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Reductive Activation of Arenes. VII.[1] Alkylation of 9-Cyanoanthracene Two-Electron Reduction Products in Liquid Ammonia.

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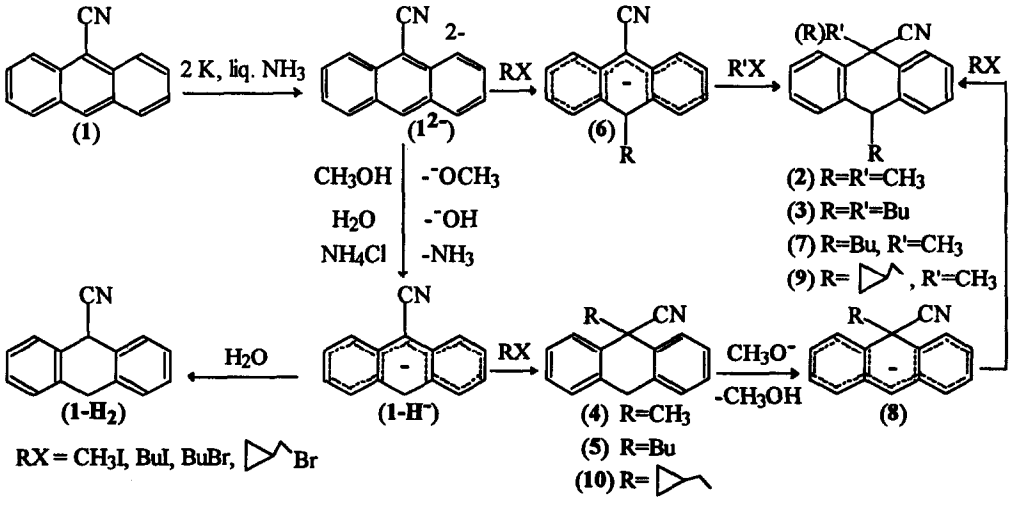
Abstract: The reactions of the 9-cyanoanthracene dianion generated by the action of two equivalents of potassium in liquid ammonia with primary alkyl iodides and bromides gave 9-cyano-9,10-dialkyl-9,10-dihydroanthracenes. The alkylation of the 9-cyano-9,10-dihydro-9-anthryl anion generated by the two-electron reduction of 9-cyanoanthracene in liquid ammonia in the presence of ammonium chloride gave 9-cyano-9-alkyl-9,10-dihydroanthracene. The results obtained by using cyclopropylmethyl bromide as model reagent suggest these reactions to proceed through S_N mechanism. The spatial structure of 9,10-dihydroanthracene derivatives obtained is discussed.

The reduction of aromatic compounds by alkaline metals in liquid ammonia with subsequent protonation or alkylation is a general method for synthesis of dihydro- and alkyldihydroaromatic compounds. The reaction may be performed with various aromatics differing in the substitution degree and the character of substituents (OR, NR_2, R, $SiMe_3$, CO_2^-, CO_2R, $CONR_2$, COR, Ph[2,3], CN[4,5]). The synthetic outcome of the reaction is determined by the regioselectivity of alkylation and the number of alkyl fragments being introduced; hence it directly depends on the nature, structure and properties of anionic intermediates formed in arene reduction[3,7]. Some authors have examined the nature of the reduction products of arenes by alkaline metals in liquid ammonia[6,7]. In the case of aromatic nitriles, it has been shown[6], that the basicity of the dianion $\mathbf{1}^{2-}$ formed in the reduction of 9-cyanoanthracene **1** by two equivalents of potassium is insufficient for its protonation in liquid ammonia. However, the dianion $\mathbf{1}^{2-}$ may be converted to the 9-cyano-9,10-dihydro-9-anthryl anion ($\mathbf{1\text{-}H}^-$) by the action of a stronger protonating agent as compared to ammonia, e.g., by methanol. One can

expect that the alkylation of the products of the two-electron reduction of nitrile **1** in liquid ammonia on the one hand, and in its mixture with methanol on the other should lead to different compounds: the di- and monoalkylated 9-cyano-9,10-dihydroanthracene respectively. Moreover, investigation of the mechanism and regioselectivity of alkylation of $\mathbf{1}^{2-}$ and $\mathbf{1\text{-}H}^-$, and comparison of these data with similar characteristics of the 9-cyanoanthracene radical anion $(\mathbf{1}^{\cdot-})$[8] make it possible to judge about the relationship between the reactivity of the above charged species and their molecular and electronic structure. In the present paper, we have examined the protonation and alkylation of the products of two-electron reduction of nitrile **1** by potassium in liquid ammonia.

RESULTS AND DISCUSSION

We have found that the reaction of nitrile **1** with two equivalents of potassium in liquid ammonia and subsequent treatment of the resulting solution with the excess of water lead to 9-cyano-9,10-dihydroanthracene ($\mathbf{1\text{-}H_2}$) in a mixture with the starting nitrile **1**. The nitrile $\mathbf{1\text{-}H_2}$ was isolated chromatographically in 82 % yield. Its structure was established by PMR and mass-spectroscopy. In addition to the signals of eight aromatic protons, the PMR spectrum of $\mathbf{1\text{-}H_2}$ contains a singlet and two doublets (J = 18.0 Hz) at 5.10, 3.92 and 4.06 ppm respectively, i.e., in the region typical of the resonance of protons in the 9- and 10-positions of 9-X-9,10-dihydroanthracenes (X is an electron-accepting group)[8,9]. The analysis of this result considering the above data about the products of two-electron reduction of nitrile **1** suggests that the dianion $\mathbf{1}^{2-}$ formed at the first stage is protonated by water at the 10-position of the aromatic nucleus having a maximal electron density[6]. The resulting anion $\mathbf{1\text{-}H}^-$ adds a proton to form the final product, nitrile $\mathbf{1\text{-}H_2}$ (scheme 1).



Scheme 1.

The consecutive action of two equivalents of potassium and of alkyl halide (CH_3I or n-BuI) on the nitrile **1** in liquid ammonia without subsequent treatment with water (Tab.1, Nos.1,2) leads to a ~6:1 mixture of 9-cyano-9,10-dialkyl-9,10-dihydroanthracene (**2**, alkyl = CH_3; **3**, alkyl = n-Bu) and 9-cyano-9-alkyl-9,10-dihydroanthracene (**4**, alkyl = CH_3; **5**, alkyl = n-Bu). The product distribution was established by PMR. Compounds **2** and **3** were isolated chromatographically. In addition to the signals of aromatic protons and the protons of two alkyl fragments, the PMR spectra of these nitriles have a signal of a proton at C10 (a quartet or a triplet depending on the alkyl fragment type). Two triplets at 3.98 and 4.16 ppm with a ~5:1 integral intensity ratio in the spectrum of nitrile **3** indicates that the compound is a mixture of two stereoisomers (for details see below). Compound **4** could not be isolated individually. Its structure was assigned by means of analysis of mass- and PMR spectra of the fraction that represents its 1:2 mixture with **2** (see Experimental) taking into account the spectral data of nitrile **5** given earlier[8].

Table 1. Conditions and Yields of Products in the Reactions of $\mathbf{1}^{2-}$ and $\mathbf{1}\text{-}H^-$ with Alkyl Halides.

No[1]	Protonating agent (H^+)	RX	Batches, mmol				Composition of products mixtures, mmol			
			nitrile	potassium	H^+	RX	nitrile **1**	monoalkyl dihydroarene	dialkyl dihydroarene	
1		CH_3I	3.00	6.60		13.00	0.15	**4** 0.42	**2**	2.30
2		BuI	3.00	6.20		6.00		**5** 0.45	**3**[2]	2.47
3[3]		1) BuI	4.00	8.20		1) 4.00			**7**	2.50
		2)CH_3I				2) 8.00				
4	CH_3OH	CH_3I	3.00	6.60	3.00	13.00		**4** 0.30	**2**	1.82
5	CH_3OH	CH_3I	2.50	5.10	2.50	25.00	0.34	**4** 0.37	**2**	1.46
6	NH_4Cl	BuBr	2.00	4.00	2.00	2.00	0.32	**5** 1.60		
7	CH_3OH	BuI	2.50	5.10	12.50	12.50	0.49	**5** 1.01	**3**[4]	0.76
8		1) 	4.00	8.20		1) 4.00		**4** 0.49	**2**	0.49
		2) CH_3I				2) 8.00			**9**	2.92
9	NH_4Cl		2.00	4.00	2.00	2.00	0.40	**10** 1.60		

Notes.

1 Experiment No.5 performed acc. to I, the others acc. to II (see Experimental).

2 Stereoisomer ratio 5:1.

3 In addition to nitrile **7**, 130 mg of a mixture of mono- and dialkyldihydroderivatives of **1** is formed (20 % of the total amount of reaction products).

4 Stereoisomer ratio 4:1.

Compounds **4** and **5**, evidently, owe their origin to the presence of residual moisture in ammonia, providing partial protonation of $\mathbf{1}^{2-}$ to form **1**-$\mathbf{H}^-$ (cf. [6]), alkylation of which leads to these products. The main reaction products, dialkyldihydroarenes **2** and **3**, are formed in the alkylation of $\mathbf{1}^{2-}$. The alkylation seems to follow the pathway similar to that considered above for the protonation of $\mathbf{1}^{2-}$ (scheme 1): the alkyl fragment adds in the 10-position of $\mathbf{1}^{2-}$ to form the 9-cyano-10-alkyl-9,10-dihydro-9-anthryl anion **6**, and further alkylation of **6** leads to the final products. In agreement with these notions, sequential addition of one equivalent of n-butyl iodide and the excess of methyl iodide to the product of two-electron reduction of nitrile **1** in liquid ammonia (Tab.1, No.3) gave mainly 9-cyano-9-methyl-10-butyl-9,10-dihydroanthracene **7** (80 % w/w of total amount of the reaction products). The following spectral data indicate the location of the alkyl fragments in nitrile **7**: a triplet at 4.10 ppm corresponding to the proton at C10 bonded to butyl, and a singlet of methyl at 1.95 ppm (see Experimental). The PMR spectrum shows that the mixture also has mono- and dialkyldihydroderivatives of **1** containing the methyl and butyl fragments. Their structures are not evident, but the position of the signals of protons at C10 and in the alkyl groups, as well as character of their splitting and intensity, shows that the alkyl groups are bonded with the sp^3-hybrid carbon atoms. The mono- and dialkyl derivatives are present in the mixture in nearly equal amounts. The amount of these compounds is about ~20 % of the reaction products. Their formation may be due to partial protonation of $\mathbf{1}^{2-}$ (see above), or to the competing reactions of alkyl halides with $\mathbf{1}^{2-}$, **1**-$\mathbf{H}^-$ and **6**. Thus, the result obtained suggests predominant para-orientation of the electrophylic attack relative to the cyano group, both in the alkylation of $\mathbf{1}^{2-}$ and in the protonation. This is in agreement with influence of the cyano group on the negative charge distribution in $\mathbf{1}^{2-}$ and with a tendency toward formation of the anion **6** that is the most stable isomer among cyanodihydroaryl anions (see [6]).

The reaction of the **1**-$\mathbf{H}^-$ anion with alkyl halides should lead to dihydroarenes **1**-$\mathbf{H_2}$ containing an alkyl fragment in the 9-position. It is known, however, that such reactions of anions are generally complicated by subsequent alkylation processes involving a base (an amide or an alkoxide) formed at the stage of protonation of the arene dianion[2,3] (see scheme 1). This leads to formation of di- and, in some cases, trialkyldihydroarenes along with the mono-derivatives[10]. Indeed, the addition of methyl iodide to the product of the two-electron reduction of **1** by potassium in liquid ammonia in the presence of methanol gave a 6:1 mixture of nitriles **2** and **4** (by PMR). When we used the "inverse quenching" procedure (an addition of the ammonia solution of the **1**-$\mathbf{H}^-$ salt, prepared as described above, to the cooled solution of methyl iodide in THF) the content of **4** among the reaction products slightly increased (cf. exp. 4 and 5 in Tab.1). This result agrees with the above assumption that dialkyldihydroarene is formed through a secondary deprotonation/alkylation reactions (see scheme 1). The lesser degree of subsequent alkylation in experiment 5 may be due to partial neutralization of the base by the excess of the alkyl halide or by the ammonium salt formed in its solvolysis. By using ammonium chloride as a protonating agent, giving no strong bases as a result of deprotonation, subsequent alkylation may be completely excluded to obtain monoalkyldihydroarene **5** in the reaction with butyl bromide (Tab.1, No.6).

As noted above, the reaction of $\mathbf{1}^{2-}$ with butyl iodide leads to the formation of nitrile **3** as a mixture of stereoisomers (5:1). A stereochemically similar result is achieved by the reaction of butyl iodide with products of the reduction of **1** by two equivalents of potassium in liquid ammonia in the presence of methanol (Tab.1, No.7), i.e., by sequential alkylation of **1**-$\mathbf{H}^-$ and **8** (scheme 1, see above). The analysis of spectral data of the reaction products and their comparison with literature data allow us to judge about the structure of

stereoisomers. As shown elsewhere (see, e.g., [11]), dihydroanthracenes typically have a nonplanar structure in which the central ring has a "boat" conformation with the alkyl substituents in predominantly pseudoaxial positions[12,13]. Thus, cis-9-cyano-9,10-dibutyl-9,10-dihydro-anthracene probably has the structure 3-a,a (fig.1; the letters a and e denote spatial arrangement of alkyl groups at C9 and C10); the trans-isomer seems to be an equilibrium mixture of the conformations 3-a,e and 3-e,a.

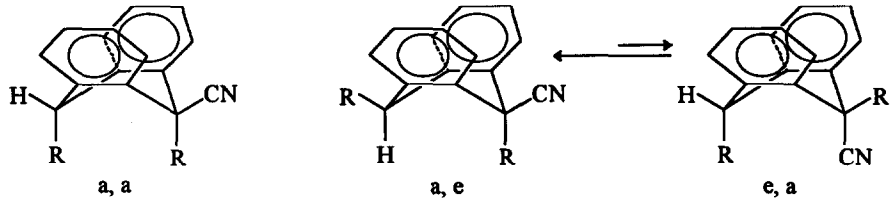


Fig. 1.

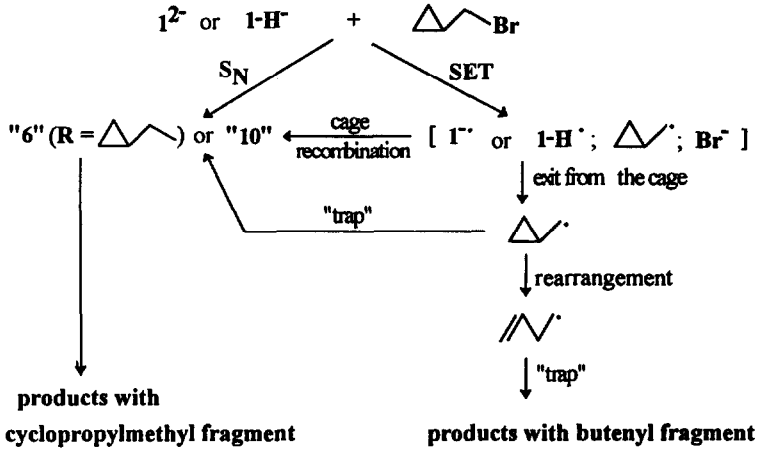
By taking into account that the pseudoequatorial protons in dihydroanthracenes generally absorb in a stronger field than the pseudoaxial ones[12], the more intense triplet at 3.98 ppm in the spectrum of 3 may be assigned to the pseudoequatorial proton in cis-isomer and triplet of lower intensity at 4.16 ppm to pseudoaxial proton of the trans-isomer existing predominantly in the 3-a,e conformation. This assignment is confirmed by the vicinal constant values of spin-spin coupling of protons at C10 and alkyl, with the greater one (7.5 Hz *vs* 5.0 Hz) belonging to triplet of cis-isomer (cf. [13]). Thus, in the reactions with $\mathbf{1}^{2-}$ and **1**-H$^-$, dibutyldihydroarene 3 is formed as a mixture of cis- and trans-isomers where the cis-isomer is predominant. However, alkylation of $\mathbf{1}^{2-}$ with methyl iodide or sequentially with butyl iodide and the excess of methyl iodide leads only to the cis-isomer of nitriles 2 and 7, since H10 manifests itself in the PMR spectra as a quartet or a triplet respectively with the vicinal spin-spin coupling constants J_{10,CH_n} = 7.0 - 7.5 Hz.

Comparison of these results with literature data[13] on the high stereoselectivity of formation of cis-dialkyldihydroarenes in the reductive alkylation of anthracene by primary alkyl halides suggests that introduction of the cyano group does not change the stereochemistry of the reactions.

As mentioned above, the spatial structures of 2 and 3 are independent of the route of the formation of these compounds. As in[13,15] we assumed that the stereoisomer product ratio is set at the stage of alkylation of their precursors (anions 6 (Tab.1, Nos.1,2,3) or anions 8 (Tab.1, Nos.4,5,7)). Comparison of the results of alkylation of anion 6 (R = n-Bu) by two different alkyl iodides is in agreement with the conclusion[13] that the size of the alkyl group in alkyl halide is a factor governing stereochemistry of the reaction. The experimental results in general are consistent with ideas on stereochemistry of the reductive alkylation of anthracene and its derivatives[9,13,15].

Let us discuss the mechanism of interaction of $\mathbf{1}^{2-}$ and **1**-H$^-$ with alkyl halides. It is known[16-18] that the dianions of arene functional derivatives in reactions with alkylating reagents may show the properties of both nucleophiles and one-electron reducing reagents. The mechanism of nucleophilic substitution is generally ascribed to the reactions of cyclohexadienyl anions, though the electron transfer to alkyl halide with further recombination of radicals is also not excluded[19]. To distinguish between these pathways one can use the reagents generating fast rearranging radicals along the SET mechanism leading to the products containing

rearranged alkyl fragment[20]. If the recombination of the alkyl radical with arene radical anion or cyclohexadienyl radical in a primary singlet pair (formed by electron transfer from the respective anion to alkyl halide) is faster than rearrangement of probing alkyl radical or its exit from the cage, then this approach wouldn't allow to distinguish this mechanism from the classical S_N mechanism (scheme 2). The kinetic and stereochemical approaches generally used to recognize the S_N mechanism do not ensure this either. Thus, to the SET channel only those variants of mechanism can reliably be assigned which include the exit of the alkyl radical from the cage.



Scheme 2.

However, the complete cage recombination seems to be unlikely in the case under consideration. According to [21], the alkyl radicals formed by photolysis of diacyl peroxides recombinate in a primary cage in pentane or decaline to 35 and 50 %, respectively, and the reasons are not seen for the rates of cage recombination of alkyl radical with radical anion or cyclohexadienyl radical to be faster. The efficiency of cage reactions is considered[22] dependable on many parameters, being dominated by viscosity of the solvent controlling the rate of diffusion exit of radicals from the cage[21,22]. The viscosity of liquid ammonia used as a solvent (0.26 sP at 238 K[23]) is close to that of pentane (0.21 sP at 303 K[22]). Increased stability of arene radical anion and cyclohexadienyl radical as compared to alkyl radical and, as a consequence, decreased rate of recombination and decreased solvating ability of ammonia in relation to pentane can only reduce the efficiency of the cage process and raise the probability of radicals exit from the cage[22]. Therefore, in the electron transfer from the arene dianion or the cyclohexadienyl anion to alkyl halide in liquid ammonia, a considerable portion of the alkyl radicals formed is expected to leave the cage. As for the possibility that the interaction of alkyl radicals escaping the cage with the "trap" could be faster than their rearrangement, it seems negligible. It has been shown by ESR[21] (detecting out-of-cage radicals) that above 173 K the cyclopropylmethyl radicals virtually completely rearrange to the butenyl radicals before they react with each other or with a solvent. According to these data, the formation of 4-pentenylcyclopropane and 1,2-dicyclopropylethane through

photolysis of cyclopropylacetyl peroxide is the result of cage recombination[21], i.e., the rate of rearrangement of cyclopropylmethyl radicals is high enough for this process to compete with cage recombination and diffusion. Moreover, the reactions of cyclopropylmethyl halides with dianions of benzophenone anil in THF at 295 K[16] or of terephthalodinitrile (in liquid ammonia at 240 K[24]), which are structurally similar to the species under this study, yield the products containing rearranged alkyl fragments. It means that in the reactions of these alkyl halides with 1^{2-} and **1**-H$^-$ the primary alkyl radical should rearrange, at least partly, before its reaction with a "trap". Even the 5-hexenyl radical formed during the Wittig rearrangement of benzhydrol 5-hexenyl ether completely rearranges after an exit from a primary cage, and then recombinates with the benzophenone radical anion (Li-salt, THF, 296 K[25]), though its rate of rearrangement ($k = 10^5$ s^{-1} [26]) is much smaller than for the cyclopropylmethyl radical ($k = 9\times10^7$ s^{-1} at 295 K, 5×10^6 s^{-1} at 240 K[27]).

Taking into account these considerations, we have chosen cyclopropylmethyl bromide as a model reagent. It has been found that the consecutive reactions of this reagent and methyl iodide with the product of two-electron reduction of **1** by potassium in liquid ammonia lead to 9-cyano-9-methyl-10-cyclopropylmethyl-9,10-dihydroanthracene **9**. In the alkylation of **1**-H$^-$, generated by the reduction of **1** in the presence of ammonium chloride, by cyclopropylmethyl bromide, 9-cyano-9-cyclopropylmethyl-9,10-dihydroanthracene **10** is formed (Tab.1, Nos.8,9). The structure of nitrile **9** is confirmed by the similarity of the PMR data relating to position of its substituents to those of **7** (see above). Spectral data of **10** coincide with those described earlier[8]. No compounds with the butenyl fragment have been detected in the mixtures.

Thus, our results suggest that the reactions of 1^{2-} and **1**-H$^-$ with primary alkyl halides occur at least predominantly by the S_N mechanism. The SET mechanism would have led to formation of pronounced amount of products with rearranged alkyl fragment. A similar conclusion has earlier been made on the same grounds for the 9-cyanoanthracene radical anion $1^{\cdot-}$ [8]. Thus, all products of nitrile **1** reduction - radical anion $1^{\cdot-}$, dianion 1^{2-}, and anion **1**-H$^-$- show nucleophilic properties in this reaction.

Comparison of the present data and previous ones[8] concerning the structure of cyanoalkyldihydroarenes formed by the reactions of one- and two-electron reduction products of **1** with alkyl halides shows that the regioselectivities inherent in these reactions are different. In the case of radical anion $1^{\cdot-}$, the ipso-position is alkylated whereas in the case of the dianion 1^{2-} the position para to the cyano group. In the reactions of 1^{2-}, the orientation of alkylation is in line with either electron density distribution in the dianion or the relative stability of the resulting anions of type **6**[6]. However, for $1^{\cdot-}$ the orientation may be determined by the distribution of the π-electronic charge (by analogy with the data of [29] for the benzonitrile radical anion), the greater part of which is on the ipso-carbon atom ($q_{ipso} = -0.253$; $q_{para} = -0.216$; calculations were carried out using optimized (RHF/PM3) geometry by the UHF/INDO method). The relative energy values of isomeric cyano substituted cyclohexadienyl radicals[30] do not explain the observed regioselectivity.

As for the synthetic aspect of these results, we note that the alkylation of $1^{\cdot-}$ [8] and **1**-H$^-$ forms monoalkyldihydroarenes of a similar structure. However, in the case of **1**-H$^-$, substrate activation by the two-electron reduction provides a higher degree of its conversion into the reaction products (80 %) compared to the radical anion (max 50 %). The alkylation of 1^{2-} affords dialkyldihydroarenes (yield 60-75 %) containing two similar or different alkyl fragments. In the latter case, one can probably change their position in the reaction product by alternating the sequence of alkyl halides introducing into the reaction.

EXPERIMENTAL

The ^{1}H-NMR spectra were recorded on Bruker AC-200 and Bruker WP-200 SY instruments for the 5 % $(CD_3)_2CO$ and $CDCl_3$ solutions using $((CH_3)_3Si)_2O$ as an internal standard. Exact values of molecular ion masses were measured by high-resolution mass-spectrometry on Finnigan MAT-8200.

The following compounds and solvents were used:

Tetrahydrofurane purified acc. to. [31].

Liquid ammonia purified by dissolving metallic sodium in it with subsequent distillation into the reactor cooled to -70 °C.

9-Cyanoanthracene prepared acc. to [32] from 9-anthraldehyde. Mp (from hexane) 175-176 °C (173-174 °C[33]).

Alkyl halides (methyl iodide, n-butyl iodide, n-butyl bromide) purified by passing through aluminium oxide with subsequent distillation, bp correspond to literature data[34].

Argon purified by passing through two glass vessels connected with a THF solution of disodium benzophenone.

Cyclopropylmethyl bromide obtained acc. to [35] from cyclopropylmethanol bought from Merck-Schuchardt.

Reduction of 9-cyanoanthracene **1** *by potassium in liquid ammonia.* To obtain the dianion $\mathbf{1}^{2-}$, potassium cut into pieces under a THF layer was added with stirring to a suspension of nitrile **1** in liquid ammonia (conc. 5×10^{-2} M) at -33 °C in an argon atmosphere. The reaction mixture was kept under this condition for 10 min.

To obtain the **1**-$\mathbf{H}^-$ anion, potassium and a protonating agent (CH_3OH, NH_4Cl) were added in series.

Reaction of the products of reduction of **1** *with alkyl halides and water.* I) A solution of the reduction products prepared as described above was added with stirring in an argon atmosphere to a THF solution of alkyl halide excess cooled to -35 °C. The mixture was stirred for 20 min, then 50 ml of diethyl ether was added. After ammonia had been evaporated, the reaction mixture was diluted with water and extracted with diethyl ether (350 ml). The consolidated ether extract was washed with water, and then dried over $MgSO_4$. The mixture of reaction products obtained after solvent evaporation was analyzed by PMR. II) The necessary amount of electrophile was added dropwise to the solution of the products of reduction of **1** prepared as described above, and the mixture was stirred until half of the initial amount of liquid ammonia evaporated. Further treatment of the reaction mixture and product analysis were carried out as described above.

Table 1 lists the batches, reagent ratio, and composition of products mixtures.

New compounds were isolated by TLC on silica gel, eluent was hexane:diethyl ether (9:1).

Purity of compounds was PMR controlled.

9-Cyano-9,10-dihydroanthracene **1**-$\mathbf{H_2}$: yield 82 %, mp 101-102 °C (ethanol), ^{1}H-NMR ($CDCl_3$) δ 7.20-7.70 (m, 8H, H1-4,5-8), 5.10 (s, 1H, H9), 3.92, 4.06 (both d, $J_{10,10'}$ = 18.0 Hz, at 1H, H10,10') ppm. HRMS calcd for $C_{15}H_{11}N$: 205.0891. Found: 205.0884.

9-Cyano-9,10-dimethyl-9,10-dihydroanthracene **2**: yield 70 %, liquid, ^{1}H-NMR ($(CD_3)_2CO$) δ 7.40-7.80 (m, 8H, H1-4,5-8), 4.23 (q, $J_{10,CH3}$ = 7.5 Hz, 1H, H10), 1.90 (s, 3H, C9CH_3), 1.48 (d, $J_{10,CH3}$ = 7.5 Hz, 3H, C10CH_3) ppm. HRMS calcd for $C_{17}H_{15}N$: 233.1205. Found: 233.1204.

9-Cyano-9,10-dibutyl-9,10-dihydroanthracene **3**: yield 76 %, liquid, ^{1}H-NMR ($(CD_3)_2CO$) δ 7.20-7.75 (m, 8H, H1-4,5-8), 3.98 (t, $J_{10,CH2}$ = 7.5 Hz, 1H, H10, cis-isomer), 4.16 (t, $J_{10,CH2}$ =5.0 Hz, 1H, H10, trans-isomer), 0.79-1.95 (m, 18H, C9Bu, C10Bu) ppm. HRMS calcd for $C_{23}H_{27}N$: 317.2144. Found: 317.2136.

9-Cyano-9-methyl-10-butyl-9,10-dihydroanthracene **7**: yield 60 %, liquid, ^{1}H-NMR ($(CD_3)_2CO$) δ 7.39-7.78 (m, 8H, H1-4,5-8), 4.10 (t, $J_{10,CH2}$ =7.0 Hz, 1H, H10), 1.95 (s, 3H, C9CH_3), 0.83-1.73 (m, 9H, C10Bu) ppm. HRMS calcd for $C_{20}H_{21}N$: 275.1674. Found: 275.1679.

9-Cyano-9-methyl-10-cyclopropylmethyl-9,10-dihydroanthracene **9**: yield 70 %, liquid, ^{1}H-NMR ($CDCl_3$) 7.34-7.79 (m, 8H, H1-4,5-8), 4.11 (t, $J_{10,CH2}$ =7.0 Hz, 1H, H10), 1.95 (s, 3H, C9CH_3), 1.60 (dd, $J_{10,CH2}$ = $J_{\alpha,\beta}$ = 7.0 Hz, C10CH_2-), 0.04-0.72 (m, 5H, c-C_3H_5) ppm. HRMS calcd for $C_{20}H_{19}N$: 273.1517. Found: 273.1557.

The structure of compound **4**, which was not isolated individually, was conjectured from the analysis of the ^{1}H-NMR spectrum of the mixture of compounds obtained in experiment 1, Table 1. The signals of nitrile **4** are 7.30-7.80 (m, 8H, H1-4,5-8), 4.06, 4.18 (both d, $J_{10,10'}$ = 19.0 Hz, at 1H, H10,10'), 1.74 (s, 3H, C9CH_3) ppm. As shown by mass-spectrometry, the mixture contains compounds with mass numbers 219 (nitrile **4**, $C_{16}H_{13}N$) and 233 (nitrile **2**, $C_{17}H_{15}N$).

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REFERENCES AND NOTES

1. Communication VI. Selivanov, B. A.; Shteingarts V. D. *Zh. Org. Khim.* Submitted for publication.
2. Rabideau, P. W. *Tetrahedron.* **1989**, *45*, 1579-1603.
3. Rabideau, P. W.; Marcinow, Z. *Organic Reactions, vol. 42;* Paquette, L. A. et al Eds.; John Wiley and Sons, Inc.: New York, **1992**; pp. 1-334.
4. Vaganova, T. A.; Bilkis, I. I.; Shteingarts, V. D. *Zh. Org. Khim.* **1986**, *22*, 2239-2240.
5. Schultz, A. G.; Macielag, M. *J. Org. Chem.* **1986**, *51*, 4983-4987.
6. Bilkis, I. I.; Vaganova, T. A.; Panteleeva, E. V.; Tananakin, A. P.; Salnikov, G. E.; Mamatyuk, V. I.; Shteingarts, V. D. *J. Phys. Org. Chem.* **1994**, 7, 153-161.
7. Mullen, K.; Huber, W.; Neumann, G.; Schnieders, C.; Unterberg, H. *J. Am. Chem. Soc.* **1985**, *107*, 801-807.

8. Bilkis, I. I.; Vaganova, T. A.; Pimnev, S. M.; Shteingarts, V. D. *Zh. Org. Khim.* **1991**, *27*, 1722-1727.
9. Rabideau, P. W.; Day, L. M.; Husted, C. A.; Mooney, J. L.; Wetzel, D. M. *J. Org. Chem.* **1986**, *51*, 1681-1686.
10. Lindow, D. F.; Cortez, C. N.; Harvey, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 5406-5412.
11. Rabideau, P. W. *Accounts Chem. Res.* **1978**, *11*, 141-147.
12. Cho, H.; Harvey, R. G.; Rabideau, P. W. *J. Am. Chem. Soc.* **1975**, *97*, 1140-1145.
13. Fu, P. P.; Harvey, R. G.; Paschal, J. W.; Rabideau, P. W. *J. Am. Chem. Soc.* **1975**, *97*, 1145-1153.
14. Harvey, R. G.; Arzadon, L. *Tetrahedron.* **1969**, *25*, 4887-4894.
15. Rabideau, P. W.; Burkholder, E. G. *J. Org. Chem.* **1979**, *44*, 2354-2357.
16. Smith, J. G.; Irwin, D. C. *J. Am. Chem. Soc.* **1980**, *102*, 2757-2759.
17. Selivanov, B. A.; Bilkis, I. I.; Danilov, I. S.; Shteingarts, V. D. *Zh. Org. Khim.* **1982**, *18*, 2143-2152.
18. Danilova, N. K.; Shteingarts, V. D. *Zh. Org. Khim.* **1986**, *22*, 785-794.
19. Bank, S.; Bank, J. F. *Organic Free Radicals.* Pryor, W. A. Eds.; Am. Chem. Soc.: Washington, 1978; pp. 343-358.
20. Bilkis, I. I.; Shteingarts, V. D. *Izv. Sib. Otd. Acad. Nauk SSSR. Ser. Khim. Nauk.* **1987**, *17*, 105-131; Newcomb, M.; Curran, D. P. *Accounts Chem. Res.* **1988**, *21*, 206-214.
21. Sheldon, R. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1970**, *92*, 4395-4404.
22. Sheldon, R. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1970**, *92*, 5175-5186.
23. Makhija, R. C.; Stairs, R. A. *Can. J. Chem.* **1970**, *48*, 1214-1218.
24. Bilkis, I.; Vaganova, T.; Panteleeva, E.; Shteingarts, V. *10 Congress IUPAC on Physical Organic Chemistry. Haifa.* **1990**; p.224.
25. Garst, G. F.; Smith, C. D. *J. Am. Chem. Soc.* **1976**, *98*, 1526-1537.
26. Lal, D.; Griller, D.; Hasband, S.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6355-6357.
27. Newcomb, M.; Glehn, A. *J. Am. Chem. Soc.* **1989**, *111*, 275-277.
28. Elving, P. G.; Markowitz, J. M.; Rosental, I. *J. Electrochem. Soc.* **1954**, *101*, 195-202.
29. Bilkis, I. I.; Vaganova, T. A.; Bobyleva, V. I.; Shteingarts, V. D. *Zh. Org. Khim.* **1991**, *27*, 48-56.
30. Birch, A. J.; Hindle, A. L.; Radom, L. *J. Am. Chem. Soc.* **1980**, *102*, 4074-4080.
31. Malykhin, E. V.; Mamatyuk, V. I.; Shteingarts, V. D. *Izv. Sib. Otd. Acad. Nauk SSSR. Ser. Khim. Nauk.* **1979**, *12*, 142-145.
32. Campagna, F.; Carrotti, A. G.; Casini, G. A. *Tetrahedron Lett.* **1977**, *21*, 1813-1816.
33. Calas, R.; Deschamps, *J. Bull. Soc. Chim. Fran.* **1950**, 1034.
34. *Spravochnik Khimika.* Nikolskij, B. P. Eds.; Goskhimizdat; Moskva, 1963.
35. Willey, G. A.; Herskowits, R. L.; Rein, B. M.; Cheng, D. C. *J. Am. Chem. Soc.* **1964**, *86*, 964-965.

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