The pentane solution was washed with 1:1 dimethyl sulfoxide–water (two 50-ml portions) and with 50% aqueous sodium chloride. The pentane solution was dried over magnesium sulfate and concentrated to a colorless oil, which crystallized when kept in the refrigerator overnight. Recrystallization from cold Skellysolve B gave 5.05 g (0.022 mol, 41%) of crystals, mp 36–37°. Two recrystallizations from cold Skellysolve B gave colorless crystals: mp 36–37°; $\nu_{C=O}$ 1625, $\nu_{C=C}$ 1600, 1575, 1495, $\nu_{=CH_2}$ 880, ν_{Ph} 780, 730, 700 cm^{-1} in Nujol; nmr ($CDCl_3$) δ 7.33 (s, 5 H, C_6H_5), 4.86 (s, 2 H, $=CH_2$), 3.8–3.15 (m, 4 H, NCH_2), 2.45–1.50 (m, 8 H, $-CH_2-$).

Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11. Found: C, 78.10; H, 8.32; N, 6.51.

1-Benzyl-5-methyleneheptamethylenimine (6).—A solution of **5** (5.05 g, 0.0220 mol) in ether (50 ml) was added to a mixture of lithium aluminum hydride (3.5 g) and ether (200 ml). The mixture was heated at reflux temperature for 5 hr. Ethyl acetate and water were added to consume the excess hydride and the inorganic solids were collected by filtration. The ether filtrate was dried over magnesium sulfate and concentrated to an oil. The oil was transferred to a 10-ml distillation flask with ether and distilled, giving 3.687 g (0.0171 mol, 78%) of colorless oil: bp 78–80° (0.05 mm); λ_{max} in 95% ethanol 258 mμ (ϵ 508), 263 (362), 268 (254); $\nu_{=CH}$ 3060, 3020, $\nu_{C=C}$ 1630, 1595, 1490, ν_{Ph} 724, 700 cm^{-1} on the oil; nmr ($CDCl_3$) δ 7.29 (m, 5 H, C_6H_5), 4.76 (s, 2 H, $=CH_2$), 3.61 (s, 2 H, $NCH_2C_6H_5$).

Anal. Calcd for $C_{15}H_{21}N$: C, 83.66; H, 9.83; N, 6.51. Found: C, 84.14, 82.96; H, 10.53, 9.93; N, 5.44, 6.18.

4-Benzylhexahydro-7a-methyl-1*H*-pyrrolizinium Perchlorate (7a). Aqueous perchloric acid (70%, 20 drops) was added to a solution of **6** (0.42 g, 0.0195 mol) in absolute ethanol (5.0 ml). The solution was heated to reflux for 90 min. Addition of ether (25 ml) caused rapid separation of a first crop of 0.148 g of colorless crystals, mp 195–198°. Recrystallization from absolute ethanol gave colorless crystals: mp 215–216°; $\nu_{C=C}$ 1580, 1495, ν_{Ph} 770, 710 cm^{-1} in Nujol; nmr (DMF-d_7) δ 4.53 (s, $PhCH_2N$), 3.63 (m, $-CH_2NCH_2-$), 2.32, 2.26 (s, $-CH_2-$), 1.75 (s, $-CH_3$).

Anal. Calcd for $C_{15}H_{22}NO_4Cl$: C, 57.05; H, 7.02; N, 4.44. Found: C, 56.79; H, 7.10; N, 4.85.

The filtrate from the isolation of product above was kept in the freezer overnight. Colorless crystals, appearing to be a mixture of **7a** and **8a**, mp 60–80°, 140–145° (0.269 g), formed and were collected: $\nu_{=CH}$ 3140, $\nu_{C=C}$ 1630, 1575, 1492, ν_{Ph} 751, 697 cm^{-1} in Nujol. Two recrystallizations from ethanol–ether gave colorless crystals, softening at 90–100°, mp 140–145°. Recrystallization of 0.16 g from absolute ethanol, preceded by heating in refluxing ethanol for 1 hr, gave colorless crystals (0.03 g), partial softening at 140–150°, mp 190–205°.

4-Benzylhexahydro-7a-methyl-1*H*-pyrrolizinium Chloride (7b). A. From Attempted Benzoylation of 1-Benzyl-5-methyleneheptamethylenimine.—A solution of **6** (0.314 g, 0.00146 mol) in dioxane (reagent grade, 5.0 ml) was added to a solution of benzoyl chloride (0.218 g, 0.00156 mol) in dioxane (5.0 ml). Crystals began forming after 30 min at room temperature and were collected after 22 hr, giving 0.289 g (0.00115 mol, 78%) of product, mp 282–284° dec. Two recrystallizations from ethanol–ether, the last preceded by decolorization with activated charcoal, gave colorless crystals: mp 295–296 subl; $\nu_{C=C}$ 1600, 1580, 1495, ν_{Ph} 770, 720 cm^{-1} in Nujol; nmr $PhCH_2N$ (δ 4.68, singlet), $-CH_2-$ (2.35, 2.29, singlets), $-CH_3$ (1.82, singlet) in dimethylformamide-d_7 at 95°.

Anal. Calcd for $C_{15}H_{22}NCl$: C, 71.54; H, 8.81; N, 5.56. Found: C, 71.46; H, 8.99; N, 5.79.

B. From Attempted Acetylation of 1-Benzyl-5-methyleneheptamethylenimine.—The above compound (**7b**) was obtained from addition of a solution of **6** (0.387 g, 0.0018 mol) in dioxane (dried over sodium, 5.0 ml) to a solution of acetyl chloride (0.153 g, 0.00195 mol) in dioxane (5.0 ml), giving, after 6 hr, 0.313 g (0.00125 mol, 69%) of product, mp 272–275° dec. The infrared spectrum in Nujol is identical with that of the above product.

1-Benzyl-1-methyl-5-methyleneheptamethyleniminium Iodide (8b).—Excess methyl iodide was added to a solution of **6** (0.143 g, 0.665 mol) in methanol (5 ml). After 3 days at room temperature, the now yellow solution was partially concentrated by evaporation on the steam bath. Ether was added to the solution, which became cloudy. Crystals slowly formed and, after cooling the mixture in the refrigerator, were collected, mp 187–189°. Two recrystallizations from methanol–ether gave colorless crystals of **8b**: mp 184–186°; nmr ($CDCl_3$) δ 7.7 (m, 5 H, $-C_6H_5$), 5.00 (s, 2 H, $=CH_2$ or $-NCH_2Ph$), 4.93 (s, 2 H, $=CH_2$ or NCH_2Ph), 3.66 (m, 4 H, $-NCH_2-$), 3.18 (s, 3 H, $-CH_3$), 2.35 (m, 8 H, $-CH_2-$).

Anal. Calcd for $C_{16}H_{24}NI$: C, 53.78; H, 6.77; N, 3.92. Found: C, 53.73; H, 6.75; N, 4.36.

Registry No.—**3**, 32674-93-4; **4**, 32674-94-5; **5**, 32674-95-6; **6**, 32674-96-7; **7a**, 32674-97-8; **7b**, 32670-60-3; **8a**, 32670-61-4; **8b**, 32653-78-4.

Reaction of Cyanide Ion with Aromatic Nitriles and Aromatic Heterocyclic Compounds in Dipolar Aprotic Solvents. Cyanide Exchange[1]

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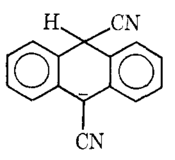
The cyanation of electronegatively substituted aromatic compounds and of unsaturated hydrocarbons containing extended π systems by treatment with sodium cyanide and an oxidizing agent in aprotic solvents offers attractive synthetic possibilities.[2] The reaction has been considered to proceed *via* reversible addition of cyanide ion to the substrate to yield a carbanion (*e.g.*, **1**, from 9-cyanoanthracene) which is then converted to the cyanation product by the action of the oxidizing agent. A similar addition of cyanide ion to a heterocyclic aromatic system has been proposed by Happ and Janzen[3] to account for the esr spectrum observed when acridine is treated with cyanide ion in air-saturated dimethylformamide (DMF); the spectrum is that of the radical anion resulting from the action of oxygen on the carbanion **2**. These authors have also studied the esr spectrum of the radical anion formed by the attack of oxygen on the 9-cyanoanthracene adduct (**1**). In the present study, undertaken before the publication of the work of Happ and Janzen, the oxidizing agent (sodium anthraquinone-α-sulfonate, α-SAS) preferred for the conversion of 9-cyanoanthracene and cyanide ion to 9,10-dicyanoanthracene has been found highly effective for the conversion of acridine and sodium cyanide to 9-cyanoacridine. This result is in accord with the postulation of the similar intermediates **1** and **2**. Further evidence for intermediates such as **1** and **2** has been sought by the use of labeled cyanide ion in reactions with electronegatively substituted aromatic compounds. The use of labeled cyanide in the



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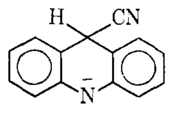

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[1] Grateful acknowledgment is made to the U. S. Army Research Office for partial support of this work [Grant DA-ARO(D)-G857].

[2] (a) B. E. Galbraith, K. E. Whitaker, and H. R. Snyder, *J. Org. Chem.*, **34**, 1411 (1969); (b) K. E. Whitaker and H. R. Snyder, *ibid.*, **35**, 30 (1970).

[3] E. H. Janzen and J. W. Happ, *ibid.*, **35**, 96 (1970).

TABLE I

CYANIDE EXCHANGE

Registry no.	Run	Substrate (S)	Mole ratio of KCN[a]:S	Temp,[b] °C	Time, hr	Radio-activity[c]	Recovery, %
1210-12-4	1	9-Cyanoanthracene	4:1	80	2	0.91	30
	2	9-Cyanoanthracene	4:1	23	5	0.348	70
	3	9-Cyanoanthracene	1:1	80	0.75	0.626	80
	4	9-Cyanoanthracene	2:1	80	0.75	0.755	69
1217-45-4	5	9,10-Dicyanoanthracene	4:1	80	5	1.09	60
5326-19-2	6	9-Cyanoacridine	4:1	65	20	0.800	67
2510-55-6	7	9-Cyanophenanthrene	4:1	100	24	0.970	70
16001-13-1	8	9-Cyano-10-phenylanthracene	4:1	100	24	0.060	65
1467-01-2	9	9-Cyano-10-methylanthracene	4:1	100	24	0.020	30
3029-30-9	10	1,4-Dicyanonaphthalene	4:1	100	3	0.068	38
	11	1,4-Dicyanonaphthalene	4:1	100	8	0.180	28
	12	4,4′-Dicyanobiphenyl	4:1	130	24	0	82
	13	1-Cyanonaphthalene	4:1	100	24	0	51
	14	2-Cyanonaphthalene	4:1	100	24	0	
	15	1,3-Dicyanobenzene	4:1	100	24	0	31
	16	1,4-Dicyanobenzene	4:1	100	24	0	
	17	1,4-Dicyanocyclohexane	4:1	100	24	0	42
	18	Stearonitrile	4:1	100	24	0	35
110-61-2	19	Succinonitrile	4:1	100	24	0.97	15

[a] The radioactivity of the potassium cyanide was 2.00 μCi of ^{14}C/mmol of the compound. [b] ±5°. [c] Radioactivity is expressed in microcuries of ^{14}C/mmol of compound. Measurements are done by liquid scintillation and are accurate to ±2%.

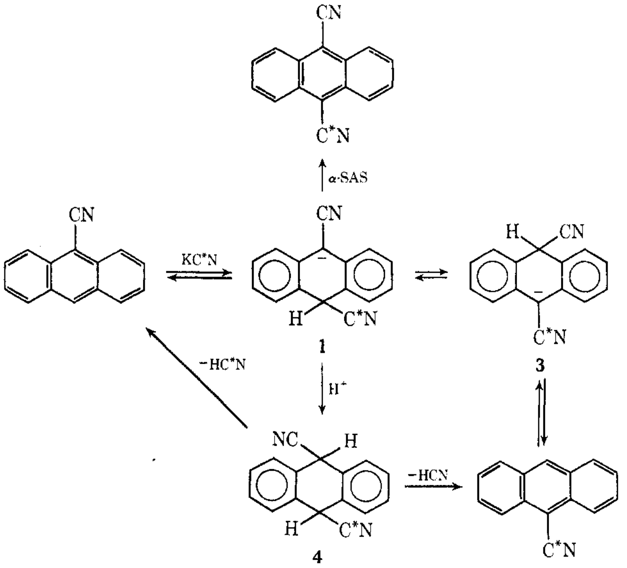
cyanation reactions also promises to afford a very simple means of introducing labeled cyano groups into certain aromatic and heterocyclic systems.

Treatment of 9-cyanoanthracene with 2 mol of carbon-14 labeled potassium cyanide in the presence of 1 mol of the quinone α-SAS at 80° for 2 hr produced an 80% yield of 9,10-dicyanoanthracene with the same millimolar radioactivity as that of the cyanide employed. A reaction run for 4 hr at 100° yielded a product of millimolar radioactivity 1.34 times that of the cyanide employed. These results would be expected if exchange occurs with the product, 9,10-dicyanoanthracene, and not with the organic reagent, 9-cyanoanthracene, under the conditions employed.

In the absence of oxidizing agent, 9-cyanoanthracene undergoes exchange with cyanide ion (run 1, Table I). Also, under the conditions used, DMF solutions of 9-cyanoanthracene and cyanide ion generate the 9,10-dicyano compound, presumably as a result of electron transfer between the carbanion formed and the parent aromatic compound.[2b] In runs 2–4, the per cent recovery and the extent of exchange are shown to depend upon the temperature, the cyanide concentration, and the duration of the reaction. As more drastic conditions are employed, the amount of labeled 9-cyanoanthracene becomes smaller and the extent of exchange becomes greater.

If the exchange reaction proceeds by the attack of cyanide ion on the carbon atom attached to the cyano group, then there should be very little difference in reactivity between 9-cyanoanthracene and 9-cyano-10-methylanthracene or between 9-cyanoanthracene and 9-cyano-10-phenylanthracene. However, the methyl- and phenyl-substituted compounds proved to be very unreactive (runs 8 and 9).

Therefore, it is most likely that the exchange reaction with 9-cyanoanthracene proceeds through the same carbanion (1) postulated as the intermediate for the cyanation reaction. The exchange might result from a proton migration in the carbanion, followed by loss of the cyanide ion; alternatively, protonation of the carbanion during the aqueous work-up, followed by the loss of hydrogen cyanide, would give the same result.



In the latter pathway, the 9,10-dicyano-9,10-dihydro derivative, **4**, corresponds to the hydrocyanation products which have been obtained in good yields from some highly unsaturated hydrocarbons by the same experimental procedure.[2a] If the exchange reaction occurs by this pathway, then the use of deuterated or tritiated water in the final hydrolysis of the reaction mixture prepared from 9-cyanoanthracene and sodium cyanide should result in the formation of deuterium or tritium labeled compounds. A solution containing 4 equiv of cyanide and 1 equiv of 9-cyanoanthracene was heated at 80° for 2 hr before the reaction mixture was added to tritiated water. The 9-cyanoanthracene was recovered in radiochemically pure form and the 10 position was found to be labeled with tritium to the extent of 39%. In a similar experiment in which deuterium oxide was used in place of tritiated water, the 10 position of 9-cyanoanthracene was found to be labeled with deuterium to the extent of 41%, as determined by deuterium analysis and nmr and mass spectral data. It thus appears that about 80% of the recovered 9-cyanoanthracene is derived from the dihydro derivative (**4**).

It would, of course, be desirable to isolate 9,10-dicyano-9,10-dihydroanthracene and study its dehydrocyanation. Severin and Schmitz have reported that 9-nitroanthracene reacts with sodium borohydride in DMF to give a solution which upon treatment with an ion exchange resin (acid form) generates 9,10-dihydro-9-nitroanthracene.[4] We have found that this process applied to 9-cyanoanthracene gives a 65% yield of 9,10-dihydro-9-cyanoanthracene, but with 9,10-dicyanoanthracene the only product isolated other than starting material was 9-cyanoanthracene, which was obtained in 50% yield. The fact that none of the reduction product of 9-cyanoanthracene was found suggests that 9-cyanoanthracene is not formed until after the excess borohydride has been destroyed by the acid treatment. It seems quite likely that the dihydrocyano compound is its precursor.

The observations mentioned above support the view that the carbanion **1** is involved in the cyanation and exchange reactions of 9-cyanoanthracene. This carbanion is formed reversibly, and in the presence of the quinone, α-SAS, it is converted to the cyanation product. Exchange does not occur with 9-cyanoanthracene in the presence of oxidizing agent, since in the aprotic reaction medium protonation of **1** cannot occur to give the dihydro intermediate **4**, as demonstrated in the initial synthesis of labeled 9,10-dicyanoanthracene, in which the millimolar radioactivity of the dicyano compound is the same as that of the $K^{14}CN$ used initially. However, under more drastic conditions it was found that both addition and exchange with the product occurred, as evidenced by the increased millimolar radioactivity in the dicyano compound. In run 5, the dinitrile was heated with a fourfold excess of labeled cyanide at 80° for 5 hr; exchange did, indeed, occur, as 27% of the cyano groups were replaced.

In the absence of added oxidizing agent the carbanion slowly undergoes electron transfer with 9-cyanoanthracene, and 9,10-dicyanoanthracene and as yet unknown reduction products are formed. Also the portion of the carbanion surviving to the end of the reaction period is converted by hydrolysis to 9,10-dicyano-9,10-dihydroanthracene, which loses hydrogen cyanide to regenerate 9-cyanoanthracene. This is the route by which exchange with radioactive cyanide occurs, but there is substantial loss in the process because of the formation of 9,10-dicyanoanthracene. The best method of preparing labeled 9-cyanoanthracene by the exchange process requires the use of highly radioactive cyanide and short reaction periods.

In other experiments (runs 6–19), various aromatic and aliphatic nitriles were treated with carbon-14 labeled potassium cyanide. Of the aromatic nitriles studied, only 9-cyanoacridine, 9-cyanophenanthrene, and 1,4-dicyanonaphthalene were found to undergo the exchange reaction. In the reaction with 9-cyanophenanthrene, none of the dicyano compound was detected; the phenanthrene derivative does not appear to undergo the electron transfer process which occurs with 9-cyanoanthracene.[2b] Of the aliphatic nitriles studied, only succinonitrile was found to undergo exchange with labeled cyanide. Since the cyanide ion is a very strong base in dipolar aprotic solvents, the reaction with succinonitrile may be explained by proton abstraction, followed by loss of cyanide and then by hydrocyanation to give labeled succinonitrile.

The reactivity of aromatic nitriles in cyanide exchange seems to depend on the ability of the substrate to form a Meisenheimer-like complex. In turn, formation of this complex depends on the ability of the cyano group to stabilize the carbanion sufficiently to compensate for the loss in aromaticity. The relative ease of addition to aromatic nuclei, anthracene > phenanthrene > naphthalene > benzene, has been correlated with the amount of stabilization energy lost in forming the adduct.[5] Thus, for example, the stabilization energy lost in going from anthracene to 9,10-dihydroanthracene is less than the loss with phenanthrene. Because the formation of a Meisenheimer complex also involves a certain loss in aromaticity, a similar argument can be made for the reactivity of simple aromatic nitriles toward exchange. This argument can also be employed to explain the successful cyanation of acridine and the unsuccessful reactions with quinoline, isoquinoline, and pyridine. For the latter compounds, the stabilization of the anionic intermediates is insufficient to compensate for the loss in aromaticity.

Experimental Section

Melting points are uncorrected and were determined with a Kofler micro hot stage apparatus. Infrared spectra were obtained by use of potassium bromide discs and a Perkin-Elmer 521 infrared spectrophotometer. Microanalyses for carbon, hydrogen, and deuterium were performed by Mr. J. Nemeth and associates. Yellow carbon-14 labeled compounds were burned to carbon-14 carbon dioxide and water. The radioactive carbon dioxide was absorbed in Hyamine hydroxide before adding a toluene scintillator and counting with a Packard liquid scintillation spectrometer. Radioactive samples which did not give colored solutions were dissolved in a toluene scintillator and counted. Yellow tritium-labeled compounds were also burned to carbon dioxide and tritium water. The radioactive water was dissolved in a dioxane-based scintillator and counted. The Bush Channels ratio method was used to correct for quenching in all radioactive samples assayed.[6]

Materials.—Unless otherwise specified, commercially available reagents were used without purification. The dimethylformamide was stored over Linde Type 4A Molecular Sieve for 2 weeks before use. Finely divided sodium cyanide (98%), potassium cyanide-^{14}C, and α-SAS were dried for 24 hr at 110° under vacuum and stored over calcium sulfate in a tightly closed container.

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[4] T. Severin and R. Schmitz, *Chem. Ber.*, **95**, 1417 (1962).

[5] F. G. Bordwell, "Organic Chemistry," Macmillan, New York, N. Y., 1963, p 540.

[6] E. T. Bush, *Anal. Chem.*, **36**, 1082 (1964).

The millimolar radioactivity of the potassium cyanide-^{14}C was 2.00 μCi of ^{14}C/mmol of compound.

General Procedure for Cyanide Exchange.—A mixture of substrate (1.0 mmol) and potassium cyanide-^{14}C (0.26 g, 4.0 mmol) in DMF (25 ml) was stirred under dry nitrogen in a 50-ml, three-necked flask equipped with a gas inlet tube dipping into the liquid, a reflux condenser with a calcium sulfate drying tube, and a thermometer. After the mixture had been heated at a specified temperature and for a specified time (see Table I), it was poured into 150 ml of a 1:1 solution of water and saturated ammonium chloride. The aqueous mixture was filtered. If the substrate was appreciably soluble in water, a chloroform extraction was used, followed by evaporation of the chloroform. Purification was accomplished by column chromatography with silica gel (20 g) and elution with cyclohexane, mixtures of cyclohexane–benzene, and finally benzene. Identification of the compounds was done by comparison with the known compounds by tlc, melting point, ir, and elemental analysis.

Preparation of 9,10-Dicyanoanthracene with Potassium Cyanide-^{14}C.—A mixture of 9-cyanoanthracene (0.20 g, 1.0 mmol), labeled potassium cyanide (0.13 g, 2.0 mmol), and α-SAS (0.31 g, 1.0 mmol) in 25 ml of DMF was heated at 80° for 2 hr. The reaction mixture was poured into water and filtered hot. The solid product (0.18 g, 80%) was purified by recrystallization from chloroform and by column chromatography. The melting point (335°) and the infrared spectrum were identical with those of 9,10-dicyanoanthracene.[2b] A sample was combusted and analyzed by liquid scintillation counting. The measured radioactivity was 2.00 μCi of ^{14}C/mmol of compound.

An identical experiment was run at 100° for 4 hr. The radioactivity of the purified 9,10-dicyanoanthracene was 2.68 μCi of ^{14}C/mmol of compound.

Preparation of 9-Phenyl-10-cyanoanthracene.—To a solution of 9-phenylanthracene (0.508 g, 2.0 mmol) in 25 ml of carbon disulfide in a 50-ml, three-necked, round-bottomed flask equipped with thermometer, addition funnel, and reflux condenser, bromine (0.32 g, 2.0 mmol) in 25 ml of carbon disulfide was added dropwise over a 30-min period at 23°. Stirring was continued for 3 hr. The excess bromine and carbon disulfide were removed by evaporation to yield a yellow solid (0.50 g) which was mixed with cuprous cyanide (1.7 g, 20 mmol) in 80 ml of DMSO and heated under reflux for 4 hr. The reaction mixture was poured into 500 ml of a 1:1 solution of water and concentrated ammonium hydroxide. The aqueous mixture was filtered to yield a brownish precipitate, which was dried. The product was extracted from the solid with chloroform to separate it from the residual cuprous cyanide. An intensely yellow solid was obtained after evaporation of the chloroform. Tlc showed two spots, one of which corresponded to 9-phenylanthracene. The mixture was separated by silica gel chromatography to give 9-phenyl-10-cyanoanthracene, mp 198–200° (lit.[7] mp 199–200°), in an overall yield of 65%.

Preparation of 9-Methyl-10-cyanoanthracene.—The method of Calas and Lalande[8] was used to prepare 9-methyl-10-cyanoanthracene from 9-methylanthracene by bromination in carbon disulfide, followed by treatment with cuprous cyanide. The latter reaction was carried out in DMSO. A yellow solid, mp 204–205 (lit.[8] mp 205°), was obtained after silica gel chromatography and crystallization from ethanol.

Hydrolysis of Reaction Mixture with Tritiated Water.—A mixture of 9-cyanoanthracene (0.20 g, 1.0 mmol) and sodium cyanide (0.20 g, 4.0 mmol) in 25 ml of DMF was heated for 2 hr at 80°. The reaction mixture was then poured into 100 ml of tritiated water (0.484 μCi of tritium/mmol of water). After purification of the yellow solid obtained, a 45% recovery of starting material was found. Combustion of a sample, followed by a liquid scintillation measurement of the water obtained, showed that the compound contained 0.19 μCi of tritium/mmol of compound.

Hydrolysis of Reaction Mixture with Deuterium Oxide.—The reaction was performed exactly as the preceding one, except that deuterium oxide (100 g) was used in the work-up. Analysis of the water obtained from a burned sample showed that 4.5% of the hydrogen present in the compound was deuterium. A mass spectrum showed a similar increase in the 204 peak; an nmr spectrum also showed a reduction in the peak at δ 8.55.

Reaction of 9-Cyanoanthracene with Sodium Borohydride.—In a three-necked, 100-ml, round-bottomed flask equpped with a reflux condenser, gas inlet, and 50-ml dropping funnel were placed 1.0 g (5.0 mmol) of 9-cyanoanthracene and 30 ml of DMF. Nitrogen was bubbled through the mixture. A solution of sodium borohydride (0.38 g, 10 mmol) in 25 ml of DMF was then added dropwise over a 0.5 hr period. The purple mixture was then stirred for an additional 2 hr at room temperature and then poured onto 50 ml of Dowex 50W-X8 acid resin which had been washed with DMF. After hydrogen evolution ceased, approximately 0.5 hr, the DMF solution was separated from the resin by suction filtration and then poured into a solution prepared from 275 ml of water and 25 ml of saturated ammonium chloride solution. The mixture was allowed to stand overnight and was then filtered to give 0.85 g of a pale yellow solid, mp 110–113°. Recrystallization from heptane gave 0.65 g of white needles, mp 115–116°.

Anal. Calcd for $C_{15}H_{11}N$: C, 87.80; H, 5.37; N, 6.83. Found: C, 87.85; H, 5.32; N, 6.73.

Reaction of 9,10-Dicyanoanthracene with Sodium Borohydride.—In a three-necked, 100-ml, round-bottomed flask equipped with a reflux condenser, gas inlet, and 50-ml dropping funnel were placed 0.228 g (1.0 mmol) of 9,10-dicyanoanthracene and 35 ml of DMF. The mixture was heated to 60°, as nitrogen was bubbled through the solution. After the 9,10-dicyanoanthracene had dissolved, a solution of sodium borohydride (0.076 g, 2.0 mmol) in 10 ml of DMF was added dropwise over a 0.5-hr period. The purple mixture was then stirred for 2 hr at 60° and poured onto 20 ml of Dowex 50W-X8 acid resin which had been washed with DMF. After hydrogen evolution had ceased, approximately 15 min, the DMF solution was separated from the resin by suction filtration. Some of the 9,10-dicyanoanthracene was lost because of its insolubility in DMF. The DMF solution was then poured into 300 ml of water containing 25 ml of saturated ammonium chloride solution. After a few minutes the mixture was filtered, and the solid obtained (0.13 g) was dried and dissolved in chloroform. The solution was then evaporated onto silica gel and put on top of a 15-g column. Elution with 1:1 benzene–cyclohexane gave 0.10 g (50%) of 9-cyanoanthracene and 0.025 g of 9,10-dicyanoanthracene.

Cyanation of Acridine.—In a 50-ml, round-bottomed flask equipped with a gas inlet, condenser, and thermometer were placed acridine (1.78 g, 10 mmol), sodium cyanide (1.0 g, 20 mmol), α-SAS (3.41 g, 10 mmol), and 40 ml of DMSO. The mixture was heated for 3 hr at 90° and was then poured into 300 ml of water containing 25 ml of 10% sodium hydroxide. After a few minutes, the mixture was filtered while it was still warm. After thorough washing, the solid was dried and dissolved in 200 ml of chloroform; decolorizing charcoal and anhydrous magnesium sulfate were added to the solution. Filtration and evaporation of the solvent gave 1.66 g (83%) of a yellow solid: mp 181–182° (lit.[9] mp 180–181°); ir 2220, 1630, 1520, 1150, 750 cm^{-1}.

Anal. Calcd for $C_{14}H_8N_2$: C, 82.35; H, 3.92; N, 13.73. Found: C, 82.36; H, 3.98; N, 13.46; mol wt, 204 (mass spectrum).

Hydrolysis of 9-Cyanoacridine-^{14}C to 9-Acridinecarbamide-^{14}C.—A mixture of the labeled 9-cyanoacridine (0.13 g, 0.800 μCi of ^{14}C/mmol of compound) and 3 ml of 90% H_2SO_4 was heated on a steam bath for 3 hr. The mixture was then poured into 200 ml of water and a 10% KOH solution was added until the pH of the solution was 11. The solid (0.146 g) was collected, washed with water, and then dried. The material was recrystallized twice from ethanol. The purified samples gave a melting point of 264–265° (lit.[10] mp 263–264°). Radioassay gave a value of 0.786 μCi of ^{14}C/mmol of 9-acridinecarbamide.

Anal. Calcd for $C_{14}H_{10}N_2O$: C, 75.68; H, 4.50; N, 12.61. Found: C, 75.42; H, 4.39; N, 12.47.

Registry No.—K*CN, 32319-17-8; 9,10-dicyanoanthracene-*2*-^{14}C, 32319-25-8; 9-cyano-9,10-dihydroanthracene, 32319-26-9; 9-acridinecarbamide-^{14}C, 32319-27-0.

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