by uv absorption. Pyridine has λ_{max} 256 nm (log ϵ 3.5); pyridine *N*-oxide has λ_{max} 255 nm (log ϵ 4.1). Distillation of a dilute solution of pyridine caused eventual disappearance of the 256-nm maximum, but end absorption persisted off scale at low wavelength; evidently an impurity had been concentrated. Distillation had no effect on the absorbance of dilute pyridine *N*-oxide solution [*N*-oxide from Aldrich was recrystallized from CCl_4; colorless plates, mp 68–69° (lit.[45] mp 65–66°), were used]. Distillation of a solution of pyridine and pyridine *N*-oxide gave a uv spectrum lacking the fine structure characteristic of pyridine, but with λ_{max} 255 nm, and going off scale as characteristic of the impurity in pyridine. The reaction mixture, after pentane extraction of II and IV, gave after distillation a residue with the uv maximum typical of pyridine *N*-oxide and the impurity; absorbance of 2.1 l. of solution was 0.60; concentration of oxide was therefore 4.3×10^{-5} *M*, total 9.1×10^{-5} mol; theoretical yield of oxide assuming 65% yield of IV was 2.7×10^{-3} mol; actual yield was 3.3% of theory.

(45) H. S. Mosher, L. Turner, and A. Carlsmith, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 828.

Registry No. —I HCl, 16547-17-4; II, 6880-03-1; IV, 614-30-2; IV picrate, 38734-75-7; monoperthalic acid, 2311-91-3; O_2, 7782-44-7; *tert*-dodecanethiol, 25103-58-6; CCl_4, 56-25-3.

Acknowledgments. —We are grateful to the Department of Chemistry at Rice University for permission to use the Varian A-56-60 nmr spectrometer while J. P. L. was attending the 159th National Meeting of the American Chemical Society in Houston, and to Professor Arthur R. Lepley for assistance in performing the CIDNP experiment. We thank Mr. David G. Jelinek (Central Michigan University) for reinvestigating the picrate of *N*-benzyl-*N*-methylaniline. This work was supported by grants from the U. S. Army Research Office, Durham, and the Graduate School of Boston University.

Mechanism of the Base-Induced Decomposition of *N*-Nitroso-*N*-methylurea

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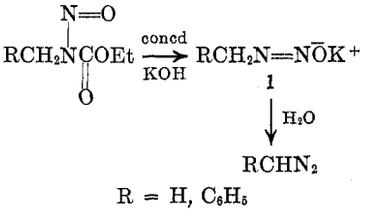
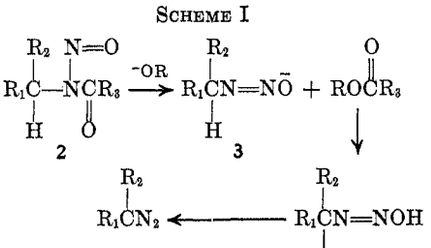
The mechanism corresponding to the base-induced decomposition of *N*-nitroso-*N*-methylurea is discussed. Evidence is presented for the decomposition which is consistent with initial abstraction of a urea proton, but not with a mechanism involving initial nucleophilic addition to the nitroso or carbonyl groups.

The base-induced decomposition of *N*-nitrosoamides, -carbamates, and -ureas to diazoalkanes has been the subject of many synthetic and mechanistic investigations. The mechanistic considerations, in particular, have stimulated considerable debate. In 1894, von Pechmann established that the hydroxide-induced decomposition of nitrosocarbamates afforded diazoalkanes.[1] Hantzsch and Lehmann[2] isolated the methyl and benzyl diazotates (**1**) and demonstrated that treatment of **1** with water afforded the corresponding diazoalkanes.



An investigation by Gutsche and Johnson[3] of the methoxide-induced decomposition of several *N*-nitroso-*N*-benzylcarbamates expanded this scheme (Scheme I) and the subsequent isolation of methyl ethyl carbonate[4] from the base-induced conversion of *N*-nitroso-*N*-cyclohexylurethane (**2a**) provided convincing evidence for a mechanism initiated by methoxide attack on the carbonyl carbon. This scheme has also been established as operative for the decomposition of *N*-nitrosoamides.[5-7] Similarly, by indicating the formation of alkyl carbamate, Applequist and McGreer[8] implied that the alkoxide-induced decomposition of *N*-nitroso-*N*-cyclobutylurea (**2b**) to diazocyclobutane was initiated by attack on the carbonyl moiety.

SCHEME I

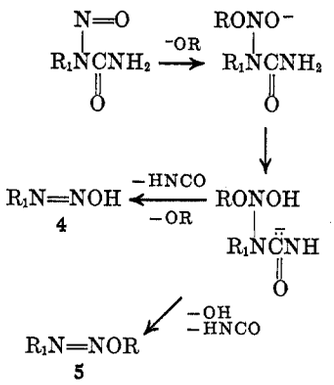


a, R_1 = H; R_2 = C_6H_{11}; R_3 = OEt
b, R_1R_2 = $(CH_2)_3$; R_3 = NH_2

In 1966, however, Jones, Muck, and Tandy[9] described experiments which appeared to exclude the Applequist and McGreer scheme as a possible mechanism for the conversion of *N*-nitroso-*N*-(2,2-diphenylcyclopropyl)urea to 2,2-diphenyldiazocyclopropane. They provided an alternate mechanism involving alkoxide attack on the nitroso moiety of the urea (Scheme II). A third mechanism which involved proton abstraction as the first step (Scheme III) was also excluded on the basis of several observations. Jones, *et al.*,[9] were careful to limit their discussion to the decomposition of *N*-nitroso-*N*-(2,2-diphenylcyclo-

(1) H. von Pechmann, *Chem. Ber.*, **27**, 1888 (1894).
(2) A. Hantzch and M. Lehmann, *Chem. Ber.*, **35**, 897 (1902).
(3) C. D. Gutsche and H. E. Johnson, *J. Amer. Chem. Soc.*, **77**, 109 (1955).
(4) F. W. Bollinger, F. N. Hayes, and S. Siegel, *J. Amer. Chem. Soc.*, **72**, 5592 (1950).
(5) R. Huisgen and J. Reinertshofer, *Justus Liebigs Ann. Chem.*, **575**, 174 (1952).
(6) R. Huisgen, *Justus Liebigs Ann. Chem.*, **573**, 173 (1951).
(7) C. D. Gutsche and I. Y. C. Tao, *J. Org. Chem.*, **28**, 883 (1963).
(8) D. E. Applequist and D. E. McGreer, *J. Amer. Chem. Soc.*, **82**, 1965 (1960).
(9) W. M. Jones, D. L. Muck, and T. K. Tandy, Jr., *J. Amer. Chem. Soc.*, **88**, 68 (1966).

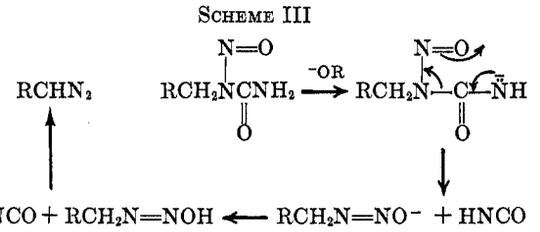
SCHEME II



propyl)urea. A subsequent review has, unfortunately, indicated the validity of the mechanistic conclusions for "several nitrosoureas."[10] We therefore wish to discuss our findings for the base-induced decomposition of *N*-nitroso-*N*-methylurea.

During the course of a study on the generation and utilization of diazomethane, it became apparent that the mechanism outlined in Scheme II was inconsistent with the alkoxide-induced decomposition of *N*-nitroso-*N*-methylurea, a transformation which might better be rationalized by the mechanism outlined in Scheme III. The experiments which led to this conclusion

SCHEME III



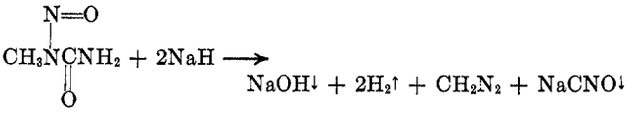
have been described briefly in a previous report.[11] A more detailed description of these experiments, with additional evidence in favor of the proton abstraction mechanism, is now presented.

Results and Discussion

Published evidence excluding the carbonyl addition mechanism (Scheme I) for the base-induced decomposition of *N*-nitroso-*N*-(2,2-diphenylcyclopropyl)urea is substantial. Jones, *et al.*,[9] found less than 1% ethyl carbamate resulting from the lithium ethoxide induced decomposition of *N*-nitroso-*N*-(2,2-diphenylcyclopropyl)urea. They also determined that ethyl carbamate, had it been formed, would have been stable to the reaction conditions, a finding which has been corroborated in this laboratory. Also, decomposition *via* the mechanism outlined in Scheme I would require the presence of at least a catalytic amount of ethanol. Alcohol-free lithium ethoxide was found to effect the decomposition of *N*-nitroso-*N*-(2,2-diphenylcyclopropyl)urea in anhydrous ether in 20 min at 0°. A similar result has been obtained in this laboratory for *N*-nitroso-*N*-methylurea. These two lines of evidence are sufficient to exclude the carbonyl addition mechanism for the decomposition of *N*-nitroso-*N*-(2,2-diphenylcyclopropyl)urea or *N*-nitroso-*N*-methylurea.

In addition, the finding that lithium 2,2-diphenylcyclopropyl diazotate was stable to lithium ethoxide–ethanol and to isocyanic acid strongly suggested that the mechanism outlined in Scheme III could not be operative for the decomposition of *N*-nitroso-*N*-(2,2-diphenylcyclopropyl)urea, since it contained the diazotate as an obligatory intermediate. In this regard the chemistry of methyl diazotate appears to differ from that of lithium 2,2-diphenylcyclopropyl diazotate. Specifically, treatment of $CH_3N{=}NO^-K^+$ with excess isocyanic acid in tetrahydrofuran at 0°, under rigorously anhydrous conditions, afforded potassium cyanate and nitrogen liberation, corresponding to the formation of diazomethane. When decomposition was effected in the presence of isocyanic acid and a less acidic carboxylic acid, the methyl carboxylate was formed. Similar results were obtained when a single equivalent of isocyanic acid was employed or when excess diazotate was present. Thus, there exists at least one diazotate whose reactivity with isocyanic acid is consistent with the mechanism outlined in Scheme III.

Clearly, this finding suggests that the proton-abstraction mechanism should not be dismissed *a priori* as incorrect for all *N*-nitroso-*N*-alkylureas. Simple considerations of acid–base equilibria make a rapid, quantitative proton transfer (urea, $pK_a \cong 16$; ethanol, $pK_a \cong 17$) an attractive first step in the decomposition. Moreover, several experiments suggest that the proton-abstraction mechanism (Scheme III) is actually operative in the decomposition of *N*-nitroso-*N*-methylurea. For example, treatment of *N*-nitroso-*N*-methylurea with sodium hydride in dry 1,2-dimethoxyethane under anhydrous conditions resulted in the decomposition of the urea to diazomethane[12] in quantitative yield, according to the following equation.



The strongly basic nature of sodium hydride (pK_a = 40) undoubtedly precludes nucleophilic addition to the nitroso group in the presence of the relatively acidic urea protons (pK_a = 16).[13] A similar result was obtained from the addition of 1 equiv of anhydrous *n*-butyllithium to a solution of *N*-nitroso-*N*-methylurea in dry 1,2-dimethoxyethane. Immediate decomposition of the urea to diazomethane was observed; this material could be used in the conversion of 1 equiv of a carboxylic acid to its methyl ester (87% yield). If the decomposition was run in the presence of a second equivalent of *n*-butyllithium, lithium methyl diazotate was formed.

The decomposition of *N*-nitroso-*N*-methylurea with hindered bases also supports this mechanism. Treatment of the urea with excess triethylamine in 1,2-dimethoxyethane effected decomposition to diazo-

(10) G. W. Cowell and A. Ledwith, *Quart. Rev., Chem. Soc.*, **24**, 1191 (1970).

(11) S. M. Hecht and J. W. Kozarich, *Tetrahedron Lett.*, 5147 (1972).

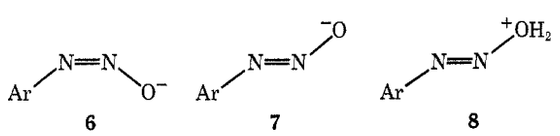
(12) *N*-Nitroso-*N*-methylurea is stable to a suspension of sodium hydroxide in dry 1,2-dimethoxyethane, under the reaction conditions.

(13) W. P. Jencks and J. Regenstein in "CRC Handbook of Biochemistry," 2nd ed, H. A. Sober, Ed., Chemical Rubber Company, Cleveland, Ohio, 1970, pp J-187–J-226.

nium products. Since triethylamine is a very hindered base, which exhibits poor nucleophilic properties as a result of this steric hindrance, the proton-abstraction mechanism (Scheme III) would seem more consistent with the observed results. Treatment of *N*-nitroso-*N*-methylurea with 1 equiv of potassium *tert*-butoxide also resulted in the rapid formation of diazomethane. Treatment with a twofold excess of potassium *tert*-butoxide resulted in the formation of potassium methyl diazotate, which rapidly decomposed to diazomethane upon addition of water.[14]

Additional supporting evidence may be obtained from the decomposition of *N*-nitroso-*N*-methylurea with anions of widely varying base strength and nucleophilic character. The mechanism outlined in Scheme III can only be operative in the presence of a strong base. In this context, it is significant that the half-life of *N*-nitroso-*N*-methylurea in the presence of phenoxide and thiophenoxide anions was ~75 and 210 sec, respectively, in the sense that phenoxide is a stronger base than thiophenoxide (although a far weaker nucleophile). Under the same conditions, the decomposition of *N*-nitroso-*N*-methylurea by hydroxide ion was too fast to measure. Further verification of base control in the decomposition was provided by the smaller amount of *N*-nitroso-*N*-methylurea decomposed by a given amount of thiophenoxide, relative to the phenoxide anion (Figure 1).

The results of decomposition obtained for *N*-nitroso-*N*-(2,2-diphenylcyclopropyl)urea and *N*-nitroso-*N*-methylurea might be considered compatible if the apparent stability of 2,2-diphenylcyclopropyldiazotate to moderately strong acids could be explained. A reasonable approach to this problem might be the initial assumption that the reaction pathway from the individual diazotates to their respective final products was achieved *via* transition states of rather different energies. For example, early work in this field[15] established the difference in reactivities of syn and anti aryl diazotates. While the syn diazotates (**6**) rapidly afforded diazonium ions, their anti isomers (**7**) yielded these products slowly, the rate-determining step in the latter case apparently involving isomerization to the syn diazotate or formation of the conjugate acid (**8**).[16] Although alkyl diazotates have not been



noted to isomerize, ostensibly owing to the instability of each of the geometrical isomers,[17] 2,2-diphenylcyclopropyldiazotate might be thought to exist largely as the less reactive anti isomer owing to steric constraints and to possess a higher energy barrier to decomposition than other alkyl diazotates on the basis of steric or electronic effects associated with the 2,2-diphenylcyclopropyl moiety. Alternatively, 2,2-diphenylcyclopropyl diazotate might be thought to form the observed ring-opened product *via* some species other than a diazoalkane, *e.g.*, a carbene.[18]

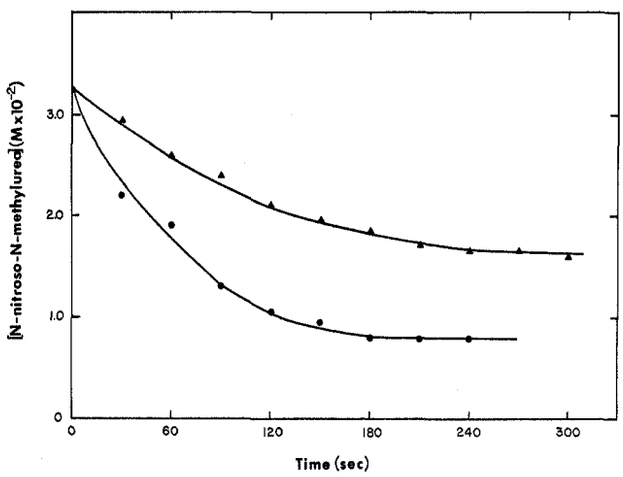


Figure 1.—Decomposition curves for *N*-nitroso-*N*-methylurea in the presence of thiophenoxide (▲) and phenoxide (●) anions, respectively.

Experimental Section

Ultraviolet spectra were recorded on a Cary 15 spectrophotometer. Infrared spectra were determined on a Perkin-Elmer 457A spectrophotometer, through the courtesy of Professor Dietmar Seyferth.

Treatment of Potassium Methyl Diazotate with Isocyanic Acid in Tetrahydrofuran.—Isocyanic acid was generated by thermolysis of cyanuric acid at 380–400° and introduced into tetrahydrofuran which had been precooled to 0°. The normality of the solution was determined by titration of an aliquot with a standardized sodium hydroxide solution. Potassium methyl diazotate (0.10 g, ~1.0 mmol) was suspended in 10 ml of THF at 0°. Isocyanic acid (~0.6 mmol) in 50 ml of THF was added and the mixture was stirred at 0° under anhydrous conditions for 3 hr, during which time gas evolution was observed. The reaction mixture was then concentrated and an infrared spectrum of the residue revealed the presence of cyanate ion (2275 cm^{-1}).

This reaction was repeated utilizing an isocyanic acid solution which contained excess *p*-nitrobenzoic acid. At the conclusion of the reaction the solution was concentrated and treated with ether. The ethereal layer was extracted with water and sodium bicarbonate solution and dried. Concentration afforded methyl *p*-nitrobenzoate in 90% yield, based on limiting diazomethane.

Decomposition of *N*-Nitroso-*N*-methylurea with Sodium Hydride in 1,2-Dimethoxyethane.—To a suspension of sodium hydride (1.00 g, 41.7 mmol) in 20 ml of 1,2-dimethoxyethane at 0° was added *N*-nitroso-*N*-methylurea (2.15 g, 20.8 mmol) in 15 ml of 1,2-dimethoxyethane. The suspension was maintained under anhydrous conditions. Gas evolution began immediately and the mixture was stirred at 0° for 3 hr. The solution slowly turned yellow owing to the generation of diazomethane. The diazomethane solution was decanted and utilized in the methylation of an excess of *p*-nitrobenzoic acid (3.43 g of ester isolated, corresponding to 91% diazomethane formation.) No *N*-nitroso-*N*-methylurea remained at the conclusion of the reaction, as judged by ultraviolet spectroscopy.

Decomposition of *N*-Nitroso-*N*-methylurea with *n*-Butyllithium in 1,2-Dimethoxyethane. One Equivalent of *n*-Butyllithium.—To a solution of *N*-nitroso-*N*-methylurea (220 mg, ~2.2 mmol) in 10 ml of 1,2-dimethoxyethane was added *n*-butyllithium (1 ml, 2.2 *M* in pentane, 2.2 mmol). Lithium cyanate (98 mg, 91%, identified by infrared spectroscopy) precipitated from solution, which assumed the yellow color indicative of diazomethane formation. The diazomethane solution was utilized in the esterifi-

(14) For Scheme II to be operative here, it would be necessary to postulate that *deprotonation* of the diazohydroxide occurred faster than its decomposition while *protonation* of the diazotate was slow.

(15) H. Zolling, "Diazo and Azo Chemistry, Aliphatic and Aromatic Compounds," Interscience, New York, N. Y., 1961.

(16) B. A. Porai-Koshits, *Zh. Org. Khim.*, **2**, 1125 (1966).

(17) E. H. White, T. J. Ryan, and K. W. Field, *J. Amer. Chem. Soc.*, **94**, 1360 (1972).

(18) For a thorough discussion of possible intermediates see (a) W. M. Jones and M. H. Grasley, *Tetrahedron Lett.*, 927 (1962); (b) ref 9; (c) W. M. Jones and J. M. Walbrick, *J. Org. Chem.*, **34**, 2217 (1969).

cation of *p*-nitrobenzoic acid (346 mg of methyl *p*-nitrobenzoate isolated, 87% yield, based on limiting CH_2N_2).

Two Equivalents of *n*-Butyllithium.—To a sodium of *N*-nitroso-*N*-methylurea (220 mg, ~2.2 mmol) in 10 ml of 1,2-dimethoxyethane under N_2 was added *n*-butyllithium (2 ml, 2.2 *M* in pentane, 4.4 mmol). A precipitate (202 mg) formed and no diazomethane generation was observed. Quenching of the isolated precipitate with H_2O afforded rapid gas liberation and diazomethane, suggesting that the precipitate was a mixture of lithium cyanate and the methyl diazotate. This was supported by the infrared spectrum of the solid, which had bands at 2275 (cyanate) and 2180 cm^{-1} (diazotate).

Decomposition of *N*-Nitroso-*N*-methylurea with Triethylamine in 1,2-Dimethoxyethane.—To a solution of *N*-nitroso-*N*-methylurea (0.50 g, ~5 mmol) in 15 ml of 1,2-dimethoxyethane at 0° was added triethylamine (2.7 ml, 25 mmol). Gas evolution began immediately and the decomposition of the urea was followed spectrophotometrically. The reaction was complete in 45 min. The final solution contained cyanate ion, as judged by infrared spectroscopy. The diazomethane generated by this procedure could be trapped by the addition of *p*-nitrobenzoic acid to the initial reaction mixture.

Decomposition of *N*-Nitroso-*N*-methylurea with Potassium *tert*-Butoxide in *tert*-Butyl Alcohol.—To a solution of potassium *tert*-butoxide (2.17 g, 19.4 mmol) in 50 ml of *tert*-butyl alcohol at 20° was added *N*-nitroso-*N*-methylurea (1.0 g, 9.7 mmol). The suspension was maintained under nitrogen and stirred for 20 min. Essentially no diazomethane was observed to have been formed. The suspension of potassium cyanate was filtered, yield 0.73 g (96%), identification by infrared spectroscopy. The filtrate was concentrated under diminished pressure to afford potassium methyl diazotate as a yellow solid, yield 0.76 g (~80%, identification by infrared spectroscopy), which rapidly decomposed (gas evolution) upon addition of water. Decomposition of the urea with 1 equiv of potassium *tert*-butoxide resulted in the rapid formation of diazomethane. The diazomethane could be utilized in the conversion of *p*-nitrobenzoic acid to its methyl ester. The yield of diazomethane (based on methyl *p*-nitrobenzoate formed in the presence of excess *p*-nitrobenzoic acid) was about 90%. Work-up of the initial reaction mixture indicated the presence of potassium cyanate (93%) and methyl diazotate (18%).

Rate of Decomposition of *N*-Nitroso-*N*-methylurea by Sodium Phenoxide and Sodium Thiophenoxide.—*N*-Nitroso-*N*-methylurea (67 mg, 0.65 mmol) was dissolved in 20 ml of 1,2-dimethoxyethane. The solution was cooled to 0° and sodium phenoxide (75 mg, 0.65 mmol) was added quickly. At 30-sec intervals, 20 μl of the solution was added to 2 ml of EtOH and acidified with 2 drops of 1 *N* hydrochloric acid solution, which quenched the reaction. The ultraviolet absorbance spectrum (A_{230}) was recorded for each aliquot and then 4 *N* sodium hydroxide solution was added to decompose the unreacted urea. The solution was reacidified and A_{230} was again recorded. The difference in each set of two spectra was employed as a measure of unreacted *N*-nitroso-*N*-methylurea. A control experiment demonstrated that all *N*-nitroso-*N*-methylurea absorbance was eliminated by the acid–base treatment and did not affect the other reactants.

Data for the phenoxide- and thiophenoxide-induced decompositions of *N*-nitroso-*N*-methylurea indicated half-lives of decomposition of ~75 and 210 sec, respectively.

Registry No.—*N*-Nitroso-*N*-methylurea, 684-93-5.

Acknowledgments.—We thank Professors C. G. Swain and F. D. Greene for helpful discussions during the course of this work.

Synthesis of 2-Aminomethylpyrroles and Related Lactams

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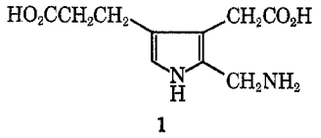
The potassium enolate of ethyl 2-methoxy-5-nitro-4-pyridinepyruvate was C-alkylated and C-acylated with methyl iodide, ethyl iodide, *n*-propyl iodide, ethyl bromoacetate, ethyl chloroformate, and benzyl chloroformate and the corresponding ethyl 2-oxobutyrate, 2-oxocaproate, 2-oxoglutarate, and the oxalacetates were obtained. The same procedure afforded the 2-benzyloxy and 2-anisyloxy oxalacetates. Reductive cyclization of the α-keto monoesters afforded the corresponding ethyl 5-methoxy-6-azaindole-2-carboxylates and in several cases also the 1,2,3,4-tetrahydro-3-oxy-6-methoxy-1,7-naphthyridin-2-ones. The 6-azaindoles were transformed with hydrobromic acid into the corresponding 6-azaindanones, which were reduced to the corresponding 2-carboxy-3-alkylpyrrole lactams. The latter were transformed into the corresponding 4-alkyl-3-carboxymethyl-2-aminomethylpyrroles. The catalytic hydrogenation of the oxalacetates, followed by cyclization of the resulting 5-aminopyridines, afforded 2,3-dicarbethoxy-6-azaindoles and 2,3-dicarbethoxy-6-azaindanone. The latter were transformed by catalytic hydrogenation into diethyl 5-oxo-3a,4,5,6-tetrahydro-1*H*-pyrrolo[2,3-*c*]pyridine-2,3-dicarboxylate which could not be saponified to a 2-aminomethylpyrrole.

The synthesis of 2-aminomethyl-3-carboxymethylpyrroles was a task of particular interest in pyrrole chemistry ever since it was conclusively established[1] that the natural metabolite porphobilinogen was a 2-aminomethyl-3-carboxymethyl-4-carboxyethylpyrrole **1**. This unique compound has no other metabolic



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analogs and, since it is the precursor of all the natural porphyrins, chlorins, and corrin derivatives,[2] it was tempting to develop a synthetic method which should afford not only porphobilinogen but also analogous 2-aminomethylpyrroles to study their chemical and biological behavior. 2-Aminomethylpyrroles proved also to be very suitable intermediates for dipyrrylmethane synthesis,[3] being in many senses more advantageous than the classical 2-bromomethyl or 2-acetoxymethylpyrrole derivatives.

In our previous work[4] we approached the problem of the synthesis of porphobilinogen **1** by considering it to be a derivative of a 5-oxo-4,5,6,7-tetrahydro-6-azaindole (pyrrole lactam) structure. The synthesis of the 6-azaindole ring was then achieved[4] by a sequence modeled on the Reissert-type synthesis of indoles, which was based on the synthesis of the ethyl *o*-nitro-4-pyr-

(1) G. H. Cookson and C. Rimington, *Biochem. J.*, **57**, 476 (1954).

(2) J. Lascelles, "Tetrapyrrole Biosynthesis and its Regulation," W. A. Benjamin, New York, N. Y., 1964, p 47.

(3) B. Frydman, S. Reil, A. Valasinas, R. B. Frydman, and H. Rapoport, *J. Amer. Chem. Soc.*, **93**, 2738 (1971).

(4) B. Frydman, M. E. Despuy, and H. Rapoport, *J. Amer. Chem. Soc.*, **87**, 3530 (1965); B. Frydman, S. Reil, M. E. Despuy, and H. Rapoport, *ibid.*, **91**, 2338 (1969).