitroso amine, was done either by column chromatography or in the following way. The solvent was evaporated under vacuum, and the residue taken up in 5% sodium hydroxide solution, which solution in turn was evaporated. This residue was then dissolved in a small amount of water, the resulting solution was acidified, and the precipitate was collected on a Buchner funnel and recrystallized from the appropriate solvent. No attempts were made to optimize the yields, which varied from 85 to 20%.

4-Nitro-3(5)-piperidylpyrazole (2b): pale yellow, mp 129 °C (from benzene); IR 3130, 2950, and 2860 (NH and CH), 1600 and 1315 cm^{-1} (NO_2); NMR (100 MHz, Me_2SO-d_6) δ 1.64 (m, 6, β and γ piperidyl H), 3.26 (m, 4, α piperidyl H), and 8.32 [s, 1, 5(3)-H]; (100 MHz, acetone-d_6) δ 1.76 (m, 6, β and γ piperidyl H), 3.36 (m, 4, α piperidyl H) and two signals for the 5(3)-H at 8.32 and 8.52 in the ratio 1:15 consistent for a 3(5)-substituted 4-nitropyrazole.[17] Anal. Calcd for $C_8H_{12}N_4O_2$: C, 48.97; H, 6.17; N, 28.56. Found: C, 48.70; H, 6.42; N, 28.56.

3(5)-N-Morpholyl-4-nitropyrazole (2c): pale yellow, mp 162 °C (from ethyl acetate); IR 3220, 3160 (CH and NH), 1600 and 1310 cm^{-1} (NO_2); NMR (100 MHz, acetone-d_6) δ 3.32 (m, 4) and 3.82 (m, 4) and two signals for the 5(3)-H in the ratio of 14:3 at 8.44 and 8.52 (see **2b**; ref 17). Anal. Calcd for $C_7H_{10}N_4O_3$: C, 42.42; H, 5.09; N, 28.27. Found: C, 42.77; H, 5.21; N, 28.08.

3(5)-Diethylamino-4-nitropyrazole (2d): pale yellow, mp 82–83 °C (sublimation); IR 3120 (NH), 1490 and 1320 cm^{-1} (NO_2); NMR ($CDCl_3$) δ 1.76 (t, 6, CH_3), 3.43 (q, 4, CH_2), and 8.26 [s, 1, 5(3)-H]. Anal. Calcd for $C_7H_{12}N_4O_2$: C, 45.64; H, 6.57; N, 30.42. Found: C, 45.54; H, 6.36; N, 30.24.

3(5)-Methyl-4-nitro-5(3)-N-piperidylpyrazole (2e): yellow crystals, mp 124 °C (petroleum ether, bp 80–100 °C); IR 3230 (NH), 1600 (C=C), 1500 and 1322 cm^{-1} (NO_2); NMR ($CDCl_3$) δ 1.70 (m, 6, CH_2), 2.56 (s, 3, CH_3), and 3.24 (m, 4, CH_2). Anal. Calcd for $C_9H_{14}N_4O_2$: C, 51.42; H, 6.71; N, 26.65; O, 15.22. Found: C, 51.02; H, 6.63; N, 26.21; O, 15.43. High-resolution mass spectrum: calcd for $C_9H_{14}N_4O_2$, 210.1117; found, 210.1120.

3(5)-Methyl-5(3)-morpholyl-4-nitropyrazole (2f): yellow crystals, mp 165 °C (ethyl acetate); IR 3230 (NH), 1600 (C=C), 1530 and 1360, 1380 cm^{-1} (NO_2); NMR ($CDCl_3$) δ 2.71 (s, 3, CH_3), 3.46 (m, 4, CH_2) and 3.96 (m, 4, CH_2). Anal. Calcd for $C_8H_{12}N_4O_3$: C, 45.28; H, 5.70; N, 26.40; O, 22.62. Found: C, 45.24; H, 5.83; N, 26.20; O, 22.73.

3-Methyl-1,4-dinitropyrazole (1d) was synthesized according to the previously described procedure[9,18] by nitration of 0.87 g of 3(5)-methyl-4-nitropyrazole in 3 mL of acetic acid by successive treatment with 0.7 mL of nitric acid (d = 1.52) and 2 mL of acetic anhydride while maintaining the temperature below 25 °C. For workup the reaction mixture was poured onto 50 mL of ice and the formed precipitate was filtered off affording 0.74 g of **1d**. Crystallization from hexane gave colorless crystals: mp 47 °C (lit. 48 °C[18]); IR 1640 and 1270 (N–NO_2), 1565 and 1370 cm^{-1} (C–NO_2); NMR ($CDCl_3$) δ 2.73 (s, 3, CH_3) and 9.13 (s, 1, H). Neutralization of the filtrate with sodium carbonate, extraction with ether, drying the ether extracts over magnesium sulfate, and evaporation of the ether afforded 0.38 g of a yellow oil. The NMR spectrum of this oil (100 MHz, $CDCl_3$) showed this oil to be a mixture of **1d** (79%) and its isomer 5-methyl-1,4-dinitropyrazole (21%), with signals for the latter compound at 3.12 (s, 3, CH_3) and 8.12 (s, 1, H) confirming that indeed in **1d** the methyl group occupies the 3 position.

Acknowledgments. We thank Steven M. Bonser for the preparation of N-nitropiperidine and N-nitromorpholine and Robert Jan Visser for performing the synthesis of **2d.** We also express our thanks to Dr. J. van Thuyl, J. van Houte, and W. C. M. M. Luyten for the mass spectral analyses and to J. Stikkelorum, A. van der Linden, and C. Erkelens for IR and NMR spectral data.

Registry No.—**1a,** 7185-93-5; **1b,** 38858-81-0; **1c,** 35852-77-8; **1d,** 62563-09-1; **2a,** 62563-10-4; **2b,** 62563-11-5; **2c,** 62563-12-6; **2d,** 62563-13-7; **2e,** 53960-82-0; **2f,** 53960-83-1; piperidine, 110-89-4; morpholine, 110-91-8; 5-methyl-1,4-dinitropyrazole, 62563-14-8.

References and Notes

(1) Pyrazoles. 15. For previous papers see: 14, J. W. A. M. Janssen, C. L. Habraken, and R. Louw, *J. Org. Chem.*, **41,** 1758 (1976); 13, J. W. A. M. Janssen, C. G. Kruse, H. J. Koeners, and C. L. Habraken, *J. Heterocycl. Chem.*, **10,** 1055 (1973).
(2) K. Schofield, M. R. Grimmett, and B. R. T. Keene, "The Azoles", Cambridge University Press, New York, N.Y., 1976.
(3) J. Miller, "Aromatic Nucleophilic Substitution", Elsevier, Amsterdam, 1968.
(4) E. Alcalde, J. M. Garcia-Maquina, and J. De Mendoza, *An. Quim.*, **70,** 959 (1974).
(5) A. N. Kost and I. I. Grandberg, *Adv. Heterocycl. Chem.*, **6,** 347 (1966).
(6) T. L. Jacobs, "Heterocyclic Compounds", Vol. V, R. C. Elderfield, Ed., Wiley, New York, N.Y., 1957, p 45.
(7) R. Fusco, "The Chemistry of Heterocyclic Compounds", Vol. 22, A. Weissberger, Ed., Interscience, New York, N.Y., 1967, p 3.
(8) M. D. Coburn, *J. Heterocycl. Chem.*, **8,** 153 (1971).
(9) (a) J. W. A. M. Janssen, H. J. Koeners, C. G. Kruse, and C. L. Habraken, *J. Org. Chem.*, **38,** 1777 (1973); (b) J. W. A. M. Janssen and C. L. Habraken, *ibid.*, **36,** 3081 (1971).
(10) J. F. Bunnett, *Q. Rev., Chem. Soc.*, **12,** 1 (1958).
(11) See, however, M. G. Reinecke and J. G. Newsom, *J. Am. Chem. Soc.*, **98,** 3021 (1976), and references cited therein.
(12) W. D. Emmons and J. P. Freeman, *J. Am. Chem. Soc.*, **77,** 4387, 4391 (1955); "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 839.
(13) D. J. Glover, *J. Phys. Chem.*, **74,** 21 (1970).
(14) B. J. Hunt and W. Rigby, *Chem. Ind. (London)*, 1868 (1967).
(15) R. K. Harris and R. A. Spragg, *J. Mol. Spectrosc.*, **23,** 158 (1967); Y. L. Chow and C. J. Colon, *Can. J. Chem.*, **46,** 2827 (1968).
(16) G. Schroll, R. G. Cooks, Per Klemmensen, and Sven-Olov Laweson, *Ark. Kemi*, **28,** 413 (1968).
(17) M. L. Roumestant, P. Viallefout, J. Elguero, and R. Jacquier, *Tetrahedron Lett.*, 495 (1969).
(18) R. Hüttel and F. Büchele, *Chem. Ber.*, **88,** 1586 (1955).