

Reductive Activation of Arenes: XIX.* Mechanism and Some Synthetic Applications of the Alkylation of Phthalodinitrile Radical Anion

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Abstract—Using cyclopropylmethyl bromide as mechanism-sensitive reagent, it was shown that the reaction of phthalonitrile radical anion with alkyl halides in liquid ammonia involves electron transfer. The effects of the nature of alkyl bromide and counterion in the radical anion salt and reaction conditions on the ratio of 2-alkylbenzonitrile, 4-alkylphthalonitrile, and 2,5-dialkylbenzonitrile were studied. Phthalodinitrile radical anion was found to undergo dimerization with formation of biphenyl-2,3',4'-tricarbonitrile. The examined transformations may underlie syntheses of phthalonitriles modified at the 4-position.

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We previously showed [2] that the alkylation of phthalonitrile radical anion (**II**) [which is generated by the action of metallic potassium on phthalonitrile **I** in liquid ammonia via single-electron transfer] with butyl, *sec*-butyl, and *tert*-butyl bromides and iodides gives products corresponding to replacement in the initial dinitrile of one cyano group (2-alkylbenzonitriles **III**), hydrogen atom (4-alkylphthalonitriles **IV**), and both these (2,5-dialkylbenzonitriles **V**). Compounds **IV** and **V** are formed from the same anionic precursor (Scheme 1), and their ratio depends on the nature of the halogen atom and structure of the alkyl fragment. The formation of products **IV** and **V** and the weak dependence of the site of alkylation on the alkyl halide structure were rationalized assuming that the reaction mechanism involves electron transfer (ET) from radical anion **II** to alkyl halide, followed by combination of the resulting alkyl radical with another radical anion **II** species.

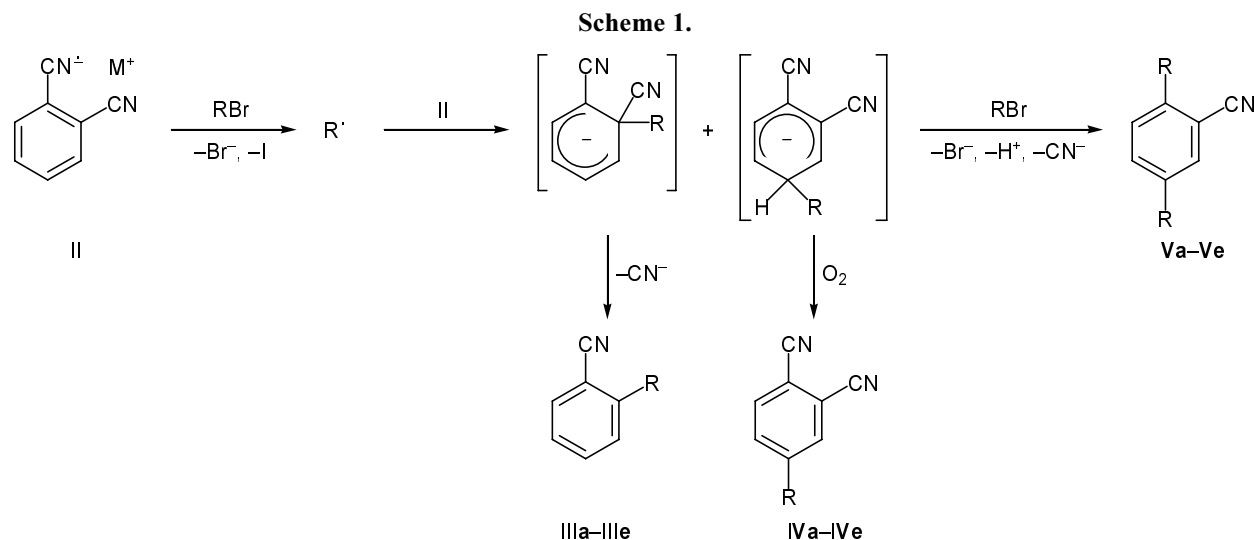
Analysis of the results of alkylation of radical anion **II** from the viewpoint of their synthetic utility led us to presume that 4-alkylphthalonitriles are potential precursors of modified phthalocyanines [3]. Interest in

phthalocyanine-based dyes and pigments has recently increased to an appreciable extent due to appearance of new fields of their possible application in technics [4] and medicine [5]. Insofar as the reaction under study provides the shortest synthetic route to such compounds, we believed it worthwhile to study in detail its mechanism and estimate the possibility of using this reaction as general approach to phthalonitriles and benzonitriles having alkyl and modified alkyl substituents.

Therefore, the present work was aimed at substantiating the proposed mechanism of alkylation of radical anion **II** on the basis of experimental data, elucidating the possibility for extending structural diversity of alkylating agents, and synthesizing substituted benzonitriles and phthalonitriles most of which (with a few exceptions, see below) were not reported previously.

In order to obtain experimental proofs for ET mechanism in the alkylation of radical anion **II** we used cyclopropylmethyl bromide as radical-clock testing reagent. Single-electron transfer reduction of cyclopropylmethyl bromide gives cyclopropylmethyl radical which quickly isomerizes into 3-butenyl radical ($k_i =$

* For communication XVIII, see [1].



$4.8 \times 10^5 \text{ s}^{-1}$ at -33°C [6]). If radical anion **II** is present in the reaction system, the isomerization of cyclopropylmethyl radical competes with its combination with radical anion **II** ($k \approx 10^9 \text{ mol l}^{-1} \text{ s}^{-1}$ [7]). On the other hand, 3-butenyl radical formed as a result of isomerization also reacts with **II**. Therefore, we should expect formation of isomeric products having nonisomerized cyclopropylmethyl fragment (n products) and isomerized 3-butenyl fragment (i products) (cf. [8]), whose ratio n/i depends on the ratio of the rates of isomerization of cyclopropylmethyl radical and its combination with radical anion **II** (Scheme 2). If the reaction under study follows nucleophilic substitution mechanism (S_{N}), the products should contain only cyclopropylmethyl fragment.

We have found that radical anion **II** with potassium as counterion reacts with cyclopropylmethyl bromide in liquid ammonia to give products with both nonisomerized [2-(cyclopropylmethyl)benzonitrile (**IIIa**) and 4-(cyclopropylmethyl)phthalonitrile (**IVa**)] and isomerized alkyl fragments [2-(but-3-en-1-yl)benzonitrile (**IIIb**) and 4-(but-3-en-1-yl)phthalonitrile (**IVb**)] (run nos. 1, 2; Table 1). The products having a cyclopropylmethyl substituent, previously unknown compounds

IIIa and **IVa**, were isolated as individual substances and were characterized by ^1H NMR, IR, and high-resolution mass spectra. Compounds **IIIb** and **IVb** with isomerized alkyl fragment were isolated only as mixtures with isomers **IIIa** and **IVa**, respectively. Analysis of these mixtures by gas chromatography–mass spectrometry showed the presence of components with the molecular weights 157 and 182, which correspond to compounds **IIIa**, **IIIb** and **IVa**, **IVb**, respectively. Signals in the ^1H NMR spectra of nitriles **IIIa**, **IIIb**, **IVa**, and **IVb** (see Experimental) were assigned by comparison with the spectra of butyl-substituted analogs [2]. The cyclopropylmethyl fragment in molecules **IIIa** and **IVa** gives rise to a doublet at δ 2.50–2.80 ppm from two protons of the α -methylene group, a multiplet at δ 0.60–1.20 ppm from the CH proton, and two multiplets in the regions δ 0.10–0.30 and 0.30–0.60 ppm from methylene protons in the cyclopropane ring. Compounds **IIIb** and **IVb** showed in the ^1H NMR spectra the following signals from the but-3-en-1-yl fragment: a multiplet at δ 5.60–6.70 ppm from the CH= proton, a 2H-multiplet at δ 4.80–5.00 ppm from the CH₂= protons, a quartet at δ 2.43 ppm from the CH₂ group in the α -position with respect to the

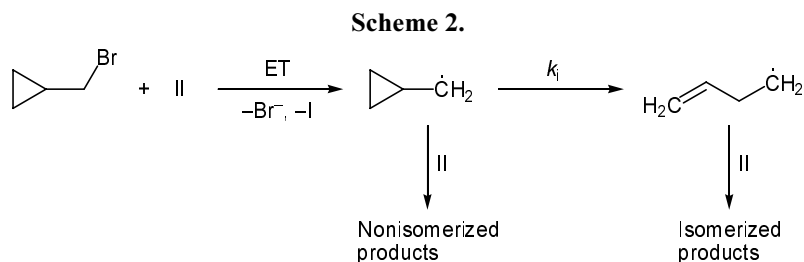


Table 1. Reactions of radical anion **II** with alkyl halides in liquid ammonia

Run no.	Amounts of reactants, mmol			II , mol/l	Time, h	Product composition, mmol (yield, mol %) ^{a, b}				
	I	metal	alkyl halide			I	III	IV	V	VI
1	5.1	K, 5.0	Cyclopropylmethyl bromide, 2.5	0.1	1	2.47	a : 0.96 (38), b : 0.03 (1.2)	a : 0.42 (17), b : 0.04 (1.6)	(< 1)	(< 1)
2	3.1	K, 3.0	Cyclopropylmethyl bromide, 1.5	0.009	3.5	1.22	a : 0.58 (39), b : 0.08 (5)	a : 0.24 (16), b : 0.11 (7)	(< 1)	
3	5.0	Na, 4.7	Octyl bromide, 2.5	0.125	1	0.94	c : 0.92 (39)	c : 0.53 (22)	c : 0.12 (5)	0.50 (21)
4	5.0	Na, 4.8	Hex-5-en-1-yl bromide, 2.5	0.1	1	2.40	d : 0.90 (38)	d : 0.50 (20)	d : 0.21 (9)	0.11 (5)
5 ^c	5.1	K, 5.0	Butyl bromide, 2.5	0.1	1	3.32	e : 0.80 (32)	e : 0.50 (20)	e : 0.10 (4)	(< 1)
6	12.5	K, 12.0	Butyl bromide, 6.25	0.25	1	5.00	e : 1.80 (30)	e : 0.85 (14)	e : 0.74 (12)	0.46 (8)
7	12.5	Na, 12.0	Butyl bromide, 6.25	0.25	1	3.40	e : 1.80 (30)	e : 1.00 (17)	e : 0.40 (7)	0.44 (7)

^a Averaged values from the results of at least two experiments are given (the error for the main products does not exceed 2%). The yields were calculated on the initial amount of the metal with account taken of the reaction stoichiometry.

^b The reaction mixture also contained unidentified compounds in an overall amount of ~5% and benzonitrile (<5%), the latter being formed via protonation of radical anion **II**.

^c Data of [2].

double bond, and a triplet at δ 2.93 ppm from protons of the CH₂ group contiguous to the aromatic ring.

The presence of but-3-en-1-yl-substituted compounds **IIIb** and **IVb** among the products indicates that the reaction involves electron transfer from radical anion **II** to alkyl halides (the results of our model experiments [8] ruled out alternative ways of isomerization of the cyclopropylmethyl moiety in the initial bromide and alkylation products). The overall *n/i* ratios [(**IIIa**+**IVa**)/(**IIIb**+**IVb**)] were equal to 20 and 4 at initial concentrations of radical anion **II** of 0.1 and 0.009 M, respectively, i.e., they approached the values typical of the electron-transfer mechanism in analogous reactions of radical anions derived from arenes [9]; similar *n/i* ratios (16 and 3, respectively) were observed experimentally in the alkylation of terephthalonitrile radical anion, which was shown to follow the ET mechanism [8]. The reduced overall *n/i* ratio at lower concentration of radical anion **II** is also consistent with the ET mechanism, in keeping with increased probability for the isomerization of initially formed cyclopropylmethyl radical as compared to its combination with radical anion **II**. However, the *ipso/para*-alkylation ratios characterizing the regioselectivity of substitution in radical anion **II** by the non-isomerized (**IIIa**:**IVa** = 2.3) and isomerized alkyl species (**IIIb**:**IVb** = 0.8) are different. A probable reason is some contribution of the S_N mechanism to the formation of compound **IIIa**. It is known that the cor-

responding ratios in the alkylation of terephthalonitrile (which is characterized by dual ET/S_N reactivity) differ by an order of magnitude [10]. Thus our results led us to conclude that radical anion **II** reacts with alkyl halides following mainly the ET mechanism.

We extended our study toward elucidating the possibility of using the reductive activation of dinitrile **I** for the synthesis of modified phthalonitriles. For this purpose, we examined the effect of such factors as the structure of alkylating agent, cation nature, and reaction conditions, on the product structure and ratio. As alkylating agents in reactions with radical anion **II** we used octyl bromide, dodecyl bromide, hex-5-en-1-yl bromide, and 1,5-dibromopentane. Bromides were taken due to their higher reactivity as compared to the corresponding chlorides [2, 11]; in addition, alkyl bromides ensured preferential formation of alkyl-substituted phthalonitriles rather than dialkyl-substituted benzonitriles, which cannot be attained using alkyl iodides (Scheme 2) [2]. We also tried sodium instead of potassium to generate radical anion **II** from phthalonitrile **I** and made attempts to perform enlarged synthesis by raising the amounts of the reactants and their concentration.

In the alkylation of radical anion **II** sodium salt with octyl bromide and hex-5-en-1-yl bromide, the product ratios were similar to those reported in [2] for the reaction with butyl bromide (cf. run nos. 3, 4, and 5; Table 1). Previously unknown 2-octylbenzonitrile

(IIIc), 4-octylphthalonitrile (IVc), 2-(hex-5-en-1-yl)benzonitrile (IIIId), 4-(hex-5-en-1-yl)phthalonitrile (IVd), and 2,5-bis(hex-5-en-1-yl)benzonitrile (Vd) were isolated as individual substances and were characterized by spectral data (see Experimental). The formation of 2,5-dioctylbenzonitrile (Vc) as minor product in run no. 3 was detected by GC-MS and ^1H NMR analysis of the reaction mixture. We can conclude that the reactivity of radical anion II almost does not change on replacement of the counterion, extension of the *n*-alkyl chain up to C_8 , and introduction of a terminal double bond into the alkylating agent. On the other hand, apart from the above listed alkyl-substituted products, the reaction mixtures contained biphenyl-2,3',4'-tricarbonitrile (VI) (a probable mechanism of its formation is discussed below). The reaction of dodecyl bromide with radical anion II sodium salt (reaction time 3 h) gave no more than 10% (overall yield, according to the GC-MS data) of alkylation products like III and IV, while the major product was tricyanobiphenyl VI (yield ~70%). An analogous pattern was observed previously in the reaction of II with butyl chloride [2]. Raising the temperature to $\sim 20^\circ\text{C}$ (the alkylation of II was carried out in THF) resulted in only a slight (up to 20%) increase of the yield of the alkylation products. We cannot propose an unambiguous explanation for the observed difference in the results of alkylation of radical anion II with dodecyl bromide, on the one hand, and with butyl and octyl bromides, on the other.

The reactions of radical anion II potassium and sodium salts with butyl bromide were performed using larger amounts of the reactants and their concentration (run nos. 6, 7; Table 1). We observed no appreciable variation in the yield of alkylation products IIIe, IVe, and Ve and their ratio. Conditions for quantitative isolation of dinitrile IVe by column chromatography on silica gel were found.

With a view to develop a synthetic route to ω -functionalized alkyl-substituted phthalonitriles, we examined the reaction of radical anion II sodium salt with 1,5-dibromopentane. According to the ^1H NMR and

GC-MS data, the product mixture was more complex than in the reactions with monobromides. Apart from ω -bromoalkyl derivatives III (18%), IV (6%), and V (2%), it contained about ~20% of at least three compounds resulting from replacement of both halogen atoms in the alkylating agent by cyano- and dicyano-phenyl groups. Obviously, the second bromine atom is replaced via reaction of initially formed products III-V with radical II. We believe that the contribution of these side processes may be reduced by changing the order of mixing of the reactant in such a way that 1,5-dibromopentane be persistently present in excess with respect to radical anion II. However, the most probable result would be increased yield of dialkyl derivatives V rather than target dinitriles IV.

Tricyanobiphenyl VI is likely to be formed according to Scheme 3, which includes dimerization of radical anion II and the subsequent irreversible decyanation of dianionic dimer VII. While studying electrochemical reduction of dicyanobenzenes by cyclic voltammetry, only isophthalonitrile radical anion was found to undergo dimerization [12]. Tricyanobiphenyl VI attracts interest as potential starting compound for the synthesis of modified phthalocyanines; therefore, we studied dimerization of radical anion II in the absence of alkylating agent under various conditions (the concentration of II and counterion nature were varied). When radical anion II sodium salt was kept in liquid ammonia at a concentration of 0.5 M for 1 h at -40 to -35°C , biphenyl VI was formed in 50% yield (run no. 1, Table 2). In this case, less than 5% of initial dinitrile I was recovered; presumably, a considerable part of II undergoes transformations involving cyano groups to give high-molecular compounds of unknown nature. Regardless of the reaction time, from radical anion II lithium salt at a concentration of 0.1 M we obtained no more than 20% of biphenyl VI (run nos. 2, 3; Table 2). Raising the concentration of II·Li to 0.3 M increased the yield of VI to 58% (run no. 4, Table 2). Unlike the reaction with the sodium salt, unreacted dinitrile I was recovered from the mixture, and the overall yield attained 70–80%. Obviously, weaker ion

Scheme 3.

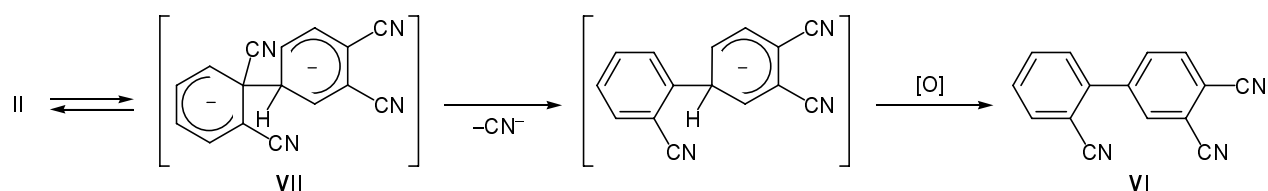


Table 2. Formation of biphenyl-2,3',4'-tricarbonitrile (**VI**) from radical anion **II** salts in liquid ammonia^a

Run no.	Amounts of reactants, mmol		II , mol/l	Reaction time, h	Product composition, mmol (yield, mol %)	
	I	alkali metal			I	VI
1	10.0	Na, 9.5	0.5	1	0.3	2.40 (50)
2	3.1	Li, 2.8	0.1	0.5	1.53	0.22 (16)
3	3.1	Li, 3.0	0.1	2	1.50	0.25 (17)
4	12.0	Li, 11.1	0.3	1	3.28	3.20 (58)

^a See notes to Table 1.

association of lithium salts in liquid ammonia, as compared to other alkaline metal salts [13], favors reduced contribution of side processes.

The results of the present study were analyzed from the viewpoint of their synthetic utility, and the following conclusions were drawn. Single-electron reductive activation of phthalonitrile (**I**) with alkali metals, followed by treatment of radical anion **II** with alkyl bromides in liquid ammonia, gives ~20% (with account taken of the stoichiometry of radical reactions) of 4-alkylphthalonitriles **IV** as potential precursors of modified phthalocyanines. Nevertheless, the examined reaction may be used as a basis for the development of acceptable synthetic procedures for the preparation of such compounds, for both starting materials and reagents are readily accessible, the process includes only one step, and the set of alkyl fragments that may be introduced into phthalonitrile molecule could be extended considerably to obtain previously inaccessible 4-alkyl derivatives. Up to now, only derivatives with methyl and *tert*-butyl groups were reported, and methods for their preparation include a number of steps and are not advantageous (as concerns the yields of the target products, calculated with respect to starting materials whose accessibility is comparable with that of phthalonitrile; see, e.g., [14, 15]). Moreover, apart from alkyl-substituted dicyanobenzenes, single-electron reduction of phthalonitrile gives rise to biphenyl-2,3',4'-tricarbonitrile (**VI**, yield ~60%) which also attracts interest as initial compound for the synthesis of modified phthalocyanines. The formation of **VI** as a minor component of a complex mixture of products obtained by electrochemical decarboxylation of silver phthalate in the presence of AgCN [16] cannot be regarded as an acceptable method for the preparation of this compound. Finally, alkylated benzonitriles formed together with phthalonitrile derivatives are undoubtedly promising as intermediate products in fine organic synthesis.

EXPERIMENTAL

The ¹H NMR spectra were recorded on a Bruker WP-200SY spectrometer from solutions in (CD₃)₂CO; the chemical shifts were measured relative to tetramethylsilane. The IR spectra were recorded in KBr (concentration 0.25 wt %) or from thin films on a UR-20 instrument. The molecular weights were determined from the high-resolution mass spectra which were obtained on a Finnigan MAT-8200 spectrometer. The reaction mixtures were analyzed by gas-liquid chromatography on an LKhM-7A instrument (2.5 × 0.002-m column; stationary phase 15% of SKTFV-83 on Chromosorb W; oven temperature programming from 100 to 300°C at 10 deg/min; carrier gas helium, flow rate 0.6 l/h). Components of the reaction mixtures were identified by GC-MS using a Hewlett-Packard G1081A system consisting of an HP 5890 Series II gas chromatograph and an HP 5971 mass-selective detector (electron impact, 70 eV; HP5 column, 30 m × 0.25 mm, film thickness 0.25 μm, stationary phase 5% of biphenyl + 95% of dimethylsiloxane; carrier gas helium, flow rate 1 ml/min; oven temperature programming in the following mode: 2 min at 50°C–10 deg/min–5 min at 280°C; injector temperature 280°C; ion source temperature 173°C; data acquisition at 1.2 scan/s, a.m.u. range 30–650).

Liquid ammonia was purified by dissolving metallic sodium therein and subsequent distillation into a reaction vessel cooled to –70°C. Tetrahydrofuran of pure grade was purified by the procedure described in [17] and was distilled over sodium diphenylketyl in a stream of argon under a pressure equal to atmospheric directly into a reaction vessel. Metallic potassium, sodium, and lithium (pure grade) were freed from the surface oxide film under a layer of anhydrous hexane. Phthalonitrile of pure grade was purified by sublimation, mp 141°C; published data [18]: mp 140–141°C. Alkyl halides were purified by passing them

through a layer of aluminum oxide and subsequent distillation just before experiment; their boiling points coincided with those given in [19]).

Phthalonitrile radical anion (II) salts. Alkali metal was added in small pieces to a suspension of dinitrile **I** in liquid ammonia (for amounts of the reactants and their concentration, see Table 1) under stirring at -33°C in an argon atmosphere or in a stream of gaseous ammonia. The mixture was then stirred for 10 min under the same conditions, and the resulting dark brown suspension of radical anion **II** salt was used in further experiments.

Alkylation of radical anion II salt. Alkyl bromide was added dropwise to a suspension of radical anion salt **II**, and the mixture was stirred in an inert atmosphere over a period specified in Table 1. The mixture was then diluted with ~ 50 ml of diethyl ether and was stirred on exposure to air until the ammonia vaporized completely. The residue was treated with 50 ml of water, and insoluble organic products were filtered off, washed with diethyl ether and water, dried in air, and analyzed by ^1H NMR, GC-MS, or GLC using authentic samples. The aqueous phase was extracted with diethyl ether (3×50 ml). The extracts were combined and dried over MgSO_4 , the solvent was distilled off, and the residue was analyzed by the above methods. Individual substances or mixtures of structurally related compounds were isolated by preparative thin-layer chromatography on plates with a fixed sorbent layer (silica gel LSL₂₅₄, $5/40$ μm , containing 13 wt % of gypsum) using hexane-diethyl ether mixtures ($\sim 8:1$ to $\sim 9:1$) as eluent; the separation process was controlled visually under UV light (after drying); separated fractions were washed off from the sorbent with diethyl ether.

2-(Cyclopropylmethyl)benzonitrile (IIIa) and 4-(cyclopropylmethyl)phthalonitrile (IVa). Cyclopropylmethyl bromide, 0.24 ml (2.5 mmol), was added dropwise to a suspension of radical anion **II** potassium salt prepared by addition of 0.19 g (5 mmol) of metallic potassium to a mixture of 0.65 g (5.1 mmol) of dinitrile **I** and 50 ml of liquid ammonia. The subsequent procedure was similar to that described above. We isolated 0.54 g of a mixture of products (run no. 1, Table 1). Separation of the mixture by TLC gave 0.11 g (0.71 mmol, 28%) of compound **IIIa** and 0.07 g (0.37 mmol, 15%) of **IVa**.

Compound **IIIa**. R_f 0.60. IR spectrum: $\nu(\text{C}\equiv\text{N})$ 2235 cm^{-1} . ^1H NMR spectrum, δ , ppm: 0.29 quint (2H,

CH_2), 0.51 quint (2H, CH_2), 1.06 sept (1H, CH), 2.74 d (2H, CH_2), 7.38 t.d (1H, 5-H, $J_o = 7.5$, $J_m = 1.5$ Hz), 7.57 m (2H, 3-H, 6-H), 7.67 t.d (1H, 4-H, $J_o = 7.5$, $J_m = 1.5$ Hz). Found: $[M]^+$ 157.0889. $\text{C}_{11}\text{H}_{11}\text{N}$. Calculated: M 157.0891.

Compound **VIa**. R_f 0.20. IR spectrum: $\nu(\text{C}\equiv\text{N})$ $2235\text{--}2240\text{ cm}^{-1}$. ^1H NMR spectrum, δ , ppm: 0.27 m (2H, CH_2), 0.54 m (2H, CH_2), 1.04 m (1H, CH), 2.71 d (2H, CH_2), 7.84 d.d (1H, 5-H, $J_o = 8$, $J_m = 1.5$ Hz), 7.94 d (1H, 6-H, $J_o = 8$ Hz), 7.96 d (1H, 3-H, $J_m = 1.5$ Hz). Found: $[M]^+$ 182.0850. $\text{C}_{12}\text{H}_{10}\text{N}_2$. Calculated: M 182.0844.

2-(But-3-en-1-yl)benzonitrile (IIIb) and 4-(but-3-en-1-yl)phthalonitrile (IVb). Cyclopropylmethyl bromide, 0.15 ml (1.5 mmol), was added to a suspension of radical anion **II** potassium salt prepared by addition of 0.12 g (3 mmol) of metallic potassium to a mixture of 0.40 g (3.1 mmol) of dinitrile **I** and 300 ml of liquid potassium. The subsequent procedure was similar to that described above. We isolated 0.34 g of a mixture of products (run no. 2, Table 1), which was separated by TLC to isolate two fractions. The first of these ($R_f \sim 0.50$), 0.09 g, was a mixture of 2-(cyclopropylmethyl)benzonitrile (**IIIa**) and 2-(but-3-en-1-yl)benzonitrile (**IIIb**) at a molar ratio of 4:1. ^1H NMR spectrum of **IIIb**, δ , ppm: 2.41 q (2H, CH_2), 2.93 t (2H, CH_2), 4.94–5.06 m (2H, $=\text{CH}_2$), 5.76–5.96 m (1H, $=\text{CH}$), 7.28–7.71 m (4H, H_{arom}). The second fraction ($R_f \sim 0.3$), 0.06 g, was a mixture of 4-(cyclopropylmethyl)phthalonitrile (**IVa**) and 4-(but-3-en-1-yl)phthalonitrile (**IVb**) at a molar ratio of 1.6:1. ^1H NMR spectrum of **IVb**, δ , ppm: 2.44 q (2H, CH_2), 2.91 t (2H, CH_2), 4.94–5.05 m (2H, $=\text{CH}_2$), 5.76–5.96 m (1H, $=\text{CH}$), 7.77–7.98 m (3H, H_{arom}). According to the GC-MS data, the molecular weights of **IIIa/IIIb** and **IVa/IVb** were 157 and 182, respectively.

2-Octylbenzonitrile (IIIc) and 4-octylphthalonitrile (IVc). Octyl bromide, 0.43 ml (2.5 mmol), was added dropwise to a suspension of radical anion **II** sodium salt prepared by addition of 0.108 g (4.7 mmol) of metallic sodium to a mixture of 0.64 g (5.0 mmol) of dinitrile **I** and 40 ml of liquid ammonia. The subsequent procedure was similar to that described above. We isolated 0.65 g of a mixture of products (run no. 3, Table 1). Separation of the mixture by TLC gave 0.15 g (0.69 mmol, 29%) of compound **IIIc** and 0.11 g (0.46 mmol, 20%) of **IVc**.

Compound **IIIc**. R_f 0.60. IR spectrum: $\nu(\text{C}\equiv\text{N})$ 2225 cm^{-1} . ^1H NMR spectrum, δ , ppm: 0.86 t (3H,

CH₃), 1.15–1.43 m [10H, (CH₂)₅], 1.67 quint (2H, CH₂), 2.84 t (2H, CH₂), 7.38 t.d (1H, 5-H, $J_o = 8$, $J_m = 1.5$ Hz), 7.46 d.d (1H, 3-H, $J_o = 8$, $J_m = 1.5$ Hz), 7.61 t.d (1H, 4-H, $J_o = 8$, $J_m = 1.5$ Hz), 7.68 d.d (1H, 6-H, $J_o = 8$, $J_m = 1.5$ Hz). Found: $[M]^+$ 215.1664. C₁₅H₂₁N. Calculated: M 215.1674.

Compound **IVc**. R_f 0.20. IR spectrum: $\nu(\text{C}\equiv\text{N})$ 2234 cm⁻¹. ¹H NMR spectrum, δ , ppm: 0.85 t (3H, CH₃), 1.12–1.40 m [10H, (CH₂)₅], 1.67 quint (2H, CH₂), 2.80 t (2H, CH₂), 7.79 d.d (1H, 5-H, $J_o = 9$, $J_m = 1.5$ Hz), 7.91 d (1H, 3-H, $J_m = 1.5$ Hz), 7.94 d (1H, 6-H, $J_o = 9$ Hz). Found: $[M]^+$ 2405.1618. C₁₆H₂₀N₂. Calculated: M 240.1626.

2-(Hex-5-en-1-yl)benzotrile (III d), 4-(hex-5-en-1-yl)phthalonitrile (IV d), and 2,5-bis(hex-5-en-1-yl)benzotrile (V d). Hex-5-en-1-yl bromide, 0.34 ml (2.5 mmol), was added dropwise to a suspension of radical anion **II** sodium salt, prepared by addition of 0.11 g (4.8 mmol) of metallic sodium to a mixture of 0.64 g (5.0 mmol) of dinitrile **I** and 50 ml of liquid ammonia. The subsequent procedure was similar to that described above. We isolated 0.68 g of a mixture of products (run no. 4, Table 1). Separation of the mixture by TLC gave 0.15 g (0.81 mmol, 34%) of compound **III d**, 0.08 g (0.38 mmol, 16%) of **IV d**, and 0.04 g (0.15 mmol, 6%) of **V d**.

Compound **III d**. R_f 0.60. IR spectrum: $\nu(\text{C}\equiv\text{N})$ 2224 cm⁻¹. ¹H NMR spectrum, δ , ppm: 1.38–1.55 m (2H, CH₂), 1.59–1.77 (2H, CH₂), 2.01–2.18 m (2H, CH₂), 2.84 t (2H, CH₂), 4.88–5.08 m (2H, =CH₂), 5.68–5.93 m (1H, =CH), 7.38 t.d (1H, 5-H, $J_o = 8$, $J_m = 1.5$ Hz), 7.46 d.d (1H, 3-H, $J_o = 8$, $J_m = 1.5$ Hz), 7.61 t.d (1H, 4-H, $J_o = 8$, $J_m = 1.5$ Hz), 7.70 d.d (1H, 6-H, $J_o = 8$, $J_m = 1.5$ Hz). Found: $[M]^+$ 184.1127. C₁₃H₁₄N. Calculated: M 184.1126.

Compound **IV d**. R_f 0.15. IR spectrum: $\nu(\text{C}\equiv\text{N})$ 2234 cm⁻¹. ¹H NMR spectrum, δ , ppm: 1.36–1.51 m (2H, CH₂), 1.61–1.78 (2H, CH₂), 2.00–2.14 m (2H, CH₂), 2.82 t (2H, CH₂), 4.87–5.05 m (2H, =CH₂), 5.68–5.92 m (1H, =CH), 7.80 d.d (1H, 5-H, $J_o = 9$, $J_m = 1.5$ Hz), 7.93 d (1H, 3-H, $J_m = 1.5$ Hz), 7.96 d (1H, 6-H, $J_o = 9$ Hz). Found: $[M]^+$ 210.1168. C₁₄H₁₄N₂. Calculated: M 210.1157.

Compound **V d**. R_f 0.75. IR spectrum: $\nu(\text{C}\equiv\text{N})$ 2224 cm⁻¹. ¹H NMR spectrum, δ , ppm: 1.33–1.52 m (4H, CH₂), 1.55–1.75 m (4H, CH₂), 2.03–2.16 m (4H, CH₂), 2.65 t (2H, CH₂), 2.81 t (2H, CH₂), 4.88–5.06 m (4H, =CH₂), 5.70–5.92 m (2H, =CH), 7.34 d (1H, 3-H, $J_o = 8$ Hz), 7.45 d.d (1H, 4-H, $J_o = 8$, $J_m = 2$ Hz),

7.52 d (1H, 6-H, 2 Hz). Found: $[M]^+$ 267.1989. C₁₉H₂₅N. Calculated: M 267.1987.

Reaction of radical anion II sodium salt with dodecyl bromide. *a.* Dodecyl bromide, 0.62 g (2.5 mmol), was added dropwise to a suspension of radical anion **II** salt, prepared by addition of 0.11 g (4.8 mmol) of metallic sodium to a mixture of 0.64 g (5.0 mmol) of phthalonitrile (**I**) and 50 ml of liquid ammonia. The mixture was stirred for 3 h at –35°C in an inert atmosphere and was then treated as described above to isolate 1.3 g of a mixture of products containing (according to the GC–MS data) 2.36 mmol of dodecyl bromide, 0.7 mmol of initial dinitrile **I**, 0.05 mmol (2%) of 2-dodecylbenzotrile, 0.17 mmol (7%) of 4-dodecylphthalonitrile, and 1.66 mmol (69%) of tricyanobiphenyl **VI** (the yields were calculated on the initial metallic sodium with account taken of the reaction stoichiometry; see Schemes 1 and 2).

b. A solution of 0.64 g (5.0 mmol) of dinitrile **I** in 40 ml of anhydrous THF was purged with argon and cooled to –70°C, and 30 ml of ammonia was condensed thereto. Metallic sodium, 0.11 g (4.8 mmol), was then added under continuous stirring in an inert atmosphere, the mixture was stirred until the ammonia vaporized and the temperature became equal to ambient, 0.62 g (2.5 mmol) of dodecyl bromide was added, and the mixture was stirred for 3 h under argon and treated as described above. We isolated 0.99 g of a mixture of products containing (according to the GC–MS data), 1.6 mmol of dodecyl bromide, 0.4 mmol of initial dinitrile **I**, 0.4 mmol (17%) of 2-dodecylbenzotrile, 0.10 mmol (4%) of 4-dodecylphthalonitrile, and 0.87 mmol (36%) of tricyanobiphenyl **VI**.

Reaction of radical anion II sodium salt with 1,5-dibromopentane. 1,5-Dibromopentane, 0.57 g (2.5 mmol), was added dropwise to a suspension of radical anion **II** salt, prepared by addition of 0.11 g (4.8 mmol) of metallic sodium to a mixture of 0.64 g (5.0 mmol) of dinitrile **I** and 70 ml of liquid ammonia. The mixture was stirred for 1 h at –35°C in an inert atmosphere and was treated as described above to isolate 0.81 g of a mixture of products containing (according to the GC–MS data), 0.37 mmol of 1,5-dibromopentane, 3.4 mmol of initial dinitrile **I**, 0.44 mmol (18%) of 2-(5-bromopentyl)benzotrile (M 251), 0.14 mmol (6%) of 4-(5-bromopentyl)phthalonitrile (M 276), 0.05 mmol (2%) of 2,5-bis-(5-bromopentyl)benzotrile (M 399), and 0.05 mmol (2%) of tricyanobiphenyl **VI**. In addition, the mixture

contained compounds with M 299 (6%), 422 (4%), and 422 (10%).

4-Butylphthalonitrile (IVe). Butyl bromide, 0.66 ml (6.3 mmol), was added dropwise to a suspension of radical anion **II** sodium salt, prepared by addition of 0.28 (12.0 mmol) of metallic sodium to a mixture of 1.60 g (12.5 mmol) of dinitrile **I** and 50 ml of liquid ammonia. The mixture was then treated according to the general procedure to isolate 0.11 g (8%) of tricyanobiphenyl **VI** as a solid material and 1.06 g of a mixture of products (run no. 7, Table 1). 4-Butylphthalonitrile (**IVe**) was isolated by column chromatography on silica gel (220 g, 3×30 cm) using hexane–diethyl ether (95:5, by volume) as eluent. Yield 0.18 g (0.98 mmol, yield 16%, purity >98%; GLC data). The spectral parameters coincided with those given in [2].

Dimerization of radical anion II. A suspension of radical anion **II** salt, prepared according to the above procedure, was stirred at -35°C for a required time and was then treated as described above (for reaction conditions and yields, see Table 2). According to the ^1H NMR and GC–MS data, the solid material separated by filtration was tricyanobiphenyl **VI**, while the ether extract contained compound **VI** and dinitrile **I**.

Biphenyl-2,3',4'-tricarbonitrile (VI). Metallic lithium, 0.08 g (11.1 mmol), was added in small pieces to a suspension of 1.64 g (12.0 mmol) of dinitrile **I** and 40 ml of liquid ammonia under stirring at -33°C in a stream of gaseous ammonia. The resulting dark brown suspension (containing radical anion **II**) was kept for 1 h under the same conditions, 50 ml of diethyl ether was added, and the mixture was stirred until the ammonia vaporized completely. The residue was treated with 50 ml of water, and the precipitate was filtered off, washed in succession with diethyl ether and water, and dried in air. Yield of compound **VI** 0.73 g (3.2 mmol, 58%), mp $256\text{--}258^{\circ}\text{C}$ (from ethanol). IR spectrum: $\nu(\text{C}\equiv\text{N})$ 2227 cm^{-1} . ^1H NMR spectrum, δ , ppm: 7.73 t.d (1H, 4-H, $J_o = 8$, $J_m = 2$ Hz), 7.79 d.d (1H, 6-H, $J_o = 8$, $J_m = 2$ Hz), 7.89 t.d (1H, 5-H, $J_o = 8$, $J_m = 2$ Hz), 7.98 d.d (1H, 3-H, $J_o = 8$, $J_m = 2$ Hz), 8.21 d.d (1H, 6'-H, $J_o = 8$, $J_m = 2$ Hz), 8.25 d.d (1H, 5'-H, $J_o = 8$, $J_m = 0.8$ Hz), 8.34 d.d (1H, 2'-H, $J_o = 2$, $J_p = 0.8$ Hz). Found: $[M]^+$ 229.0639. $\text{C}_{15}\text{H}_7\text{N}_3$. Calculated: M 229.0639.

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REFERENCES

- Panteleeva, E., Shchegoleva, L., Vysotsky, V., Pokrovsky, L., and Shteingarts, V., *Eur. J. Org. Chem.*, 2005, p. 2558.
- Bil'kis, I.I., Panteleeva, E.V., and Shteingarts, V.D., *Russ. J. Org. Chem.*, 1998, vol. 34, p. 1631.
- Hanack, M., Heckmann, H., and Polley, R., *Meth. Org. Chem. (Houben–Weil)*, 1998, vol. E9d; McKeown, N.B., *Phthalocyanine Materials: Synthesis, Structure, and Function*, Cambridge: Cambridge Univ., 1998; Mikhalenko, S.A., Barkanova, S.V., Lebedev, O.L., and Luk'yanets, E.A., *Zh. Obshch. Khim.*, 1971, vol. 41, p. 2735.
- Phthalocyanines: Properties and Applications*, Leznoff, C.C. and Lever, A.B.P., Eds., New York: VCH, 1989–1996, vols. 1–4; Johannsen, M. and Joergensen, K.A., *J. Org. Chem.*, 1994, vol. 59, p. 214; Sirlin, S.C., *Pure Appl. Chem.*, 1989, vol. 61, p. 1625; Emmelius, M., Pawlowski, G., and Vollmann, H.W., *Angew. Chem.*, 1989, vol. 101, p. 1475.
- Luk'yanets, E.A., *Ros. Khim. Zh.*, 1998, vol. 42, p. 9; Bonnett, R., *Chem. Soc. Rev.*, 1995, vol. 24, p. 19; Vol'pin, M.E., Krainova, N.Yu., Moskaleva, I.V., Novodarova, G.N., Vorozhtsov, G.N., Gal'perin, M.G., Kaliya, O.L., Luk'yanets, E.A., and Mikhalenko, S.A., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1996, p. 2105; del Rey, B., Keller, U., Torres, T., Rojo, C., and Agullo-Lopez, F., Marti, C., Brasselet, S., Ledoux, I., and Zyss, J., *J. Am. Chem. Soc.*, 1998, vol. 120, p. 12808.
- Newcomb, M. and Glenn, A., *J. Am. Chem. Soc.*, 1989, vol. 111, p. 275.
- Newcomb, M. and Curran, D.P., *Acc. Chem. Res.*, 1988, vol. 21, p. 206.
- Bil'kis, I.I., Panteleeva, E.V., Tananakin, A.P., and Shteingarts, V.D., *Zh. Org. Khim.*, 1994, vol. 30, p. 882.
- Garst, J.F. and Smith, C.D., *J. Am. Chem. Soc.*, 1976, vol. 98, p. 1520.
- Bil'kis, I.I., Panteleeva, E.V., Tananakin, A.P., and Shteingarts, V.D., *Russ. J. Org. Chem.*, 1997, vol. 33, p. 652.
- Bil'kis, I.I., Vaganova, T.A., Bobyleva, V.I., and Shteingarts, V.D., *Russ. J. Org. Chem.*, 1991, vol. 27, p. 48.
- Sertel, M., Yildiz, A., Gambert, R., and Baumgartel, H., *Electrochim. Acta*, 1986, vol. 31, p. 1287; Gennaro, A., Maran, F., Maye, A., and Vianello, E., *J. Electroanal. Chem.*, 1985, vol. 185, p. 353; Gennaro, A., Romanin, A.M., Severin, M.G., and Vianello, E., *J. Electroanal. Chem.*, 1984, vol. 169, p. 279; Gennaro, A., Maye, A., Maran, F., and Vianello, E., *Electrochim. Acta*, 1988, vol. 33, p. 167.

13. Smith, H., *Organic Reactions in Liquid Ammonia*, New York: Wiley, 1963; Bil'kis, I.I., Selivanov, B.A., and Shteingarts, V.D., *Zh. Org. Khim.*, 1986, vol. 22, p. 794; Selivanov, B.A. and Shteingarts, V.D., *Russ. J. Org. Chem.*, 2001, vol. 37, p. 1719.
14. Siege, W.O., Ferris, F.C., and Mucci, P.A., *J. Org. Chem.*, 1977, vol. 42, p. 3442.
15. Fischer, T.H. and Meierhoefer, A.W., *J. Org. Chem.*, 1978, vol. 43, p. 220.
16. Fields, E.K., US Patent no. 3970658, 1976; *Chem. Abstr.*, 1977, vol. 86, no. P 139650.
17. Malykhin, E.V., Mamatyuk, V.I., and Shteingarts, V.D., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim.*, 1979, no. 12, p. 145.
18. *Dictionary of Organic Compounds*, Heilbron, J. and Bunbury, H.M., Eds., London: Eyre and Spottiswoode, 1943, vol. 3, p. 479.
19. *Aldrich Catalogue/Handbook of Fine Chemicals*, 2002–2003.