The Reaction of 9-Nitroanthracene with Sodium Cyanide in Dimethylformamide

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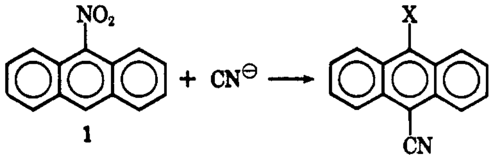
The interaction of 9-nitroanthracene with sodium cyanide in DMF at room temperature gives a solution which exhibits an electron paramagnetic resonance signal and from which a series of products, including 9-cyano-10-nitroanthracene, 9-amino-10-cyanoanthracene, 9,10-dicyanoanthracene, 9-cyano-10-anthranol, and 9-cyano-10-anthrone can be isolated. Product distributions under a variety of reaction conditions have been studied. Product formation is discussed in terms of oxidation–reduction of a Meisenheimer adduct and nucleophilic substitution.

The reaction of cyanide ion with certain hydrocarbons in aprotic polar solvents has been shown to proceed readily at room temperature.[2] Hydrocarbons studied shared one significant structural feature, a polarized double bond conjugated with an extended π system. Addition of the cyanide ion resulted in an extensively delocalized carbanion which could be oxidized to the corresponding unsaturated nitrile or protonated to the hydrocyanation product.

Nucleophilic attack of cyanide ion on aromatic nitro compounds has been documented principally in connection with the von Richter reaction.[3] In heated solutions of protic solvents, the nitro group is lost and the incoming cyanide function is ultimately hydrolyzed. The mechanism of the von Richter reaction has been the subject of much study.[4]

We wish to report the facile interaction of sodium cyanide with aromatic nitro compounds in aprotic polar solvents. With simple aromatic nitro compounds, including nitrobenzene, α-nitronaphthalene, and 9-nitroanthracene, a dark green, blue, or brown coloration develops with intensity and rapidity that vary with temperature, aromatic substrate, and solvent. At ambient temperature, coloration develops most rapidly in dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and hexamethylphosphoramide.



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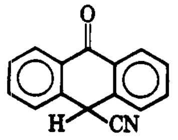
2a, X = NO_2
b, X = NH_2
c, X = CN
d, X = OH



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Treatment of 9-nitroanthracene (**1**) with sodium cyanide in DMF under nitrogen at room temperature resulted in the formation of a series of compounds: 9-cyano-10-nitroanthracene (**2a**), 9-amino-10-cyanoanthracene (**2b**), 9,10-dicyanoanthracene (**2c**), 9-cyano-10-anthranol (**2d**), and 9-cyano-10-anthrone (**3**). When the reaction was allowed to proceed in an oxygen atmosphere, anthraquinone also was formed.

Product distributions from the interaction of cyanide ion with 9-nitroanthracene under a variety of reaction conditions are summarized in Table I. In experiments A–D and G–J, the DMF was dried for 24 hr or more over molecular sieves; no special drying techniques were employed with experiments E and F. Less than 10% of 9-nitroanthracene was recovered from any of these reactions.

Two techniques resulted in higher per cent conversions to nitronitrile **2a** than the per cent yields reported in Table I (see Table II). The first involved halting reactions within 0.5 hr of mixing by adding excess dimethyl sulfate or gaseous hydrogen chloride. In the second procedure, measured amounts of dry hydrogen chloride, sufficient to react with only a portion of the sodium cyanide, were added to the mixture before the substrate, so that reaction of the latter occurred in the presence of both sodium cyanide and hydrogen cyanide. Conversion to dinitrile **2c** was lower than to the nitronitrile in each case except experiment M, where it was 17%. All experiments in Table II were carried out at room temperature except when addition of reagents caused warming.

Several products were isolated only under specific reaction conditions. A 6.8% conversion to 9-cyano-10-methoxyanthracene was achieved in experiment L, presumably as a result of methylation of cyanoanthranol **2d** by dimethyl sulfate. From experiment G, a 14.1% yield of 9-cyano-10-(4′-hydroxy)phenoxyanthracene (**2**, X = OC_6H_4OH) was isolated. In experiments such as N, where dry hydrogen chloride was introduced in excess into reaction systems, 10–19% conversions to 9-cyanoanthracene were observed. A trace of this material (<2%) also was obtained from experiment L.

The stability to reaction conditions of major components of the product mixture was tested. Whereas neither aminonitrile **2b** nor cyanoanthranol **2d** was affected by sodium cyanide in DMF at room temperature, 9-cyano-10-nitroanthracene reacted to give a 58% conversion to dinitrile **2c**. The interaction of nitronitrile with hydrogen chloride is not responsible for formation of 9-cyanoanthracene, as shown by a

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[1] Grateful acknowledgment is made of the support of this work by the U. S. Army Research Office (Grants DA-ARO(D) 31-124-G679 and G857).

[2] (a) H. R. Snyder and B. E. Galbraith, *J. Org. Chem.*, **32**, 380 (1967). (b) H. R. Snyder, B. E. Galbraith, and K. E. Whitaker, unpublished work.

[3] (a) V. von Richter, *Ber.*, **8**, 1418 (1875), and earlier papers. (b) J. F. Bunnett and M. M. Rauhut, *J. Org. Chem.*, **21**, 944 (1956), and earlier papers in the series.

[4] (a) M. Rosenblum, *J. Am. Chem. Soc.*, **82**, 3796 (1960). (b) D. Samuel, *J. Chem. Soc.*, 1318 (1960). (c) E. F. Uhlman and E. A. Bartkus, *Chem. Ind.* (London), 93 (1962). (d) K. M. Ibne-Rasa and E. K. Koubak, *J. Org. Chem.*, **28**, 3240 (1963).

TABLE I

INTERACTION OF SODIUM CYANIDE WITH 9-NITROANTHRACENE IN DIMETHYLFORMAMIDE

Expt	Substrate/cyanide	Other reactants	% **2a**	% **2b**	% **2c**	% **2d**	% **3**
A[a,b,c]	1/3		<1[o]		18[o]	0	34.7[v]
B[a,b,c]	1/3		1[p]	15.5[q]	14[p]	16.2[r,s]	16.7[r,w]
C[a,b,c]	1/3[i]		<1[o]	15.2[q]	20[o]	26.7[r,s]	0[x]
D[a,b,c]	1/3	KOH[j]	<1[o]	15.1[q]	16[o]	25.6[r,s]	11.2[r,w]
E[d,b,e]	1/4	H_2O[k]	5[o]	18.3[q]	13[o]	26.0[r,s]	Trace[r,w]
F[f,b,e]	1/3	Anthraquinone-2-sulfonic acid[l]	0[o]	15.6[p]	23[o]	33.8[r]	0
G[a,b,c]	1/3[i]	Hydroquinone[m]	0[o]	21.8[q]	9[o]	22.1[r,t]	0
H[g,h,c]	1/3[i]		0[o]	19.8[q]	9[o]	48.0[r,t]	0
I[a,b,c]	1/3[i]		<1[o]	20.0[q]	14[o]	16.8[u]	21.6[u]
J[a,b,c]	1/3	$NaNO_2$[n]	2[o]	17.2[q]	18[o]	39.4[r]	Trace[r]

[a] An 18-hr reaction time. [b] At ambient temperature. [c] Substrate, 2.5 mmoles. [d] A 12-hr reaction time. [e] Substrate, 1.0 mmole. [f] A 9-hr reaction time. [g] A 6-hr reaction time. [h] At 80–85°. [i] NaCN dried at 110°. [j] 0.5 mmole. [k] 10% aqueous DMF as solvent. [l] Sodium salt, 1.0 mmole. [m] 5.0 mmoles. [n] 10.0 mmoles. [o] For infrared analysis, spectra were run using potassium bromide pellets with potassium thiocyanate as an internal standard; see S. E. Wiberley, J. W. Sprague, and J. E. Campbell, *Anal. Chem.*, **29**, 210 (1957). [p] Column chromatography. [q] From precipitated hydrochloride. [r] Reaction mixture acidified with NH_4Cl. [s] Soluble in dilute NaOH. [t] From precipitated ammonium salt. [u] Keto-enol mixture isolated from salt precipitated on dilution of reaction mixture with ether. [v] Reaction mixture acidified with concentrated HCl. [w] Insoluble in dilute NaOH. [x] Material may have decomposed on work-up.

TABLE II

YIELDS OF 9-CYANO-10-NITROANTHRACENE ON SPECIAL WORK-UP

Expt	Substrate/cyanide	% **2a**[i]	% **1** recovered	Other reactants
K[a,b]	1/1.4	7[j]	35	Gaseous HCl
L[c,d]	1/1.5	11[j]	45	Dimethyl sulfate
M[e,f]	1/2.2	11[k]	28	Gaseous HCl[l]
N[g,h]	1/1.2	6[k]	68	Gaseous HCl[m]

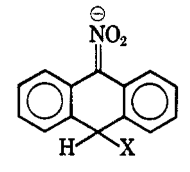
[a] Excess HCl added after 0.5 hr. [b] Substrate, 0.45 mmole. [c] Excess dimethyl sulfate (30 mmoles) added after 0.25 hr. [d] Substrate, 10.0 mmoles. [e] A 25-hr reaction time. [f] Substrate, 18.0 mmoles. [g] An 18-hr reaction time. [h] Substrate, 1.0 mmole. [i] Conversion. [j] By column chromatography. [k] By infrared analysis. [l] 25 mmoles. [m] 1.0 mmole.

control experiment, but with potassium hydroxide in DMF, the nitro group of **2a** is easily replaced, giving an almost quantitative yield of the cyanoanthrone and cyanoanthranol tautomers. A positive Griess test[5] for nitrite ion was obtained from the latter experiment as well as from the interaction of 9-nitroanthracene with sodium cyanide.

A sample of 9-nitroanthracene in the presence of cyanide ion in DMF gave rise to an epr signal which reached maximum intensity within 45 min and then grew weaker until it was of negligible intensity after 3.5 hr.

Discussion

The variety of products observed from the reaction of sodium cyanide with 9-nitroanthracene suggests a somewhat complicated series of simultaneous and consecutive processes. The initial step is probably the formation of intermediate **7a**, a type of Meisenheimer complex.[6] A similar complex (**7b**) of 9-nitroanthracene with sodium methoxide in DMSO has been studied recently by nmr spectroscopy.[7] The striking difference between **7a** and **7b** is the propensity for the former to undergo further spontaneous transformations under mild reaction conditions.



7a, X = CN
b, X = OCH_3

Two compounds, 9-cyano-10-nitroanthracene and 9-amino-10-cyanoanthracene, represent products of oxidation and reduction of complex **7a**. One mechanism which accounts for the formation of both of these products is outlined in Scheme I. Electron transfer is a recognized process for reduction of nitro compounds to amines,[8] and it accounts for the observed paramagnetic character of our reaction solutions.

It has not been possible to assign epr signals to specific radicals or anion radicals.[9a] However, 9-nitroanthracene is known to be a good electron acceptor,[9b] and furthermore, nitronitrile **2a** and nitrosonitrile **11** may also compete for electrons, freeing 9-nitroanthracene for interaction with cyanide.

Experiment G was run in anticipation that hydrogen abstraction from hydroquinone would favor formation of 9-amino-10-cyanoanthracene *via* intermediate **10** at the expense of nitronitrile **2a** and subsequent nucleophilic substitution products of the latter. Examination of Table I shows that the yield of the amine was increased; however, the reduced yield of dinitrile in this case undoubtedly reflects a successful competition by the hydroquinone anion with cyanide ion in reaction with **2a**.

An alternative explanation for the increase of the yield of the amine on addition of hydroquinone is that the latter functions as a proton source in a mechanism such as that outlined in Scheme II. In the absence of protons, the nitroso intermediate **11** could be obtained by loss of hydroxide ion *via* **12**. A weakness of this mechanism is that it does not explain the formation of 9-cyano-10-nitroanthracene.

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(5) Ilosvay Modification, Test 1574, Merck Index, 5th ed, Merck and Co., Inc., Rahway, N. J., 1940, p 745.

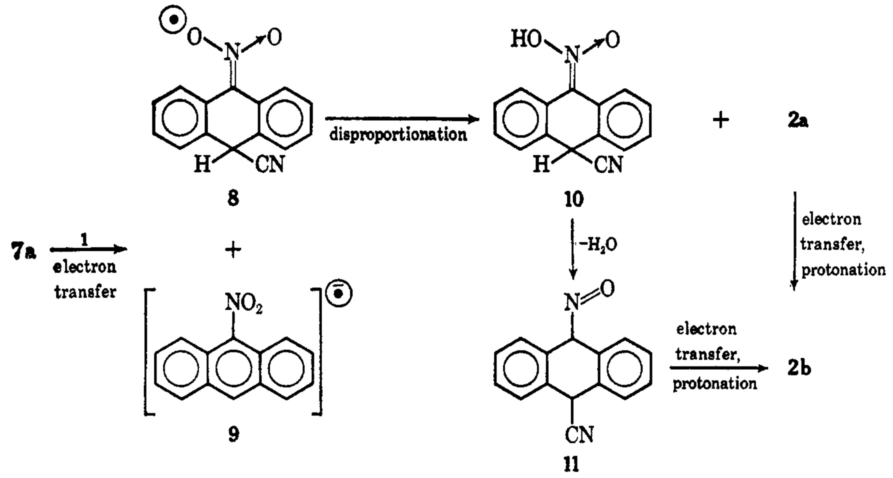
(6) J. Meisenheimer, *Ann.*, **323**, 205 (1902).

(7) R. Foster, C. A. Fyfe, P. H. Emslie, and M. I. Foreman, *Tetrahedron*, **23**, 227 (1967).

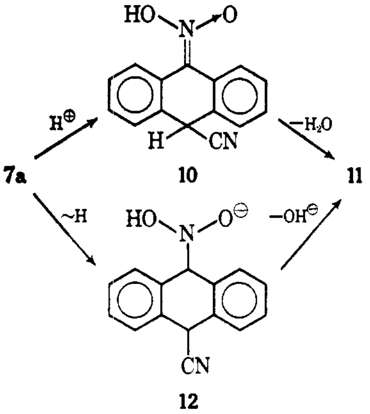
(8) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 73–77.

(9) (a) The lack of published coupling constants for the anion radical of 9-nitroanthracene may be due to its instability; see J. Q. Chambers, *Dissertation Abstr.*, **26**, 52 (1965). (b) A. Ishitani and S. Nagakura, *Bull. Chem. Soc. Japan*, **38**, 367 (1965).

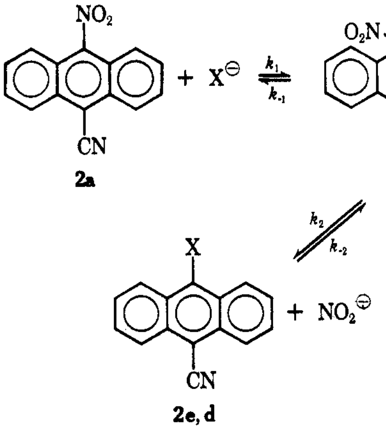
SCHEME I



SCHEME II



SCHEME III



Experiment F reflects an attempt to increase the yield of 9-cyano-10-nitroanthracene by oxidation of intermediate **7a**. This technique has shown considerable utility in dealing with the cyanide adducts of unsaturated hydrocarbons[2b] and its failure here is due, undoubtedly, not to lack of formation of nitronitrile, but to efficient interaction of **2a** with nucleophiles in the system. Experiments K and L were interrupted before nucleophilic attack could minimize the yield of nitronitrile; in experiments M and N, reduction of alkalinity of the medium by conversion of part of the sodium cyanide to hydrogen cyanide may explain the higher yield of **2a**.

Several factors, working in concert, account for the facility with which 9-cyano-10-nitroanthracene undergoes nucleophilic substitution with loss of nitrite ion. First, the ability of polar aprotic solvents to enhance reactivity of anions is well known.[10] Second, as in the case of 9-nitroanthracene, the nitronitrile should be subject to a certain amount of inhibition of resonance due to steric interaction of the nitro group with the 1,8-*peri* hydrogens.[11] Steric factors are capable of regulating the course of nucleophilic substitutions,[12] and given the stabilization of intermediate **13** by the nitrile function it seems likely that the sequence in Scheme III accounts for the production of 9,10-dicyanoanthracene and 9-cyano-10-anthranol. A basic solution of hydroquinone would give rise to the (4'-hydroxy)phenoxy compound by a similar process.

In experiment J of Table I, a large excess of nitrite ion, added at the beginning of the reaction, failed to increase the yield of nitronitrile at the expense of its substitution products. Conversion of 9-cyano-10-anthranol to its salt in basic solution provides a rationale for its stability, and there are several possible explanations for the undiminished yield of the dinitrile. The second nitrile function may lend considerably more stability to the dinitrile than does the sterically hindered nitro group to the nitronitrile **2a** (thermodynamic control),[13] or alternatively there may be high efficiency of C–NO_2 bond cleavage relative to C–CN cleavage in intermediate **13** ($k_2 \gg k_{-1}$, kinetic control).

Experimental Section[14]

Materials.—Unless otherwise specified, commercially available reagents were used without purification. Dimethylformamide (Mallinckrodt "Analytical Reagent") was distilled before use in epr experiments; controls showed the undistilled solvent to be suitable for preparative experiments. Aldrich 9-nitro-

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(10) A. J. Parker, *Quart. Rev.*, **16**, 163 (1962).

(11) J. Trotter, *Can. J. Chem.*, **37**, 1009 (1959).

(12) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, pp 455–456.

(13) Only unreacted dinitrile was recovered from treatment of 9,10-dicyanoanthracene with a tenfold excess of sodium nitrite at 80–90° in DMF.

(14) Melting points were determined with a Kofler microstage apparatus equipped with calibrated thermometers. Microanalyses were performed by Mr. J. Nemeth and his associates, and mass spectra were obtained by Mr. J. Wrona, with an Atlas CH 4 spectrometer. A Perkin-Elmer 521 infrared spectrophotometer was utilized for infrared spectra, and ultraviolet spectra were run on a Perkin-Elmer 202 spectrophotometer. Electron paramagnetic resonance spectra were obtained from a Varian V 4500-10A spectrophotometer.

anthracene was recrystallized from 30% benzene in hexane and melted at 149–150°.

General Procedure for Treatment of 9-Nitroanthracene with Sodium Cyanide in DMF.—The sodium cyanide was added to the desired amount of solvent (usually 8–10 ml per mmole of substrate) in a flask fitted with gas inlet and Drierite tubes. (A condenser was used with heated reactions.) The magnetically stirred DMF–sodium cyanide mixture was flushed with nitrogen for at least 1 hr before addition of 9-nitroanthracene and other reagents employed with each particular reaction.

Isolation and Identification of Products. 9-Cyano-10-nitroanthracene (2a).—Direct filtration of reaction solutions yielded a mixture of **2a** and dinitrile **2c** in experiments K and L, and some additional material was isolated by chromatography of the mixture obtained on dilution of the filtrate with water in experiment L. Best separation of nitronitrile and dinitrile was achieved by chromatography on silica gel, developing and eluting with a 50:50 mixture of benzene–cyclohexane. Quantitative infrared calculations[15] were based on the prominent band in 9-cyano-10-nitroanthracene at 810 cm^{-1}. Other medium-strong bands are (in potassium bromide): 2220, 1520, 1440, 1370, 1330, 1280, 1265, 1170, and 760 cm^{-1}. The ultraviolet and visible spectra show λ_{max} at 217, 257, 370, 387, and 406 mμ. Recrystallized from benzene, the nitronitrile yielded the analytical data below and sublimed at 317°.

Anal. Calcd for $C_{15}H_8N_2O_2$: C, 72.64; H, 3.25; N, 11.30; mol wt, 248. Found: C, 72.48; H, 3.21, 3.27, 3.26; N, 11.24; mol wt, 248 (mass spectrum).

9-Cyano-10-nitroanthracene was oxidized to anthraquinone (infrared spectrum coincident with authentic material) by the method used previously to oxidize methyl 9-nitro-10-anthroate.[16]

The nitronitrile was independently synthesized as follows. The nitration of 9-bromoanthracene was attempted along lines of the procedure of Barnett and Cook.[17] A slurry of 10.3 g (0.04 mole) of 9-bromoanthracene (Aldrich, recrystallized from ethanol, mp 100.5–105.5°) was stirred vigorously into 40 ml of acetic acid, and the temperature was regulated to remain below 30°.

Nitric acid (2.6 ml, 70%, sp gr = 1.42, 0.04 mole) was added dropwise over a period of 15 min. The reaction mixture was stirred 1 hr at 25–30° and 1 hr at 40–50° and poured into 100 ml of water. The supernatant liquid was decanted, and the yellow solid was washed four times with 100-ml portions of water, decanting the washes each time. The resultant solid was dried and chromatographed on silica gel, developing and eluting with cyclohexane and benzene. The yield of crude 9-bromo-10-nitroanthracene was 0.8 g or 7%. A 20% yield of 9,10-dibromoanthracene, mp 226° (lit.[18] mp 226°), was obtained as a by-product. The crude bromonitro compound was used in the preparation of **2a** below; subsequent chromatography on silica gel showed it to be contaminated with 9,10-dibromoanthracene. The 9-bromo-10-nitroanthracene from the second chromatogram melted at 330° with decomposition and yielded the analytical data below. Strong–medium infrared bands are (in potassium bromide): 1515, 1440, 1360, 1315, 1275, 1265, 900, 795, and 850 cm^{-1}.

Anal. Calcd for $C_{14}H_8BrNO_2$: C, 55.68; H, 2.69; N, 4.64; mol wt, 302. Found: C, 56.00; H, 3.02; N, 4.58; mol wt, 302 (mass spectrum).

A modification of the method of Friedman and Schechter[19] was used as crude 9-bromo-10-nitroanthracene (0.50 g, 1.6 × 10^{-3} mole) was refluxed under nitrogen for 6.5 hr in 30 ml of DMF with cuprous cyanide (0.15 g, 1.7 × 10^{-3} mole). The solution was cooled to 50° and poured into a mixture of 0.5 ml of ethylenediamine in 60 ml of water. Material precipitated on cooling was chromatographed on silica gel, developing and eluting with benzene–cyclohexane. Along with some impure starting material and 9,10-dicyanoanthracene, 0.14 g (34% yield) of nitronitrile **2a** was obtained, slightly contaminated with anthraquinone, which was removed by recrystallization from chloroform. The resultant material yielded an infrared spectrum coincident with the compound obtained from 9-nitroanthracene and sodium cyanide.

9-Amino-10-cyanoanthracene (2b).—Dilution of a filtered reaction solution with brine yielded a mixture of compounds which contained essentially all of the amine produced in the reaction. This could be isolated by chromatography but was most easily obtained by precipitating the hydrochloride from dry ether with dry hydrochloric acid. The hydrochloride was not significantly soluble in H_2O (the free amine is insoluble in dilute acid), and treatment with 5% sodium bicarbonate readily yielded the aminonitrile. It exhibited the following infrared spectrum (in potassium bromide, medium–strong bands): 3460, 3550, 3250, 2210, 1645, 1560, 1450, 1440, 1395, 1295, 995, 975, 750, and 640 cm^{-1}. Recrystallized from benzene, the amine showed mp 262–263°.

Anal. Calcd for $C_{15}H_{10}N_2$: C, 82.64; H, 4.62; N, 12.85; mol wt, 218. Found: C, 82.55; H, 4.45; N, 12.89; mol wt, 218 (mass spectrum).

Oxidation of the amine with sodium dichromate in acetic acid yielded anthraquinone (infrared spectrum coincident with authentic material).

The diacetamide was made by heating the amine (50 mg) for 2 hr with 5 ml of acetic anhydride. It was recrystallized twice from cyclohexane and showed nitrile (2220 cm^{-1}) and amide (1720 cm^{-1}) bands in the infrared spectrum, mp 198–200°.

Anal. Calcd for $C_{19}H_{14}N_2O_2$: C, 75.56; H, 4.67; N, 9.28; mol wt, 302. Found: C, 75.36; H, 4.48; N, 9.22; mol wt, 302 (mass spectrum).

9,10-Dicyanoanthracene (2c).—The dinitrile, essentially insoluble in cold DMF, was immediately filtered from cooled reaction solutions as reactions were halted. Nitronitrile **2a**, a frequent contaminant, could be removed by recrystallization from DMF. Medium–strong infrared bands (in potassium bromide) are: 2220 and 2215 (lit.[16] 2222.5 cm^{-1} with second weak band), 1620, 1450, 1440, 1280, 1380, 1170, 1155, 765, and 630 cm^{-1}. The ultraviolet and visible spectra showed (in ethanol) signals at λ_{max} 220, 261, 378, 400, and 424 mμ. The dinitrile sublimed at 335° (lit.[20] mp 335–336°). It was hydrolyzed to the half-amide, mp 349–351° (lit.[20] mp 357–358°), which showed strong infrared bands at 2220 (nitrile) and 1640 cm^{-1} (amide).

9-Cyano-10-anthranol (2d).—Dilution of reaction mixtures with brine, followed by filtration, yielded a slightly fluorescent, yellow-green filtrate. The percentage of enol obtained by neutralization and ether extraction of the filtrate was quite dependent on the acid used, and saturation with ammonium chloride was most effective. The cyanoanthranol was readily soluble in aqueous alkali,[21a] from which it could be recovered, mainly as enol, by acidification with concentrated hydrochloric acid. It was soluble in ether and a convenient separation from impurities involved precipitation of the salt from ether with ammonia followed by treatment with dilute acid. It was recrystallized from acetic acid, with mp 263–268°, and from methanol, mp 255–265° (lit.[20] mp 294–295°).[21b] The cyanoanthranol showed the following medium–strong infrared bands (in potassium bromide): 3240 (broad), 2220, 1565, 1430, 1390, 1320, 1290, 1200, and 755 cm^{-1}.

Anal. Calcd for $C_{15}H_9NO$: C, 82.26; H, 4.14; N, 6.40; mol wt, 219. Found: C, 82.24; H, 4.12; N, 6.10; mol wt, 219 (mass spectrum).

The methyl ether was prepared by dissolving 50 mg of enol in 5 ml of acetone and 0.5 ml of 66% aqueous potassium hydroxide and adding 0.5 ml of dimethyl sulfate. The solid obtained on dilution with water was recrystallized from ethanol, mp 177.5–178.5° (lit.[20] mp 177–178°).

9-Cyano-10-anthrone (3).—Acidification of filtered, aqueous reaction mixtures with concentrated hydrochloric acid yields mainly the ketone. In one experiment (I of Table I), after both benzene and chloroform were added to a reaction mixture with no effect and drawn off *in vacuo*, addition of ether caused considerable precipitation, and a mixture of dinitrile and a water-soluble substance was filtered. The water-soluble material yielded a precipitate on acidification which was a mixture of the keto–enol tautomers. The keto form is virtually insoluble in cold aqueous alkali and ether.[21a] It dissolves in DMF, giving a yellow-green solution, from which a mixture of the keto–enol

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[15] See Table I, footnote *o*.

[16] R. O. C. Norman and P. D. Ralph, *J. Chem. Soc.*, 2221 (1961).

[17] E. de B. Barnett and J. W. Cook, *ibid.*, **125**, 1084 (1924).

[18] E. de B. Barnett, *Org. Syn.*, **1**, 209 (1941).

[19] L. Friedman and H. Schechter, *J. Org. Chem.*, **26**, 2522 (1961).

[20] C. Dufraisse and J. Mathieu, *Bull. Soc. Chim. France*, 302 (1947).

[21] (a) The relative solubilities of the keto–enol isomers in aqueous alkali and their interconversion in organic solvents parallels the behavior of anthrone and anthranol; see L. F. Fieser and M. Fieser, "Organic Chemistry," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1956, pp 767–769. (b) On repeated crystallization, neither of the keto–enol pair melted sharply, due probably to contamination by tautomer.

pair is recovered on treatment with acid. A solution of cyanoanthrone in benzene is thermochromic, showing a dark brown coloration when hot that fades on cooling. Medium-strong infrared bands (in potassium bromide) for 9-cyano-10-anthrone are: 1675, 1595, 1450, 1320, 1270, 930, 810, 760, 720, and 680 cm^{-1}. It shows almost negligible nitrile absorption at 2200 cm^{-1}. From benzene-cyclohexane it has mp 192° with considerable decomposition.

Anal. Calcd for $C_{15}H_9NO$: C, 82.26; H, 4.14; N, 6.40; mol wt, 219. Found: C, 81.79; H, 4.00; N, 6.07, 6.41; mol wt, 219 (mass spectrum).

9-Cyano-10-methoxyanthracene.—This compound was isolated in experiment L by chromatography of the mixture of products precipitated on dilution of the reaction mixture with water. It exhibited an infrared spectrum identical with that of the authentic material.

9-Cyanoanthracene.—This compound was isolated by chromatography of the water-insoluble materials obtained in reactions worked up with excess dry hydrogen chloride. After recrystallization from ethanol, it showed mp 174-176° (lit.[22] mp 174-175°). Strong infrared bands were noted (in potassium bromide) at 2220, 895, 840, 770, and 720 cm^{-1}.

9-Cyano-10-(4′-hydroxy)phenoxyanthracene.—Subsequent to removal of aminonitrile **2b** from water-insoluble material in experiment G, column chromatography yielded the hydroquinone adduct. Recrystallized from carbon tetrachloride, it showed mp 231-232°. Strong-medium bands in the infrared spectrum are (in potassium bromide): 3340, 2220, 1500, 1470, 1440, 1405, 1370, 1285, 1190, 1085, 820, 760, and 730 cm^{-1}.

Anal. Calcd for $C_{21}H_{13}NO_2$: C, 81.10; H, 4.21; N, 4.50; mol wt, 311. Found: C, 80.57; H, 4.35; N, 4.50; mol wt, 311 (mass spectrum).

Nucleophilic Substitution Reactions of 9-Cyano-10-nitroanthracene. Reaction with Sodium Cyanide.—After a 1-hr nitrogen flush of a mixture of sodium cyanide (0.05 g, 10^{-3} mole) in 5 ml of DMF, nitronitrile (0.10 g, 4 × 10^{-4} mole) was added, and the mixture was stirred under nitrogen at room temperature for 6 hr. Filtration yielded 67 mg of crude 9,10-dicyanoanthracene, contaminated to about 20% with nitronitrile. Column chromatography ultimately yielded pure dinitrile for unequivocal identification. Only traces of other compounds were obtained from this reaction.

Treatment with Potassium Hydroxide.—A mixture of potassium hydroxide (0.11 g, 2 × 10^{-3} mole) in 5 ml of DMF was flushed for 1 hr with nitrogen, and nitronitrile (0.03 g, 1.0 × 10^{-4} mole, known to be contaminated with anthraquinone) was added. After stirring for 17 hr under nitrogen, filtration yielded 6.5 mg of a solid identified by infrared analysis as anthraquinone. The filtrate was diluted with 45 ml of water and saturated with ammonium chloride. Extraction with ether and evaporation yielded an orange oil (DMF) from which 13 mg of an orange solid precipitated on dilution with water. Infrared analysis showed that this was a mixture of 9-cyano-10-anthranol and 9-cyano-10-anthrone. Recrystallization from acetic acid yielded material whose infrared spectrum showed it to be rich in enol **2d**.

Paramagnetic Resonance Study.—A 5-ml sample of 2 × 10^{-3} *M* sodium cyanide in DMF was flushed for 0.5 hr with nitrogen in a side-arm dropping funnel attached at the lower end to a flat epr cell such that the nitrogen exited through the cell. A sample of 9-nitroanthracene (5.6 mg, 2.5 × 10^{-5} mole) was added, stirred thoroughly by the nitrogen stream, and dropped into the epr cell. An eight-peak spectrum with a 28-gauss line width was observed which did not vary in complexity but diminished in intensity considerably within 3.5 hr.

Registry No.—9-Nitroanthracene, 602-60-8; sodium cyanide, 143-33-9; DMF, 68-12-2; **2a**, 14789-43-6; **2b**, 14789-44-7; diacetamide of **2b**, 14789-50-5; **2c**, 1217-45-4; **2d**, 14789-46-9; **3**, 14789-47-0; 9-bromo-10-nitroanthracene, 14789-48-1; 9-cyano-10-(4′-hydroxy)phenoxyanthracene, 14789-49-2.

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The Favorskii Rearrangement of *cis*- and *trans*-Carvone Tribromides. I. Primary Amines[1]

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The action of primary amines in ether or methanol on *trans*-carvone tribromide II leads to exclusive Favorskii rearrangement and affords iminolactones VII and unsaturated amides VIII. *cis*-Carvone tribromide undergoes a Favorskii rearrangement with amines in methanol to yield the same iminolactones; however, 1,2-elimination of hydrogen bromide occurs in ether to give the bromo unsaturated ketone XIII. Contrary to statements in the literature, it is shown that α-axial halo ketones undergo the Favorskii rearrangement. The importance of solvent polarity in determining the reaction path followed by an α-halo ketone is again emphasized.

Substantial quantities of carvenolide I were required during an investigation of the synthesis of various iridolactones.[3] The preparation of carvenolide I reported by Wallach[4] involved treatment of carvone tribromide II with ammonia to give a basic intermediate, formulated as III or IV, which was converted into carvenolide by steam distillation. It is difficult to visualize a mechanism for the transformation of III or IV into carvenolide I; consequently, we were prompted to reexamine the intermediate "amino ketone." The basic intermediate was isolated in 36% yield from the reaction of carvone tribromide II and ammonia in amyl alcohol using the procedure described by Wallach.[4] Although this compound was too unstable to permit complete characterization, spectral data indicated it possessed the constitution represented by formula V. The nmr spectrum of the basic intermediate was identical with that of carvenolide I except for the presence of a very broad, one-proton signal centered at 6.1 ppm, while the infrared spectrum displayed C=N and N-H stretching vibrations at 6.01 and 3.01 μ, respectively. The extremely facile hydrolysis to carvenolide I is also in accord with the formulation of the intermediate as the iminolactone V (Scheme I).

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