

N-Alkoxydipyrromethenes

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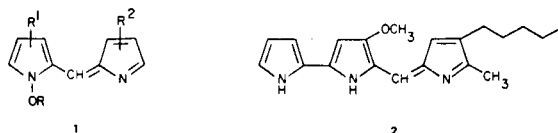
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2-Cyano-*N*-hydroxypyrroles are *O*-alkylated and the nitrile function reduced to the corresponding aldehyde with diisobutylaluminum hydride. Condensation with pyrroles in the presence of hydrogen bromide gives the difficultly purified *N*-alkoxydipyrromethanes.

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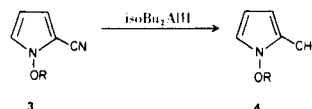
There has been much interest recently in the synthesis of *N*-substituted porphyrinogens (1) and the preparation of an *N,N',N'',N'''*-tetramethylporphyrinogen has been reported (2). Such compounds are of interest for both theoretical (nonplanarity, aromaticity) and practical (ease of complex formation with metals, biological activity) reasons. We have developed a simple route to 2-cyano-*N*-hydroxypyrrole and its derivatives from 2-azidopyridine 1-oxides (3), and it was felt that this would permit us to develop approaches to *N*-hydroxydipyrromethenes derivatives (1) and thence to *N*-hydroxy (or alkoxy)-porphyrinogens. Also of great interest was the fact that a 5-(2-pyrryl)dipyrromethene, Prodigiosin (2), showed definite activity against *Plasmodium berghei* in mice and exhibited no cross-resistance with chloroquine, but did exhibit appreciable levels of toxicity at the 160 mg/kg body weight dose (4). It was hoped that an *N*-hydroxy (or alkoxy) derivative of 2 would show similar activity



without the accompanying toxicity. This paper describes successful efforts to synthesize compounds of the type 1.

Attempts to reduce 2-cyano-*N*-hydroxypyrrole (3; R = H) or its *O*-acetyl derivative (3; R = CH₃CO) failed to lead to any isolable product. The reaction of 3 (R = H) with pyrrole in the presence of hydrogen chloride did not give any of the desired *N*-hydroxydipyrromethene and, indeed, as is becoming clear, the nitrile function in 3 seems to be very resistant to electrophilic attack. 1-Benzyloxy-2-cyanopyrrole (3; R = PhCH₂) was not reduced to the corresponding aldehyde under Stephens conditions (stannous chloride-hydrochloric acid) or with lithium triethoxyaluminum hydride. Treatment of 3

(R = PhCH₂) with Magic Methyl followed by addition of pyrrole again did not lead to the isolation of any ketone. On the other hand, 3 (R = PhCH₂) could be reduced to the corresponding aldehyde (4; R = CH₂Ph) in good yield using diisobutylaluminum hydride. 1-Methoxy- (4; R = CH₃) and 1-*p*-anisoxypyrrole-2-carboxaldehyde (4; R = *p*-CH₃OC₆H₄CH₂) were prepared similarly.

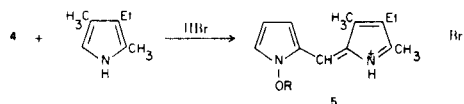


Condensation of 4 (R = CH₂Ph) with pyrrole in the presence of hydrobromic acid did not give any material showing the characteristic (5) ultraviolet spectrum of a dipyrromethene. On the other hand, condensation with 2,4-dimethyl-3-ethylpyrrole in ethereal hydrogen bromide gave 1-benzyloxy-2-[3,5-dimethyl-4-ethyl-2*H*-pyrrol-2-ylidene)methyl]pyrrole hydrobromide (5) as greenish crystals. Inhalation of this solid caused strong irritations. The structure of 5 was confirmed by its uv spectrum (λ max 462 nm), its mass spectrum (M⁺, m/e 306) (C₂₀H₂₂N₂O) (5-HBr), and its nmr spectrum. The latter exhibited lines at δ 13.32 (due to -NH =) 8.82 (dd, 1H, J_{3,4} = 5.2, J_{3,5} = 1.1 Hz, H₃ (or H₅)), 7.39 (br s, 6H, C₆H₅ and H₅ (or H₃)), 7.04 (s, 1H, -CH=), 6.48 (dd, 1H, J_{3,4} = 5.2, J_{4,5} = 3 Hz, H₄), 5.25 (s, 2H, OCH₂Ph), 2.92 (s, 3H, Me), 2.44 (q, 2H, J = 7.5 Hz, CH₂CH₃), 2.16 (s, 3H, Me), 1.09 (t, 3H, J = 7.5 Hz, CH₂CH₃).

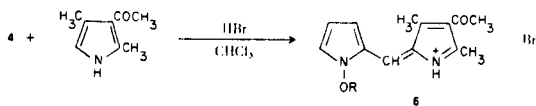
Attempts to regenerate the *N*-hydroxy function by debenylation of 3 (R = CH₂Ph), 4 (R = CH₂Ph) or 5 (R = CH₂Ph) failed. Since a *p*-methoxybenzyloxy group is reported to be cleaved smoothly at room temperature by trifluoroacetic acid (6) 2-cyano-*N*-hydroxypyrrole was treated with sodium hydride and then *p*-methoxybenzyl chloride in *N,N*-dimethylformamide to give 3 (R = CH₂C₆H₄-*p*-OMe) which was reduced to the aldehyde

with diisobutylaluminum hydride. Though *p*-methoxybenzyl alcohol was obtained on cleavage of these molecules with acid the remaining fragment could not be isolated. Cleavage with hydrogen bromide gave *p*-methoxybenzyl bromide and unidentified tars.

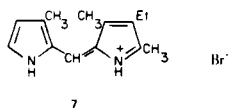
Condensation of **4** ($R = p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2$) with 2,4-dimethyl-3-ethylpyrrole with hydrogen bromide in ether gave the dipyrromethene (**5**; $R = p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2$). In this case, as in all subsequent examples of **5**, great care had to be taken to avoid the intrusion of metal ions in



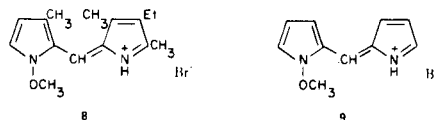
solution during the synthesis or purification of the methene, otherwise highly colored metal complexes contaminated the product that were extremely difficult to remove. We subsequently made it a practice to use demineralized water and highly purified reagents and solvents to avoid this problem as much as possible. Problems also arose occasionally because of the formation of salts containing more than one equivalent of hydrogen bromide and eventually the condensations were carried out using molar equivalents of reagents and a given volume of a standard solution of hydrogen bromide in chloroform in the cold. This permitted the successful condensation of **4** ($R = p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2$) with 3-acetyl-2,4-dimethylpyrrole to give **6** though, as with all the *N*-alkoxydipyrromethenes reported here, purification proved to be extremely difficult and tedious. In some cases, the spectral data suggested that the benzyloxy or *p*-methoxybenzyloxy group had been partially cleaved during reaction in the presence of hydrogen bromide. Indeed, when 1-(*p*-methoxybenzyloxy)-3-methylpyrrole-2-carboxaldehyde was condensed in ether with 2,4-dimethyl-3-ethylpyrrole in a stream of dry hydrogen bromide the product isolated analyzed correctly for the de-*p*-methoxybenzyloxyated dipyrromethene (**7**).



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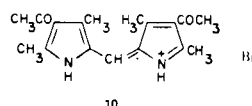


In the hope of avoiding the latter problem, 1-methoxypyrrole-2-carboxaldehyde (**4**; $R = \text{Me}$) was condensed with various pyrroles in chloroform containing hydrogen bromide. In this way, **5** ($R = \text{Me}$), **6** ($R = \text{Me}$, as the sesquihydrobromide salt), **8** and **9** could be obtained, but again analytical purity was only achieved after considerable

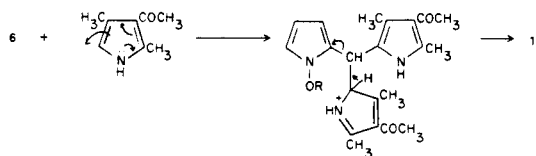


labor. The dipyrromethenes from **4** and ethyl 3-methylpyrrole-2-carboxylates could never be obtained pure.

A remarkable result was obtained when the crude red paste obtained from **4** ($R = p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2$) and 3-acetyl-2,4-dimethylpyrrole was treated with picric acid in chloroform. Instead of the picrate corresponding to **6**, the product proved to be the symmetrical dipyrromethene **10**. The mechanism of its formation is unclear but it



could involve nucleophilic attack by 3-acetyl-2,4-dimethylpyrrole (either unchanged or regenerated somehow from the crude product) upon **6** followed by acid-catalyzed elimination (retro-aldol) of the *N*-alkoxyppyryl unit.



EXPERIMENTAL

Melting points are uncorrected.

Reagents.

The preparation of 2-cyano-*N*-hydroxypyrrole and 2-cyano-*N*-hydroxy-3-methylpyrrole has been described (3).

1-Benzyloxy-2-cyanopyrrole (**3**; $R = \text{CH}_2\text{Ph}$).

A solution of 2-cyano-*N*-hydroxypyrrole (0.70 g.), benzyl chloride (1.65 g.) and pyridine (1.35 ml.) in dry chloroform (40 ml.) was stirred at room temperature for 48 hours. A saturated aqueous solution of sodium carbonate (10 ml.) was added and stirring was continued for another 72 hours. The mixture was extracted with chloroform (3 x 10 ml.), the organic layer was dried (magnesium sulfate) and evaporated to dryness to give a dark oil (1.6 g.). Chromatography on a column of silica gel (30 g.) followed by elution with benzene gave 1-benzyloxy-2-cyanopyrrole (860 mg., 67%), b.p. $73^\circ/2\text{mm.}$; ir (film): 2218 cm^{-1} ($\text{C}\equiv\text{N}$); nmr (carbon tetrachloride): δ 7.31 (s, 5H, Ph), 6.67 (dd, 1H, $J_{4,5} = 3.0$, $J_{3,5} = 1.5$ Hz, H_5), 6.47 (dd, 1H, $J_{3,4} = 4.5$, $J_{3,5} = 1.5$ Hz, H_3), 5.89 (dd, 1H, $J_{3,4} = 4.5$, $J_{4,5} = 3.0$ Hz, H_4), 5.11 (s, 2H, CH_2); mass spectrum m/e 198 (M^+ , 3), 91 (100).

Anal. Calcd. for $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}$: C, 72.71; H, 5.08. Found: C, 72.76; H, 5.10.

2-Cyano-1-methoxypyrrole (**3**; $R = \text{CH}_3$).

Sodium hydroxide (0.2 g.) and methyl iodide (1.43 g.) were added to 2-cyano-*N*-hydroxypyrrole (0.54 g.) in methanol (10 ml.) and the solution was boiled under reflux for 2 hours. It was then poured into ice-water (50 ml.), and the mixture extracted with chloroform (6 x 25 ml.). The dried (sodium sulfate) chloroform

extracts were evaporated *in vacuo* to give a dark liquid which was chromatographed on basic alumina. Elution with benzene gave 2-cyano-1-methoxypyrrole (0.49 g., 80%), b.p. 68°/0.5 mm.; ir (film): 2220 cm⁻¹; nmr (deuteriochloroform): δ 7.05 (dd, 1H, J_{3,4} = 5, J_{3,5} = 2.1 Hz, H₃), 6.7 (dd, 1H, J_{4,5} = 3.5, J_{3,5} = 2.1 Hz, H₅), 6.15 (dd, 1H, J_{3,4} = 5, J_{3,5} = 2.1 Hz, H₄), 4.1 (s, 3H, OCH₃).

Anal. Calcd. for C₆H₆N₂O: C, 59.01; H, 4.95; N, 22.95. Found: C, 59.29; H, 5.05; N, 22.76.

2-Cyano-1-methoxy-3-methylpyrrole.

This was prepared similarly (99.5% yield) and had b.p. 40-41°/0.15 mm.; nmr (neat): δ 7.0 (d, 1H, H₅), 5.9 (d, 1H, H₄), 4.12 (s, 3H, OCH₃), 2.15 (s, 3H, CH₃).

Anal. Calcd. for C₇H₈N₂O: C, 61.78; H, 5.80. Found: C, 61.88; H, 5.88.

2-Cyano-1-(*p*-methoxybenzyloxy)pyrrole (3; R = *p*-CH₃OC₆H₄CH₂).

To a solution of 2-cyano-*N*-hydroxypyrrole (6.0 g.) in dry dimethylformamide (25 ml.) cooled in an ice-bath was slowly added a slurry of sodium hydride (3.0 g., 57% oil dispersion) in dry ether with stirring. *p*-Methoxybenzyl chloride (9.7 ml.) was then added and the solution was stirred overnight. It was diluted with water (50 ml.), extracted with ether (3 x 50 ml.), the extracts dried (magnesium sulfate) and concentrated to give a dark oil. Column chromatography on silica gel and elution with benzene gave a yellow oil (13 g., 93%) which, on bulb-to-bulb distillation (bath temperature 158-160°/0.25 mm.), gave 3 (R = *p*-CH₃OC₆H₄CH₂); ir (film): 2850 (s) (OCH₃), 2240 cm⁻¹ (C≡N); nmr (carbon tetrachloride): δ 6.95 (AB q, 4H, J = 8 Hz, Ar), 6.61 (dd, 1H, J_{4,5} = 3; J_{3,5} = 2 Hz, H₅), 6.43 (dd, 1H, J_{3,4} = 4.5; J_{3,5} = 2 Hz, H₃), 5.83 (dd, 1H, J_{3,4} = 4.5, J_{4,5} = 3 Hz, H₄), 5.01 (s, 2H, OCH₂Ar), 3.68 (s, 3H, OCH₃).

Anal. Calcd. for C₁₃H₁₂N₂O₂: C, 68.37; H, 5.30. Found: C, 68.36; H, 5.40.

2-Cyano-1-(*p*-methoxybenzyloxy)-3-methylpyrrole.

This was prepared similarly to the above starting from 2-cyano-1-hydroxy-3-methylpyrrole and was obtained in 81% yield, b.p. 156°/0.25 mm.; ir (film): 2855, 2240 cm⁻¹; nmr (carbon tetrachloride): δ 6.96 (AB q, 4H, J = 8 Hz, Ar), 6.45 (d, 1H, J_{4,5} = 3 Hz, H₅), 5.64 (d, 1H, J_{4,5} = 3 Hz, H₄), 4.98 (s, 2H, OCH₂Ar), 3.70 (s, 3H, OCH₃), 2.12 (s, 3H, CH₃).

Anal. Calcd. for C₁₄H₁₄N₂O₂: C, 69.39; H, 5.82. Found: C, 69.71; H, 6.12.

1-Benzyloxy-2-aldehyde (4; R = CH₂Ph).

A solution of 1-benzyloxy-2-cyanopyrrole (3.0 g.) in dry ether (5 ml.) was stirred under dry, oxygen-free nitrogen and treated with a solution of diisobutylaluminum hydride (3.2 ml.) in dry ether (40 ml.) over a period of 25 minutes. The solution was stirred for 1.5 hours at room temperature and then boiled under reflux for 1.75 hours. It was then cooled in ice and a solution of water (1.5 ml.) in tetrahydrofuran (25 ml.) was added. The solution was shaken with *N* hydrochloric acid (2 x 150 ml.), the organic layer separated and the aqueous layer extracted with ether (2 x 70 ml.). The combined ether layers were washed with 2% sodium carbonate solution (75 ml.), water (75 ml.) and dried (magnesium sulfate). Evaporation gave a light orange-yellow oil (2.35 g., 76%) which showed a single spot on tlc and was purified further by bulb-to-bulb distillation (bath temperature 120°/0.05 mm.) to give the aldehyde; ir (chloroform): 2765,

2720 (w), 1662 cm⁻¹ (vs); nmr (carbon tetrachloride): δ 9.47 (s, 1H, CHO), 7.28 (s, 5H, Ph), 6.66 (m, 2H, H₃ and H₅), 5.87 (dd, 1H, J_{3,4} = 5, J_{4,5} = 3 Hz, H₄), 5.11 (s, 2H, OCH₂Ph); mass spectrum m/e (relative intensity): 201 (M⁺, 0.05), 91 (100).

Anal. Calcd. for C₁₂H₁₁NO₂: C, 71.62; H, 5.51; N, 6.96. Found: C, 71.84; H, 5.45; N, 7.09.

The following *N*-alkoxypyrrole-2-aldehydes were similarly prepared:

1-(*p*-Methoxybenzyloxy)pyrrole-2-aldehyde (4; R = *p*-CH₃OC₆H₄CH₂).

This compound was prepared in 63% yield, b.p. 150°/0.25 mm.; ir (film): 2850 (OCH₃), 1672 cm⁻¹ (CHO); 2,4-dinitrophenylhydrazone, m.p. 146-148° (from ethanol).

Anal. Calcd. for C₁₉H₁₇N₅O₆: C, 55.47; H, 4.17. Found: C, 55.72; H, 4.36.

1-(*p*-Methoxybenzyloxy)-3-methylpyrrole-2-aldehyde.

This compound was prepared in 65% yield, b.p. 155°/0.25 mm.; ir (film): 2852, 1670 cm⁻¹.

Anal. Calcd. for C₁₄H₁₅NO₃: C, 68.57; H, 6.12. Found: C, 68.62; H, 5.95.

1-Methoxypyrrole-2-aldehyde (4; R = CH₃).

This compound was prepared in 64% yield, b.p. 43°/0.2 mm.; ir (film): 1680 cm⁻¹; nmr (deuteriochloroform): δ 9.38 (s, 1H, CHO), 6.82 (dd, 1H, J_{4,5} = 3.0, J_{3,5} = 2.0 Hz, H₅), 6.46 (dd, 1H, J_{3,4} = 4.5, J_{3,5} = 2 Hz, H₃), 5.77 (dd, 1H, J_{3,4} = 4.5, J_{4,5} = 3.0 Hz, H₄), 3.74 (s, 3H, OCH₃).

Anal. Calcd. for C₆H₇NO₂: C, 57.60; H, 5.60. Found: C, 57.79; H, 5.72.

1-Methoxy-3-methylpyrrole-2-aldehyde.

This compound was prepared in 91.2% yield, b.p. 53-54°/0.2 mm.; ir (film): 1660 cm⁻¹; nmr (deuteriochloroform): δ 9.79 (s, 1H, CHO), 6.92 (d, 1H, H₅), 5.93 (d, 1H, H₄), 4.13 (s, 3H, OCH₃), 2.42 (s, 3H, CH₃).

Anal. Calcd. for C₇H₉NO₂: C, 60.43; H, 6.47. Found: C, 60.61; H, 6.55.

1-Benzyloxy-2-[(3,5-dimethyl-4-ethyl-2*H*-pyrrol-2-ylidene)methyl]pyrrole Hydrobromide (5; R = CH₂Ph).

A solution of 1-benzyloxy-2-aldehyde (100 mg.) and 2,4-dimethyl-3-ethylpyrrole (65 mg.) in dry ether was treated with 2 drops of 48% hydrobromic acid and the solution kept at 10° for 1/2 hour. The dark greenish solid was dissolved in methanol and precipitated with ether, filtered, washed with dry ether and recrystallized from ether-methanol to give 5 (R = CH₂Ph) as dark green crystals, m.p. >300°.

Anal. Calcd. for C₂₀H₂₃BrN₂O: C, 62.02; H, 5.99. Found: C, 62.05; H, 5.99.

2-[(3,5-Dimethyl-4-ethyl-2*H*-pyrrol-2-ylidene)methyl]-1-(*p*-methoxybenzyloxy)pyrrole Hydrobromide (5; R = *p*-CH₃OC₆H₄CH₂).

A solution of 1-(*p*-methoxybenzyloxy)pyrrole-2-aldehyde (1.3 mmoles) and 2,4-dimethyl-3-ethylpyrrole (1.3 mmoles) in dry ether (5 ml.) was treated with 48% hydrobromic acid (2 drops). After 1/2 hour at room temperature the ether was decanted and treated once more with 48% hydrobromic acid. The operation was repeated once more, all the precipitated solid was collected, filtered, dissolved in methanol (10 ml.) and the product precipitated with ether (50 ml.) (60% yield); λ max (methanol): 496 nm.

Anal. Calcd. for C₂₁H₂₅BrN₂O₂: C, 60.43; H, 6.04. Found: C, 60.29; H, 5.82.

Alternate General Method for Synthesis of Dipyrromethenes.

The 1-alkoxypyrrole (1.0 mmole) in chloroform (20-25 ml.) was treated with a standard solution of dry hydrogen bromide (1.1 mmoles) in chloroform. The suspension was kept at 10° with occasional shaking. The solid was filtered on a sintered glass funnel, washed with chloroform and recrystallized. Thus were obtained:

2-[(3,5-Dimethyl-4-ethyl-2*H*-pyrrol-2-ylidene)methyl]-1-methoxy-pyrrole Hydrobromide (**5**; R = CH₃).

This compound was prepared in 80% yield, m.p. >300° (from ether-chloroform).

Anal. Calcd. for C₁₄H₁₉BrN₂O: C, 54.01; H, 6.15. Found: C, 53.91; H, 6.08.

2-[(3,5-Dimethyl-4-ethyl-2*H*-pyrrol-2-ylidene)methyl]-1-methoxy-3-methylpyrrole Hydrobromide (**8**).

This compound was prepared in 86% yield, m.p. >300° (from ether-chloroform); ir. (potassium bromide): 1640 cm⁻¹.

Anal. Calcd. for C₁₅H₂₁BrN₂O: C, 55.40; H, 6.51. Found: C, 55.32; H, 6.51.

1-Methoxy-2-(2*H*-pyrrol-2-ylidenemethyl)pyrrole Hydrobromide (**9**).

This compound was prepared in 94% yield, m.p. >300° (chloroform).

Anal. Calcd. for C₁₀H₁₁BrN₂O: C, 47.08; H, 4.35; N, 10.98. Found: C, 47.28; H, 4.79; N, 10.79.

2-[(4-Acetyl-3,5-dimethyl-2*H*-pyrrol-2-ylidene)methyl]-1-methoxy-pyrrole Sesquihydrobromide (**6**; R = CH₃).

This compound was prepared in 64% yield, m.p. >300° (chloroform); ir (potassium bromide): 1640 cm⁻¹.

Anal. Calcd. for C₁₄H₁₆N₂O₂·1.5HBr: C, 46.15; H, 4.95. Found: C, 46.32; H, 4.56.

2-[(4-Acetyl-3,5-dimethyl-2*H*-pyrrol-2-ylidene)methyl]-1-(*p*-methoxybenzyloxy)pyrrole Hydrobromide (**6**; R = *p*-CH₃OC₆H₄CH₂).

This compound was prepared in 74% yield, m.p. >300°; ir 1620 cm⁻¹ (C=N).

Anal. Calcd. for C₂₁H₂₃BrN₂O: C, 58.46; H, 5.37. Found: C, 58.65; H, 5.47.

Dipyrromethene Hydrobromide **10**.

The brick red paste obtained by bubbling hydrogen bromide gas through a solution of 1-(*p*-methoxybenzyloxy)pyrrole-2-aldehyde (0.23 g.) and 3-acetyl-2,4-dimethylpyrrole (0.15 g.) in chloroform (25 ml.) was treated with picric acid (0.23 g.) in chloroform (25 ml.). After a few hours the green solid (0.20 g.) which precipitated was filtered and recrystallized from chloroform-ether and had m.p. 193-194°; ir (potassium bromide): 1670, 1620 cm⁻¹; mass spectrum m/e (relative abundance): 285 (20), 284 (C₁₇H₂₀N₂O₂⁺, 100).

Anal. Calcd. for C₁₇H₂₁BrN₂O₂: C, 55.89; H, 5.79; N, 7.67. Found: C, 56.15; H, 5.86; N, 7.53.

Acknowledgments.

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REFERENCES AND NOTES

- (1) R. Grigg, A. Sweeney, G. D. Dearden, A. H. Jackson, and A. W. Johnson, *Chem. Commun.*, 1273 (1970). A. H. Jackson and G. R. Dearden, *Ann. N. Y. Acad. Sci.*, **206**, 151 (1973). W. K. McEwen, *J. Am. Chem. Soc.*, **68**, 711 (1946). A. H. Corwin and W. M. Quattlebaum, *ibid.*, **58**, 1081 (1936). R. C. Ellingson and A. H. Corwin, *ibid.*, **68**, 1112 (1946).
- (2) B. Franck and C. Wegner, *Angew. Chem. Int. Ed. Engl.*, **14**, 424 (1975).
- (3) R. A. Abramovitch and B. W. Cue, Jr., *J. Org. Chem.*, **38**, 173 (1973); *Idem.*, *Heterocycles*, **1**, 227 (1973); **2**, 297 (1974). *Idem.*, *J. Am. Chem. Soc.*, **98**, 1478 (1976).
- (4) A. J. Castro, *Nature*, **213**, 903 (1967).
- (5) R. W. Guy and R. A. Jones, *Aust. J. Chem.*, **19**, 1871 (1966).
- (6) B. Frydman, G. Biddain, and J. C. Repetto, *J. Org. Chem.*, **38**, 1824 (1973).