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Reductive Activation of Arenes: XV.* Anionic Products of *m*-Tolynitrile Reduction with Sodium in Liquid Ammonia, and Their Alkylation**

T. A. Vaganova, E. V. Starokon', and V. D. Shteingarts

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia

Abstract—From results of oxidation, protonation, and alkylation of the products arising in one- or two-electron reduction of *m*-tolunitrile with sodium in liquid ammonia followed a conclusion that these products are respectively anion-radical of the compound and 3-methyl-1-cyano-2,5-cyclohexadienyl anion. The reaction of both reduction products with alkyl halides gives rise to compounds of ipso-alkylation with respect to cyano group: the corresponding alkyltoluenes and 1-alkyl-3-methyl-1-cyclohexadienes. The ratio of these products depends on the structure of alkyl halide. The possibility to prepare selectively m-alkyltoluenes by reaction of the product of two-electron reduction of *m*-tolunitrile with alkyl halides was demonstrated.

Within the framework of systematic study on reductive activation of functional arenes to reactions with electrophilic agents we demonstrated formerly that anionic products of one- and two-electron reduction of aromatic mononitriles produced by alkali metal in the liquid ammonia react with primary alkyl halides with replacement of the cyano group and/or with ipso-addition disregarding the character of the aromatic moiety (phenyl [2, 3], 1-naphthyl [3, 4], 9-anthracenyl [5, 6]). In the mechanistic study with the use of model reagent of "radical clock" type we established that all reduced forms of the above mononitriles, anion-radicals, cyclodihydroaryl anions, and in the latter case dianion, played in these processes the role of nucleophiles. The introduction of an additional electron-withdrawing substituent, the second cyano group, into position *2* or *4* of benzonitrile crucially changes the reaction mechanism and related thereto alkylating orientation. In reactions of anion-radicals formed from terephthalonitrile and phthalonitrile with alkyl halides occurred electron transfer followed by recombination of the anion-radical with alkyl radical. As a result both cyano group and hydrogen were substituted in ~4:1 ratio [7, 8]. The reactivity of terephthalonitrile dianion is

of dual character and depends on the nature of the alkyl halide [9].

The present study is an extension of this research aimed to elucidation by an example of cyanoarenes of the effect of structural factors on regioselectivity and on alkylation mechanism of the anionic reduced forms of functional arenes with electron-donor substituents. First of all we considered the methyl group. As show published data [10, 11] the anion-radicals of tolunitriles generated electrochemically in DMF in millimolar concentration were quite stable and thus it was possible to investigate their reaction with alkyl halides. Taking into consideration the available data on unsubstituted aromatic nitriles [1–6] it seems presumable to generate these anion-radicals in sufficient concentrations for performing chemical experiments. Besides in [11] was made a conclusion from the electrochemical data, that anion-radicals of tolunitriles even in reactions with primary alkyl halides exhibit both nucleophilic and electron-donor reactivity. In comparison with results we formerly had obtained for anion-radical of benzonitrile [2] and dinitriles [7, 8] the above facts showed that the introduction of a methyl group into the anion-radical of benzonitrile changed the pattern of its reactivity; therewith in the case of *para*-isomer the change was similar to that produced by electron-withdrawing cyano group. However the approach used by Sorensen *et al.* [11] cannot reveal the orientation of anion-radical alkylation inherent to each mechanism. Yet it

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* For communication XIV see [1].

is known that as a rule the change of reaction mechanism is accompanied by the altered orientation and therefore by another set of alkylation products [7–9, 11–13]. Such data give the basis for conclusions on the reaction mechanism on the structural level. In the light of the above the goal of this study was performing one- and two-electron reduction of *m*-tolunitrile (**I**) with sodium in liquid ammonia, chemical testing of the nature of arising anionic reduction products, and establishing of the character of alkylation products obtained therefrom.

The reduced forms were generated along the procedure that we had frequently used before in the same purpose [1–9]: the reduction was carried out by adding one or two equiv of metallic sodium to a solution of nitrile **I** in the liquid ammonia at –33°C. The study of reactivity of the anion-radical of *m*-tolunitrile (**II**) might be hampered by its high basicity, aptitude to disproportionation or dimerization. Since the reduction potentials of benzonitrile [14] and nitrile **I** [11] have close values, and the benzonitrile anion-radical is stable in the liquid ammonia, it is presumable that the basicity of anion-radical **II** is also insufficient to be protonated by ammonia. The difference between the first and the second reduction potential for benzonitrile and tolunitriles is no less than 0.5 V [11, 14], and this provides a possibility to regard anion-radical **II** as not apt to disproportionation using the reasoning previously applied to the anion-radical of terephthalonitrile [7]. To prevent the two-electron reduction at generation of the anion-radicals we used 10–15% excess of a substrate with respect to the alkali metal. We checked the degree of transformation of the initial compound under these conditions by reaction with oxygen. The recovery of the initial compound in such experiments indicates that no deep transformations irreversibly changing its structure have occurred (see, e.g., [4, 7, 15]). On the other hand, it is an evidence of stability of the anion-radical as a product of one-electron reduction. It was established that at treating with oxygen the product of one-electron reduction of nitrile **I** with sodium in liquid ammonia preliminary kept for 30 min the initial nitrile **I** is recovered to 75% from the amount charged.*

To ensure the completeness of the two-electron reduction in this case was used ~2.2 equiv of sodium.

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* In experiments carried out in liquid ammonia with solutions of concentration ~0.01 M and with amount of reagents ~0.5 g the relatively volatile organic compounds usually are not quantitatively recovered for the compounds are carried away with evaporated ammonia.

It was established that oxidation with oxygen of the product of the two-electron reduction of nitrile **I** did not result in recovery of the initial compound. After evaporation of ammonia, dilution of the reaction mixture with water, and extraction we isolated only 1-% of *m*-toluamide. It is known [16] that at two-electron reduction of benzonitrile with potassium in the liquid ammonia arises a very basic dianion that is protonated with ammonia to yield 1-cyano-2,5-cyclo-hexadien-1-yl anion. Basing on these data it may be expected that dianion of tolunitrile (**I**) also undergoes protonation affording 3-methyl-1-cyano-2,5-cyclo-hexadien-1-yl anion (**III**). Apparently the oxidation of anion **III** gives rise to the corresponding methyl-cyclohexadienone (see, e.g., [5]) that by reaction with oxygen in an alkaline medium provides products of deep oxidation, probably with cleavage of the benzene skeleton and/or polymers that are not extracted from the water solution. In contrast, the protonation of the product of two-electron reduction of nitrile **I** with water results in recovery of ~70% of the initial nitrile. Taking into account that in reactions with unsubstituted 1-cyano-2,5-hexadien-1-yl anion an electrophile adds to the ipso-position with respect to cyano group [4] it is presumable that at treating with water anion **III** forms 3-methyl-1-cyano-2,5-cyclo-hexadiene that in the course of the workup transforms into the initial nitrile **I**.

Thus the reported data in combination with the known facts on reduction of aromatic nitriles in the liquid ammonia [2–9] and with results of electro-chemical reduction of nitrile **I** [10, 11] permit the assumption that its one- and two-electron reduction in liquid ammonia performed in this study furnishes respectively anion-radical **II** and anion **III** sufficiently stable for investigation of their reactivity with respect to alkyl halides.

The alkylation of the reduced forms of nitrile **I** was carried out by adding alkyl halides to their solutions in liquid ammonia at –33°C. The analyses of compounds mixtures formed was performed by ^{1}H NMR spectroscopy, GLC, and GC-MS. The reagents ratio and products composition are given in a table, the spectral characteristics are listed in EXPERI-MENTAL.

It was established that the products of one-electron and two-electron reduction of nitrile **I** with sodium reacted with butyl bromide to afford mainly 3-butyl-toluene (**IV**) (table, runs nos. 1, 2). This compound and the other alkyltoluenes (see below) are described in the literature (see, e.g., [17]) but spectral data sufficient for identification are lacking. Therefore we

Reaction between products of nitrile **I** reduction with sodium in liquid ammonia and alkyl halides

Run no.	Quantity of reagents, mmol			Composition of reaction products, mmol (GLC data)`		
	nitrile **I**	sodium	AlkHlg	nitrile **I**	alkyltoluene	cyanodialkylcyclohexadiene
1	3.5	3.0	BuBr 1.6	0.81	(**IV**) 1.39	(**V**) 0.07
2	3.0	6.5	BuBr 6.5	0.05	(**IV**) 2.16	(**V**) 0.08
3	3.0	6.5	BuI 6.5	0.02	(**IV**) 2.48	(**V**) 0.02
4	3.0	6.5	BuCl 6.5	1.49	(**IV**) 0.75	(**V**) 0.02
5	3.0	6.5	*i*-BuBr 6.5	0.01	(**VII**) 1.90	(**X**) 0.30
6	3.0	6.5	*s*-BuI 6.5	0.01	(**VIII**) 1.92	(**XI**) 0.52
7[b]	3.0	6.5	*c*-HexBr 6.5	0.70	(**IX**) 0.40	(**XII**) 0.99

` Data averaged for 2–3 runs. [b] The mixture of reaction products contained ~0.9 mmol of cyclohexene.

isolated the compounds synthesized from the mixtures obtained by chromatography, and their structure was confirmed by spectral method. The ^{1}H NMR spectrum of compound **IV** by the position and pattern of the signals resembles that of its structural analog, 3-ethyltoluene [18]: *m*-Dialkylbenzenes have a characteristic multiplet in the region δ 6.5–7.0 ppm, and although the individual signals of the four aromatic protons cannot be singled out, the pattern cannot be mistaken for the corresponding spectra of the *ortho*- or *para*-isomers. Alongside arene **IV** and initial nitrile **I** in the products mixture is present in a small quantity (2–3%) a previously unknown 1-butyl-3-methyl-1-cyano-2,5-cyclohexadiene (**V**). The assignment of the signals in its ^{1}H NMR spectrum was done basing on the spectrum of 1-butyl-1-cyano-2,5-cyclohexadiene [3]. The singlet of methyl group at the double bond appears at δ 1.77 ppm; the signals of the butyl moiety attached to C^1 and geminal with respect to cyano group are shifted upfield as compared to the signals of this substituent in an aromatic ring; the protons of the methylene C^4H_2 group give rise to a typical multiplet at   2.57 ppm. In the resonance region of olefin protons three groups of signals are observed: The most upfield multiplet (δ 5.35 ppm) having no splitting with $J_{H,H}$ ~10 Hz that is characteristic of a vicinal coupling through a double bond belongs to a proton at C^2 adjacent to a methyl group. The protons attached to C^5 and C^6 in analogous structures appear as doublets of triplets in the region δ 5.60–6.00 ppm ($J_{H,H}$ 10 and ~3 Hz). However in the spectrum of compound **V** the signal of H^6 proton has a more complicated pattern presumably because of specific stereochemistry of the compound (cf. [3, 6]). The structure assumed for nitrile **V** is also confirmed by the data of high-resolution mass spectrometry.

Thus in both cases form the same products with the only difference, that the yield of alkylation products with anion radical **II** according to GLC data attains ~48% with respect to sodium used; in keeping with the typical stereochemistry in reaction of anion-radical with electrophile it corresponds to the reaction completion to 95%. At the same time the two-electron reduction product is virtually completely consumed, and butyltoluene **IV** forms consequently in ≥70% yield.
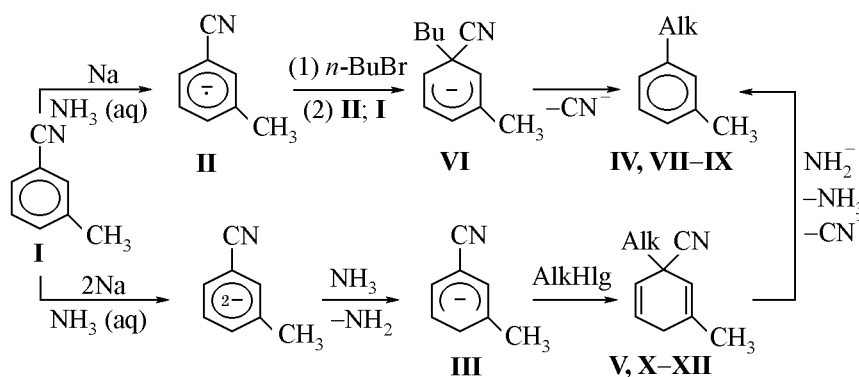
Alk = Bu (**IV, V**), *i*-Bu (**VII, X**), *s*-Bu (**VIII, XI**), *c*-Hex (**IX, XII**).

Basing on the structure of the alkylation products **IV** and **V** obtained, and taking into account the data on orientation of protonation and alkylation of the reduced forms of benzonitrile [2, 3] the reaction of butyl bromide with the products of one- and two-electron reduction of nitrile **I** may be described by the following scheme:

Anion-radical **II**, the product of one-electron reduction of nitrile **I**, is alkylated into the ipso-position with respect to cyano group affording 1-alkyl-cyano-3-methylcyclohexadien-4-yl anion **VI** that either suffers decyanation to give arene **IV** or takes up a proton providing cyanodialkylcyclohexadiene **V**. At the lack of an efficient proton source the second reaction route occurs to a small degree. Dianion generated by two-electron reduction of nitrile **I** is protonated by ammonia giving anion **III** (cf. [3, 18] that on alkylation furnishes cyanodialkylcyclohexadiene **V**. However in this case in the mixture arises an equivalent amount of amide ion that effects dehydrocyanation of nitrile **V** with formation of dialkylarene **IV**.

In order to elucidate the effect of halogen nature and alkyl structure on the alkylation process of the reduced forms under investigation we carried out reaction of the product of two-electron reduction of nitrile **I** with a series of alkyl halides. We established that a dialkylarene **IV** was the main product of anion **III** alkylation disregarding the halogen nature (Hlg = Cl, Br, I) in butyl halide (see table, runs nos. 2–4). However in reaction with butyl chloride a considerable amount of initial nitrile **I** is recovered. Taking into account a similar result obtained at protonation of the product of two-electron reduction of nitrile **I** (see above) it is presumable that butyl chloride shows not only electrophilic but also CH-acidic properties. A similar change in reaction direction was previously observed in reaction of two-electron reduction products obtained from benzonitrile and 1-naphthonitrile in going from butyl iodide and butyl bromide to butyl chloride [3].

Variation of alkyl moiety was performed in the following series: BuBr, *i*-BuBr, *s*-BuBr, *c*-HexBr, *t*-BuBr (see table, runs nos.2, 5–7). It was established that in reactions of the above alkyl halides with the product of two-electron reduction of nitrile **I** were obtained the corresponding alkyltoluenes: 3-iso-butyl-toluene (**VII**), 3-sec-butyltoluene (**VIII**), 3-cyclo-hexyltoluene (**IX**), and the corresponding 1-alkyl-1-cyano-3-methyl-2,5-cyclohexadienes: 1-iso-butyl-1-cyano-3-methyl-2,5-cyclohexadiene (**X**), 1-sec-butyl-1-cyano-3-methyl-2,5-cyclohexadiene (**XI**), 1-cyano-

1-cyclohexyl-3-methyl-2,5-cyclohexadiene (**XII**). Alkyltoluenes **VII–IX** have been described in the literature (see, e.g., [17]), and cyclohexadienes **X–XII** were synthesized for the first time. Compounds **VII–XII** were isolated from the mixtures by chromatography, their structure was established from spectral data analogous to the corresponding spectra of compounds **IV, V**. Alongside the mentioned compounds in the reaction mixtures were present unidentified compounds in overall amounts not exceeding ≤5% (GLC data), and in reaction with cyclohexyl bromide alongside with ~20% of the recovered initial nitrile some cyclohexene was detected. The reaction of the product of two-electron reduction of nitrile **I** with *tert*-butyl bromide did not result in alkylation, and 85% of the initial nitrile **I** was recovered.

The results of runs nos 2, 5–7 presented in the table show that irrespective of the structure of the alkyl moiety the alkylation occurs at the *ipso*-position with respect to cyano group (see the scheme). Similarly to the data obtained previously both for anion-radicals of aromatic nitriles [2, 4–6] and cyano-dihydroaryl anions [3, 6] the above mentioned results testify to the occurrence of S_N reaction mechanism. In both cases this orientation corresponds to the position with maximum localization of the negative charge [6, 7, 17]. In contrast, on introducing the second cyano group into the anion-radical of benzo-nitrile resulting in the change of its reactivity from nucleophilic to electron-donating one [7, 8] the alkylation occurs both in the ipso and unsubstituted position of the ring. Additional proof that in reaction with alkyl halides anion **III** plays the role of nucleophile is the lack of reaction with tert-butyl bromide which provides alkylation products by E_T mechanism [8, 9, 19]. To a certain extent the tert-butyl bromide may be regarded as a test reagent for primary evaluation of the reactivity of an anionic species that may react both by S_N and E_T mechanisms. Nonetheless the above reasoning provides only indirect evidence for the occurrence of the S_N mechanism in reactions of anion-radical **II** and anion **III** with alkyl halides. To obtain direct proofs the reactions should be performed with model reagents that would fix various structural fragments in the reaction products depending on the reaction mechanism. This study is planned for the future.

It is obvious that the ratio of alkylarene to cyclo-hexadiene in the reactions with branched alkyl halides is quite different from that observed at the use ot primary alkyl halides. Within the framework of the above scheme the growth of diene **X–XII** content in

the reaction products should be apparently ascribed to the increasing aptitude of alkyl halide with branched alkyl to operate as CH-acid with hydrogen halide elimination; this assumption is supported by the detection of cyclohexene among the products obtained in run no.7 (see table). This process ensures more effective neutralization of sodium amide and thus decreases the dehydrocyanation of the primary reaction product. The recovery of the initial nitrile in reaction with cyclohexyl bromide, same as in reaction with butyl chloride, is probably due to basic properties of anion **III** that compete with its nucleophilicity.

In conclusion let us consider the synthetic opportunities of the results obtained. The most general alkylation method for aromatic ring is traditionally Friedel–Krafts reaction that within over a century of its investigation has undergone numerous modifications resulting in creation of new catalysts and reagents [20]. However the opportunity to prepare individual dialkylbenzenes by this reaction remains very limited. Therefore the alternative methods of aromatic ring alkylation are also under lively development; they are mostly concerned with the use of organometallic reagents [21]. The alkylation of reduced forms of easily available tolunitriles performed in this study by an example of nitrile **I** may be regarded as such alternative approach to aromatic ring alkylation. The compounds corresponding to ipso-alkylation of anion-radical **II** and cyanomethylcyclohexadienyl anion **III**, *m*-alkyltoluenes **IV, VII–IX**, in both cases form as the main product. Taking into account the high degree of nitrile **I** conversion the reaction between the product of its two-electron reduction and alkyl halides may be used for preparation of individual *m*-alkyltoluenes.

EXPERIMENTAL

^{1}H NMR spectra were registered on spectrometer Bruker WP-200SY from solutions in CDCl$_3$. The precise values of molecular ions mass were measured by high-resolution mass spectrometry on Finnigan MAT-8200 instrument. Reaction mixtures were analyzed by GLC on chromatograph LKhM-7A under the following conditions: stationary phase 15% SKTFV-83 on Chromosorb W, oven temperature programmed from 100 to 300°C at a rate 10°C/min, carrier gas helium, flow rate 0.6 1h^{-1}, column 2500×2 mm. The GC-MS measurements were carried out on a Hewlett-Packard system G1081A composed of a gas chromatograph HP 5890 of series **II** and mass-selective detector HP 5971, ionizing electrons

energy 70 eV, column HP5 (5% of diphenylsiloxane, 95% dimethylsioxane), 30×0.25×0.25 m, carrier gas helium, heating mode: 2 min at 50°C, then 10°/min, 5 min at 200°C, evaporator temperature 280°C, ion source temperature 173°C. The data sampling rate 1.2 scan/sec in the mass region 30–650 a.u.

The following compounds and solvents were used in the study: Liquid ammonia was purified by dissolving sodium metal with subsequent evaporation into a reactor cooled to –70°C. The oxides from the surface of sodium metal of "pure" grade were removed under a layer of dry hexane. *m*-Tolunitrile was obtained by procedure from [22] from *m*-toluic acid, bp 57–58°C (3 mm Hg), publ. 84°C (10 mm Hg) [23]. Alkyl halides were purified by passing through alumina followed by distillation; boiling points were consistent with published data [23].

Reduction of *m*-tolunitrile (I) with sodium in the liquid ammonia. To a solution of nitrile **I** in liquid ammonia (of concn. 0.05 M) at –33°C was added while stirring a required amount of sodium metal, and then the reaction mixture was maintained at the same conditions for 10–30 min.

REACTIONS OF REDUCTION PRODUCTS OF *m*-TOLUNITRILE (**I**) WITH ELECTROPHILIC REAGENTS

Oxidation of reduction products of *m*-tolunitrile (I). Through the solutions of reduction products obtained from nitrile **I** by the action of 3.0 mmol of sodium (0.069 g) on 3.3 mmol of nitrile **I** (0.386 g) or of 6.5 mmol of sodium (0.149 g) on 3.0 mmol of nitrile **I** (0.351 g) was passed for 15–20 min a flow of oxygen dried by passing through a layer of calcium chloride. The reaction mixture was stirred for 20 min, and then was added 5 ml of methanol and 50 ml of ethyl ether. The reaction mixture was stirred to complete evaporation of liquid ammonia, and to the residue 50 ml of water was added. The ether layer was separated, the water layer was extracted with ether (2×50 ml), the combined ether solutions were washed with water and dried on MgSO$_4$. After distilling off the solvent the residue was analyzed by ^{1}H NMR and GLC. On oxidation of the product of one-electron reduction 0.3 g of compound was obtained containing 96% of initial nitrile I (yield 75%). On oxidation of the product of two-electron reduction *m*-toluamide was isolated (0.042 g, ~10%).

Protonation of the product of two-electron reduction of *m*-tolunitrile (I). To a solution of a product of two-electron reduction of nitrile I obtained

by treating with 6.5 mmol of sodium (0.149 g) 3.0 mmol of nitrile **I** (0.351 g) was added dropwise while stirring 0.01 mol of water (0.18 ml). The reaction mixture was kept for 29 min, and then 50 ml of ethyl ether was added. Further workup was carried out as above. On removing the solvent 0.25 g (~70%) of initial nitrile **I** was obtained.

Reaction of reduction products of *m*-tolunitrile (I) with alkyl halides. To a solution of reduction products prepared by the above described procedure was added alkyl halide in amount and at reagents ratio indicated in the table. The reaction mixture was stirred till evaporation of the half of liquid ammonia (~0.5 h), and then 50 ml of ethyl ether was added. Further workup was carried out as above. The composition of reaction products mixtures was determined from ^{1}H NMR spectra, GLC and GC-MS analyses (see table). Individual compounds were isolated by column chromatography on silica gel 40/8- μ, eluent hexane–ethyl ether, 95:5 by volume, or by TLC on plates with a fixed layer of sorbent (silica gel LSL_{254} 6/40 μ with addition of 13 wt% of gypsum), eluent hexane–ethyl ether, 9:1 by volume. The visualization of spots was under UV irradiation of the dried plate. The structure of compounds was derived from ^{1}H NMR and high resolution mass spectra.

By separation of compounds mixture obtained in reaction of two-electron reduction product of nitrile **I** and sec-butyl bromide (table, run no.6) we isolated a fraction containing according to ^{1}H NMR and GC-MS data nitrile **I** and 1-sec-butyl-1-cyano-3-methyl-2,5-cyclohexadiene (**XI**) (*M* 175). In the ^{1}H NMR spectrum of the mixture to compound **XI** [$CDCl_3$, δ, ppm] correspond the signals: 0.80–1.70 m (9H, C_4H_9), 1.77 s (3H, CH_3), 2.57 m (2H, H^4), 5.35 m (1H, H^2), 5.61 m (1H, H^6), 6.03 m (1H, H^5).

Characteristics of individual compounds: **3-Butyltoluene (IV).** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.90 t (3H, CH_3), 1.33 m (2H, CH_2), 1.57 m (2H, CH_2), 2.27 s (3H, CH_3), 2.55 t (2H, CH_2), 6.91–7.18 m (4H, H^{2,4,5,6}). Found: *M* 148.1252. $C_{11}H_{16}$. Calculated: *M* 148.1251.

3-*iso*-Butyltoluene (VII). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.94 d (6H, 2CH_3), 1.89 sept (1H, CH), 2.36 s (3H, CH_3), 2.47 d (2H, CH_2), 6.95–7.20 m (4H, H^{2,4,5,6}). Found: *M* 148.1250. $C_{11}H_{16}$. Calculated: *M* 148.1251.

3-*sec*-Butyltoluene (VIII). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.83 t (3H, CH_3), 1.23 d (3H, CH_3), 1.59 m (2H, CH_2), 2.34 s (3H, CH_3), 2.56 m (1H, CH), 6.95–7.25 m (4H, H^{2,4,5,6}). Found: *M* 148.1246. $C_{11}H_{16}$. Calculated: *M* 148.1251.

3-Cyclohexyltoluene (IX). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.38 m (4H, 2CH_2), 1.78 m (4H, 2CH_2), 2.02 m (2H, CH_2), 2.27 s (3H, CH_3), 4.27 m (1H, CH), 6.91–7.19 m (4H, H^{2,4,5,6}). Found: *M* 174.1411. $C_{13}H_{18}$. Calculated: *M* 174.1408.

1-Butyl-1-cyano-3-methyl-2,5-cyclohexadiene (V). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, 2 stereoisomers: 0.84 m (3H, CH_3), 1.10–1.70 (6H, [CH_2)$_3$], 1.77 s (3H, CH_3), 2.57 m (2H, H^4) 5.35 m (1H, H^2), 5.60 d.t, 5.61 d.t (1H, H^6), 6.03 d.t (1H, H^5). $J_{H,H}^{5,6}$ 10 Hz, $J_{H,H}^{5,4}$ 3.5 Hz, $J_{H,H}^{6,4}$ 2 Hz. Found: *M* 175.1359. $C_{12}H_{17}N$. Calculated: *M* 175.1360.

1-*iso*-Butyl-1-cyano-3-methyl-2,5-cyclohexa-2,5-diene (X). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, 2 stereoisomers: 0.91 d (6H, 2CH_3), 1.62 d (2H, CH_2), 1.72 s (3H, CH_3), 1.74 m (1H, CH), 2.55 m (2H, H^4), 5.34 m (1H, H^2), 5.62 d.t, 5.63 d.t (1H, H^6), 5.88 d.t (1H, H^5). $J_{H,H}^{5,6}$ 10 Hz, $J_{H,H}^{5,4}$ 3.5 Hz, $J_{H,H}^{6,4}$ 2 Hz. Found: *M* 175.1362. $C_{12}H_{17}N$. Calculated: *M* 175.1360.

1-Cyano-1-cyclohexyl-3-methyl-2,5-cyclohexa-diene (XII). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, 2 stereoisomers: 1.12 m (4H, 2CH_2), 1.73 s (3H, CH_3), 1.78 m (7H, 3CH_2, CH), 2.53 (2H, H^4), 5.28 m (1H, H^2), 5.55 d.t, 5.56 d.t (1H, H^6), 5.93 d.t (1H, H^5), $J_{H,H}^{5,6}$ 10 Hz, $J_{H,H}^{5,4}$ 3.5 Hz, $J_{H,H}^{6,4}$ 2 Hz. Found: *M* 201.1514. $C_{14}H_{19}N$. Calculated: *M* 201.1517.

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