

Reductive Activation of Arenes: XIII.* Reaction with Butyl Bromide of Anionic Products Formed by Reduction of 9,10-Dicyanoanthracene with Potassium in Liquid Ammonia**

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Abstract—Reduction of 9,10-dicyanoanthracene with one equivalent of metallic potassium in liquid ammonia at -33°C gives a product which almost does not react with butyl bromide. By contrast, the two-electron reduction product reacts with butyl bromide to form, depending on the reaction conditions and procedure for treatment of the reaction mixture, one of the three compounds: 10-butyl-9-cyanoanthracene, 10-butyl-10-cyano-9,10-dihydroanthracen-9-one, or 9,10-dibutyl-9,10-dicyano-9,10-dihydroanthracene. Relatively stable 10-butyl-9,10-dicyano-9,10-dihydro-9-anthryl anion was presumed to be a common precursor of these products.

While studying reductive activation of functionally substituted arenes to electrophilic reagents, we showed the possibility for alkylation of aromatic nitriles via replacement of the amino group and/or *ipso*-addition by the action of primary alkyl halides on the corresponding one- or two-electron reduction products; the substrates were benzonitrile, 1-cyanonaphthalene, and 9-cyanoanthracene [2–6]. Introduction of an additional electron-acceptor substituent, the second cyano group, into position 2 or 4 of benzonitrile radically changes the mechanism and regioselectivity of alkylation of the reduced forms: reactions of terephthalodinitrile and phthalodinitrile radical anions with alkyl halides follow the electron-transfer mechanism, and products of replacement of the cyano group and hydrogen atom are formed at a ratio of $\sim 4:1$ [7, 1]. Terephthalodinitrile dianion shows a dual reactivity, depending on the alkyl halide nature [8].

We thought it important to elucidate whether the observed effect of cyano group as electron-acceptor substituent in benzene derivatives is general. The

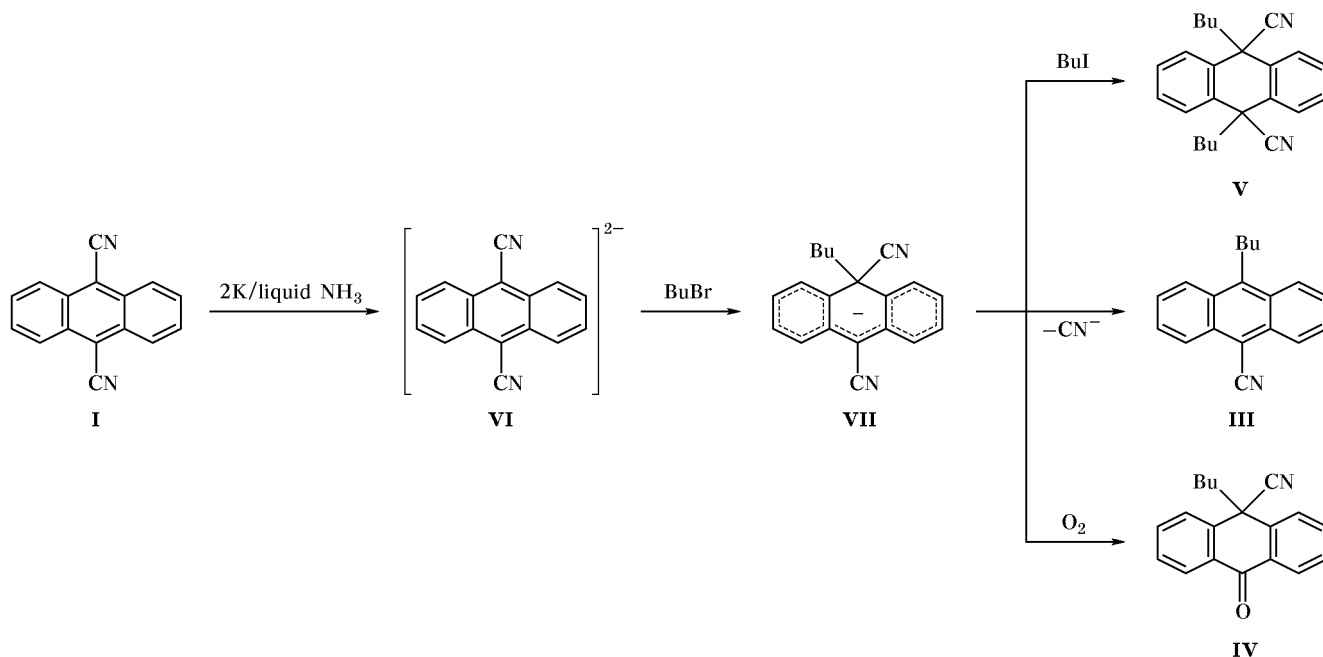
present communication reports on the first step of study in this line. We tried to determine the state of reduction products of 9,10-dicyanoanthracene (**I**) with potassium in liquid ammonia on the basis of the results of their subsequent protonation, oxidation, and reaction with butyl bromide and to compare these results with those obtained by us previously for 9-cyanoanthracene [4, 5].

It is known that electrochemical oxidation of dinitrile **I** by cyclic voltammetry in acetonitrile is characterized by reversible one-electron wave [9], indicating that the corresponding radical anion is stable under these conditions. In the present work substrate **I** was reduced by the procedure which was previously used in a number of analogous cases [1–8]: 1 or 2 equiv of metallic potassium was added to a suspension of dinitrile **I** in liquid ammonia at -33°C under argon. As a result, dark violet solutions containing reduction products were formed. In order to get information on the structure of one-electron reduction products, the ammonia solution was treated with water and ammonium chloride. In both cases, addition of the protonating agent only slightly changed the color of the solution. The latter turned colorless only on exposure to air (after addition of diethyl ether and vaporization of ammonia). The isolated solid product was initial dinitrile **I** containing a small amount (less

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Scheme 1.



than 2%) of 9-cyanoanthracene (**II**). The latter may be formed by decyanation of **I**, which is typical of reactions of reduced forms of cyanoarenes with protic reagents [1–8]. These results suggest that possible transformations of the radical anion derived from dinitrile **I**, e.g., dimerization [2, 4], are reversible (if occurred). The high basicity of compound **I** may be the factor complicating study of its reactivity. However, it was shown previously [5, 8] that even more basic 9-cyanoanthracene and terephthalodinitrile dianions are stable toward liquid ammonia.

Treatment of the one-electron reduction product with butyl bromide for less than 3 h gave only traces of compounds containing butyl group in the anthracene core. The extremely low conversion of dinitrile **I** in this reaction may be due to high electron affinity ($E_{1/2} = -0.9$ V [9, 10]) and hence low reactivity of its radical anion, as compared with the radical anion derived from nitrile **II** ($E_{1/2} = -1.34$ V [11]); the conversion of the latter in the reaction with butyl bromide attains ~80% [4]. By contrast, the two-electron reduction product of dinitrile **I** reacted with butyl bromide under argon to give ~80% of 9-butyl-10-cyanoanthracene (**III**) (see table). In addition, the product mixture contained initial dinitrile **I** and a number of minor products whose yield did not exceed 1–2%: nitrile **II** (which is likely to be formed by the action of traces of water), 10-butyl-10-cyano-9,10-dihydroanthracen-9-one (**IV**), and 9,10-dibutyl-9,10-dicyano-9,10-dihydroanthracene (**V**) (Scheme 1).

Compounds **III–V** were not reported previously; they were isolated by chromatography, and their structure was confirmed by the ^1H NMR, IR, and high-resolution mass spectra (see Experimental).

The formation of the major product, nitrile **III**, can be explained in terms of the scheme proposed previously for analogous reactions of terephthalodinitrile [8]. It includes *ipso*-alkylation of dianion **VI** to give anion **VII**. Further transformations of anions like **VII** [1–8] can include protonation or alkylation with formation of dihydroarenes and decyanation with formation of substituted arene. Among dihydroaryl anions of the benzene, naphthalene, and anthracene series containing one or two cyano groups, only 10-alkyl-10-cyano-9,10-dihydro-9-anthryl anion formed by alkylation of reduced 9-cyanoanthracene species [4, 5], is more prone to give the corresponding dihydroarene, while the other dihydroaryl anions undergo mainly decyanation.

Presumably, a small amount of anthrone **IV** is formed by the action of traces of oxygen on anion **VII**. Although the latter is fairly resistant to decyanation, it is readily oxidized in the presence of oxygen by a mechanism typical for analogous transformations of benzyl cyanides [12]. When alkylation of the two-electron reduction product was carried out in air, anthrone **IV** was formed in a yield of up to 80%, whereas the yield of nitrile **III** decreased to 1–2% (see table). Hasegava *et al.* observed [13] a similar relation between the ratio of products formed by

Reactions of 9,10-dicyanoanthracene (**I**) reduction products with butyl halides

Amounts of reactants, mmol			Composition of products, mmol (GLC data)				
dinitrile I	potassium	butyl halide	dinitrile I	nitrile II	nitrile III	anthrone IV	dinitrile V
2.0	4.0	BuBr, ^a 4.0	0.10	0.04	1.60	0.02	0.02
2.0	4.0	BuBr, 4.0	0.10	0.04	0.02	1.58	0.02
2.0	4.0	BuBr, ^a 4.0	0.02	0.02	0.02	0.08	1.68
		BuI, ^b 4.0					

^a Under argon. ^b Butyl iodide was added 0.5 h after the reaction started, and the mixture was kept for an additional 3 h.

base-catalyzed transformations of 9-X-9,10-dicyano-9,10-dihydroanthracenes (X = CH₂OEt, CH₂SEt), i.e., substituted anthracenes and anthrones, and the temperature, solvent nature, and the presence of oxygen.

The low yield of nitrile **III** in the above experiment indicate a high stability of anion **VII** which undergoes decyanation only at elevated temperature (after vaporization of ammonia). The low reactivity of anion **VII** also follows from the small concentration (1–2%) of dialkyldicyano derivative **V** in product mixtures obtained by reactions with excess butyl bromide. Dinitrile **V** was obtained as the major product when butyl bromide and butyl iodide were added in succession through a time interval of 30 min to the solution formed by two-electron reduction of dinitrile **I** with potassium in liquid ammonia, and the resulting mixture was kept at –35°C for at least 3 h (see table). In this case, compound **V** was a mixture of stereoisomers at a ratio of ~5:3; one of these was isolated in the pure state by chromatography. Its ¹H NMR spectrum contained signals at δ 0.64, 1.20, and 2.35 ppm from protons of the butyl groups; signals at δ 0.82, 1.23, 1.49, and 1.93 ppm in the spectrum of isomeric mixture **V** were assigned to the butyl group protons of the second stereoisomer. It is known that dihydroanthracenes are characterized by nonplanar structure with the central ring having a *boat* conformation [14]. The fact that each isomer gives only one set of signals from the two butyl groups indicates *cis* configuration of the alkyl substituents which occupy either pseudoaxial or pseudoequatorial positions. Comparison of the chemical shifts of the α-CH₂ protons (δ 2.35 and 1.93 ppm, intensity ratio ~5:3) with analogous parameters of *cis*- and *trans*-9,10-dibutyl-9-cyano-9,10-dihydroanthracenes (δ 1.80–2.00 and 2.40 ppm for pseudoaxial and pseudoequatorial α-CH₂ groups, respectively [5]) suggests pseudoequatorial orientation of the butyl groups in the major isomer of **V**.

Our results show that alkylation of the dianion generated from dinitrile **I** by the action of potassium

in liquid ammonia gives rise to a relatively stable dihydroanthryl anion **VII** with geminal cyano and butyl groups. Depending on the reaction conditions (such as temperature, presence of oxygen, and reactivity of alkyl halide), anion **VII** can be converted into three types of products: substituted anthracene **III**, anthrone **IV**, or dihydroanthracene **V**. The mechanism of alkylation of dinitrile **I** dianion, leading to formation of anion **VII**, can include several competing paths, e.g., direct nucleophilic attack on alkyl halide or initial one-electron transfer from the dianion to alkyl halide, followed by combination of the resulting radical anion of **I** and alkyl radical. Elucidation of this problem requires the use of reagents which can be fixed in the products as specific structural fragments, depending on the particular reaction path. This will be the subject of our further investigations.

EXPERIMENTAL

The ¹H NMR spectra were recorded on a Bruker WP-200SY instrument from solutions in CDCl₃. The IR spectra were measured on a Bruker Vector 22 spectrometer from samples pelleted with KBr. The molecular weights were determined from the high-resolution mass spectra which were obtained on a Finnigan MAT-8200 mass spectrometer. The reaction mixtures were analyzed by GLC on a Hewlett-Packard HP 5890 gas chromatograph using an HP-5 column (15000 × 0.53 mm; 5% of biphenyl, 95% of dimethylsiloxane); heat-conductivity detector; carrier gas helium, flow rate 5 ml/min; oven temperature: 1 min at 40°C, 10 deg/min to 240°C; injector temperature 200°C; detector temperature 240°C. The products were identified by gas chromatography–mass spectrometry on a Hewlett-Packard G1081A system consisting of an HP 5890 Series II gas chromatograph and an HP 5971 mass-selective detector; energy of ionizing electrons 70 eV; HP-5 capillary column, 30 m × 0.25 mm × 0.25 μm; carrier gas helium, flow

rate 1 ml/min; oven temperature: 2 min at 50°C, 10 deg/min to 280°C (5 min); injector temperature 280°C; ion source temperature 173°C; data acquisition at 1.2 scan/s in the amu range from 30 to 650.

Liquid ammonia was purified by dissolving metallic sodium and subsequent distillation into a reaction flask cooled to -70°C. 9,10-Dicyanoanthracene was synthesized from 9,10-dibromoanthracene by the procedure described in [15]; mp 334–335°C (from chloroform). Butyl bromide and butyl iodide were purified by passing through a layer of aluminum oxide and subsequent distillation; their boiling points coincided with published data [16]. Metallic sodium and potassium of pure grade were used. Argon of pure grade was dried by passing through a layer of calcined calcium chloride.

Reduction of 9,10-dicyanoanthracene (I) with potassium in liquid ammonia. To a suspension of dinitrile **I** in liquid ammonia ($c = \sim 5 \times 10^{-2}$ M), stirred at -33°C, we added metallic potassium (preliminarily cut into small pieces under a layer of hexane), and the mixture was stirred for 10 min at that temperature.

Reactions of one-electron reduction products of 9,10-dicyanoanthracene (I) with protonating agents. To a solution of one-electron reduction products obtained by the above procedure from 0.251 g (1.1 mmol) of dinitrile **I** and 0.039 g (1 mmol) of potassium we added 10 mmol of water or ammonium chloride. The mixture was kept until liquid ammonia vaporized by half (~0.5 h), and 30–40 ml of diethyl ether was added. When ammonia vaporized completely, 50 ml of water was added. The ether layer was separated, the aqueous layer was extracted with chloroform (2 × 50 ml), and the combined extracts were washed with water and dried over MgSO₄. Removal of the solvent gave 226 mg of a solid product which contained (according to the ¹H NMR and GLC data), 98% of initial dinitrile **I** and 2% of 9-cyanoanthracene (**II**).

Reactions of 9,10-dicyanoanthracene reduction products with butyl halides. The amounts of the reactants and the compositions of products mixtures are given in table. To a solution obtained by reduction of dinitrile **I** with potassium in liquid ammonia (see above) we added butyl bromide. The mixture was stirred for 0.5 h at -33 to -35°C and treated by the procedure described above. The products were identified and quantitated by ¹H NMR spectroscopy and GC-MS. Previously unknown compounds were isolated by thin-layer chromatography on silica gel using chloroform as eluent and were analyzed by spectral methods.

9-Butyl-10-cyanoanthracene (III). mp 108–109°C (from hexane). ¹H NMR spectrum (CDCl₃), δ , ppm: 1.00 t (3H, CH₃), 1.60–1.80 m [4H, (CH₂)₂], 3.73 t (2H, CH₂), 7.50–7.70 m (4H, 2-H, 3-H, 6-H, 7-H), 8.26 d and 8.37 d (2H each, 1-H, 4-H, 5-H, 8-H). IR spectrum, ν , cm⁻¹: 2210 (C≡N), 2930–2950 (C–H, aliph.), 3060–3080 (C–H, arom.). Found: M^+ 259.1358. C₁₉H₁₇N. Calculated: M 259.1361.

10-Butyl-10-cyano-9,10-dihydroanthracen-9-one (IV). mp 75–76°C (from hexane). ¹H NMR spectrum (CDCl₃), δ , ppm: 0.65 t (3H, CH₃), 0.86 m (2H, CH₂), 1.03 m (2H, CH₂), 2.16 t (2H, CH₂), 7.55 t.d and 7.71 t.d (2H each, 2-H, 3-H, 6-H, 7-H), 7.85 d.d and 8.30 d.d (2H each, 1-H, 4-H, 5-H, 8-H). IR spectrum, ν , cm⁻¹: 1710 (C=O), 2120 (C≡N), 2880–3080 (C–H), 3060–3080 (C–H, arom.). Found: M^+ 275.1312. C₁₉H₁₇NO. Calculated: M 275.1310.

cis-9,10-Dibutyl-9,10-dicyano-9,10-dihydroanthracene (V). mp 173–174°C (from hexane). IR spectrum, ν , cm⁻¹: 2220 (C≡N), 2860–3080 (C–H). ¹H NMR spectrum (CDCl₃), δ , ppm: *e,e*-isomer: 0.64 m (10H, 2CH₃CH₂), 1.20 m (4H, 2CH₂), 2.35 t (4H, 2CH₂), 7.49 m and 7.71 m (4H each, H_{arom}). Found: M^+ 342.2089. C₂₄H₂₆N₂. Calculated: M 342.2096; *a,a* isomer: 0.82 t (6H, 2CH₃), 1.23 m (4H, 2CH₂), 1.49 m (4H, 2CH₂), 1.93 t (4H, 2CH₂), 7.49 and 7.80 m (4H each, H_{arom}). Found: M^+ 342.2102. C₂₄H₂₆N₂. Calculated: M 342.2096.

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