

Anal. Calcd for $C_{18}H_{21}Cl$: C, 79.24; H, 7.76. Found: C, 78.87; H, 7.74.

Preparation of 1,2,3,4-Tetrahydro(4a,9a-dichloromethano)fluorene (2a). A. Chloroform-Potassium *t*-Butoxide. Chloroform (11.94 g, 0.10 mole) in anhydrous benzene (50 ml) was added over a 35-min period under nitrogen to a cold, stirred mixture of **1a** (8.51 g, 0.05 mole) and potassium *t*-butoxide⁹ (0.11 mole) in anhydrous benzene (100 ml). The mixture was processed as described for the conversion of **4** to **6**. The yellow oil (11.86 g, 94% yield) obtained by chromatography (alumina, 250 g) solidified. Recrystallization of this product from ethanol gave **2a** as a pale yellow solid, mp 86.5–87° (mixed up with that described below, 86–87.5°).

B. Phenyl(trichloromethyl)mercury. The reaction of **1a** (8.5 g, 0.05 mole) with phenyl(trichloromethyl)mercury (19.8 g, 0.05 mole) in hot benzene (100 ml) was carried out for 65 hr as described for reaction with **4**. The yellow solid (10.21 g, 81% yield, mp 84–86°), obtained subsequent to removal of phenylmercuric chloride (14.0 g, 90%), was recrystallized from ethanol to give **2a** as a white solid (mp 86.5–87.5°). The cyclopropane **2a** showed: nmr spectrum (25% in $DCCl_3$) C_6H_4 (complex, τ 2.67–2.98, wt 4), benzylic CH_2 (AB quartet, τ 6.35, 6.64, 6.80, and 7.09; $J_{AB} = 17.5$ cps, wt 2), CH_2 (complex, τ 7.56–8.18, wt 4), and CH_2 (complex, and τ 8.32–8.86, wt 4).

Anal. Calcd for $C_{14}H_{14}Cl$: C, 66.42; H, 5.57; Cl, 28.01. Found: C, 66.41; H, 5.59; Cl, 27.58.

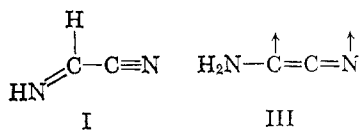
Hydrogen Cyanide Dimer. Aminocyanocarbene

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Abstract: The synthesis and properties of aminocyanocarbene are described. Thermal and photolytic decomposition of the sodium (Vb) and lithium (Vc) salts of 1-cyanoformamide *p*-toluenesulfonylhydrazone gives diaminomaleonitrile, a tetramer of hydrogen cyanide, as the major product. Irradiation of Vc at -196° in 2-methyltetrahydrofuran glass forms a yellow product, identified as aminocyanocarbene, absorbing in the range 332–450 $m\mu$ with the principal maximum at 391 $m\mu$. No epr signals characteristic of a triplet methylene were observed. These results indicate that aminocyanocarbene is a singlet ground-state compound possessing considerable dipolar character. Aminocyanocarbene may be a key intermediate in hydrogen cyanide polymerization and in prebiological organic synthesis.

Base-catalyzed polymerization of hydrogen cyanide yields a mixture of products which includes a tetramer (diaminomaleonitrile),^{1,2} a pentamer (adenine),² polymeric amino acid precursors,³ and black, intractable solids believed to have fused tetrahydropyridine structures.¹ Whatever the reactions leading to these products, it is reasonable to suppose that a key step would be dimerization of hydrogen cyanide. In the absence of experimental evidence it has been widely assumed that HCN dimer is iminoacetonitrile (I).¹ An alternative structure has been proposed by Kliss and Matthews⁴ who have argued that I would spontaneously tautomerize to aminocyanocarbene.



The prediction that aminocyanocarbene is of lower energy than I has been supported by LCAO–MO calculations of Serre and Schneider⁵ who suggest that its stability results from electron delocalization in a triplet ground state. Electron paramagnetic resonance (epr) experiments have established the existence of triplet ground states for two related compounds, cyanomethyl-

ene^{6,7} and dicyanomethylene.⁸ In the parent compound, cyanomethylene, the triplet state with delocalization of unpaired electrons in mutually orthogonal orbitals extending over the C–C–N system is evidently preferred to a 1,3-dipolar singlet state with paired electrons residing primarily on the more electronegative terminal nitrogen atom. For aminocyanocarbene, however, the effect of the amino group on this electron distribution may be significant. Delocalization of the unshared pair of amino electrons^{9,10} into an unoccupied p orbital of the carbene center followed by further delocalization over the nitrile group could be sufficiently stabilizing to cause the ground state to be singlet (II), with considerable dipolar character. Two ground-state structures for aminocyanocarbene must therefore be considered, the singlet II and the triplet III. In this paper we describe the synthesis and properties of aminocyanocarbene and the determination of its ground spin state.

Results

1. Synthesis and Reactions of Aminocyanocarbene.

A synthetic route was devised for generating aminocyanocarbene *via* aminocyanodiazomethane (IV) since polymerization of hydrogen cyanide proceeds too

(1) T. Völker, *Angew. Chem.*, **72**, 379 (1960), and references cited therein.

(2) R. Sanchez, J. Ferris, and L. E. Orgel, *Science*, **153**, 72 (1966), and references cited therein.

(3) (a) C. N. Matthews and R. E. Moser, *Nature*, **215**, 1230 (1967); (b) C. N. Matthews and R. E. Moser, *Proc. Natl. Acad. Sci. U. S. A.*, **56**, 1087 (1966), and references cited therein.

(4) R. M. Kliss and C. N. Matthews, *ibid.*, **48**, 1300 (1962).

(5) J. Serre and F. Schneider, *J. Chim. Phys.*, **61**, 1655 (1964).

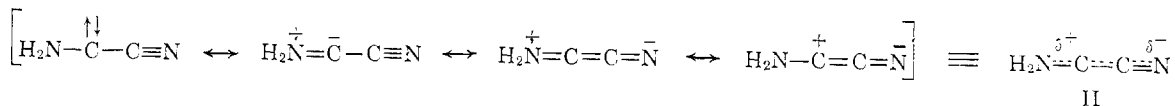
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(7) R. A. Bernheim, R. J. Kempf, J. V. Gramas, and P. S. Skell, *ibid.*, **43**, 196 (1965).

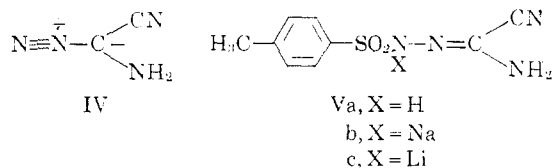
(8) E. Wasserman, L. Barash, and W. A. Yager, *J. Am. Chem. Soc.*, **87**, 2075 (1965).

(9) J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964, pp 168, 172.

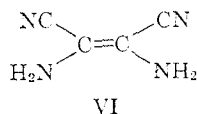
(10) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p 204.



rapidly to permit ready isolation of the dimer. The unstable diazo compound IV was formed and decomposed *in situ* by the method of Bamford and Stevens.¹¹⁻¹³ The necessary precursor, 1-cyanoformamide *p*-toluenesulfonylhydrazone (Va), was readily synthesized from *p*-toluenesulfonylhydrazine and excess cyanogen. Sodium and lithium salts (Vb and Vc) of Va were then used in the decomposition experiments.



When a slurry of the sodium salt Vb was heated or irradiated in dry diglyme rapid decomposition occurred, accompanied by evolution of the theoretical volume of nitrogen. As Vb was used up during the course of the reaction, a solid gradually precipitated which subsequently was shown to be sodium *p*-toluenesulfinate. Evaporation of the reaction solution gave pale yellow crystals of diaminomaleonitrile (VI), mp



182-184°, and a small amount of black intractable solid. Photolytic decomposition of Vb in other aprotic solvents (*e.g.*, pentane or benzene) proceeded more slowly (2-4 hr) than in diglyme but gave essentially the same products. When either decomposition was carried out in the presence of hydroxylic solvents, even in trace amounts, the solutions rapidly darkened and gave only black tars.

In contrast to the sodium salt Vb, the lithium salt Vc is very soluble in diglyme. Heating a diglyme solution of Vc gave nitrogen, lithium *p*-toluenesulfinate, and VI, the yield of the latter being approximately half of that obtained from the sodium salt. Photolysis in diglyme did not give VI. Instead, the salt decomposed rapidly (5-10 min) to hydrogen cyanide and a black tarry solid with an infrared spectrum resembling that of high molecular weight HCN polymers prepared by alkaline catalysis.¹ When a slurry of Vc in *n*-pentane was irradiated, the reaction became slow, as in the case of Vb, and VI was obtained in high yield (75-80%).

Attempts to trap aminocyanocarbene have, so far, been unsuccessful. Photolytic decomposition of Vb and Vc in diglyme in the presence of carbene traps such as norbornene, 2,3-dimethyl-2-butene, triphenylphosphine, and benzene gave VI as the only isolable nitrogenous product.

2. Absorption Spectrum of Aminocyanocarbene. We recently have shown¹⁴ that irradiation of salts of

(11) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).

(12) W. G. Dauben and F. G. Willey, *J. Am. Chem. Soc.*, **84**, 1497 (1962).

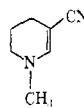
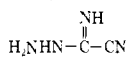
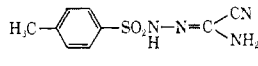
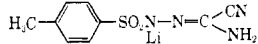
(13) G. M. Kaufman, J. A. Smith, G. S. Vander Stouw, and H. Schechter, *ibid.*, **87**, 935 (1965), and references cited therein.

(14) R. E. Moser, J. M. Fritsch, and C. N. Matthews, *Chem. Commun.*, 770 (1967).

p-toluenesulfonylhydrazones in a frozen glass at -196° generates corresponding methylenes. This technique, which has special application in studying methylenes formed from nonisolable diazo compounds, was extended to salt Vc. Photolysis of Vc in 2-methyltetrahydrofuran (MTHF) glass at -196° with filtered (Pyrex) or unfiltered radiation led to the appearance of a yellow color which survived for at least 24 hr at this temperature but rapidly disappeared when the sample was warmed sufficiently to permit diffusion through the matrix. Hydrogen cyanide and nitrogen were evolved when the matrix melted. The yellow color must therefore be due to a reactive species¹⁵ which readily eliminates hydrogen cyanide. The absorption spectrum (Figure 1) showed a broad band in the region 332-450 mμ with the principal maximum at 391 mμ, the *p*-toluenesulfonyl absorption tail being taken as base line.

It is likely that the reactive species is aminocyanocarbene formed by loss of sulfinate and nitrogen from Vc. Isomerization to I, possible in spite of matrix rigidity,¹⁶ is ruled out by the fact that conjugated nitriles including iminoacetonitriles absorb at wavelengths less than 300 mμ (Table I). Further, assignment of

Table I. Longest Wavelength Absorption Maxima of Conjugated Nitriles

Compound	λ_{max} , mμ	ϵ_{mol}
CH ₂ =CHCN	190 ^a	6,300 (neat)
	278 ^b	18,300 (ethanol)
	255 ^c	8,200 (acetonitrile)
	245 ^c	12,000 (ethanol)
	288 ^c	9,950 (water)

^a "The Chemistry of Acrylonitrile," 2nd ed, American Cyanamid Company, New York, N. Y., 1959, p 6. ^b K. Schenker and J. Druey, *Helv. Chim. Acta*, **42**, 1960 (1959). ^c Present work.

absorption bands at 332-450 mμ to aminocyanocarbene is consistent with the results reported for other carbeneoid compounds. Merer and Travis¹⁷ have described the absorption spectrum of cyanomethylene generated from diazoacetonitrile by vapor phase photolysis. Bands observed at 280-340 mμ were attributed to transitions within the triplet manifold. The same authors have shown¹⁸ that chlorocarbene and fluorocarbene, possessing singlet multiplicity in their ground states, exhibit $1_A''-1_A'$ transitions at 550-820 and 430-600 mμ, respectively. Diarylmethylenes, in general, absorb near 300 mμ and in the visible range.¹⁵

(15) A. M. Trozzolo and W. A. Gibbons, *J. Am. Chem. Soc.*, **89**, 239 (1967), and references cited therein.

(16) E. Wasserman and W. A. Yager, *J. Phys. Chem.*, **71**, 201 (1967).

(17) A. J. Merer and D. N. Travis, *Can. J. Phys.*, **43**, 1795 (1965); **44**, 353 (1966).

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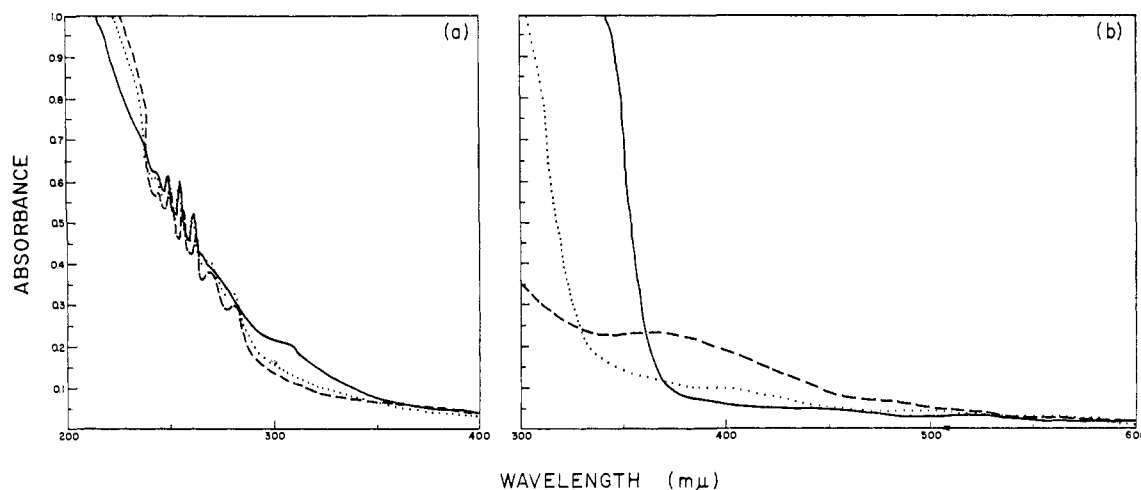


Figure 1. Photolysis of 1-cyanoformamide *p*-toluenesulfonylhydrazone lithium salt in 2-methyltetrahydrofuran at 77°K: a, 10^{-5} M, b, 10^{-3} M; pathlength 0.4 cm.; — before photolysis, ---- after photolysis (15 min), ···· after melting and refreezing.

Evidence from electronic spectra thus implicates aminocyanocarbene as the reactive intermediate formed by decomposition of Vc. Conclusive structural determination awaits further analysis of rotational and vibrational features of the spectrum.

3. Determination of the Ground Spin State of Aminocyanocarbene. Since epr measurements have been useful in determining the ground-state multiplicity of a number of methylenes,^{6-8,14} aminocyanocarbene was examined for long-lived triplet spin resonance absorptions. Solutions of Vc in MTHF (*ca.* 10^{-3} M), deaerated and sealed in quartz tubes, were frozen at -196° and photolyzed in the epr cavity¹⁴ for periods ranging from 5 min to 2 hr, using both unfiltered and filtered radiation (Pyrex and Jena UG-1 and WG-1 filters). Decomposition of Vc to aminocyanocarbene under these reaction conditions was indicated by the formation during irradiation of a yellow color which persisted as long as the matrix was held at -196° . Spectra recorded during and after photolysis showed no epr absorptions characteristic of triplet methylenes⁶⁻⁸ in the region 0–10 kgauss. A free spin absorption at 3295 gauss (frequency: 9243 Mc), which grew in intensity with irradiation time when no filters were employed, resulted from photodecomposition of the glass (MTHF).¹⁴ This signal was eliminated by carrying out photolyses with light of wavelength longer than 2300 Å. Epr studies thus show that aminocyanocarbene has singlet multiplicity in the ground state.

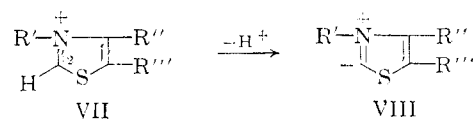
Discussion

We conclude that thermal or photolytic decomposition¹² of the salts of 1-cyanoformamide *p*-toluenesulfonylhydrazone (Va) produces aminocyanocarbene which possesses a singlet ground state (II). Further, the formation of typical products of HCN polymerization in these reactions suggests that HCN dimer has the same structure.

When II exists in low concentration, as in the melted MTHF matrix, unimolecular elimination of hydrogen cyanide can occur. In the presence of high concentrations of the precursor salts Vb or Vc, displacement reactions of II with the salts or with the diazo intermediate IV take place instead to give diaminomaleonitrile (VI). Bimolecular reactions of this type occur readily with

suspensions of the salts but apparently not with solutions in which photolytic destruction occurs too rapidly for VI to be formed. Failure of olefins to act as carbene traps reflects the weakly electrophilic character of II.

The stability of singlet aminocyanocarbene is analogous to that of the immonium ylids^{9,10,19} formed by deprotonation of N-substituted thiazolium salts (VII). Breslow¹⁹ has shown that the lability of the C-2 protons of these salts results largely from high s character of multiply bonded carbon, the inductive effect of the adjacent charged nitrogen, the resonance contribution



of carbene-like structures, and delocalization of the electron pair onto sulfur. Combined, these factors impart an unusual degree of stability to the resulting ylid VIII and account for the enzymatic activity of thiamine. The same factors favoring loss of a proton from a thiazolium salt would tend to favor rearrangement of iminoacetonitrile to aminocyanocarbene by proton migration. An even higher degree of stabilization of the resulting carbene might be assumed because of the greater electronegativity of the nitrile group relative to sulfur and the further opportunities for delocalization of paired electrons.

These conclusions and other experimental evidence³ support the hypothesis⁴ that aminocyanocarbene is a key intermediate in hydrogen cyanide polymerization and, therefore, in prebiological organic synthesis.

Experimental Section

Materials. *p*-Toluenesulfonylhydrazine (Aldrich Chemical Co.) was recrystallized from chloroform (mp 112°). Cyanogen (Matheson Co.), sodium hydride (Metal Hydrides, 53% in mineral oil), and lithium hydride (Alfa Inorganics) were used without further purification. 2-Methyltetrahydrofuran and diglyme were distilled under nitrogen from lithium aluminum hydride.

Apparatus. Preparative scale photodecompositions were carried out in a water-jacketed Pyrex vessel using an Hanovia 140-w, high-pressure Hg Utility Lamp. Irradiation of samples in an optical-

(19) R. Breslow, *J. Am. Chem. Soc.*, **80**, 3719 (1958).

transmission cavity on a Varian V-4502-15 epr spectrometer was by a General Electric AH-6 high-pressure Hg lamp, used with or without filters as indicated. Ultraviolet and visible spectra were recorded on Bausch and Lomb Model 505 or Cary Model 14 spectrometers, and infrared spectra on a Beckman Model IR-4 spectrometer. The 4-mm pathlength cell used in recording frozen glass spectra was cooled with liquid nitrogen in a small unsilvered quartz dewar flask. All *p*-toluenesulfonylhydrazone salt solutions were prepared in a nitrogen-filled drybox and deaerated and sealed *in vacuo*. Microanalyses were carried out by Galbraith Laboratories, Knoxville, Tenn.

1-Cyanoformamide *p*-Toluenesulfonylhydrazone (Va) and Salts Vb and Vc. A solution of *p*-toluenesulfonylhydrazine (27.0 g, 0.14 mole) in ethanol (1 l.) was added with stirring over a period of 2 hr to an ice-water-cooled solution of cyanogen (36.0 g, 0.70 mole) in ethanol (400 ml). The cold mixture was stirred for 15 min, diluted with water (20 ml), and allowed to warm to room temperature over a period of 12 hr. Unreacted cyanogen and solvent were removed rapidly *in vacuo* at 40°, and the yellow solid residue was recrystallized from aqueous methanol (175 ml, 4H₂O:3CH₃OH, v/v). Further purification was effected upon precipitation of the hydrazone from tetrahydrofuran by addition of petroleum ether which gave light yellow platelets (17.0 g, 0.07 mole), mp 204–205° dec.

Anal. Calcd for C₉H₁₀N₄O₂S: C, 45.2; H, 4.7; N, 23.5; S, 13.4; mol wt, 238.3. Found: C, 45.53; H, 4.44; N, 23.24; S, 13.33; mol wt, 249 (ethanol).

The infrared spectrum (KBr) showed N–H stretching bands at 3440, 3330, and 3200 cm⁻¹ and C≡N absorption at 2260 cm⁻¹. Other strong peaks occurred at 1660, 1325, and 1180 cm⁻¹. The nmr spectrum (CH₃CN, TMS internal standard) consisted of an A₂B₂ multiplet centered at τ 2.35 (four protons), a sharp spike at τ 7.53 (three protons), and a broad band centered at τ 4.20 (three protons). Ultraviolet absorption maxima occurred at 224 m μ (ϵ 12,600) and 245 m μ (ϵ 12,000) in ethanol.

Treatment of the hydrazone (10% sodium in tetrahydrofuran) with equivalent amounts of sodium hydride or lithium methoxide (1.77 *N* in methanol) gave the corresponding salts in quantitative yield. They were obtained as white solids (Vb, mp 215° dec, and Vc, mp 175° dec) by precipitation from tetrahydrofuran with ether. Their ultraviolet spectra showed two maxima at 222 m μ (ϵ 8530) and 288 m μ (ϵ 9950) in H₂O with the longer wavelength band extending to 360 m μ .

A reference compound, 1-cyanoformamide hydrazone, mp 83–85° (from ethyl acetate-carbon tetrachloride), was prepared by addition of 85% hydrazine hydrate (8.85 g, 0.15 mole) to cyanogen (10.0 g, 0.19 mole) in cold ethanol (150 ml).

Anal. Calcd for C₂H₄N₄: C, 28.6; H, 4.8; N, 66.7; mol wt,

84.08. Found: C, 28.61; H, 4.84; N, 66.59; mol wt, 86 (acetone).

Thermal Decomposition of *p*-Toluenesulfonylhydrazone Salts. A stirred suspension of the sodium salt Vb (0.60 g, 2.3 mmoles) in diglyme (40 ml) was heated to 140–150° under a dry nitrogen atmosphere. As the reaction proceeded to completion (ca. 2 hr), the theoretical amount of nitrogen was evolved and passed through a CaCl₂ tube into a gas buret. Sodium *p*-toluenesulfinate, λ_{\max} 259 and 263 m μ (0.1 *N* aqueous NaOH), was filtered off, and the yellow filtrate was concentrated to 3 ml *in vacuo* at room temperature. Addition of ether (20 ml) precipitated a black solid (0.008 g) which was filtered off. The filtrate was clarified with charcoal and evaporated to dryness *in vacuo*. The solid residue, recrystallized from benzene-2-propanol, gave yellow crystals of diaminomaleonitrile (VI), (0.096 g, 0.9 mmole), mp 182–184°. Infrared (KBr) spectra of the product and an authentic sample of diaminomaleonitrile (VI) were identical.

The infrared spectrum (KBr) of the black ether-insoluble residue was similar to that of polymer obtained by base-catalyzed polymerization of hydrogen cyanide, with principal absorption maxima at 3450, 2245, and 1650 cm⁻¹.

Pyrolytic decomposition of the lithium salt in diglyme under identical conditions gave diaminomaleonitrile (VI) in approximately half the yield obtained from the sodium salt.

Photolytic Decomposition of *p*-Toluenesulfonylhydrazone Salts. A stirred slurry of *p*-toluenesulfonylhydrazone sodium salt Vb (0.26 g, 1.0 mmole) in dry diglyme (20 ml) was irradiated under nitrogen in a water-cooled (ca. 10°), sealed Pyrex tube. As the reaction proceeded the initial slurry briefly dissolved and then was replaced with a suspension of sodium *p*-toluenesulfinate. Decomposition was completed within 2 hr as indicated by nitrogen release. In other runs the volume of nitrogen evolved was found to be the theoretical amount. The yellow reaction solution was worked up as in the thermal reactions and diaminomaleonitrile (VI) (0.015 g, 0.13 mmole), mp 182–184°, was collected.

In contrast to the sodium salt, the lithium salt Vc gave no diaminomaleonitrile (VI) when photolyzed in diglyme solution. Suspended in *n*-pentane, however, photolysis of the lithium salt followed by addition of tetrahydrofuran gave VI, the yield in this case being approximately equal to that obtained from the sodium salt in a comparable reaction.

Acknowledgments. We thank Dr. W. Landgraf and Mr. G. Bulow of Varian Associates, Palo Alto, Calif., and Dr. J. R. Miller, of Shell Oil Co., Wood River, Ill., for assistance in epr studies, and Professor M. J. S. Dewar for helpful comments.