Reductive activation of arenes

22.* Reactions of the terephthalonitrile radical anion and dianion with α,ω-dibromoalkanes. New evidence for the charge transfer complex as a key intermediate in the reactions of the dianion**

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The major products of reactions of the terephthalonitrile radical anion with α,ω-dibromoalkanes $Br(CH_2)_nBr$ (n = 3—5) were 4-(ω-bromoalkyl)benzonitriles. Analogous reactions of the terephthalonitrile dianion mainly yielded α,ω-bis(4-cyanophenyl)alkanes. Both transformations are convenient one-step routes to otherwise not easily accessible compounds that are valuable as versatile building blocks. The results of alkylation allow one to suggest that reactions of the dianion with intermediate 4-(ω-bromoalkyl)benzonitriles proceed more rapidly than those with the starting α,ω-dibromoalkanes. This was confirmed by competitive reactions of the dianion with 4-(ω-bromoalkyl)benzonitriles and the corresponding alkyl bromides. To explain such a ratio of the reaction rates, a mechanism was proposed for the reaction of the dianion with 4-(ω-bromoalkyl)benzonitriles. According to this mechanism, a charge transfer complex is a key reaction intermediate.

Key words: terephthalonitrile, radical anion, dianion, α,ω-dibromoalkanes, 4-(ω-bromoalkyl)benzonitriles, α,ω-bis(4-cyanophenyl)alkanes, charge transfer complexes, reaction mechanisms.

Reactions of anionic intermediates (radical anions, dianions, and cyclohexadienyl anions) formed in the reductive activation of aromatic compounds with electrophiles (first of all, alkyl halides) have long attracted the attention of researchers for both synthetic purposes and investigations of their mechanisms. In the latter case, the key factor is a competition between nucleophilic substitution (S_N) and electron transfer (ET). A structural approach involving correlation between the nature and ratio of reaction products and the structure of the alkyl halide and the reduced anionic form of arene[2] is very efficient for such investigations. Unlike physical methods used to study the mechanisms of the above reactions, this approach provides additional important information on a possible scope of synthetic applications of such transformations.

In connection with this, one- and two-electron reduction of arenes with electron-withdrawing functions (NO_2, COR, and CN)[3] is most attractive because the presence of the latter allows generation of long-lived reduced anionic forms in preparative amounts for use as highly reactive synthons. The cyano group holds a special position among the aforementioned functions since the reduced anionic forms of aromatic nitriles can be easily generated, combine relative stability and high reactivity toward alkyl halides, and, in contrast to analogous reduced forms of nitro compounds and ketones, can be alkylated in the aromatic fragment only.[4—10] A combination of the above characteristics allows development of new and unprecedentedly simple approaches to the synthesis of otherwise not easily accessible functionalized cyanoarenes and cyanodihydroarenes, which are versatile building blocks in fine organic synthesis.

Earlier, it has been shown that one- and two-electron reduction of terephthalonitrile (**1**) with an alkali metal in liquid ammonia yields radical anion ($\mathbf{1}^{\bullet-}$)[7] and dianion ($\mathbf{1}^{2-}$)[8] of this dinitrile, respectively, which are sufficiently stable under the generation conditions. The fact that dianion $\mathbf{1}^{2-}$ is promising for use in *para*-cyanophenylation has been illustrated with a developed one-step synthesis

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of 4-alkylbenzonitriles in 50—90% yields[8,11] from this dianion and various alkyl halides. Evidently, it would be reasonable to extend the range of reagents involved in reactions with the reduced anionic forms of dinitrile **1** for achieving synthetically significant results.

The present study was devoted to reactions of radical anion $\mathbf{1}^{\bullet -}$ and dianion $\mathbf{1}^{2-}$ with α,ω-dibromoalkanes $Br(CH_2)_nBr$ (n = 3—5) in liquid ammonia. We used these reagents because the expected products would contain a functionalized alkyl fragment, which can be further modified in a variety of ways. If these reactions proceeded like reactions of radical anion $\mathbf{1}^{\bullet -}$ and dianion $\mathbf{1}^{2-}$ with primary alkyl bromides,[7,8] one could expect that reaction products are 4-(ω-bromoalkyl)benzonitriles and α,ω-bis(4-cyanophenyl)alkanes, which are very promising for subsequent use as building blocks (also in the context of synthetic approaches based on reductive activation). An additional prerequisite has been provided by the formation of ω-haloalkylated products in reactions of the reduced anionic forms of benzonitrile,[12] nitrobenzene,[13] naphthalene,[14] anthracene,[15] and 3,4-diphenylcinnoline[16] with α,ω-dihaloalkanes.

Results and Discussion

Addition of $Br(CH_2)_nBr$ to an equivalent amount of the sodium salt of radical anion $\mathbf{1}^{\bullet -}$ in liquid ammonia ("normal" order of addition) led to the corresponding 4-(ω-bromoalkyl)benzonitriles **2**—**4** (n = 3—5, respectively) in 15—25% yields (according to the reaction stoichiometry that requires two equivalents of radical anion $\mathbf{1}^{\bullet -}$ for the formation of one equivalent of the alkylation product, the resulting dinitrile **1** (1 equiv.) being easily recovered), α,ω-bis(4-cyanophenyl)alkanes **5**—**7** (n = 3—5, respectively) in 5—14% yields (in this case, four equivalents of radical anion $\mathbf{1}^{\bullet -}$ are required to obtain one equivalent of the product), and α-(4-cyanophenyl)-ω-(2,5-dicyanophenyl)alkanes **8**—**10** (n = 3—5, respectively) in 1—3% yields (Scheme 1; Table 1, entries *1*, *2*, *4*). Other products depending on the structure

Table 1. Reactions of the sodium salts of radical anion $\mathbf{1}^{\bullet -}$ and dianion $\mathbf{1}^{2-}$ with α,ω-dibromoalkanes

Entry	Anionic reduced form of **1** (mmol)	$Br(CH_2)_nBr$		Composition of the products according to GLC-MS and ^{1}H NMR data, mmol (mol.%)[a]		
		n	Amount (mmol)	Primary alkylation products	Repeated alkylation products	Ratio of the *ipso*/*ortho*-alkylation products
1[b]	$\mathbf{1}^{\bullet -}$ (4.8)	3	5.0	**2**, 0.39 (16); **11**, 0.32 (13); **12**, 0.30 (12)	**5**, 0.06 (5); **8** (<1)	2.6
2	$\mathbf{1}^{\bullet -}$ (4.8)	4	5.0	**3**, 0.48 (20); **13**, 0.34 (14)	**6**, 0.17 (14); **9**, 0.04 (3)	2.0
3[c]	$\mathbf{1}^{\bullet -}$ (4.8)	4	25.0	**3**, 0.56 (23); **13**, 0.24 (10)	**6** (≤1)	2.3
4	$\mathbf{1}^{\bullet -}$ (4.8)	5	5.0	**4**, 0.60 (25); **14**, 0.06 (2)	**7**, 0.07 (6); **10** (≤1)	11
5	$\mathbf{1}^{2-}$ (4.8)	3	5.0	**2** (≤1)	**5**, 1.49 (62); **8**, 0.1 (4); **20** (≤1); **22**, 0.36 (22)	19
6	$\mathbf{1}^{2-}$ (10.0)	3	5.0	**2** (≤1)	**5**, 2.06 (41); **8**, 0.43 (9); **20**, 0.35 (7); **22**, 0.64 (19)	7
7	$\mathbf{1}^{2-}$ (5.0)	4	5.0	**3**, 0.06 (2)	**6**, 1.15 (46); **9**, 0.15 (6); **21**, 0.63 (25)	12
8	$\mathbf{1}^{2-}$ (2.5)	4	1.3	**3**, 0.03 (1)	**6**, 0.88 (70); **9**, 0.04 (3); **21**, 0.025 (2)	23
9[d]	$\mathbf{1}^{2-}$ (25.0)	4	12.5	—	**6**, 7.91 (63); **9** (≤1); **23**, 1.58 (19)	—[e]
10	$\mathbf{1}^{2-}$ (2.5)	4	5.0	**3**, 0.03 (1)	**6**, 0.81 (66); **9**, 0.1 (8)	8
11[c]	$\mathbf{1}^{2-}$ (5.0)	4	25.0	**3**, 0.19 (4)	**6**, 2.30 (92); **9**, 0.06 (1)	—[e]
12[f]	$\mathbf{1}^{2-}$ (5.0)	4	10.0	**3**, 0.49 (10)	**6**, 1.74 (70); **9**, 0.15 (6)	15
13	$\mathbf{1}^{2-}$ (5.0)	5	5.0	—	**7**, 2.18 (87); **10**, 0.06 (2)	36
14	$\mathbf{1}^{2-}$ (10.0)	5	5.0	**4** (≤1)	**7**, 4.48 (90); **10**, 0.23 (4)	20

[a] The data are averaged over no less than two parallel experiments; the deviation for the major products does not exceed 5%. The mixtures of the reaction products from radical anion $\mathbf{1}^{\bullet -}$ contain, apart from the compounds listed in the table, the starting dinitrile **1** (~2.5 mmol) and a dibromoalkane (up to 1.5 mmol).

[b] The mixture also contains benzonitrile and its alkylation products (in total, ~0.35 mmol).

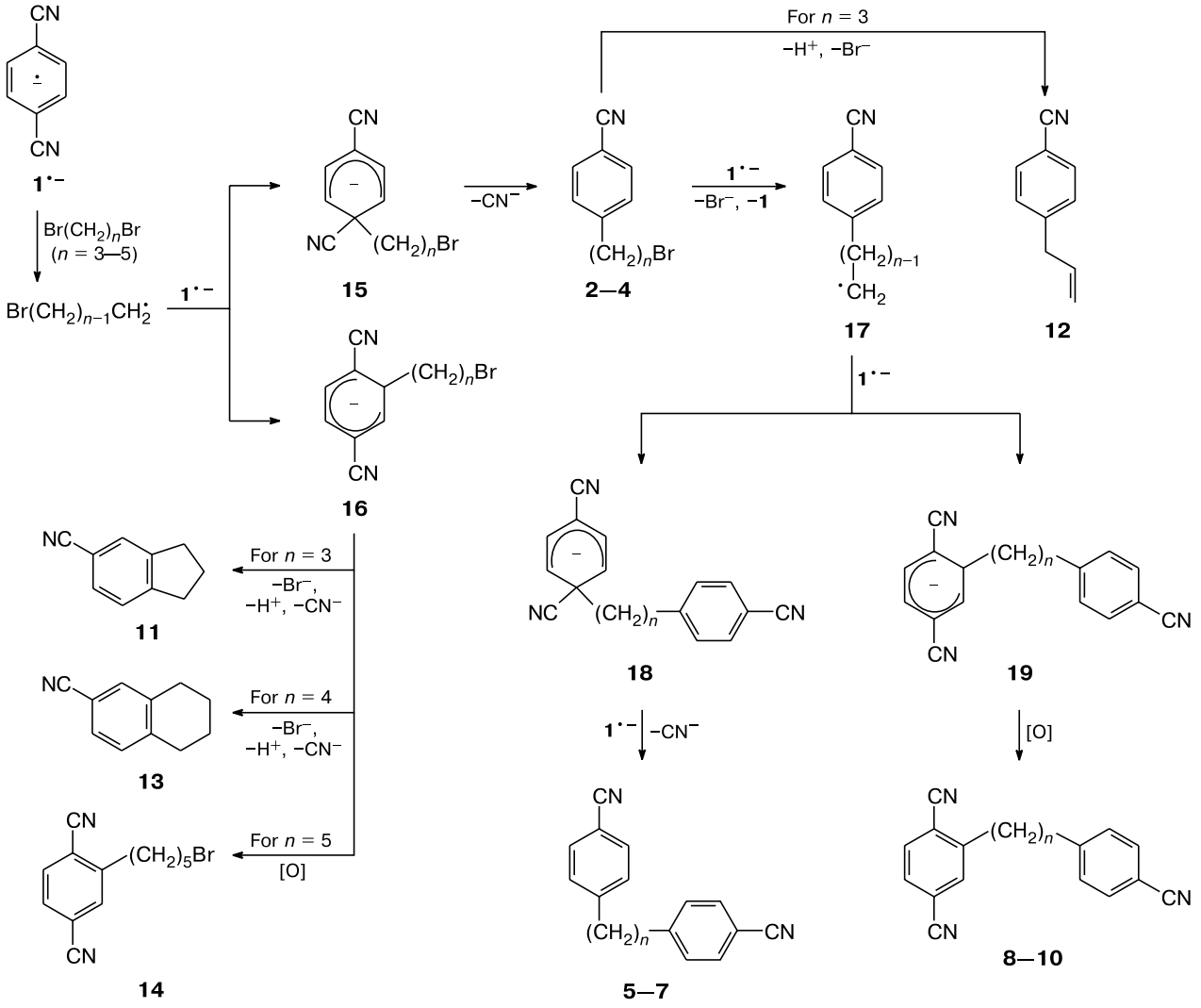
[c] The inverse quenching technique was used. The mixture also contains 1,4-dibromobutane (~20 mmol).

[d] The concentration of the salt of dianion $\mathbf{1}^{2-}$ was 0.5 mol L^{-1} in this entry and 0.1 mol L^{-1} in the others.

[e] Not estimated because of a large error in the determination of the content of the minor (*ortho*-alkylation) product.

[f] The reaction was carried out in THF.

Scheme 1



n = 3 (**2**, **5**, **8**), 4 (**3**, **6**, **9**), 5 (**4**, **7**, **10**)

of dibromoalkane included 5-cyanoindane (**11**) (13%) and 4-allylbenzonitrile (**12**) (12%) from dibromopropane, 2-cyano-5,6,7,8-tetrahydronaphthalene (**13**) (10%) from dibromobutane, and 2-(5-bromopentyl)-1,4-dicyanobenzene (**14**) (4%) from dibromopentane.

Bromoalkylbenzonitriles **2**—**4** have been described[17—21] without spectroscopic characterization. In the present work, we isolated these compounds and confirmed their structures by ^{1}H NMR, IR, and high-resolution mass spectra (see Experimental). Diphenylalkanes **5**—**7** were isolated from products of the reactions of dianion $\mathbf{1}^{2-}$ (see below), spectroscopically characterized (see Experimental), and used to identify these compounds in reaction products from radical anion $\mathbf{1}^{\bullet-}$. The structures of minor products **8**—**10** were proposed from ^{1}H NMR and GLC-MS data by analogy with the products of reactions of radical anion $\mathbf{1}^{\bullet-}$ with alkyl halides.[7] The spectroscopic characteristics of nitrile **12** fully agree with the published data.[22] The earlier described indane **11** [23] (for the IR spectrum, see Ref. 24) and tetrahydronaphthalene **13** [25,26] (for the mass spectrum, see Ref. 27) were isolated as a mixture with compound **12** (~1 : 1) and in the individual state, respectively, while unknown dinitrile **14** was isolated as a mixture with the starting compound **1**.

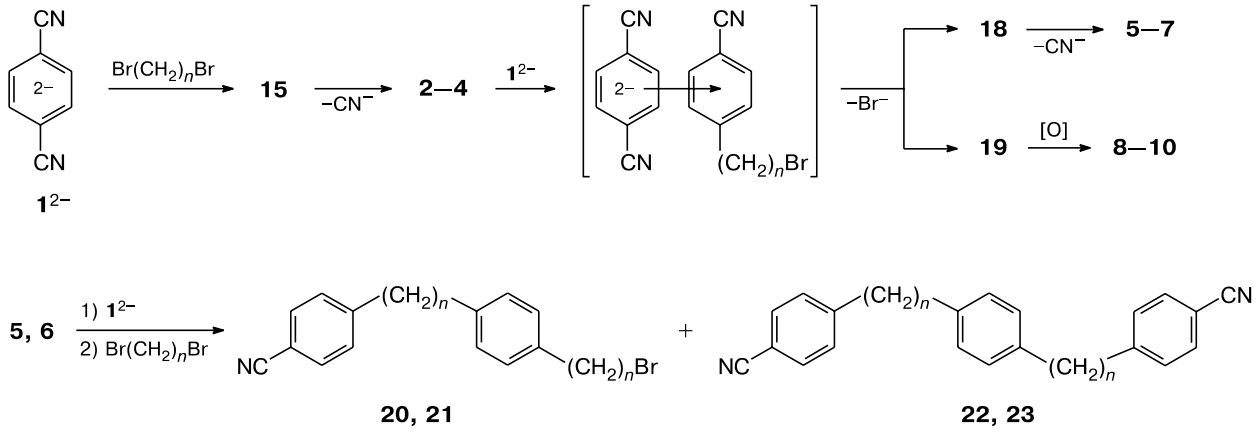
When considering possible pathways to the aforementioned products (see Scheme 1), one should note that they are all formed by substitution of an alkyl fragment for either the cyano group (*ipso*-alkylation) or the H atom (*ortho*-alkylation) in radical anion $\mathbf{1}^{\bullet-}$. Obviously, immediate precursors of bromoalkylbenzonitriles **2**—**4** are dicyanocyclohexadienyl anions **15**, which undergo rapid

elimination of the cyanide ion (*cf.* Refs 6—8). Allylbenzonitrile **12** probably results from dehydrobromination of the initially formed nitrile **2** under the action of basic components of the reaction mixture. This is in agreement with the presence of benzonitrile and its alkylated derivatives in reaction products (see Table 1, Note to entry *1*) because benzonitrile is known[7,8] to form *via* protonation of the reduced anionic forms of dinitrile **1**. The presence of dinitrile **14** in the reaction products obtained from 1,5-dibromopentane suggests the formation of cyclohexadienyl anion **16** during the *ortho*-alkylation of radical anion $\mathbf{1}^{\bullet -}$. Most likely, indane **11** and tetralin **13** are produced in the reactions of radical anion $\mathbf{1}^{\bullet -}$ with 1,3-dibromopropane and 1,4-dibromobutane, respectively, *via* intramolecular replacement of the Br atom from anion **16** (similar cyclization has been observed in electrochemical generation of an anthracene radical anion in the presence of 1,3-dihaloalkanes[28]) followed by dehydrocyanation of the cyclization products. Double cyanoarylation (probably due to secondary reactions of radical anion $\mathbf{1}^{\bullet -}$ with bromoalkylbenzonitriles **2**—**4**) give diphenylalkanes **5**—**7** and minor products **8**—**10**. We found that their yields decrease with an increase in the dibromoalkane/$\mathbf{1}^{\bullet -}$ ratio. In addition, the "inverse" quenching technique (a solution of the salt of radical anion $\mathbf{1}^{\bullet -}$ in liquid ammonia is slowly added to 1,4-dibromobutane to ensure a constant excess of the latter with respect to nitrile **3**) minimizes the amounts of "secondary" products (see Table 1, entries *2*, *3*). On the whole, the nature and ratio of the products obtained in the reactions of radical anion $\mathbf{1}^{\bullet -}$ with dibromoalkanes indicate that the primary and secondary transformations have comparable rates and probably follow the same ET mechanism (see Scheme 1). ω-(4-Cyanophenyl)alkyl radical **17** arising from the electron transfer from radical anion $\mathbf{1}^{\bullet -}$ to bromoalkylbenzonitriles **2**—**4** undergoes recombination with radical anion $\mathbf{1}^{\bullet -}$ at its *ipso*- or *ortho*-positions to form the corresponding cyclohexadienyl anions **18** or **19**. Loss of the cyanide ion by anion **18** gives products **5**—**7** as the result of the replacement of the cyano group, while oxidation of anion **19** yields products **8**—**10** due to the replacement of the H atom.

For discussion of the mechanism of the reactions of radical anion $\mathbf{1}^{\bullet -}$ with dibromoalkanes, it is significant that the ratio of the *ipso*- and *ortho*-alkylation products (*ipso*/*ortho*) in the reactions with dibromopropane and dibromobutane was approximately two (see Table 1). As shown earlier[5,7] for reactions of radical anion $\mathbf{1}^{\bullet -}$ with monohaloalkanes, this is indicative of the ET mechanism and reflects the regioselectivity of diffusion recombination of radical anion $\mathbf{1}^{\bullet -}$ with an alkyl radical (in this case, with ω-bromoalkyl or ω-(4-cyanophenyl)alkyl one; see Scheme 1). When moving to dibromopentane, the *ipso*/*ortho* ratio increases to 11 (see Table 1, entry *4*). This can be due, at least in part, to different natures of the products formed from anion **16**: neither cyanoindane **11** nor cyanotetralin **13** changes under the reaction conditions, while dicyanophenylpentyl bromide **14** most likely undergoes further transformations. For instance, it is not improbable that the formation of compound **10** results from alkylation of radical anion $\mathbf{1}^{\bullet -}$ with bromide **14**.

Alkylation of the disodium salt of dianion $\mathbf{1}^{2-}$ with α,ω-dibromoalkanes in liquid ammonia (Scheme 2) while mixing the reagents in a "normal" way mainly gives α,ω-bis(4-cyanophenyl)alkanes **5**—**7** in 40—90% yields (for the amounts of the reagents and the ratio of the products, see Table 1, entries *5*—*10*, *13*, *14*). Primary (**2**—**4**) and repeated alkylation products (**8**—**10**) were detected in substantially smaller amounts (below 10%). More profound transformations give 4-{3-[4-(3-bromopropyl)phenyl]propyl}benzonitrile (**20**) and 1,4-bis[3-(4-cyanophenyl)propyl]benzene (**22**) in a reaction of

Scheme 2



n = 3 (**20**, **22**), 4 (**21**, **23**)

dianion $\mathbf{1}^{2-}$ with dibromopropane and, according to ^{1}H NMR and GLC-MS data, their analogs **21** and **23** (20—25% yields) in a reaction with dibromobutane (see Scheme 2; Table 1, entries *5—9*). Obviously, these compounds are formed *via* reduction of diphenylalkanes **5** and **6** with dianion $\mathbf{1}^{2-}$ followed by reactions of their reduced anionic forms with dibromoalkanes.

Compounds **5** and **6** have been described earlier[29—31] but selective spectroscopic data have been reported only for the latter;[32,33] data for compounds **7**, **20**, and **22** are lacking. All these products were isolated by chromatography and characterized by spectroscopic data (see Experimental).

Although the products of the reactions of dianion $\mathbf{1}^{2-}$ with various α,ω-dibromoalkanes differ in composition, the corresponding bis(cyanophenyl)alkanes **5—7** are dominant in all the cases. The increase in their yields when moving from dibromopropane and dibromobutane to dibromopentane is probably due to the lower reduction rate and, consequently, the lower rate at which dinitrile **7** is involved in subsequent transformations, compared to its analogs **5** and **6**. A plausible reason is that the solubility of these compounds in liquid ammonia decreases in this order. With a reaction of dianion $\mathbf{1}^{2-}$ with 1,4-dibromobutane as an example, we showed that the yield of the major product **6** is lowered when dianion $\mathbf{1}^{2-}$ is used in both an excess and deficient amount with respect to dibromide, as well as when the concentrations of the reagents are increased and the reaction time is extended. This is associated with further reactions of dinitriles **5** and **6** with dianion $\mathbf{1}^{2-}$, which is evident from the increased yields of compounds **20—23** (see Table 1). The reactions of dianion $\mathbf{1}^{2-}$ with 1,5-dibromopentane are least sensitive to the aforementioned factors and are most selective.

We attempted to stop the reaction of dianion $\mathbf{1}^{2-}$ with 1,4-dibromobutane at the formation of primary alkylation product **3** by employing the inverse quenching technique (see Table 1, entry *11*). However, bis(cyanophenyl)butane **6** remained dominant (90% yield) under these conditions, undergoing little further transformations.

Thus, the outcomes of the reactions of radical anion $\mathbf{1}^{\bullet-}$ and dianion $\mathbf{1}^{2-}$ with α,ω-dibromoalkanes mainly differ in the nature of the major products: primary alkylation products (bromoalkylbenzonitriles **2—4**) from radical anion $\mathbf{1}^{\bullet-}$ and repeated alkylation products (bis(cyanophenyl)alkanes **5—7**) from dianion $\mathbf{1}^{2-}$. It is unlikely that this is due to the different states of the salts of the two reduced forms in liquid ammonia (visually, the sodium salt of radical anion $\mathbf{1}^{\bullet-}$ forms a solution, while the disodium salt of dianion $\mathbf{1}^{2-}$ forms a suspension). In each case, the nature and composition of the products are determined by the competition between the starting dibromoalkane and the formed bromoalkylbenzonitrile in the reaction with the anionic reagent, whose state is identical for both the competing bromides.

Apparently, the discovered difference in the outcomes of the alkylation of radical anion $\mathbf{1}^{\bullet-}$ and dianion $\mathbf{1}^{2-}$ suggests much more rapid reactions of dianion $\mathbf{1}^{2-}$ with primary alkylation products **2—4** than with the starting dibromoalkanes, while the rates of the reactions of radical anion $\mathbf{1}^{\bullet-}$ with both the alkylating reagents are close to each other. Also, the different outcomes can hardly be attributed to the low solubilities of dibromoalkanes in liquid ammonia since in the reactions of radical anion $\mathbf{1}^{\bullet-}$, they are sufficient for primary and repeated alkylation to proceed at comparable rates. Nevertheless, to verify the assumption of the possible influence of the solvent nature, we replaced liquid ammonia by THF after the generation of dianion $\mathbf{1}^{2-}$ and carried out a reaction of the latter with 1,4-dibromobutane (see Table 1, entry *12*). However, although the yield of bromobutylbenzonitrile **3** (10%) was slightly higher (see Table 1, *cf.* entries *10* and *12*), the reaction outcome was generally the same: the major product was bis(cyanophenyl)butane **6** (70%).

To check the above rate ratio of the primary and repeated alkylation of dianion $\mathbf{1}^{2-}$, we carried out its competitive reaction with, on the one hand, 4-(ω-bromoalkyl)benzonitriles **2** and **3** and, on the other hand, 1-bromopropane and 1-bromobutane, respectively. In the both cases, the reactions mainly gave double alkylation products **5** and **6** (21% both) and **8** and **9** (7 and 10%, respectively) and the products of their further transformations **22** and **23** (15 and 14%, respectively). The total yields of the products of the reactions of dianion $\mathbf{1}^{2-}$ with nitriles **2** and **3** were 3—4 times higher than the yields of 4-propyl- (**24**) and 4-butylbenzonitrile (**25**) (14 and 12%, respectively) formed in the reactions of dianion $\mathbf{1}^{2-}$ with the corresponding alkyl bromides.

It is highly improbable that the discovered difference in the rates of the reactions of dianion $\mathbf{1}^{2-}$ with, on the one hand, α,ω-dibromoalkanes and alkyl bromides and, on the other hand, 4-(ω-bromoalkyl)benzonitriles is due to the different electronic effects of the ω-(4-cyanophenyl) and ω-bromoalkyl substituents on the ease of the reductive cleavage of the C—Br bond in the alkylating reagent since the length of the polymethylene chain separating the reaction center and the substituent is sufficiently long in all cases. We assume that the alkylation of dianion $\mathbf{1}^{2-}$ with dibromoalkanes and bromoalkylbenzonitriles follow different mechanisms.

Like reactions with *n*-alkyl bromides,[8] highly selective primary *ipso*-alkylation of dianion $\mathbf{1}^{2-}$ with α,ω-dibromoalkanes most likely occurs as an S_N reaction. In contrast, analogous reactions of radical anion $\mathbf{1}^{\bullet-}$, which follow the ET mechanism, are not highly regioselective.[5,7] It should be noted that reactions of the electrochemically generated anthracene radical anion with alkyl halides are highly regioselective in the case of the S_N mechanism and

poorly regioselective in the case of the ET mechanism.[15] Apparently, the specific feature that distinguishes the reactions of dianion $\mathbf{1}^{2-}$ with dinitriles **2**—**4** from its reactions with dibromoalkanes may be the formation in the former of a charge transfer complex (CTC) between dianion $\mathbf{1}^{2-}$ and the cyanophenyl fragment of reagent **2**—**4** (see Scheme 2), which is similar to that proposed earlier[34] for reactions of dianion $\mathbf{1}^{2-}$ with arenecarbonitriles. This assumption agrees with data on the formation of CTC between arenes and their reduced anionic forms[35] and on the detection of CTC as a key intermediate of ET reactions.[36] Then such a CTC may be transformed into anion of the type **18** either in a synchronous single-step way or according to the intracomplex ET mechanism. In the latter case, the electron is transferred from dianion $\mathbf{1}^{2-}$ first to the cyanophenyl fragment of reagent **2**—**4** involved in CTC formation and then to the dissociating C—Br bond. The resulting radical anion $\mathbf{1}^{\bullet -}$ and 4-cyanophenylalkyl radical **17** undergo recombination to give cyclohexadienyl anion **18**, which further yields products **5**—**7**. Possible evidence for this mechanism is provided by some contribution of *ortho*-alkylation leading to anion **19**. The substantially higher ratio of *ortho*/*para*-alkylation in this case compared to similar reactions of radical anion $\mathbf{1}^{\bullet -}$ (~2) does not exclude, in our opinion, this possibility since recombination of radical anion $\mathbf{1}^{\bullet -}$ and radical **17** occurs in a primary cage with a structure given by the structure of the preceding CTC rather than in the diffusion regime (see Scheme 2). Diffusion recombination characterized by low selectivity occurs according to the ET mechanism in the alkylation of radical anion $\mathbf{1}^{\bullet -}$.[7]

Assessing the potential synthetic value of the results presented above, we should note that bromoalkylbenzonitriles **2**—**4** are promising for use as bifunctional electrophiles. The single-step way in which the process occurs and the accessibility of the starting compounds can largely compensate for low (~20%) yields of nitriles **2**—**4** in the alkylation of radical anion $\mathbf{1}^{\bullet -}$ with α,ω-dibromoalkanes compared to earlier conducted multistep syntheses of the same products in total ~15% yields.[17—21] Functionalized bisarylalkanes, including compounds **5** and **6**, are part of wavelength converters in semiconductor lasers,[29] used to prepare biologically active[31] and macrocyclic compounds,[33] and are obviously valuable for fine organic synthesis as building blocks with a wide range of possible applications. The developed approach to their synthesis with dianion $\mathbf{1}^{2-}$ as a synthon of *para*-cyanophenylation of dibromoalkanes offers an advantage over the previous multistep syntheses because its efficient single-step procedure ensures substantially higher yields of the target products (60—90% *vs.* ~15% (see Refs 29—31)) with respect to the starting reagents with comparable accessibilities.

Experimental

^{1}H NMR spectra were recorded on a Bruker AC-200 instrument in acetone-d_6 or $CDCl_3$. IR spectra were recorded on a Vector-22 instrument (Bruker). The exact masses of molecular ions were determined by high-resolution mass spectrometry on a Finnigan MAT-8200 instrument. The components were identified by GLC-MS on a Hewlett Packard G1081A setup consisting of an HP 5890 Series II gas chromatograph and an HP 5971 mass-selective detector (ionizing energy 70 eV, HP5 column (5% poly(diphenylsiloxane), 95% poly(dimethylsiloxane)), 30 m × 0.25 mm × 0.25 μm, helium as a carrier gas, 1 mL min^{-1}; column heating conditions: 2 min at 50 °C, heating at a rate of 10 deg min^{-1}, 5 min at 280 °C; evaporation chamber temperature 280 °C; ion source temperature 173 °C; data were collected at a rate of 1.2 scan s^{-1} in the mass range from 30 to 650 amu.

Liquid NH_3 was purified by distillation over metallic sodium to a reaction vessel cooled to −70 °C; THF was dehydrated by reflux over sodium benzophenone ketyl and distilled under argon to a reaction vessel immediately before use. An oxide layer from metallic sodium was removed under dry hexane. Dibromoalkanes were purified by passing through alumina followed by distillation. Terephthalonitrile was purified by sublimation *in vacuo*, m.p. 222 °C (*cf.* Ref. 37: m.p. 222—223 °C).

Generation of radical anion $\mathbf{1}^{\bullet -}$ and dianion $\mathbf{1}^{2-}$. Metallic Na (0.95 equiv. for $\mathbf{1}^{\bullet -}$ and 2.10 equiv. for $\mathbf{1}^{2-}$) was added to a stirred suspension of dinitrile **1** in liquid NH_3 (25—50 mL) in an atmosphere of evaporating NH_3 at −33 °C. The resulting dark green solution of the salt of radical anion $\mathbf{1}^{\bullet -}$ or the resulting black-brown suspension of the salt of dianion $\mathbf{1}^{2-}$ were used in subsequent transformations.

Reactions of radical anion $\mathbf{1}^{\bullet -}$ and dianion $\mathbf{1}^{2-}$ with α,ω-dibromoalkanes (general procedure). α,ω-Dibromoalkane (for the specified amount, see Table 1) was added dropwise in an inert atmosphere of evaporating NH_3 to a stirred solution of the salt of radical anion $\mathbf{1}^{\bullet -}$ or a stirred suspension of the salt of dianion $\mathbf{1}^{2-}$ in liquid NH_3; the starting solution(suspension) turned red-brown. The reaction mixture was kept under the same conditions for 40—50 min and brought in contact with air. Diethyl ether (30—50 mL) was added and stirring was continued to complete evaporation of the NH_3. After water (50 mL) was added, the solid precipitate was filtered off, successively washed with Et_2O and water, and dried in air. The product from the liquid fraction was extracted with Et_2O (3×40 mL). The combined ethereal extract was washed with water to neutral pH, dried over $MgSO_4$, and concentrated. The compositions of the mixtures of products were determined from ^{1}H NMR spectra and GLC-MS data. Individual compounds were isolated by recrystallization from hexane or by TLC on a fixed sorbent (silica gel LSL_{254} 5/40 μ with added gypsum (13 wt.%), hexane—Et_2O (6—9) : 1 (v/v) as an eluent). The result of separation was checked visually by irradiation of dried plates with UV light. The fractions of the products were washed out from the sorbent with Et_2O. The compositions of the fractions were analyzed by the ^{1}H NMR and GLC-MS methods.

4-(3-Bromopropyl)benzonitrile (2), 5-cyanoindane (11), and 4-allylbenzonitrile (12). A reaction of radical anion $\mathbf{1}^{\bullet -}$ with 1,3-dibromopropane (see Table 1, entry *l*) gave a mixture of products from which nitrile **2** (0.080 g, 15%) was isolated as a

colorless oil, R_f 0.3 (hexane—Et_2O, 6 : 1). IR (thin film), ν/cm^{-1}: 2228 (C≡N). ^{1}H NMR (acetone-d_6), δ: 2.10—2.25 (m, 2 H, CH_2); 2.86 (t, 2 H, $ArCH_2$, J = 9 Hz); 3.47 (t, 2 H, CH_2Br, J = 9 Hz); 7.45 (d, AA´BB´ system, 2 H, H(3), H(5), J = 8 Hz); 7.68 (d, AA´BB´ system, 2 H, H(2), H(6), J = 8 Hz). High-resolution MS, found: m/z 222.9994 [M]$^+$. $C_{10}H_{10}NBr$. Calculated: M = 222.9997. Indane **11** (0.26 mmol) and nitrile **12** (0.24 mmol) were detected in a fraction with R_f ~0.8. For this fraction, ^{1}H NMR ($CDCl_3$), δ: 2.10 (quint, 2 H, CH_2, J = 9 Hz); 2.90—2.97 (m, 4 H, 2 CH_2); 7.27 (d, 1 H, H(7), J = 9 Hz); 7.39 (dd, 1 H, H(6), J = 9 Hz, J = 1 Hz); 7.46 (d, 1 H, H(4), J = 1 Hz) (the signals relate to compound **11**); 3.34 (d, 2 H, $ArCH_2$, J = 7 Hz); 5.10 (dd, 1 H, =CH_2, J = 16.7 Hz, J = 2.0 Hz); 5.13 (dd, 1 H, =CH_2, J = 10.2 Hz, J = 2.0 Hz); 5.93 (ddt, 1 H, =CH—, J = 16.7 Hz, J = 10.2 Hz, J = 6.6 Hz); 7.28 (d, AA´BB´ system, 2 H, H(3), H(5), J = 8.4 Hz); 7.56 (d, AA´BB´ system, 2 H, H(2), H(6), J = 8.4 Hz) (the signals relate to compound **12**). GLC-MS revealed two peaks with m/z 143 ([M]$^+$).

4-(4-Bromobutyl)benzonitrile (3) and 2-cyano-5,6,7,8-tetrahydronaphthalene (13). A reaction of radical anion $\mathbf{1}^{\bullet-}$ with 1,4-dibromobutane (see Table 1, entry *2*) gave a mixture of products from which nitrile **3** (0.091 g, 16%) was isolated as a colorless oil, R_f 0.3 (hexane—Et_2O, 6 : 1). IR (thin film), ν/cm^{-1}: 2227 (C≡N). ^{1}H NMR (acetone-d_6), δ: 1.67—1.94 (m, 4 H, 2 CH_2); 2.74 (t, 2 H, $ArCH_2$, J = 9 Hz); 3.50 (t, 2 H, CH_2Br, J = 9 Hz); 7.43 (d, AA´BB´ system, 2 H, H(3), H(5), J = 8.4 Hz); 7.67 (d, AA´BB´ system, 2 H, H(2), H(6), J = 8.4 Hz). High-resolution MS, found: m/z 237.0150 [M]$^+$. $C_{11}H_{12}NBr$. Calculated: M = 237.0153. Tetrahydronaphthalene **13** (0.038 g, 10%) was isolated as a viscous white solid, R_f 0.5 (hexane—Et_2O, 6 : 1), m.p. 20 °C (*cf.* Ref. 38: m.p. 20—21 °C). IR (KBr), ν/cm^{-1}: 2230 (C≡N). ^{1}H NMR ($CDCl_3$), δ: 1.77—1.82 (m, 4 H, 2 CH_2); 2.73—2.80 (m, 4 H, 2 $ArCH_2$); 7.11 (d, 1 H, H(4), J = 8 Hz); 7.31 (dd, 1 H, H(3), J = 8 Hz, J = 1.5 Hz); 7.32 (d, 1 H, H(1), J = 1.5 Hz). High-resolution MS, found: m/z 157.0893 [M]$^+$. $C_{11}H_{11}N$. Calculated: M = 157.0891.

4-(5-Bromopentyl)benzonitrile (4) and 2-(5-bromopentyl)-1,4-dicyanobenzene (14). A reaction of radical anion $\mathbf{1}^{\bullet-}$ with 1,5-dibromopentane (see Table 1, entry *4*) gave a mixture of products from which nitrile **4** (0.121 g, 20%) was isolated as a colorless oil, R_f 0.5 (hexane—Et_2O, 6 : 1). IR (thin film), ν/cm^{-1}: 2227 (C≡N). ^{1}H NMR (acetone-d_6), δ: 1.38—1.56, 1.58—1.68, 1.81—1.95 (all m, 2 H each, CH_2); 2.73 (t, 2 H, $ArCH_2$, J = 8 Hz); 3.48 (t, 2 H, CH_2Br, J = 8 Hz); 7.45 (d, AA´BB´ system, 2 H, H(3), H(5), J = 8 Hz); 7.76 (d, AA´BB´ system, 2 H, H(2), H(6), J = 8 Hz). High-resolution MS, found: m/z 252.1531 [M]$^+$. $C_{12}H_{14}NBr$. Calculated: M = 252.1533. Bromopentyldicyanobenzene **14** (0.05 mmol) was detected in a fraction with R_f ~0.2 with the starting dinitrile **1** (0.03 mmol). For compound **14**, ^{1}H NMR ($CDCl_3$), δ: 1.43—1.59 (m, 2 H, CH_2); 1.60—1.78, 1.82—1.97 (both m, 4 H each, 4 CH_2); 2.88 (t, 2 H, $ArCH_2$, J = 8 Hz); 3.40 (t, 2 H, CH_2Br, J = 7 Hz); 7.55 (dd, 1 H, H(5), J = 8.6 Hz, J = 1.5 Hz); 7.60 (d, 1 H, H(3), J = 1.5 Hz); 7.70 (d, 1 H, H(6), J = 8.6 Hz). GLC-MS revealed a peak with m/z 276 ([M]$^+$).

1,3-Bis(4-cyanophenyl)propane (5). A reaction of dianion $\mathbf{1}^{2-}$ with 1,3-dibromopropane (see Table 1, entry *5*) gave a mixture of products from which compound **5** (0.266 g, 45%) was isolated as a white solid, R_f 0.2 (hexane—Et_2O, 8 : 1), m.p. 94—95 °C (*cf.* Ref. 25: m.p. 94—95 °C). IR (KBr), ν/cm^{-1}: 2227 (C≡N). ^{1}H NMR (acetone-d_6), δ: 1.97—2.08 (m, 2 H, CH_2); 2.75 (t, 4 H, 2 $ArCH_2$, J = 8 Hz); 7.42 (d, 2 AA´BB´ systems, 4 H, H(2´), H(6´), H(2″), H(6″), J = 8 Hz); 7.68 (d, 2 AA´BB´ systems, 4 H, H(3´), H(5´), H(3″), H(5″), J = 8 Hz). High-resolution MS, found: m/z 246.1126 [M]$^+$. $C_{17}H_{14}N_2$. Calculated: M = 246.1157.

1,5-Bis(4-cyanophenyl)pentane (7). A reaction of dianion $\mathbf{1}^{2-}$ with 1,5-dibromopentane (see Table 1, entry *14*) gave a mixture of products from which compound **7** (1.030 g, 75%) was isolated as a white solid, R_f 0.3 (hexane—Et_2O, 8 : 1), m.p. 117 °C. IR (KBr), ν/cm^{-1}: 2226 (C≡N). ^{1}H NMR (acetone-d_6), δ: 1.31—1.45 (m, 2 H, CH_2); 1.61—1.76 (m, 4 H, 2 CH_2); 2.71 (t, 4 H, 2 $ArCH_2$, J = 8 Hz); 7.41 (d, 2 AA´BB´ systems, 4 H, H(2´), H(6´), H(2″), H(6″), J = 8 Hz); 7.66 (d, 2 AA´BB´ systems, 4 H, H(3´), H(5´), H(3″), H(5″), J = 8 Hz). High-resolution MS, found: m/z 274.1468 [M]$^+$. $C_{19}H_{18}N_{22}$. Calculated: M = 274.1469.

4-{3-[4-(3-Bromopropyl)phenyl]propyl}benzonitrile (20). A reaction of dianion $\mathbf{1}^{2-}$ with 1,3-dibromopropane (see Table 1, entry *6*) gave a mixture of products from which compound **20** (0.034 g, 2%) was isolated as a white solid, R_f 0.15 (hexane—Et_2O, 9 : 1). IR (KBr), ν/cm^{-1}: 2227 (C≡N). ^{1}H NMR (acetone-d_6), δ: 1.85—2.18 (m, 4 H, 2 CH_2); 2.56—2.79 (m, 6 H, 3 $ArCH_2$); 3.45 (t, 2 H, CH_2Br, J = 8 Hz); 7.14 (s, 4 H, H(2´), H(3´), H(5´), H(6´)); 7.41 (d, AA´BB´ system, 2 H, H(3), H(5), J = 8 Hz); 7.66 (d, AA´BB´ system, 2 H, H(2), H(6), J = 8 Hz). High-resolution MS, found: m/z 341.0779 [M]$^+$. $C_{19}H_{20}NBr$. Calculated: M = 341.0779.

1,4-Bis[3-(4-cyanophenyl)propyl]benzene (22). A reaction of dianion $\mathbf{1}^{2-}$ with 1,3-dibromopropane (see Table 1, entry *6*) gave a mixture of products from which compound **22** (0.145 g, 8%) was isolated as a white solid, R_f 0.4 (hexane—Et_2O, 9 : 1), m.p. 280 °C. Found (%): C, 84.71; H, 6.94; N, 8.32. $C_{26}H_{24}N_2$. Calculated (%): C, 85.68; H, 6.64; N, 7.69. IR (KBr), ν/cm^{-1}: 2226 (C≡N). ^{1}H NMR (acetone-d_6), δ: 1.68—1.72 (m, 4 H, 2 CH_2); 2.27—2.35, 2.98—3.04 (both m, 4 H each, 4 $ArCH_2$); 7.08—7.12 (m, 4 H, H(2), H(3), H(5), H(6)); 7.44 (d, 2 AA´BB´ systems, 4 H, 2 H(2´), 2 H(6´), J = 8 Hz); 7.67 (d, 2 AA´BB´ systems, 4 H, 2 H(3´), 2 H(5´), J = 8 Hz).

Reaction of dianion $\mathbf{1}^{2-}$ with 1,4-dibromobutane in THF. Dinitrile **1** (0.64 g, 5 mmol) was placed in a three-neck flask fitted with a stirrer, a bubbler, and a gas outlet. Tetrahydrofuran (50 mL) was distilled under argon to the flask. Ammonia (30 mL) was condensed with continuous stirring at −70 °C and then metallic Na (0.24 g, 10.25 mmol) was added. The ammonia was evaporated in an argon flow (~30 min). 1,4-Dibromobutane (1.2 mL, 10 mmol) was added under argon with continuous stirring at 10 °C to the resulting dark brown suspension of the disodium salt of dianion $\mathbf{1}^{2-}$ in NH_3-saturated THF. The reaction mixture was stirred in an inert atmosphere for 40 min and then treated and analyzed as described above. A mixture of products obtained (2.01 g) mainly contained 1,4-bis(4-cyanophenyl)butane (**6**) (70%) (for the complete composition of the products, see Table 1, entry *12*).

Reaction of dianion $\mathbf{1}^{2-}$ with 1,4-dibromobutane under inverse quenching. Dinitrile **1** (0.64 g, 5 mmol) was placed in a two-neck dropping funnel fitted with a pressure equalization arm, a stirrer, and a gas outlet. Liquid NH_3 (50 mL) was condensed with continuous stirring at −70 °C into the funnel. Metallic Na (0.24 g, 10.2 mmol) was added with stirring in an atmosphere of evaporating NH_3. The resulting suspension of the

disodium salt of dianion $\mathbf{1}^{2-}$ was added dropwise for 20 min to a stirred solution of 1,4-dibromobutane (3 mL, 25.0 mmol) in THF (3 mL) cooled to −30 °C. The reaction mixture was kept for 10 min and treated according to the standard procedure to give a mixture of products (4.52 g) (for the composition, see Table 1, entry *11*). Bis(4-cyanophenyl)butane **6** was isolated by crystallization from hexane—benzene (4 : 1 v/v).

1,4-Bis(4-cyanophenyl)butane (6). Yield 0.58 g (90%), m.p. 132 °C (*cf*. Ref. 30: m.p. 133—134 °C). IR (KBr), ν/cm^{-1}: 2227 (C≡N). ^{1}H NMR (acetone-d_6), δ: 1.63—1.72 (m, 4 H, 2 CH_2); 2.75 (t, 4 H, 2 CH_2, J = 8 Hz); 7.42 (d, 2 AA´BB´ systems, 4 H, H(2´), H(6´), H(2″), H(6″), J = 8 Hz); 7.67 (d, 2 AA´BB´ systems, 4 H, H(3´), H(5´), H(3″), H(5″), J = 8 Hz). High-resolution MS, found: m/z 260.1309 $[M]^+$. $C_{18}H_{16}N_2$. Calculated: M = 260.1313.

Competitive reactions of dianion $\mathbf{1}^{2-}$ with 4-(ω-bromoalkyl)benzonitriles 2 and 3 and *n*-alkyl bromides. ***A.*** A solution of compound **2** (0.18 g, 0.79 mmol) and PrBr (0.07 mL, 0.79 mmol) in THF (3 mL) was added dropwise to a stirred suspension of the salt of dianion $\mathbf{1}^{2-}$ prepared from dinitrile **1** (0.10 g, 0.78 mmol) and metallic Na (0.037 g, 1.60 mmol) in liquid NH_3 (25 mL). The reaction mixture was treated as described above to give a mixture (0.24 g) of compounds **5** (21%), **8** (7%), **20** (15%), **24** (14%), and **1** (7%) (GLC-MS and ^{1}H NMR data).

B. A solution of compound **3** (0.17 g, 0.72 mmol) and BuBr (0.077 mL, 0.72 mmol) in THF (3 mL) was added dropwise to a stirred suspension of the salt of dianion $\mathbf{1}^{2-}$ prepared from dinitrile **1** (0.09 g, 0.72 mmol) and metallic Na (0.035 g, 1.51 mmol) in liquid NH_3 (25 mL). The reaction mixture was treated as described above to give a mixture (0.26 g) of compounds **6** (21%), **9** (10%), **23** (17%), **25** (12%), and **1** (11%) (GLC-MS and ^{1}H NMR data).

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