

## Electron Spin Resonance Studies of Radical Formation in Nucleophilic Addition Reactions. II. Cyanide Ion Addition to Electrophilic Compounds. The N-Methyl-9-cyanoacridanyl Radical<sup>1</sup>

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The electron spin resonance spectrum of N-methyl-9-cyanoacridanyl radical has been obtained by the cyanide ion addition to N,N'-dimethyl-9,9'-biacridinium dinitrate (lucigenin) in dimethyl sulfoxide or -formamide. The same radical is produced upon the addition of cyanide ion to air-saturated solutions of N-methylacridinium salts or N-methyl-9-cyanoacridan. N-methyl-9-cyanoacridanyl radical is found to be unusually stable to oxygen. A carbanion air-oxidation mechanism is suggested for radical production. Radicals are also produced in the addition of cyanide to acridine, acridine N-oxide, 9-cyanoanthracene, N-methylpyridinium iodide, N,3,5-trimethylpyridinium iodide, and N-methyl-3-carbamoylpyridinium iodide. Structural assignments have been made from all the radicals produced except for the last-named compound by the aid of coupling constants derived from molecular orbital calculations.

In a previous report we have described the results of an electron spin resonance (esr) study of the addition of hydroxide ion to N,N'-dimethyl-9,9'-biacridinium dinitrate (lucigenin, abbreviated DBA<sup>2+</sup>) in the absence of air or oxidizing agent.<sup>2</sup> The initial addition of hydroxide to DBA<sup>2+</sup> is followed by ionization of the carbinol to the pinacolate. Dissociation of the pinacolate to N-methylacridone ketyl is postulated, although this radical has not been detected. Three types of esr spectra are obtained, depending on the concentration of base and time after mixing. Structures have been assigned to two of these spectra. The radicals are believed to be produced by N-methylacridone ketyl reduction of DBA<sup>2+</sup> and the hydroxide addition product of DBA<sup>2+</sup>. These reactions are accompanied by weak chemiluminescence, probably due to the one-electron oxidation of N-methylacridone ketyl.

In previous studies of chemiluminescence of DBA<sup>2+</sup> in biological systems, it has been shown that cyanide ion enhances the light emission under normal conditions of chemiluminescence.<sup>3</sup> Our results on the hydroxide ion addition to DBA<sup>2+</sup> suggested that similar addition and radical-formation reactions might be taking place with cyanide ion and DBA<sup>2+</sup>. An esr study of this reaction and of other cyanide additions to electrophilic aromatic compounds is reported here. Included are DBA<sup>2+</sup>, N-methylacridinium chloride, N-pyridinium iodide, N-methyl-3,5-dimethylpyridinium iodide, N-methyl-3-carbamoylpyridinium iodide (N-methylnicotinamide), acridine, acridine N-oxide, and 9-cyanoanthracene. In all cases, readily detectable esr signals can be obtained in the presence of air. From analyses of the esr spectra, assignments for the structures of the radicals are made. Details of the stoichiometry and kinetics of radical formation will be reported in future publications.

### Experimental Section

**Equipment.**—The equipment used for this study has been described.<sup>2</sup>

(1) This work was supported by the Atomic Energy Commission, Contract AT-(40-L)-2851.

(2) E. G. Janzen, J. B. Pickett, J. W. Happ, and W. DeAngelis, *J. Org. Chem.*, **35**, 88 (1970).

(3) J. R. Totter, *Photochem. Photobiol.*, **3**, 231 (1964).

**Chemicals.**—Acridine and 3,5-dimethylpyridine were obtained from Aldrich Chemical Co. Lucigenin was obtained from K & K Laboratories, Inc.; 9-cyanoanthronitrile and nicotinamide were obtained from Eastman Organic Chemicals. Other chemicals were commercially available and were of reagent grade.

1-Methylpyridinium iodide was prepared from pyridine and methyl iodide, mp 116–117° (lit. mp 117°).<sup>4</sup> The reaction of 3,5-dimethylpyridine with methyl iodide gave 1,3,5-trimethylpyridinium iodide, mp 270–271° (lit. mp 270°).<sup>5</sup> 1-Methyl-3-carbamoylpyridinium iodide was prepared from nicotinamide and methyl iodide, mp 205–206° (lit. mp 206.5–207.0°).<sup>6</sup>

10-Methylacridinium chloride was synthesized by treating acridine with dimethyl sulfate followed by ion exchange with NaCl to form the chloride salt according to the method of Albert,<sup>7</sup> mp 182–183° dec (lit. mp 183° dec). 9-Cyano-10-methylacridinium chloride was prepared from 9-cyanoacridine and dimethyl sulfate followed by ion exchange with NaCl. Recrystallization from absolute ethanol gave orange crystals, mp 195–196°<sup>8</sup> dec. 9-Cyanoacridine was synthesized from acridine and KCN by the method of Lehmstedt and Dostal, mp 179–180° (lit. mp 181°).<sup>9</sup> 9,10-Dihydro-9-cyano-10-methylacridan was prepared from the reaction of 10-methylacridinium chloride with KCN according to the procedure of Kaufmann and Albertini, mp 142–143° (lit. mp 143°).<sup>10</sup>

Acridine N-oxide was prepared from acridine and *p*-nitroperbenzoic acid in chloroform, mp 168–169° (lit. mp 169°).<sup>11</sup>

### Results and Discussion

**9-Cyanoacridanyl Radical.**—The addition of potassium cyanide to DBA<sup>2+</sup> in nitrogen-purged solutions of DBA<sup>2+</sup> in dimethyl sulfoxide (DMSO) or dimethylformamide (DMF) results in a change in color from amber to cherry red. A weak esr signal is detected, which can be resolved into the same spectrum as shown in Figure 1. The coupling constants extracted from the spectrum are listed in Table I. The radical is thought to be N-methyl-9-cyanoacridanyl radical (II), produced by the following reaction (eq 1). The structural assignment has been confirmed by electrolytic reduction of N-methyl-9-cyanoacridinium chloride. The same spectrum as shown in Figure 1 is obtained.

(4) E. M. Kosower, *J. Amer. Chem. Soc.*, **77**, 3883 (1955).

(5) J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 859 (1961).

(6) R. N. Lindquist and E. H. Cordes, *J. Amer. Chem. Soc.*, **90**, 1269 (1968).

(7) A. Albert, "The Acridines," St. Martin's Press, New York, N. Y., 1966, pp 343, 344.

(8) F. Kehrman and M. Sandoz, *Ber.*, **51**, 388 (1918); F. McCapra, D. G. Richardson, and Y. C. Chang, *Photochem. Photobiol.*, **4**, 1111 (1965).

(9) K. Lehmstedt and F. Dostal, *Chem. Ber.*, **72**, 804 (1939).

(10) C. Kaufmann and A. Albertini, *Ber.*, **42**, 1999 (1909).

(11) M. Ionescu, I. Goia, and H. Mantsch, *Rev. Roum. Chim.*, **11**, 243 (1966); G. Anthoine, J. Nasielski, E. Vander Donckt, and N. Vanlautre. *Bull. Soc. Chim. Belg.*, **76**, 230 (1967).

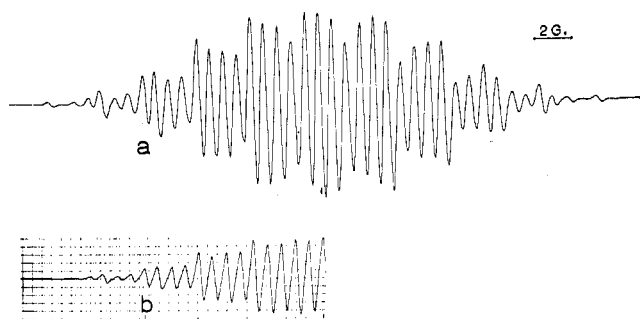
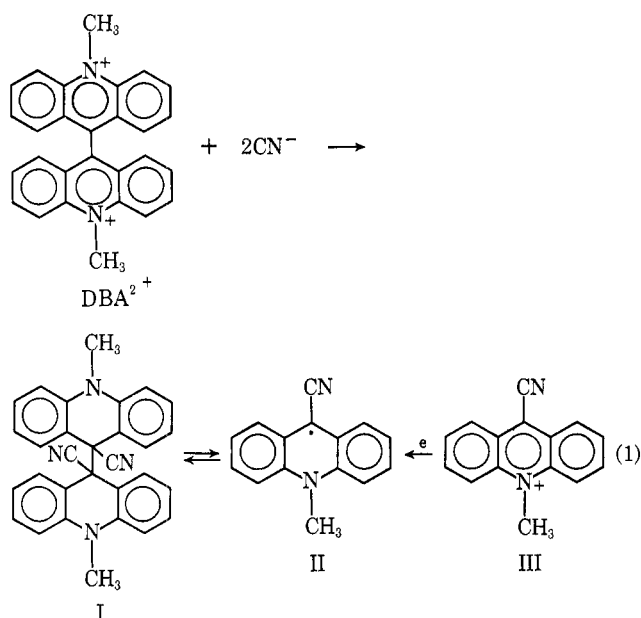


Figure 1.—(a) ESR spectrum of N-methyl-9-cyanoacridanyl radical produced from 0.008 M N-methyl-9-cyanoacridan in DMSO saturated with potassium cyanide and air; (b) computer-simulated spectrum using the coupling constants listed in Table I.



Although radical II has not been reported before, a number of stable radicals of similar structure are known. Certain 9-substituted xanthyl radicals are stable at room temperature (9-phenyl,<sup>12a</sup> 9-isopropyl,<sup>12b</sup> and 9-*sec*-butyl,<sup>12b</sup>) although temperatures of above 78 and 86° are required for the detection of 9-methyl- and 9-ethylxanthyl radicals.<sup>12b</sup> Diphenylmethoxymethyl<sup>13</sup> and diphenylcyanomethyl<sup>14</sup> radicals have also been detected at 139 and 185°, respectively. The coupling constants of these radicals are shown in Table I for comparison. The assignment of coupling constants has been made on the basis of molecular orbital calculations (see following paragraph), by analogy to the xanthyl radicals, and by deuterium substitution in the methyl group.

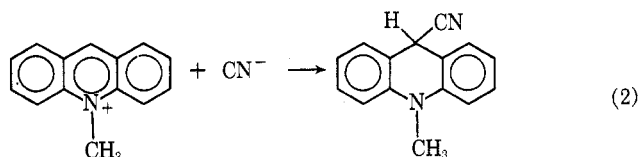
N-Methyl-9-cyanoacridanyl radical is also obtained in the addition of cyanide ion to N-methylacridinium chloride in DMF, DMSO, or DMSO-water mixtures. The highest concentration of radical is obtained in initially air-saturated solutions containing excess cyanide. Under these conditions the solution turns from yellow to cherry red.

(12) (a) M. D. Sevilla and G. Vincow, *J. Phys. Chem.*, **72**, 3641 (1968); (b) *ibid.*, **72**, 3647 (1968).

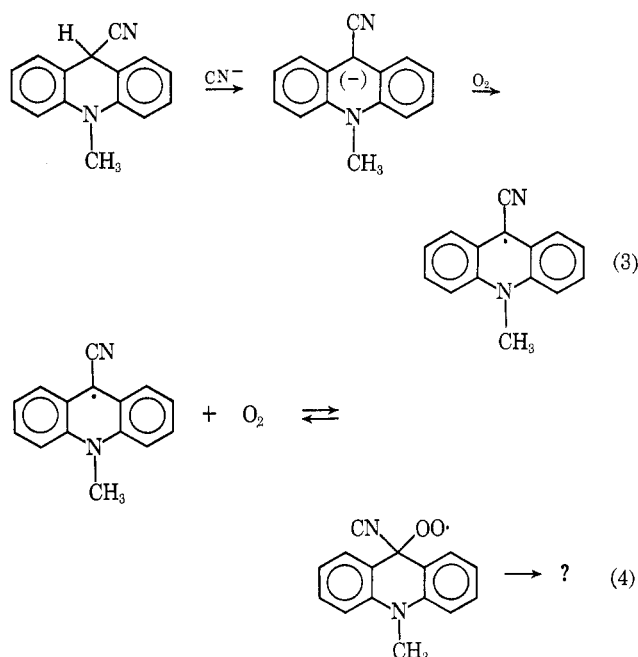
(13) G. E. Hartzell, C. J. Bredeweg, and B. Loy, *J. Org. Chem.*, **30**, 3119 (1965).

(14) By the thermal dissociation of tetraphenylsuccinonitrile in nitrobenzene: O. W. Maender, unpublished results.

Similar results are obtained from reactions with N-methyl-9-cyanoacridan, which can readily be isolated from the addition of 1 mol of cyanide to N-methylacridinium chloride.<sup>7,10,15</sup> This compound exhibits a readily detectable ESR signal in the crystalline solid



state. The signal is apparently stable for long periods of time and is not sensitive to air or oxygen. In solution N-methyl-9-cyanoacridan gives a weak signal due to N-methyl-9-cyanoacridanyl radical. Upon addition of cyanide ion a cherry red solution develops and the signal increases in intensity. Introduction of air or oxygen first leads to a large increase in signal intensity and finally to a slow decay in the signal. The absorption of significant amounts of oxygen begins after *ca.* 1 mol of cyanide ion has been added to N-methylacridinium chloride. The rate of oxygen absorption is fairly rapid in the presence of excess cyanide. The oxygen absorption of N-methyl-9-cyanoacridan is very slow under the same conditions. These observations suggest a carbanion oxidation mechanism with the 9-cyanoacridanyl radical as a "stable" radical intermediate (eq 3 and 4). In the presence of other bases



(*e.g.*, *t*-BuOK), the same red color develops. Cyanide ion in DMSO solution also produces the characteristic colors of the carbanion of diphenylacetonitrile (red) and 9-phenylfluorene (pale yellow). Of interest is the unusual stability of the N-methyl-9-cyanoacridanyl radical to oxygen. Clearly, the equilibrium between the radical and oxygen and the peroxy radical favors the acridanyl radical. In the triphenylmethyl radical system the same equilibrium favors triphenylmethyl at

(15) R. M. Acheson, "Acridines," Interscience Publishers, New York, N. Y., 1956, pp 234-262.

TABLE I  
HYPERFINE COUPLING CONSTANTS OF FREE RADICALS PRODUCED IN CYANIDE ADDITIONS

| Free radical | Registry no. | $A_1^H$   | $A_2^H$                | $A_3^H$              | $A_4^H$                | $A_5^N$              | $A_{10}^N$           | $A_{CH_3}^H$         |
|--------------|--------------|---|------------------------|----------------------|------------------------|----------------------|----------------------|----------------------|
|              | 22027-31-2   | 2.79 <sup>a</sup><br>2.69 <sup>b</sup><br>2.83 <sup>c</sup> | <0.25<br><0.23<br>0.15 | 2.16<br>2.23<br>1.9  | <0.25<br><0.23<br>0.56 | 1.38<br>1.33<br>1.59 | 3.55<br>3.56<br>3.31 | 2.74<br>0.42<br>3.12 |
|              | 21482-68-8   | 3.31 <sup>a</sup>   | 0.86                   | 3.81                 | 0.74                   |                      |                      |                      |
|              | 22027-38-9   | 1.98 <sup>a</sup>   | 1.12                   | 2.55                 |                        | 1.42                 |                      |                      |
|              | 3710-06-3    | 3.37 <sup>a</sup>   | 1.23                   | 3.37                 |                        |                      |                      |                      |
|              | 22040-09-1   | 3.00 <sup>a</sup><br>2.11 <sup>c</sup>                      | 1.00<br>0.51           | 1.13<br>1.05         | 1.47<br>1.53           | 0.76<br>1.17         | 5.80<br>6.29         |                      |
|              | 22027-32-3   | 4.46 <sup>a</sup><br>4.14 <sup>c</sup>                      | <0.28<br>0.17          | 1.68<br>2.66         | 1.18<br>1.78           | 1.04<br>0.86         | 2.79<br>3.37         |                      |
|              | 22027-33-4   | 2.20 <sup>a</sup><br>2.21 <sup>c</sup>                      | <0.40<br>0.80          | <0.40<br>0.80        | 2.20<br>2.21           | 1.16<br>1.31         |                      |                      |
|              | 22027-34-5   | 0.52 <sup>a</sup><br>0.38 <sup>c</sup>                      | 3.63<br>3.88           |                      |                        | 2.13<br>2.21         | 6.51<br>6.14         | 5.68<br>5.79         |
|              | 22087-72-5   | 3.97 <sup>a</sup><br>3.91 <sup>d</sup><br>4.14 <sup>c</sup> | 0.66<br>0.60<br>1.26   | 3.31<br>3.30<br>3.28 | 0.66<br>0.60<br>0.41   |                      | 0.66<br>0.60<br>0.73 | 0.66<br><0.3<br>0.69 |

<sup>a</sup> Hyperfine coupling constants in this row extracted from spectra obtained. <sup>b</sup> Same as footnote *a* for deuterated methyl derivative. <sup>c</sup> Coupling constants in this row predicted from molecular orbital calculations; see text. <sup>d</sup> Same as footnote *a* for ethyl derivative.

100°. <sup>16</sup> Details on the oxidation of these systems will be published later.

In addition to cyanide ion, other nucleophiles were tested for radical formation in the presence of *N*-methylacridinium chloride in DMSO, DMF, or 90:10 DMSO-water mixtures. A partially degassed DMSO solution saturated with potassium *t*-butoxide added to *N*-methylacridinium chloride gave a ten-line spectrum, shown in Figure 2. The solution was emerald green in color. The spectrum is assigned to the 9-*t*-butoxy-*N*-methylacridanyl radical produced by reactions similar to eq 2 and 3. In this spectrum,  $A_1^H = A_3^H = A_{CH_3}^H = 2.9$ ,  $A_N = 2.9$ , and  $A_2^H = A_4^H = <1.5$  G.

(16) E. G. Janzen, F. J. Johnston, and C. L. Ayers, *J. Amer. Chem. Soc.*, **89**, 1176 (1967); C. L. Ayers, E. G. Janzen, and F. J. Johnston, *ibid.*, **88**, 2610 (1966).

The addition of sodium, potassium, and benzyltrimethylammonium hydroxide (*i.e.*, in the latter case Triton B in aqueous methanol) did not produce sufficient quantities of free radicals to be detectable by esr.

The reaction of *N*-methyl- and *N*-ethylacridinium iodide with sodium sulfide in DMF or DMSO solutions containing oxygen produces a dark red-brown solution which gives a strong esr signal. No signal is observed in the absence of oxygen. An overmodulated spectrum gives five broad lines separated by 3.8 G. Similar spectra have been observed for the ketyls of *N*-methylacridone,<sup>2</sup> xanthen-9-one,<sup>17a</sup> thioxanthen-9-one,<sup>17b</sup> xanthene-9-thione,<sup>17c</sup> and thioxanthene-9-thione.<sup>17a</sup>

(17) (a) E. G. Janzen and C. M. DuBose, Jr., *J. Phys. Chem.*, **70**, 3372 (1966); (b) E. T. Kaiser and D. H. Eargle, Jr., *J. Amer. Chem. Soc.*, **85**, 1821 (1963); (c) H. C. Heller, *ibid.*, **89**, 4288 (1967).

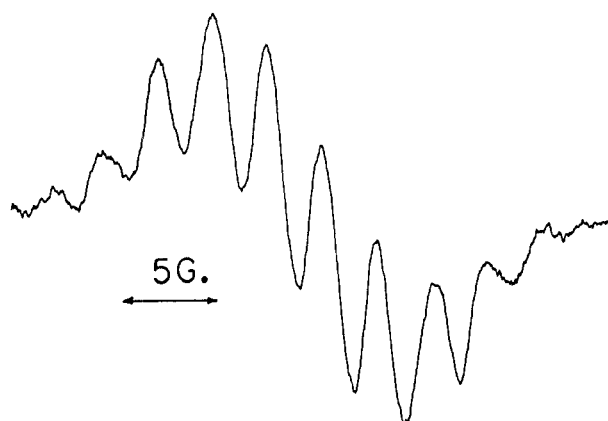
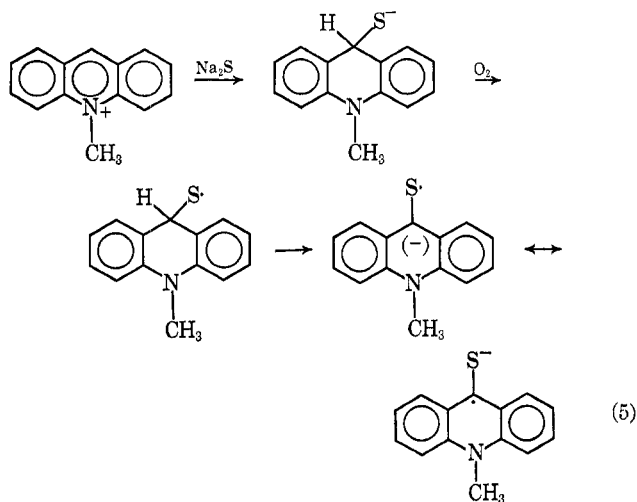


Figure 2.—Spectrum assigned to N-methyl-9-*t*-butoxyacridanyl radical obtained from 0.01 *M* N-methylacridinium iodide in partially degassed DMSO saturated with potassium *t*-butoxide.

These radical anions have  $g$  values of 2.00332, 2.00355, 2.0348, 2.00571, and 2.00577, respectively. The thio-ketyls have significantly higher  $g$  values than the oxy-ketyls. A  $g$  value of 2.00512 was observed for the radical obtained in the above reaction. A well-resolved spectrum is shown in Figure 3. The coupling constants extracted from the spectrum for the N-methyl and ethyl derivatives are given in Table I. The computer-simulated spectrum using these values is shown in Figure 3. On the basis of the probable chemistry involved, the relatively high  $g$  value, and the good fit realized with spin densities obtained from molecular orbital calculations (Table I), we conclude that the radical produced in the sodium sulfide addition to N-alkylacridinium iodides in DMF or DMSO is the N-alkyl-9-thioacridone ketyl. The following route for its formation is visualized (eq 5). In support of this



mechanism is the known nucleophilic additions of sodium sulfide<sup>18a</sup> or sodium thiophenoxylate<sup>18a</sup> to N-methyl-9-phenylacridinium chloride to produce the corresponding 9-mercapto- or 9-thiophenoxy-N-methyl-9-phenylacridan. The oxygen oxidation of thiolate anions produces disulfides presumably *via* thiyl radical intermediates.<sup>18b</sup>

(18) (a) A. Hantzsch and A. Horn, *Chem. Ber.*, **35**, 877 (1902); J. F. Bunnett, C. F. Hauser, and K. V. Nahabedian, *Proc. Chem. Soc.*, 305 (1961); (b) T. J. Wallace, H. Pobiner, and A. Schriesheim, *J. Org. Chem.*, **29**, 888 (1964).

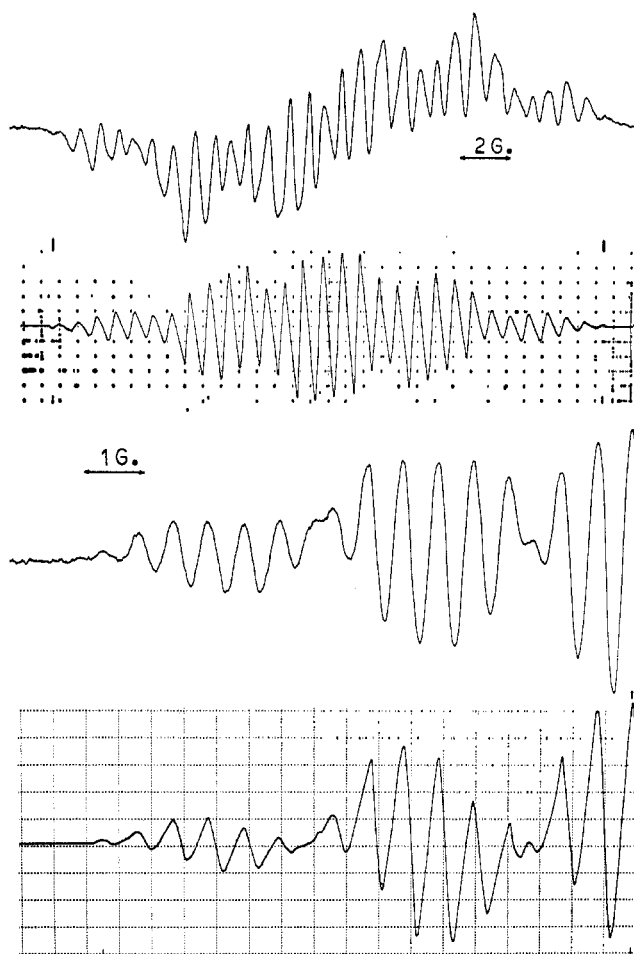
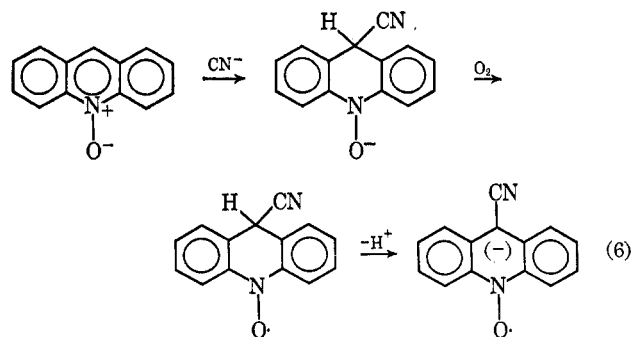


Figure 3.—(a) Recorded and simulated spectrum of N-methyl-9-thioacridone ketyl produced from 0.01 *M* N-methylacridinium iodide in DMSO saturated with  $\text{Na}_2\text{S}$  and air; (b) high-field half of the resolved and simulated spectrum of N-ethyl-9-thioacridone ketyl produced as described in a.

Sodium phenoxide, aniline, sodium bisulfite, sodium nitrite, and potassium thiocyanate under similar conditions did not produce sufficient quantities of free radicals to be detectable by esr.

**Other Cyanide Additions.**—The addition of cyanide ion to acridine N-oxide in air-saturated DMF gives the spectrum shown in Figure 4. By analogy to the cyanide addition to N-methylacridinium chloride, the radical is either the neutral nitroxide radical or the nitroxide radical anion (eq 6). The



coupling constants extracted from the spectrum are given in Table I. A good analogy for the neutral nitroxide is diphenyl nitroxide. The coupling constants for this radical are  $A_N = 10.35$ ,  $A^H_{\text{ortho,para}} =$

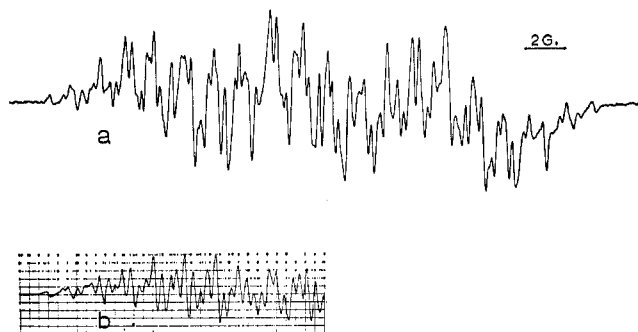
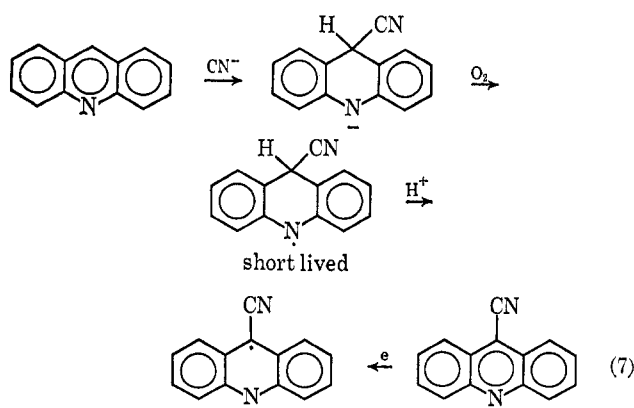


Figure 4.—(a) Spectrum of 9-cyanoacridine nitroxide anion obtained from 0.005 *M* acridine N-oxide in partially degassed DMF saturated with KCN; (b) simulated spectrum using values given in Table I.

1.97, and  $A_{meta}^H = 0.84$  G.<sup>19a</sup> The spectrum in Figure 4 should have larger nitrogen and aromatic hydrogen coupling constants if it were due to the neutral nitroxide. Moreover, the spectrum does not show a large coupling due to one hydrogen, but instead a small (nitrogen) triplet coupling is detected. On this basis the spectrum is assigned to the 9-cyanoacridine nitroxide radical anion. Similar pyridine nitroxide radical anions have been shown to be fairly stable to oxygen,<sup>19b</sup> e.g., 4-cyano, 4-carbomethoxy, 4-nitro, 4-acetyl, 4-aldehyde, and 4-benzoylpyridine N-oxide radical anions. The latter three can be produced by the basic oxygen oxidation of 4-ethyl, 4-methyl, or 4-carbinol and 4-benzoylpyridine N-oxide, respectively.

The addition of cyanide ion to acridine in air-saturated DMF or DMSO gives the spectrum shown in Figure 5. This spectrum is thought to be due to 9-cyanoacridine radical anion. Verification of this assignment has been obtained by electrolytic reduction of 9-cyanoacridine at  $-1.2$  V vs. standard calomel electrode. The same spectrum as in Figure 5 is observed. The hyperfine coupling constants are shown in Table I. The radical is believed to be produced by the following reactions (eq 7).



The addition of cyanide ion to an air-saturated solution of 9-cyanoanthracene in DMF produces the esr spectrum shown in Figure 6.

By analogy to previous reactions and on the basis of symmetry, the radical is thought to be 9,10-dicyanoanthracene radical anion. The electrolytic reduction of 9-cyanoanthracene in DMF at  $-0.9$  V vs. standard

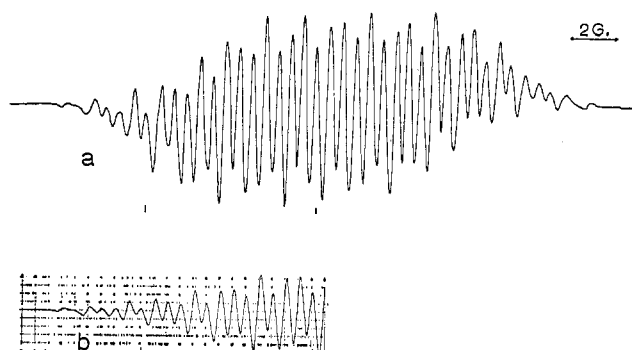


Figure 5.—(a) Spectrum of 9-cyanoacridine anion radical obtained from 0.005 *M* acridine in DMF saturated with KCN and air; (b) simulated spectrum using values given in Table I.

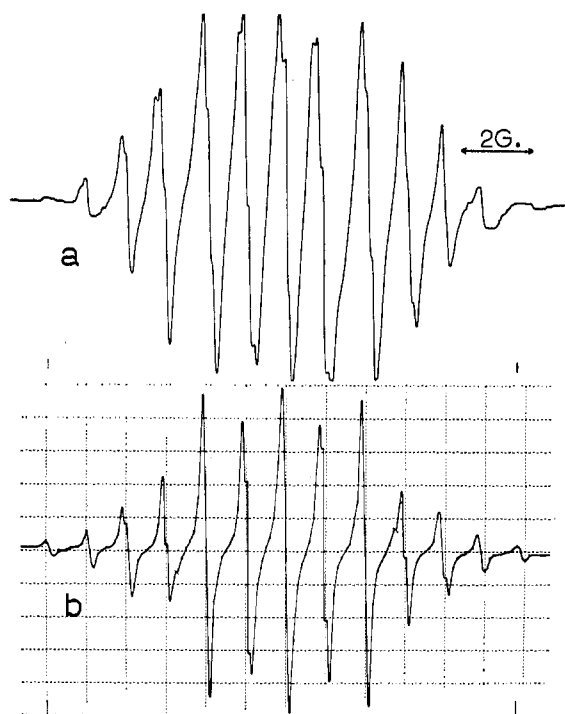
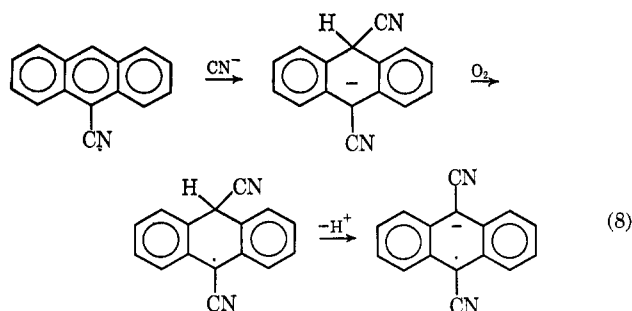


Figure 6.—(a) Spectrum of 9,10-dicyanoanthracene anion radical produced from 0.01 *M* 9-cyanoanthracene in DMF saturated with KCN and air; (b) simulated spectrum using values given in Table I.

saturated calomel electrode gives a spectrum due to 9-cyanoanthracene radical anion, which is clearly different from the spectrum in Figure 6. The formation of 9,10-dicyanoanthracene radical anion is thought to proceed as follows (eq 8).

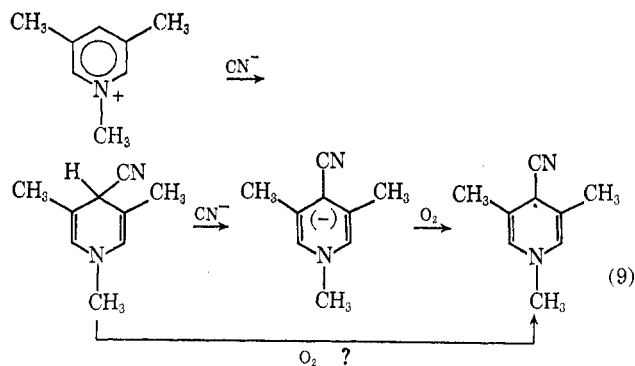


(19) (a) P. B. Ayscough and F. P. Sargent, *J. Chem. Soc., B*, 907 (1966); (b) E. G. Janzen and J. W. Happ, *J. Phys. Chem.*, **73**, 3335 (1969); see also T. Kubota, K. Nishikida, H. Miyazaki, K. Iwatani, and Y. Oishi, *J. Amer. Chem. Soc.*, **90**, 5080 (1968).

Esr spectra have also been obtained from cyanide addition to other electrophilic aromatic compounds, e.g., 9-nitroanthracene, but these spectra are not well

understood at this time and will be reported on in the future. The reaction of cyanide ion with N-methylpyridinium iodide in partly nitrogen-purged DMF or DMSO produces a blue-green solution accompanied by a strong esr signal. The analysis of the spectrum gives coupling constants which are in good agreement with the previously reported methyl viologen radical:<sup>20a</sup>  $A_N = 4.18$ ,  $A^H_{CH_3} = 3.96$ , and  $A^H_{CH} = 1.50$  and  $1.24$  G. It has previously been found that 4-cyanopyridyl radicals dimerize to produce methyl viologen radical<sup>20b</sup> in polar solvents. In dimethoxyethane the monomer appears to be more stable and detectable by esr for 2-3 days.<sup>21</sup> Our results are thus consistent with an air oxidation of the cyanide addition product of N-methylpyridinium salt in excess cyanide to 4-cyanopyridyl radical.

The 4-cyano-3,5-dimethylpyridyl radical is expected to be more stable to dimerization. The addition of potassium cyanide to 3,5-N-trimethylpyridinium iodide in partly nitrogen-purged DMF produces the spectrum shown in Figure 7. The detection of this radical has previously been reported,<sup>21</sup> but the spectrum and coupling constants have not been published. In Table I the coupling constants obtained for 4-cyanopyridyl<sup>21</sup> are given along with the values extracted from the spectrum in Figure 7. The reaction producing radicals is believed to be as in eq 9. Our data does not permit a choice of oxidation mechanism at this time.



A weak esr signal is obtained from the addition of potassium cyanide to N-methyl-3-carbamoylpyridinium iodide in partly nitrogen-purged solutions of DMF or DMSO. The spectrum contains 17 peaks with a 1.25-G spacing. Insufficient resolution prevents further analysis of the spectrum.

**Chemiluminescence.**—Chemiluminescence is observed in the air oxidation of N-methyl-9-cyanoacridan in the presence of cyanide ion, as well as in the cyanide addition to DBA<sup>2+</sup>, N-methylacridinium chloride, and 9-cyanoanthracene. No light emission was seen in the cyanide addition to acridine or acridine N-oxide. Further details will be published later.

**Molecular Orbital Calculations.**—McLachlan<sup>22</sup> molecular orbital calculations were used to estimate  $\pi$ -electron spin densities. The relations  $\alpha_X = \alpha + \delta_X\beta$  and  $\beta_{CX} = \gamma_{CX}\beta$  define the heteroatom coulomb and

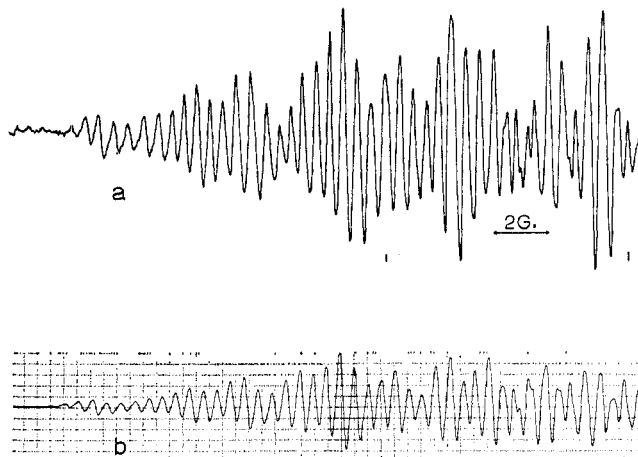


Figure 7.—(a) Spectrum of 4-cyano-3,5-N-trimethylpyridyl radical produced from 0.008 M N,3,5-trimethylpyridinium iodide in DMF saturated with KCN and air; (b) simulated spectrum using values given in Table I.

resonance integral parameters,  $\delta$  and  $\gamma$ , as functions of the coulomb and resonance integrals,  $\alpha$  and  $\beta$ , for C-C bonds in benzene.

Previous studies on nitrile anion radicals have established acceptable values for cyano parameters. The values  $\delta_N = 1.0$ ,  $\gamma_{CN} = 2.0$ , and  $\gamma_{CC'} = 0.9$  for benzonitrile radical anions<sup>23</sup> are very similar to the values  $\delta_N = 1.1$  and  $\gamma_{CN} = 2.0$  used for cyanopyridinyl anion radicals.<sup>24,25</sup> These latter parameters gave satisfactory results with the neutral and anion nitrile radicals listed in Table I.

The heterocyclic nitrogen parameters  $\delta_N = 1.2$  and  $\gamma_{CN} = 1.0$  have been used successfully for a number of cation radicals.<sup>26-28</sup> For substituted pyridine N-oxide radical anions,  $\delta_N = 1.5$ ,  $\delta_O = 1.60$ , and  $\gamma_{NO} = 1.5$  have been used.<sup>19</sup> Changing  $\delta_N$  to 1.8 improved the calculations for 9-cyanoacridine nitroxide. Good agreement between molecular orbital calculations and experimental results has been obtained for diazine anion radicals<sup>29</sup> with  $\delta_N = 0.75$  and  $\gamma_{CN} = 1.0$ . Better results were obtained for 9-cyanoacridine anion radical when  $\delta_N$  was changed to 1.1. In order to find a set of parameters that would correctly predict the heterocyclic nitrogen coupling in the neutral radicals, the nitrogen parameters were varied ( $0.5 \leq \delta_N \leq 1.5$  and  $\gamma_{CN} = 1.0$ ) while the cyano parameters were kept constant. Good agreement was obtained with  $\delta_N = 1.1$  and  $\gamma_{CN} = 1.0$ .

The coupling constants for the thiobenzophenone ketyl<sup>17c</sup> have been satisfactorily predicted using the thioketyl heteroatom parameters,  $\delta_S = 2.0$  and  $\gamma_{CS} = 1.0$ . Very good agreement was obtained for N-methyl-9-thioacridone ketyl when  $\delta_S = 2.0$  and  $\gamma_{CS} = 1.0$  and  $\delta_N = 1.5$  and  $\gamma_{CN} = 0.8$  were used.

The McConnell equation<sup>30-32</sup> relates proton hyper-

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fine coupling constants to calculated spin densities on contiguous carbon atoms. Values of  $Q = 24^{23,33,34}$  have

$$a_H = Q_{CH\rho C}$$

been used for aromatic nitriles and a value of 27 has been used in nitrogen heterocyclic nitriles. A value of  $Q = 27^{19,24}$  was found to predict hydrogen coupling constants best in this study.

The following equations relate the cyano nitrogen coupling to the spin densities on nitrogen and carbon.

$$a_N(C\equiv N) = (16.1 \pm 0.7) \rho_N + (9.0 \pm 4.7) \rho_C \text{ (Jones)}^{24}$$

$$a_N(C\equiv N) = \pm(23.1 \pm 1.4) \rho_N \mp (6.8 \pm 2.2) \rho_C$$

(Rieger and Fraenkel)<sup>23</sup>

The nitrogen couplings calculated from the former equation agree better with the observed values and are well within the established error limits of the equation.

The magnitude of the heterocyclic nitrogen coupling is presumed to depend on the spin densities on the nitrogen and on its neighboring carbon atoms.  $Q^{C_{CN}}$

$$a_N = Q^{N_N} \rho_N + Q^{C_{CN}} \rho_C$$

is small and frequently negligible. Values for  $Q^{N_N}$  and  $Q^{C_{CN}}$  in nitrogen heterocyclic anion radicals are  $30.9 \pm 2$  and  $-2 \pm 2$ , respectively.<sup>35,36</sup> For N-methylphenothiazyl cation radical the value for  $Q^{N_N}$  is 28.8 and  $Q^{C_{CN}}$  is neglected.<sup>28</sup> The latter values give a better fit to the observed heterocyclic nitrogen coupling constants for the neutral and anion radicals described in this work (Table I). For 9-cyanoacridine nitroxide,  $a_N = 35.61\rho_N - 0.93\rho_C$  was used.<sup>19</sup>

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An equation similar to the McConnell expression has been employed for methyl proton coupling constants<sup>23,33</sup>

$$a^{H_{CCH_3}} = Q^{H_{CCH_3}\rho C}$$

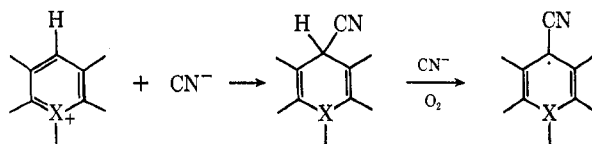
where  $Q^{H_{CCH_3}} = 27.2$ . The N-methyl proton coupling has been related to the spin density on nitrogen in N-methylphenothiazyl cation radical by a similar relationship<sup>28</sup>

$$a^{H_{NCH_3}} = Q^{H_{NCH_3}\rho N}$$

with  $Q^{H_{NCH_3}} = 27.2$  giving satisfactory results. A value of  $Q^{H_{NCH_3}} = 27.2$  gave good results for the neutral radicals in Table I.

### Conclusion

The formation of radicals or radical anions in the cyanide ion addition to compounds with electrophilic sites in air-saturated dipolar solvents appears to be a general reaction. Whether the radical produced is



neutral or charged depends on the charge of the substrate; positively charged compounds produce neutral radicals and neutral compounds produce radical anions. The radical-producing reaction is probably facilitated by the acidifying effect of the cyanide group on the  $\alpha$  proton.

**Registry No.**—N-Ethyl-9-thioacridone ketyl, 22027-35-6; N-methyl-9-*t*-butoxyacridanyl radical, 22027-36-7.

## Alkylations of Benzene and *p*-Xylene with 1-Chloro-2-methylpropane, 1-Chloro-2-methylbutane, and 2-Chloro-3-methylbutane. Effects of Steric Hindrance and Catalyst Activity on Product Distribution<sup>1a</sup>

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Alkylation of *p*-xylene with isobutyl chloride (1-chloro-2-methylpropane) and aluminum chloride gave isobutyl- and *sec*-butyl-*p*-xylene in low yields; larger amounts of *t*-butyltoluene derivatives were formed. Alkylation of benzene with 1-chloro-2-methylbutane and 2-chloro-3-methylbutane, using aluminum chloride at 25°, gave 2-methyl-3-phenylbutane and *t*-pentylbenzene in the ratio 82:18. In reactions at 0°, the initial major product from both pentyl chlorides was *t*-pentylbenzene; the proportion of 2-methyl-3-phenylbutane increased with time until an 82:18 ratio was reached. Using nitromethane-modified aluminum chloride catalyst, the only monoalkylation product from either pentyl chloride was *t*-pentylbenzene. Alkylation of *p*-xylene with 1-chloro-2-methylbutane and aluminum chloride gave 2-methyl-3-*p*-xylylbutane as the only pentylylene; 2-methyl-3-tolylbutane and *t*-pentyltoluene were also produced, in a ratio of 88:12. The data show that alkylations of benzene by the primary and secondary pentyl chlorides of the present study produce *t*-pentylbenzene initially, followed by isomerization to 2-methyl-3-phenylbutane when unmodified aluminum chloride catalyst is used. Mechanisms for the reactions are discussed—in particular, alternative possibilities for the production of 2-methyl-3-phenylbutane.

The alkylation of benzene with either *t*-butyl or isobutyl chloride and aluminum chloride catalyst gives only *t*-butylbenzene.<sup>2</sup> Alkylation of *o*-xylene with

(1) (a) Paper XXII in the series "New Friedel-Crafts Chemistry." Presented in part at the Tetrasectional American Chemical Society Meeting, Bartlesville, Okla., March 15, 1969; (b) Robert A. Welch Predoctoral Fellow, 1963–1966, NASA Trainee, 1966–1967.

(2) R. M. Roberts and D. Shienhthong, *J. Amer. Chem. Soc.*, **82**, 732 (1960).

*t*-butyl alcohol and boron trifluoride gives 1,2-dimethyl-4-*t*-butylbenzene.<sup>3</sup>

Similar alkylations of *p*-xylene, where substitution *ortho* to a methyl group must occur, are, however, quite different. Considerable steric hindrance must be overcome to accomplish introduction of a tertiary group

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