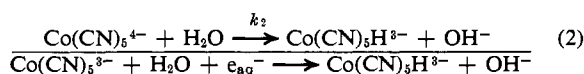
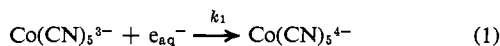


gonne National Laboratory's ARCO linear accelerator, in accord with the general procedures described elsewhere.³ Experimental conditions were maintained so as to ensure the rapid ($t_{1/2} \sim 0.1 \mu\text{sec}$) scavenging of OH radicals, either by methanol ($\sim 10^{-2} M$) in the case of the $\text{Co}(\text{CN})_5^{3-}$ solutions, or by H_2 ($\sim 0.1 M$, achieved by using a high-pressure cell⁴ containing 100 atm of H_2) in the case of the other solutions. The pH, in each case, was maintained at 13; under these conditions H atoms were rapidly ($t_{1/2} \sim 0.35 \mu\text{sec}$) converted by OH^- to e_{aq}^- so that, for our purposes, e_{aq}^- was effectively the only reactive species generated by the pulse radiolysis. The reactions of the hydrated electrons with the cobalt complexes were monitored spectrophotometrically as previously described,³ the spectra of transient species being deduced from the absorbance changes accompanying their formation and/or decay. The overall stoichiometries of the reactions were confirmed in steady-state irradiation experiments using a ^{60}Co γ source.

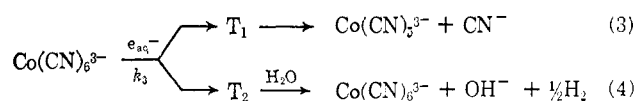
Pulse radiolysis experiments on aqueous solutions of $\text{Co}(\text{CN})_5^{3-}$ ($\sim 10^{-5} M$), in which the generation and decay of e_{aq}^- were followed at 578 nm ($\epsilon = 1.1 \times 10^4 M^{-1} \text{cm}^{-1}$), revealed a reaction between e_{aq}^- and $\text{Co}(\text{CN})_5^{3-}$ which obeyed the second-order rate law, $k_1 \cdot [e_{\text{aq}}^-][\text{Co}(\text{CN})_5^{3-}]$, with $k_1 = (1.4 \pm 0.1) \times 10^{10} M^{-1} \text{sec}^{-1}$. The initial product of this reaction is a transient, identified below as pentacyanocobaltate(I) ($\lambda_{\text{max}} 280 \text{ nm}$, $\epsilon_{\text{max}} \sim 8 \times 10^3$), which undergoes first-order decay ($k_2 = (1.0 \pm 0.1) \times 10^5 \text{ sec}^{-1}$) to yield $\text{Co}(\text{CN})_5\text{H}^{3-}$. In D_2O solutions the value of k_1 was substantially the same as in H_2O , whereas the value of k_2 was reduced to $1.6 \times 10^4 \text{ sec}^{-1}$, one-sixth its value in H_2O . We interpret these observations in terms of the following reaction sequence.



Pentacyanocobaltate(I), $\text{Co}(\text{CN})_5^{4-}$, has previously been proposed as an intermediate in the electrochemical oxidation of $\text{Co}(\text{CN})_5\text{H}^{3-}$,² in the electrochemical reduction of $\text{Co}(\text{CN})_5^{3-}$,⁵ and in the base-catalyzed oxidation of $\text{Co}(\text{CN})_5\text{H}^{3-}$ by $\text{Co}(\text{CN})_5\text{I}^{3-}$ ⁶ and by benzoquinone.¹

Pulse radiolysis experiments were also performed on aqueous solutions of various cobalt(III) cyanide complexes, including $\text{Co}(\text{CN})_6^{3-}$, $\text{Co}(\text{CN})_5\text{OH}^{3-}$, and $\text{Co}(\text{CN})_5\text{I}^{3-}$, in the hope of generating and characterizing the corresponding unstable transient six-coordinate cobalt(II) species, $\text{Co}^{\text{II}}(\text{CN})_6^{4-}$, $\text{Co}^{\text{II}}(\text{CN})_5\text{OH}^{4-}$, etc. These experiments yielded somewhat more complicated results, the significance of which is not yet fully established. For example, electron capture by $\text{Co}(\text{CN})_6^{3-}$ ($\sim 10^{-4} M$) occurred with a second-order rate constant, $k_3 = (5.0 \pm 0.5) \times 10^9 M^{-1} \text{sec}^{-1}$, corresponding to complete electron capture with $t_{1/2} \sim 1.5 \mu\text{sec}$. The initially observed products following electron capture were two distinct transients, T_1 ($\lambda_{\text{max}} 280 \text{ nm}$, $\epsilon = 7 \times 10^3$; $\lambda_{\text{max}} 965 \text{ nm}$, $\epsilon \sim 5 \times 10^2$) and T_2 ($\lambda_{\text{max}} 270\text{--}275$

nm, $\epsilon \sim 10^3$), which decayed with half-lives of $\sim 10^{-3}$ and 10^{-5} sec , respectively, in accord with the pattern depicted by eq 3 and 4, to yield $\text{Co}(\text{CN})_5^{3-}$ ($\sim 50\%$) and $\text{Co}(\text{CN})_6^{3-}$ ($\sim 50\%$), respectively.



While the available information does not provide an entirely convincing basis for the identification of T_1 and T_2 , plausible suggestions are that T_2 corresponds to $\text{Co}^{\text{II}}(\text{CN})_6^{4-}$ (with properties perhaps best described as those of an "electron-adduct" of $\text{Co}(\text{CN})_6^{3-}$),⁹ whereas T_1 (whose spectrum resembles that of $\text{Co}(\text{CN})_5^{3-}$) might be a linkage isomer of $\text{Co}(\text{CN})_5^{3-}$, such as $\text{Co}(\text{CN})_4\text{NC}^{3-}$. The latter could arise through the rapid dissociation of a precursor such as $\text{Co}(\text{CN})_4(\text{NC})_2^{4-}$, which has been proposed as one of the products of electron irradiation of solid $\text{K}_3\text{Co}(\text{CN})_6$.¹⁰

Qualitatively similar results (in each case corresponding to two transients, one of which reverts to the parent compound and the other, which decays to $\text{Co}(\text{CN})_5^{3-}$) were also obtained in pulse radiolysis experiments on aqueous solutions of other cobalt(III) cyanide complexes including $\text{Co}(\text{CN})_5\text{OH}^{3-}$, $\text{Co}(\text{CN})_5\text{I}^{3-}$, and $\text{Co}(\text{CN})_5\text{NCS}^{3-}$.^{11,12}

Acknowledgments. Based on work performed under the auspices of the U. S. Atomic Energy Commission. The award of an Argonne Universities Association-Argonne National Laboratory fellowship to one of us (G. D. V.) is gratefully acknowledged.

(7) An intermediate of this composition has previously been postulated⁸ in the "outer-sphere" oxidation of $\text{Co}(\text{CN})_5^{3-}$ to $\text{Co}(\text{CN})_6^{3-}$, by $\text{Co}(\text{NH}_3)_6^{3+}$ and other cobalt(III) complexes.

(8) J. P. Candlin, J. Halpern, and S. Nakamura, *J. Amer. Chem. Soc.*, **85**, 2517 (1963).

(9) An analogous transient, $\text{Au}(\text{CN})_2^{2-}$, also exhibiting properties of an "electron-adduct," has been observed³ in pulse radiolysis experiments on $\text{Au}(\text{CN})_2^-$ solutions. Such "electron-adducts" appear to be distinctly characteristic of cyanide complexes.

(10) J. Danon, R. P. A. Muniz, A. O. Caride, and I. Wolfson, *J. Mol. Struct.*, **1**, 127 (1967).

(11) We are grateful to Professor H. B. Gray, D. Gutterman, and G. Rossman of the California Institute of Technology for samples of these compounds and for valuable discussions.

(12) Preliminary pulse radiolysis experiments on aqueous solutions of $\text{Mo}(\text{CN})_8^{4-}$ yielded analogous results.¹¹ Electron capture by $\text{Mo}(\text{CN})_8^{4-}$ occurs with a rate constant of $7.1 \times 10^9 M^{-1} \text{sec}^{-1}$, yielding two transients, one of which decays with a rate constant of $1.3 \times 10^2 \text{ sec}^{-1}$ to $\text{Mo}(\text{CN})_7^{4-} + \text{CN}^-$ ($\sim 60\%$), and the second with a rate constant of $2 \times 10^4 \text{ sec}^{-1}$, presumably reverting to $\text{Mo}(\text{CN})_8^{4-}$.

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The Stereochemical Course of Deamination of Acyclic Secondary Carbinamines in Water. The Role of Micelles¹

Sir:

Carbinol formation *via* aqueous HNO_2 deamination of acyclic secondary carbinamines is reported to involve

(1) Presented at the 158th National Meeting of the American Chemical Society, Sept 8, 1969, New York, N. Y.

(3) A. S. Ghosh-Mazumdar and E. J. Hart, *Advances in Chemistry Series*, No. 81, American Chemical Society, Washington, D. C., 1968, p 193, and references cited therein.

(4) E. M. Fielden and E. J. Hart, *Radiat. Res.*, **33**, 426 (1968).

(5) A. A. Vičėk, *Pure Appl. Chem.*, **10**, 61 (1961).

(6) J. Halpern and M. Pribanić, unpublished data.

net inversion.² This conclusion appeared in Ingold's influential treatise³ and persists in more recent works.⁴ Our observation of a stereochemical discrepancy in the deamination of 2-aminooctane⁵ has led us to determine the stereochemical course of deamination of six amines of structure RCH(NH₂)CH₃. The results force revision of the belief that such amines deaminate with "racemization and inversion,"^{2a-4} refine our conception of the deamination reaction, and, in an initial observation of its kind, implicate alkylammonium ion micelles as agents of stereochemical control.

Deamination of 2-aminobutane has been described.⁵ The other amines were resolved *via* their tartrate salts.⁶ Enantiomeric compositions were ascertained by glpc analysis of derived diastereomeric trifluoroacetyl-L-prolylamides.⁷ Amines were deaminated with aqueous HNO₂. Nitrogen evolution was generally quantitative. Product mixtures contained 2-alkanol, 1- and 2-alkenes, and smaller quantities of 2-alkanone, 3-alkanol, and 2-alkyl nitrite. 2-Alkanols were purified by preparative glpc (Carbowax); optical purities were polarimetrically determined on neat alkanol samples.⁸ Final results appear in Table I.⁹

Table I. Stereochemistry of 2-Alkanol Formation^a

R in RCH(NH ₂)CH ₃	Stereochemistry ^b	± av dev _n , % ^c	Cmc, ^d M
C ₂ H ₅ ^e	22.9% (net) invn	0.43	
<i>n</i> -C ₃ H ₇	22.9% invn	2.23	>1.81
<i>n</i> -C ₄ H ₉	19.0% invn	0.62	0.89 ^f
<i>n</i> -C ₅ H ₁₁	3.5% invn	0.44	0.24
<i>n</i> -C ₆ H ₁₃ ^g	6.0% retn		0.041
<i>n</i> -C ₈ H ₁₇	11.8% retn	0.52	

^a Aqueous HNO₂ deamination of RCH(NH₂)CH₃, 0.76 M, in 1.6 M NaNO₂, pH 4 (HClO₄). Polarimetry details will appear in the Ph.D. Thesis of D. W. R. ^b Controls demonstrated optical stability of the alcohols to experimental procedures. ^c Average deviation of *n* deaminations. ^d Critical micelle concentration of racemic RCH(NH₃⁺)CH₃, H₂O, 1.61 M NaClO₄, pH 4 (HClO₄); average deviation ~ ±0.02 M. ^e Initial concentration 0.4–0.6 M.^{2b,5} ^f Cmc with 1.61 M; NaNO₂ 0.83 M; NaCl, 0.87 M. ^g See Table II.

There is an apparent dependence of stereochemistry on chain length when R > C₄H₉. Moreover, the stereochemistry of deamination of 2-aminooctane is *concentration dependent* (Table II).

Clearly, present mechanisms for the deamination reaction,²⁻⁴ which take no account of chain length or concentration effects, are incomplete. Consider Table I, in which appear critical micelle concentrations (cmc's) for RCH(NH₃⁺)CH₃, determined under conditions

(2) (a) P. Brewster, F. Hiron, E. D. Hughes, C. K. Ingold, and P. A. D. S. Rao, *Nature*, 166, 179 (1950); (b) K. B. Wiberg, Ph.D. Thesis, Columbia University, New York, N. Y., 1950; (c) A. Streitwieser, Jr., *J. Org. Chem.*, 22, 861 (1957).

(3) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 397.

(4) P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. 1, W. A. Benjamin, Inc., New York, N. Y., 1965, p 37.

(5) R. A. Moss and S. M. Lane, *J. Amer. Chem. Soc.*, 89, 5655 (1967).

(6) F. G. Mann and H. W. G. Porter, *J. Chem. Soc.*, 456 (1964).

(7) B. Halpern and J. W. Westley, *Chem. Commun.*, 34 (1966).

(8) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, 45 (1911).

(9) Configurational correlation of 2-aminoalkanes and 2-alkanols is available.^{10,11}

(10) M. Vogel and J. D. Roberts, *J. Amer. Chem. Soc.*, 88, 2262 (1966).

(11) J. A. Mills and W. Klyne, *Progr. Stereochem.*, 1, 194 (1954).

Table II. Concentration Dependence of 2-Aminooctane Deamination^a

[2-Aminooctane], ^b M	Stereochemistry ^c
0.76	6% (net) retn
0.39 ^d	0% racmzn
0.15	7% invn
0.076	18% invn
0.029	27% invn
0.015	23% invn ^e

^a Other conditions as above. ^b Initial concentration. ^c Optical purity of 2-octanol was determined by gc analysis of derived L-acetyllactate diastereomeric esters, ±1%: R. A. Moss, D. W. Reger, and E. M. Emery, submitted for publication; E. Gil-Av, R. Charles-Sigler, G. Fischer, and D. Nurok, *J. Gas. Chromatog.*, 4, 51 (1966); H. C. Rose, R. L. Stern, and B. L. Karger, *Anal. Chem.*, 38, 469 (1966). ^d Reference 5. ^e 24% using HCl rather than HClO₄.

analogous¹² to those of the deamination reactions. Note that the stereochemistry of the deaminative process deviates from the "normal" value, *ca.* 23% net inversion, and *moves toward retention when the initial amine concentration exceeds the cmc of the related ammonium ion*.¹⁴ (At pH 4 alkylamines exist almost completely as alkylammonium ions.) Since alkylammonium ion cmc's decrease as R lengthens, more of the total deamination reaction (at constant initial amine concentration) proceeds in the presence of micelles, the longer the R group; a "chain length" effect results. A possible rationale for micellar action follows. RNH₂ is in equilibrium with RNH₃⁺, and, if [RNH₃⁺] > cmc, free RNH₂ may be solubilized by the micelle and deaminate mainly in the micellar phase.¹⁵ The stereochemistry of micellar deamination should be *retention*, since the micellar region is considerably less polar than water.¹³ Deaminative processes in solvents of substantially lower polarity than water generally show retention stereochemistry.¹⁶

When the initial 2-aminooctane concentration is below the cmc of 2-octylammonium ion (Table II), deamination stereochemistry becomes "normal" or similar to values in Table I for those amines for which [RNH₃⁺] < cmc. Moreover, when the initial 2-octylammonium ion concentration is below the cmc, further dilution no longer increases inversion (Table II) because all deamination occurs in the absence of micelles. At intermediate concentrations (*e.g.*, twice cmc), substantial deamination occurs in the *presence and absence* of micelles and observed stereochemistry is a blend of the characteristic stereochemistries for the two processes. The deaminations of 2-aminoheptane (Table I) and 2-aminooctane (0.15 M, Table II) are representative. When initial alkylammonium ion concentration greatly exceeds the cmc, almost all deamination probably is micellar. The deaminations of 2-

(12) The anion is perforce different, but anion variation is seen to have a minor effect in the present case. The presence of product alkanol during the deamination reaction will make the cmc's slightly lower than those reported in Table I. Critical micelle concentrations were determined by surface tensiometry.¹³

(13) L. R. Romsted and E. H. Cordes, *J. Amer. Chem. Soc.*, 90, 4404 (1968), and therein.

(14) Optically active 2-octylammonium ion has a larger cmc (0.058 M) than the racemic ion. We are investigating this effect further. Phenomena of similar magnitude and direction for the other amines would not affect subsequent arguments.

(15) For leading references to micellar organic reactions, see R. B. Dunlap and E. H. Cordes, *J. Amer. Chem. Soc.*, 90, 4395 (1968).

(16) E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1968, p 440 ff.

aminooctane and 2-aminodecane (6–12% net retention at 0.76 *M*) represent the latter case, which is probably an extreme for this type of system.

The traditional mechanistic concepts of nitrous acid deamination²⁻⁴ are thus incomplete. The reaction stereochemistry is concentration dependent for a given amine and chain length dependent for homologous amines at certain given concentrations. We suggest that alkylammonium ion micelles are responsible for these effects. We are exploring these and related phenomena.

Acknowledgments. We thank Professor B. Halpern, who determined enantiomeric compositions of the newly resolved amines; the National Science Foundation, the National Institutes of Health, and the Petroleum Research Fund for financial support; Allied Chemical Company for a fellowship (D. W. R.); and Professor U. P. Strauss for helpful discussions. We also thank Dr. Stuart Lane, whose observation⁵ triggered this study.

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Phosphonitrilic Radical Anions

Sir:

We wish to report the preparation of the first cyclophosphazene (phosphonitrilic) radical anions, together with their electron spin resonance spectra. The information derived from a study of these species is applicable to the controversial question of bonding in phosphorus–nitrogen systems.¹⁻¹¹

Radical anions of organic aromatic species are well known, and those of inorganic heterocyclic compounds such as borazines have also been reported.¹² Unsuccessful previous attempts have been made to prepare cyclophosphazene radical anions by treatment of $[\text{NP}(\text{C}_6\text{H}_5)_2]_3$ with an alkali metal,¹³ but decomposition products, such as biphenyl, were the only reaction products detected. We have prepared the radical anions of a number of phosphazenes by electrolytic techniques with the use of dimethylformamide solvent and *t*-butylammonium halides or perchlorate as the supporting electrolyte. The formation of one-electron reduced species was followed by polarography, coulometry, and cyclic voltammetry. Reductions were also performed within the cavity of an esr spectrometer at potentials near the $E_{1/2}$ values.

(1) M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, *J. Chem. Soc.*, 2423 (1960).

(2) D. P. Craig, *ibid.*, 997 (1959).

(3) D. P. Craig, M. L. Heffernan, R. Mason, and N. L. Paddock, *ibid.*, 1376 (1961).

(4) D. P. Craig and N. L. Paddock, *ibid.*, 4118 (1962).

(5) D. W. J. Cruickshank, *ibid.*, 5486 (1961).

(6) D. A. Brown and C. G. McCormack, *ibid.*, 5385 (1964).

(7) N. L. Paddock, *Quart. Rev.* (London), 18, 168 (1964).

(8) D. P. Craig and K. A. R. Mitchell, *J. Chem. Soc.*, 4682 (1965).

(9) H. R. Allcock, "Heteroatom Ring Systems and Polymers," Academic Press, New York, N. Y., 1967, Chapter 3.

(10) K. A. R. Mitchell, *J. Chem. Soc.*, 2683 (1968).

(11) K. A. R. Mitchell, *Chem. Rev.*, 69, 157 (1969).

(12) D. F. Shriver, D. E. Smith, and P. Smith, *J. Amer. Chem. Soc.*, 86, 5153 (1964).

(13) D. Chapman, S. H. Glarum, and A. G. Massey, *J. Chem. Soc.*, 3140 (1963).

Certain phosphazenes could not be reduced at potentials more positive than -3 V (relative to a saturated calomel electrode). These included $[\text{NP}(\text{OC}_6\text{H}_5)_2]_3$, $[\text{NP}(\text{OC}_6\text{H}_5)_2]_n$, $[\text{NP}(\text{NHC}_6\text{H}_5)_2]_3$, $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_3$, $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_4$, $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$, $[\text{NP}(\text{OCH}_3)_2]_3$, and $[\text{NP}(\text{O}_2\text{C}_6\text{H}_4\text{-}o)]_3$ (where $n \approx 15,000$). No esr spectra were detected during attempted reduction of these species. The halophosphazenes (NPF_2)₃, (NPCl_2)₃, (NPCl_2)₄, and (NPBr_2)₃ showed spurious polarographic behavior, part of which was attributed to ligand ionization at low negative potentials.

However, the following compounds¹⁴ showed well-defined one-electron polarographic reduction peaks: hexaphenylcyclophosphazene, $[\text{NP}(\text{C}_6\text{H}_5)_2]_3$, I; octaphenylcyclophosphazene, $[\text{NP}(\text{C}_6\text{H}_5)_2]_4$, II; hexa(*p*-nitrophenoxy)cyclophosphazene, $[\text{NP}(\text{OC}_6\text{H}_4\text{-NO}_2)_2]_3$, III; tris(2,3-dioxynaphthyl)cyclophosphazene, $[\text{NP}(2,3\text{-O}_2\text{C}_{10}\text{H}_6)]_3$, IV; tris(1,8-dioxynaphthyl)cyclophosphazene, $[\text{NP}(1,8\text{-O}_2\text{C}_{10}\text{H}_6)]_3$, V; tris(2,2'-dioxybiphenyl)cyclophosphazene, $[\text{NP}(2,2'\text{-O}_2\text{C}_{12}\text{H}_8)]_3$, VI; and tris-1,3,5-triphenyltris-1,3,5-trifluoroethoxycyclophosphazene, $[\text{NP}(\text{C}_6\text{H}_5)(\text{OCH}_2\text{-CF}_3)]_3$, VII. $E_{1/2}$ values (relative to sce) are as follows: I, -2.65 ; II, -2.67 ; III, -1.24 ; IV, -1.83 dec; V, -2.15 ; VI, -2.33 ; VII (*trans*), -2.45 V. Cyclic voltammetric experiments indicated that the radicals derived from I, II, and VII had a shorter lifetime (< 1 sec) than those from III and IV (> 10 sec). However, polarographic and prolonged, low-frequency cyclic voltammetric experiments suggested that, with the exception of IV, irreversible decomposition of the radical is not the primary deactivation process.

The esr spectra of the radical anions from the two phenylphosphazenes I and II consisted of an unresolvable singlet at $g = 2$ with a 20–30-G band width. A series of careful experiments designed to vary the solvent, temperature, concentration, and polarographic technique failed to produce hyperfine splitting in this spectrum. On the other hand, hyperfine splitting was readily observed in the spectra derived from III (13–15 lines), IV (5 lines), and V (15–20 lines). It is considered unlikely that these spectra result solely from secondary decomposition products. Thus, termination of reduction during esr experiments was followed by a simple decay of each spectrum with no secondary spectra being evident. Also, in the case of the phenyl derivatives I and II, the esr spectrum of biphenyl (the most likely decomposition product) was not seen, although it was readily visible when small amounts of biphenyl were added. No esr signals have yet been detected from the radical anions of VI and VII, presumably because of their short lifetime.

These observations can be interpreted as follows. Reduction of a phosphazene to the radical anion apparently does not occur unless the side group itself is independently reducible in the same potential range or unless an aryl group is bonded directly to phosphorus. For example, *p*-nitroanisole or substituted naphthalenes

(14) Compounds I and II were prepared by the method of D. L. Herring and C. M. Douglas, *Inorg. Chem.*, 4, 1012 (1965); derivatives III and V were synthesized from $(\text{NPCl}_2)_3$ and the appropriate phenol or diol (H. R. Allcock and E. J. Walsh, unpublished work); compounds IV and VI were prepared as described previously (H. R. Allcock and R. L. Kugel, *Inorg. Chem.*, 5, 1016 (1966)); the *cis* or *trans* isomers of VII were formed by reaction of sodium trifluoroethoxide with the appropriate $[\text{NPCl}(\text{C}_6\text{H}_5)]_3$ precursor, itself synthesized by the method of B. Grushkin, M. G. Sanchez, and R. G. Rice, *ibid.*, 3, 623 (1964).