Reductive activation of arenes
21.* Reaction of products of two-electron reduction of arenecarbonitriles by alkali metals in liquid ammonia with bromo- and dibromoalkanes**

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Reductive alkylation of benzonitrile, *ortho*-, *meta*-, *para*-tolunitriles, and 1-naphthonitrile by sequential action of alkali metal and alkyl bromide in liquid ammonia results in corresponding alkylarenes and 1-alkyl-1-cyanocyclohexa-2,5-dienes. The experimental conditions for target synthesis of the specified products are found. A method of synthesis of 1-(ω-bromoalkyl)-1-cyanocyclohexa-2,5-dienes based on the interaction of two-electronic reduction products of aromatic nitriles with α,ω-dibromoalkanes $Br(CH_2)_nBr$ (n = 3—5) is developed.

Key words: aromatic nitriles, reductive alkylation, cyanocyclohexadienyl anions, 1-alkyl-1-cyanocyclohexa-2,5-dienes, 1-(ω-bromoalkyl)-1-cyanocyclohexa-2,5-dienes.

Two-electron reduction of arenecarbonitriles, namely, benzonitrile, naphthonitrile, cyanoanthracene,[2] and *ortho*-, *meta*-, and *para*-tolunitriles[1] by alkali metals in liquid NH_3 allows one to generate preparative amounts of stable cyclohexadienyl anions that are highly reactive in the reactions with electrophilic reagents, in particular, alkyl halides.[3] The primary products of such reactions, namely, dihydroarenes alkylated at the saturated carbon atom possess a versatile reactivity. Therefore, they can be used as initial compounds in fine organic synthesis, *e.g.*, as building blocks[4] in the design of analogs of natural biologically active compounds, such as fungicides and insecticides, reagents for generation of free radicals, *etc*.

Production of cyclohexadienyl anions as mentioned above is accompanied by the formation of an equivalent amount of amide ions. Under the action of amide ions the primary alkylation products of anions, that is, alkylcyanodihydroarenes undergo dehydrocyanation to give alkylarenes (Scheme 1).

The overall yield of alkylation products is 55 to 90%, and the dihydroarene/alkylarene ratio varies in the range 0.1—0.5 depending on the nature of the substrate and alkyl halide. For instance, the proportion of dihydroarene increases both upon replacement of the naphthyl fragment by phenyl one[5] and introduction of Me group at *para*-position of the substrate,[5—7] which seems to be due to a decrease in the CH-acidity of the primary dihydroarene. Besides, the percentage of dihydroarene depends on the nature of alkyl halide and increases on going from chlorides to iodides.[5] It also increases upon branching of the alkyl fragment[6] probably owing to more efficient neutralization of amide ion by alkyl halides or products of their ammonolysis. It should be emphasized that the major reaction product is always the alkylarene.

The aim of this work was to establish the experimental conditions suitable for minimization of the yields of dehydrocyanation products and for the use of products of two-electron reduction of cyanoarenes in liquid NH_3 as synthons for cyanodihydroarylation of alkyl halides. With this purpose we studied the effects of the nature of alkali metal, proton-donor additives and cosolvent, the reagent ratio, and the order of mixing of reagents on the ratio of the products of reductive alkylation of aromatic nitriles. Additionally, we studied the interaction of cyclohexadienyl anions with α,ω-dibromoalkanes. This is the first example of alkylation of such anions using dihalogenides.

Results and Discussion

Cyclohexadienyl anions were generated from benzonitrile (**1**), its methyl derivatives, namely, *ortho*- (**2**),

* For Part 20, see Ref. 1.

** Dedicated to the memory of Academician V. A. Koptyug on the occasion of the 75th anniversary of his birth.

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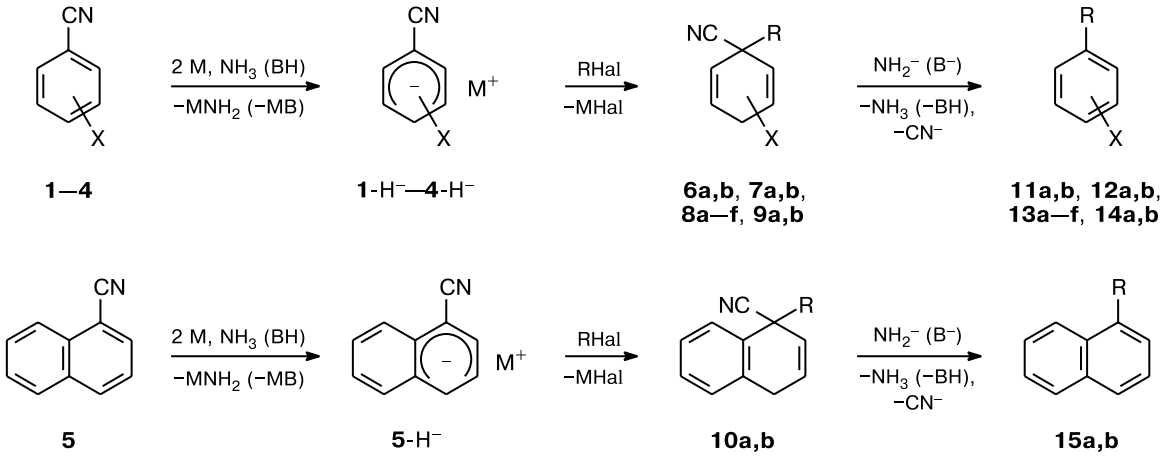
Scheme 1



X = H (**1**, **6a,b**, **11a,b**), *o*-Me (**2**, **7a,b**, **12a,b**), *m*-Me (**3**, **8a—f**, **13a—f**), *p*-Me (**4**, **9a,b**, **14a,b**);
M = Li, Na, K; BH = Bu^{t}OH, NH_4Cl, Bu^{t}Cl; Hal = Br, I;
R = Bu (**6a**, **7a**, **9a—12a**, **14a**, **15a**), $(CH_2)_5Br$ (**6b**, **7b**, **9b—12b**, **14b**, **15b**);
8, **13:** R = Bu (**a**), Bu^i (**b**), Me (**c**), $(CH_2)_3Br$ (**d**), $(CH_2)_4Br$ (**e**), $(CH_2)_5Br$ (**f**)

meta- (**3**), and *para*-tolunitriles (**4**), and 1-naphthonitrile (**5**). As was found earlier for anions **1**-H$^-$, **3**-H$^-$—**5**-H$^-$ (see Scheme 1) and established in this work for anion **2**-H$^-$, 1-alkyl-1-cyano-1,4-dihydroarenes **6—10** formed after adding a primary alkyl halide to sodium salts of cyclohexadienyl anions in liquid NH_3 (procedure *A*) undergo almost complete dehydrocyanation and transform into alkylarenes **11—15** (see Scheme 1 and Table 1).

The conditions for reductive alkylation of aromatic nitriles were optimized in order to obtain compounds **6—10** taking the reactions of anion **3**-H$^-$ with primary alkyl halides as an example. We studied the effect of proton-donor additives, cosolvent, nature of alkali metal, and order of mixing of the reagents on the extent of dehydrocyanation of alkylcyanodihydroarenes **8**. The reagents used and the reagent ratios are listed in the Experimental and

Table 1. Effect of reaction conditions on the ratio of products of the reductive alkylation of nitriles **1—5** in liquid NH_3 (see Scheme 1)

Nitrile	M	Cosolvent	Protonating agent	RHal	Alkylation procedure*	Product yield (mol.%)**		Diene/Arene
						Diene	Arene	
1 [5]	K	—	—	BuBr	*A*	13 (**6a**)	42 (**11a**)	0.3
1	Li	THF	Bu^{t}OH	BuBr	*B*	88 (**6a**)	1 (**11a**)	88
2	Na	—	—	BuBr	*A*	1 (**7a**)	54 (**12a**)	0.02
2	Li	THF	Bu^{t}OH	BuBr	*B*	93 (**7a**)	3 (**12a**)	31
3 [6]	Na	—	—	BuBr	*A*	1 (**8a**)	83 (**13a**)	0.01
3 [6]	Na	—	—	Bu^{i}Br	*A*	10 (**8b**)	63 (**13b**)	0.2
3	Na	—	NH_4Cl	Bu^{i}Br	*A*	28 (**8b**)	34 (**13b**)	0.8
3	Na	—	Bu^{t}Cl	Bu^{i}Br	*A*	35 (**8b**)	27 (**13b**)	1.3
3	Na	THF	Bu^{t}OH	Bu^{i}Br	*A*	28 (**8b**)	51 (**13b**)	0.6
3	Li	THF	Bu^{t}OH	Bu^{i}Br	*A*	47 (**8b**)	27 (**13b**)	1.7
3	Na	—	—	Bu^{i}Br	*B*	1 (**8b**)	53 (**13b**)	0.02
3	Na	—	—	MeI	*B*	45 (**8c**)	3 (**13c**)	15
3	Li	THF	Bu^{t}OH	BuBr	*B*	88 (**8a**)	7 (**13a**)	13
4 [7]	Na	—	—	BuBr	*A*	27 (**9a**)	61 (**14a**)	0.4
4	Li	THF	Bu^{t}OH	BuBr	*B*	73 (**9a**)	1 (**14a**)	73
5 [5]	K	—	—	BuBr	*A*	2 (**10a**)	68 (**15a**)	0.03
5	Li	THF	Bu^{t}OH	BuBr	*B*	79 (**10a**)	2 (**15a**)	39

* *A* and *B* denote the conventional and reverse order of mixing of reagents (see Experimental).
** According to GLC/MS and ^{1}H NMR spectroscopy data.

the reaction product yields are given in Table 1. The previously unknown alkylation products were isolated from the reaction mixtures and characterized spectroscopically (see Experimental).

Amide ions were neutralized using NH_4Cl, Bu^tOH, and Bu^tCl. *tert*-Butyl chloride acting as protonating agent undergoes elimination and transforms into isobutylene. These reagents were added to solutions of the reduction products of nitrile **3** prior to treatment with alkyl halide. Then, alkylation was performed and the reaction mixtures were neutralized with an excess of ammonium chloride. Neutralization of amide-ion with NH_4Cl and Bu^tCl causes the **8b**/**13b** ratio to increase to 0.8 and 1.3, respectively. Adding an equivalent amount of Bu^tOH to the solution of sodium salt of anion **3**-H^- in ammonia causes no decrease in the contribution of the secondary transformations. Reduction of nitrile **3** by sodium in the presence of Bu^tOH with THF as cosolvent (THF : ammonia = 1 : 5 v/v) leads to a decrease in the yield of the dehydrocyanation product (**8b**/**13b** ratio equals 0.6). When sodium is replaced by lithium, the **8b**/**13b** ratio increases to 1.7. A decrease in the extent of dehydrocyanation on going from sodium to lithium is likely due to lower basicity of lithium salts in liquid ammonia compared to sodium salts.[8]

The reaction of two-electron reduction products of benzonitrile and *ortho*-methoxybenzonitrile by lithium in the NH_3/THF/Bu^tOH system with benzyl bromide and 3-bromo-1-chloropropane results in 65—80% yields of substituted cyanocyclohexadienes.[9] Dehydrocyanation of these compounds is efficiently inhibited by neutralizing the reaction mixture with NH_4Cl after alkylation.[9] In contrast to this, the highest yield of diene **8b** achieved in this work under similar conditions is at most 50%, the dehydrocyanation product **13b** being also formed in nearly 30% yield.

The results obtained suggest that alkylation of cyclohexadienyl anion on slow addition of the alkylating agent to the solution of the two-electron reduction product of nitrile is accompanied by the dehydrocyanation of diene. Cyanocyclohexadienes **6—10** formed as a result of protonation of cyclohexadienyl anions are oxidized to initial nitriles upon treatment of the reaction mixture or undergo transformation into cyclohexadienyl anions under the action of bases followed by alkylation.

In this connection one could expect that dehydrocyanation will be most efficiently inhibited by reversing the order of reagent mixing, *i.e.*, on slow addition of the solution of cyclohexadienyl anion salt to an excess alkyl halide (procedure *B*). Here, alkylcyanocyclohexadiene is formed in the presence of minimum amounts of bases (cyclohexadienyl anion and amide ion) that are neutralized faster than in conventional mixing due to the presence of excess alkyl halide and ammonium ion produced as a result of ammonolysis of the alkyl halide. Earlier,[5] we showed that alkylation of the sodium salts of anions **1**-H^- and **5**-H^- with a large excess of MeI allows one to reduce the extent of dehydrocyanation of the primary reaction product to 10%. However, from our experiments carried out in this study it follows that the result of alkylation performed using the reverse order of reagent mixing strongly depends on both the reactivity of the alkyl halide and the conditions for generation of cyclohexadienyl anion. For instance, as with conventional mixing of reagents, the interaction of the sodium salt of anion **3**-H^- with an excess of Bu^iBr results in isobutyltoluene **13b** as the major product. The extent of dehydrocyanation considerably decreases only in the reaction with a more reactive methyl iodide (ammonolysis rates for MeI and Bu^iBr differ by several orders of magnitude[10]), namely, the dihydroarene/alkylarene ratio is 15 and the yield of the major reaction product (**8c**) reaches a value of 45%. Therefore, the effect of the reverse order of reagent mixing in the alkylation of sodium salt of anion **3**-H^- in the presence of sodium amide manifests itself only when using those alkyl halides that are comparable with MeI in reactivity. Reduction of nitrile **3** under lower-basicity conditions, that is, by lithium in a NH_3/THF mixture in the presence of Bu^tOH followed by slow addition of the solution of the salt of anion **3**-H^- thus generated to an excess of BuBr leads to preferred formation of cyclohexadiene **8a** in 88% yield (**8a**/**13a** ratio is ~13).

In order to check the general character of the procedure employed, we carried out a series of experiments with nitriles **1**, **2**, **4**, and **5** and established that the reactions of anions **1**-H^-, **2**-H^-, **4**-H^- and **5**-H^- generated under these conditions with BuBr in all cases result in preferred formation of the corresponding alkylcyanodihydroarenes **6a**, **7a**, **9a**, and **10a** in ~70—90% yields. This makes it possible to consider the proposed procedure for reductive alkylation of aromatic mononitriles synthetically valuable.

In order to extend the field of application of this method for synthesis of functionalized cyanocyclohexadienyl compounds, it was appropriate to extend the spectrum of the alkylating agents by involving dihaloalkanes in the reactions with cyclohexadienyl anions. We studied the interaction of anions **1**-H^-—**5**-H^- with α,ω-dibromoalkanes including three to five carbon atoms in the main chain. ω-Haloalkylated products can be obtained in the reactions of the anions formed in the reduction of monocyanobenzenes,[9] nitrobenzene,[11] naphthalene,[12] and 3,4-diphenylcinnoline[13] with α,ω-dihaloalkanes. Bromide reagents were chosen because other alkyl halides are prone to involvement in side reactions, in particular, substitution of both halogen atoms in diiodoalkanes or protonation of anionic reduced forms of nitriles by chloroalkanes that possess the properties of CH-acids.[5]

We established that the reactions of anion **3**-H^- generated by reduction of nitrile **3** by lithium in NH_3/THF

Table 2. Reaction of products of two-electron reduction of aromatic nitriles **1—5** by lithium in NH_3/THF/Bu^{t}OH mixture with $Br(CH_2)_nBr$ (procedure *B*)

Nitrile	*n*	Yield of reaction products (mol.%)*	
		Dihydroarene	Bromoalkylarene
3	3	92 (**8d**)	3 (**13d**)
3	4	71 (**8e**)	—
3	5	75 (**8f**)	9 (**13f**)
3 **	5	50 (**8f**)	11 (**13f**)
1	5	72 (**6b**)	18 (**11b**)
2	5	75 (**7b**)	2 (**12b**)
4	5	67 (**9b**)	7 (**14b**)
5	5	54 (**10b**)	11 (**15b**)

* According to GLC/MS and ^{1}H NMR spectroscopy data.
** Experiment was carried out following procedure *A*; the mixture of products also contained compounds **16** (18%) and **17** (7%).

mixture in the presence of Bu^{t}OH with 1,3-dibromopropane, 1,4-dibromobutane, and 1,5-dibromopentane carried out using the reverse order of the addition of the reagents result in the corresponding 1-(ω-bromoalkyl)-1-cyano-3-methylcyclohexa-2,5-dienes **8d—f** (see Scheme 1 and Table 2) as the major products. Here, the extent of dehydrocyanation of compounds **8d—f** to give 3-(ω-bromoalkyl)toluenes **13d—f** is low. Taking the interaction of anion **3**-H$^-$ with 1,5-dibromopentane as an example, we studied the possibility of the synthesis of substituted dienes using a conventional order mixing of reagents, which does not require a large excess of alkyl halide. This results in diene **8f** and toluene **13f** in a 4.5 : 1 ratio. Additionally, considerable amounts of the substitution products of the second bromine atom, namely, 1,5-di(1-cyano-3-methylcyclohexa-2,5-dienyl)pentane (**16**) and 1-cyano-3-methyl-1-[5-(3-methylphenyl)pentyl]cyclohexa-2,5-diene (**17**) are formed. Compounds **16** and **17** were not isolated in individual form, but they were detected in the mixtures of reaction products (see Table 2) by GLC/MS and ^{1}H NMR spectroscopy. Therefore, a slow addition of dibromoalkane to a solution of the salt of anion **3**-H$^-$ is accompanied by the formation of rather large amounts of secondary products corresponding to both dehydrocyanation of diene **8f** and replacement of a bromine atom in **8f** or in toluene **13f**, whereas the procedure involving the reverse order of reagent mixing permits almost complete inhibition of side processes.

Reactions of anions **1**-H$^-$, **2**-H$^-$, **4**-H$^-$, and **5**-H$^-$ with 1,5-dibromopentane under similar conditions also result in 5-bromopentylcyanodihydroarenes **6b**, **7b**, **9b**, and **10b** as the major products (yields 55—75%). The minor reaction products, bromoalkylarenes **11—15**, were reported earlier.[14] Their content in the mixtures was estimated based on ^{1}H NMR spectroscopy and GLC/MS data.

The following conclusions can be drawn. The results of the reaction of cyanodihydroaryl anions **1**-H$^-$—**5**-H$^-$ (two-electron reduction products of aromatic mononitriles in liquid ammonia) with alkyl halides strongly depend on the reaction conditions, namely, the nature of the counterion, protonating agents, cosolvent, reagent ratio, and the order of mixing of reagents. By varying these factors it is possible to carry out target synthesis of alkylcyanocyclohexadienes or alkylarenes.

We established specific conditions for reductive alkylation of nitriles **1—5** (lithium as reducing agent, equivalent amount of Bu^{t}OH, THF as cosolvent, reverse order of mixing of reagents) under which one can almost completely inhibit the side transformations initiated by bases and obtain 1-alkyl-1-cyano-1,4-dihydroarenes in high yields. In addition to alkyl halides, α,ω-dibromoalkanes are also involved in the reaction with the reduced forms of cyanoarenes. This made it possible to elaborate a method for the synthesis of 1-(ω-bromoalkyl)-1-cyano-1,4-dihydroarenes. The synthesis of such compounds is of great value because cyclohexadienes functionalized at the saturated carbon atom are potential synthons for the synthesis of analogs of natural biologically active compounds.[4] The method of synthesis of alkyl- and dialkylarenes also seems to be quite valuable. Traditionally, the most common method of alkylation of the aromatic nucleus is the Friedel—Krafts reaction.[15] However, this reaction is inappropriate for obtaining a broad spectrum of individual dialkylbenzenes. Other methods of alkylation of the aromatic nucleus, mainly involving organometallic reagents, are intensively developing.[16] Alternative methods also include the reductive alkylation of available aromatic nitriles employed in this work, which can be used to obtain alkylbenzenes, -toluenes, and -naphthalenes.

Experimental

^{1}H NMR spectra were recorded with a Bruker AC-200 spectrometer in $CDCl_3$. IR spectra were recorded with a Bruker Vector-22 instrument for slice measurements. The precise molecular weights of ions were determined by high resolution mass spectrometry with a Finnigan MAT-8200 instrument. GLC/MS identification of mixture components was performed using a Hewlett Packard G1081A setup comprising an HP 5890 Series II gas chromatograph and an HP5971 mass selective detector; electron ionization energy of 70 eV; HP5 column (5% of diphenyl and 95% of dimethylsiloxane), 30 m × 0.25 mm × 0.25 μm; with helium as carrier gas, flow rate 1 mL min^{-1}; column temperature programming from 50 °C (2 min) at an increment of 10 deg min^{-1} to 280 °C (5 min); injector temperature 280 °C; ion source temperature 173 °C; data acquisition rate 1.2 scan s^{-1} in the mass range 30 to 650 amu.

Liquid NH_3 was purified by dissolving metallic sodium followed by distillation to a reaction vessel cooled to −70 °C; THF was purified by boiling over benzophenone ketyl followed by distillation in argon atmosphere. The oxide films were removed

from alkali metals under an anhydrous hexane layer. Alkyl halides and dihaloalkanes were purified by passing through alumina followed by distillation. Nitriles **1—5** were distilled over P_2O_5.

Generation of two-electron reduction products of nitriles 1—5 (general procedure). 1). To a solution of 2.5 mmol of nitrile **1**, **3**, or **5** in liquid NH_3 (50 to 55 mL, concentration ~$5 \cdot 10^{-2}$ mol L^{-1}), alkali metal (5.2 mmol) was added with stirring in inert atmosphere at −35 °C and the reaction mass was kept for 5 to 10 min under the same conditions.

2). To a solution of alkali metal (5.2 mmol) in liquid NH_3 (50 mL), a solution of nitrile **2** or **4** (2.5 mmol) in abs. THF (5 mL) was added with stirring at −35 °C and the reaction mass was kept for 5 to 10 min under the same conditions.

When generating the reduced forms using the protonating agents, Bu^tCl or NH_4Cl (2.5 mmol) was added to the solution of the nitrile reduction products and Bu^tOH (2.5 mmol) was added to the nitrile solution in NH_3/THF (5 : 1, v/v) mixture prior to adding metal, and the solutions of the reduction products were allowed to stay for 15 to 20 min.

Reaction of products of two-electron reduction of nitriles 1—5 with alkyl halides (general procedure). ***A.*** To a solution of the reduction product, alkyl halide (6 mmol) was added dropwise with stirring at −35 °C. The reaction mixture was kept for 30 min under the same conditions and then an excess of NH_4Cl (~5 g) and Et_2O (50 mL) were added sequentially. The mass obtained was stirred until complete evaporation of NH_3 and water (50 mL) was added to the residue. The ethereal layer was separated and the aqueous layer was extracted with ether (2×50 mL). The combined organic extracts were washed with water and dried with $MgSO_4$. The compositions of the mixtures of the reaction products were determined based on the ^{1}H NMR spectroscopy, GLC, and GLC/MS data; the values averaged over the results of at least two runs (deviation was at most 5%) are listed in Tables 1 and 2. Individual compounds were separated by column chromatography or TLC (with silica gel as sorbent and hexane—diethyl ether mixture (9 : 1, v/v) as eluent). The separation process was monitored visually upon exposure of Silufol plates to UV light. The yields of the target products were at least 80% of their content in the mixtures. The structures of the compounds isolated were established by ^{1}H NMR and IR spectroscopy and by high resolution mass spectrometry.

***B* (Reverse order of mixing of reagents).** To a solution of alkyl halide (25—30 mmol) in THF (1 : 1, v/v) cooled to −10—0 °C, a solution of the reduction product was added with stirring over a period of 20 to 30 min. The reaction mixture was stirred for 10 min and then an excess of NH_4Cl (~5 g) and 50 mL of diethyl ether was added sequentially. Subsequent treatment and analysis of the mixtures of the reaction products were performed as described above.

1-(5-Bromopentyl)-1-cyanocyclohexa-2,5-diene (6b). ^{1}H NMR, δ: 1.20—1.45 (m, 4 H, 2 CH_2); 1.52—1.71, 1.73—1.90 (both m, 2 H, CH_2); 2.61—2.70 (m, 2 H, H(4)); 3.36 (t, 2 H, CH_2); 5.60 (dt, 2 H, H(2), H(6), J = 10.0 Hz, J = 2.0 Hz); 5.91 (dt, 2 H, H(3), H(5), J = 10.0 Hz, J = 3.5 Hz). IR, ν/cm^{-1}: 2230 (C≡N). Found: M = 253 (GLC/MS). $C_{12}H_{16}BrN$. Found: m/z 252.0493 $[M - 1]^+$. $C_{12}H_{15}BrN$. Calculated: M − 1 = 252.0388.

1-Butyl-1-cyano-2-methylcyclohexa-2,5-diene (7a). ^{1}H NMR, δ: 0.82 (t, 3 H, Me, J = 9.0 Hz); 1.00—1.31 (m, 4 H, 2 CH_2); 1.58—1.91 (m, 2 H, CH_2); 1.77—1.79 (m, 3 H, Me); 2.53—2.64 (m, 2 H, H(4)); 5.50 (dt, 1 H, H(6), J = 10.0 Hz, J = 2.0 Hz); 5.57—5.65 (m, 1 H, H(3)); 5.88 (dtd, 1 H, H(5), J = 10.0 Hz, J = 3.0 Hz, J = 1.0 Hz). IR, ν/cm^{-1}: 2229 (C≡N). Found: m/z 175.13586 $[M]^+$. $C_{12}H_{17}N$. Calculated: M = 175.13609.

1-(5-Bromopentyl)-1-cyano-2-methylcyclohexa-2,5-diene (7b). ^{1}H NMR, δ: 1.01—1.25, 1.26—1.43 (both m, 2 H, CH_2); 1.59—1.90 (m, 4 H, 2 CH_2); 1.77—1.79 (m, 3 H, Me); 2.53—2.64 (m, 2 H, H(4)); 3.29 (t, 2 H, CH_2, J = 9.0); 5.50 (dt, 1 H, H(6), J = 10.0 Hz, J = 2.0 Hz); 5.57—5.65 (m, 1 H, H(3)); 5.88 (dtd, 1 H, H(5), J = 10.0 Hz, J = 3.0 Hz, J = 1.0 Hz). IR, ν/cm^{-1}: 2229 (C≡N). Found: m/z 267.06202 $[M]^+$. $C_{13}H_{18}BrN$. Calculated: M = 267.06231.

1-Cyano-1,3-dimethylcyclohexa-2,5-diene (8c). ^{1}H NMR, δ: 1.43 (s, 3 H, C(1)Me); 1.71 (s, 3 H, C(3)Me); 2.50—2.59 (m, 2 H, H(4)); 5.32—5.39 (m, 1 H, H(2)); 5.64 (dq, 1 H, H(6), J =10.0 Hz, J = 2.0 Hz); 5.84 (dt, 1 H, H(5), J = 10.0 Hz, J = 3.6 Hz). IR, ν/cm^{-1}: 2228 (C≡N). Found: m/z 133.0872 $[M]^+$. $C_9H_{11}N$. Calculated: M = 133.0891.

1-(3-Bromopropyl)-1-cyano-3-methylcyclohexa-2,5-diene (8d). ^{1}H NMR, δ: 1.73 (s, 3 H, Me); 1.74—2.00 (m, 4 H, 2 CH_2); 2.52—2.61 (m, 2 H, H(4)); 3.37 (t, 2 H, CH_2, J = 9.0 Hz); 5.27—5.34 (m, 1 H, H(2)); 5.59 (dq, 1 H, H(6), J = 10.0 Hz, J = 2.0 Hz); 5.94 (dt, 1 H, H(5), J = 10.0 Hz, J = 3.5 Hz). IR, ν/cm^{-1}: 2228 (C≡N). Found: M = 239 (GLC/MS). $C_{11}H_{14}BrN$. Found: m/z 238.0238 $[M - 1]^+$. $C_{11}H_{13}BrN$. Calculated: M − 1 = 238.0232.

1-(4-Bromobutyl)-1-cyano-3-methylcyclohexa-2,5-diene (8e). ^{1}H NMR, δ: 1.35—1.53, 1.59—1.77 (both m, 2 H, CH_2); 1.75 (s, 3 H, Me); 1.77—1.95 (m, 2 H, CH_2); 2.52—2.59 (m, 2 H, H(4)); 3.36 (t, 2 H, CH_2, J = 9.0 Hz); 5.27—5.33 (m, 1 H, H(2)); 5.59 (dq, 1 H, H(6), J = 10.0 Hz, J = 2.0 Hz); 5.92 (dt, 1 H, H(5), J = 10.0 Hz, J = 3.4 Hz). IR, ν/cm^{-1}: 2228 (C≡N). Found: m/z 253.0467 $[M]^+$. $C_{12}H_{16}BrN$. Calculated: M = 253.0432.

1-(5-Bromopentyl)-1-cyano-3-methylcyclohexa-2,5-diene (8f). ^{1}H NMR, δ: 1.25—1.54 (m, 4 H, 2 CH_2); 1.57—1.75 (m, 2 H, CH_2); 1.76 (s, 3 H, Me); 1.77—1.95 (m, 2 H, CH_2); 2.51—2.59 (m, 2 H, H(4)); 3.38 (t, 2 H, CH_2, J = 9.0); 5.29—5.36 (m, 1 H, H(2)); 5.61 (dq, 1 H, H(6), J = 10.0, J = 2.0 Hz); 5.92 (dt, 1 H, H(5), J = 10.0 Hz, J = 3.4 Hz). IR, ν/cm^{-1}: 2227 (C≡N). Found: m/z 267.0631 $[M]^+$. $C_{13}H_{18}BrN$. Calculated: M = 267.0623.

1-(5-Bromopentyl)-1-cyano-4-methylcyclohexa-2,5-diene (9b). ^{1}H NMR, δ: 1.05, 1.09 (both d, 3 H, Me, J = 6.0); 1.25—1.50 (m, 4 H, 2 CH_2); 1.59—1.76, 1.77—1.94 (both m, 2 H, CH_2); 2.67—2.74 (m, 1 H, H(4)); 3.35 (t, 2 H, CH_2, J = 9.0 Hz); 5.56, 5.58 (both dd, 2 H, H(2), H(6), J = 10.0 Hz, J = 2.0 Hz); 5.82 (dd, 2 H, H(3), H(5), J = 10.0 Hz, J = 3.0 Hz). IR, ν/cm^{-1}: 2231 (C≡N). Found: m/z 267.0630 $[M]^+$. $C_{13}H_{18}BrN$. Calculated: M = 267.0623.

1-(5-Bromopentyl)-1-cyano-1,4-dihydronaphthalene (10b). ^{1}H NMR, δ: 1.26—1.53 (m, 4 H, 2 CH_2); 1.58—1.77, 1.70—1.89 (both m, 2 H, CH_2); 3.21—3.38 (m, 2 H, H(4)); 3.36 (t, 2 H, CH_2, J = 9.0 Hz); 5.88 (dt, 1 H, H(2), J = 10.0 Hz, J = 2.0 Hz); 6.21 (dt, 1 H, H(3), J = 10.0 Hz, J = 3.5 Hz); 7.18—7.54 (m, 4 H, H(5)—H(8)). IR, ν/cm^{-1}: 2227 (C≡N). Found: m/z 304.2321 $[M]^+$. $C_{16}H_{18}BrN$. Calculated: M = 304.2313.

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