Chemically induced dynamic nuclei polarization and free radicals in the reaction of triethylaluminum with nitrobenzene

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The reaction of triethylaluminum with nitrobenzene in hydrocarbon solvents was studied by GC-MS and CIDNP techniques. Radical intermediates participating in a complex process of reduction and alkylation of nitrobenzene were observed in the reaction products (nitrobenzene radical anion, ethyl radical, and nitroxyl radical), and routes of their formation and decay were discussed.

Key words: CIDNP, radicals, radical mechanism, trialkylaluminum, nitrobenzene.

It is known that the reactions of nitrobenzene (NB) with aryl-[1] and alkylmagnesium halides[2] occur through the stages of radical formation and are accompanied by effects of chemically induced dynamic nuclei polarization (CIDNP).[2] In this work, we report on the observation of CIDNP effects (the negative polarization (emission, E) and positive polarization (enhanced absorption, A) in the reaction of triethylaluminum (TEA) with NB and the study of the radical stages by the CIDNP technique.

Reactions of NB with organoaluminum compounds are virtually unstudied. Examples of reduction of nitrobenzene,[3] phenylhydroxylamine,[3] azoxybenzene, and azobenzene by triisobutylaluminum,[4] which are the products of reduction of NB, have been published. In all cases, except for azobenzene, aniline, *N*-isobutylaniline, *o*-isobutylaniline, *p*-isobutylaniline, and azobenzene were observed in the reaction products. Aniline and *N*-isobutylaniline are formed in the reaction with azobenzene.

Our experiments showed that the reactions of NB with TEA in cyclohexane or pentane at room temperature occur vigorously with exothermic effects and result in various products of reduction and alkylation of NB: aniline, *N*-ethylaniline, and *o*- and *p*-ethylanilines (Table 1).

The reaction of TEA with NB followed by hydrolysis gives, along with the compounds listed above, ethyl-substituted NB, three isomers of diethylaminobenzene, two isomers of triethylaminobenzene, and minor amounts of ethane and ethylene (see Table 1). The reduction of NB by triisobutylaluminum affords similar products of reduction and alkylation.

When solutions of NB and TEA in cyclohexane are mixed directly in the detector of an ^1H NMR spectrometer, the spectra exhibit negatively polarized signals of methylene protons of the ethyl group bound to the benzene ring (2.49 ppm, q, E) (Fig. 1, spectrum *1*). The ^{13}C NMR spectra contain a positively polarized signal corresponding to the carbon atom of the same methylene group (29.8 ppm, A). In addition, the protonic spectra exhibit emission of the singlet signal of methyl protons of ethane (0.83 ppm, E), which is formed during the reaction and dissolved in the reaction mixture. The presence of the polarized signals in the NMR spectra indicate unambiguously that radical intermediates are formed. This is confirmed by the fact that the ESR spectrum of the reaction mixture in THF at low and room temperatures exhibits a triplet with the same intensity, which is characteristic of a nitrogen-containing paramagnetic center with the hyperfine coupling (HFC) constant of spin of an unpaired electron with the nitrogen nucleus a_N = 1.67 mT that is typical of ni-

Table 1. Products of the reaction of $PhNO_2$ with Et_3Al in hexane

Compound	Yield (%)
$PhNH_2$	15.4
PhNHEt	13.7
$2\text{-}EtC_6H_4NH_2$	9.1
$4\text{-}EtC_6H_4NH_2$	5.0
$EtC_6H_4NO_2$ (mixture of isomers)	1.7
Diethylaminobenzene	5.81
(two isomers)	1.24
	18.3
Triethylaminobenzene	5.3
(two isomers)	1.24
Nonidentified	15.4
products	7.9

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1979—1982, October, 1998.

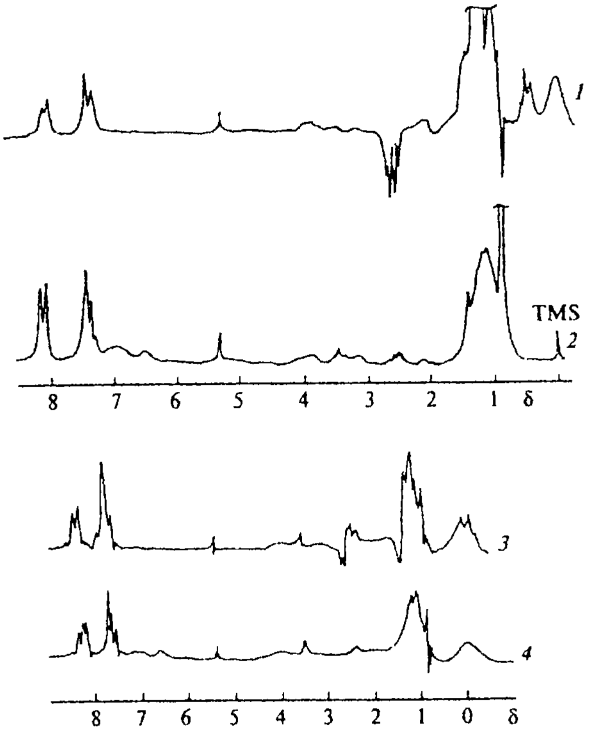


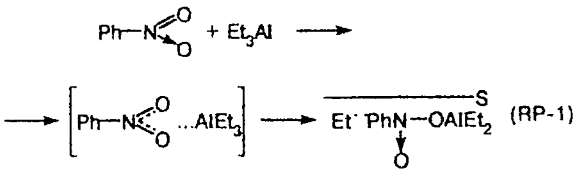
Fig. 1. ^{1}H NMR spectra of the Et_3Al—$PhNO_2$ (1 : 2) reaction system: *1*, during the reaction in cyclohexane-d_{12} (FT, 100 MHz) 3—4 s after mixing of the reagents; *2*, products of the reaction in cyclohexane-d_{12}; *3*, during the reaction in dioxane-d_8 at 60 °C 40 s after the beginning of heating (CW, 60 MHz); and *4*, reaction products in dioxane-d_8.

troxyl radicals.[5] The signal of the NB radical anion, which was initially expected, has an HFC constant with the nitrogen nucleus within 0.8—1.0 mT[6] depending on the conditions. The complex of the radical anion with ions of alkali metals and magnesium has an HFC constant within 0.9—1.2 mT.[7] Therefore, it is improbable to assign the triplet signal to the radical anion. It is most likely that, unlike the reaction with the Grignard reaction,[2] the reaction under study does not provide conditions for stabilization of the NB radical anion.

It is seen from the reaction products obtained that the complex multistage process of NB reduction is accompanied by alkylation of the aromatic ring.

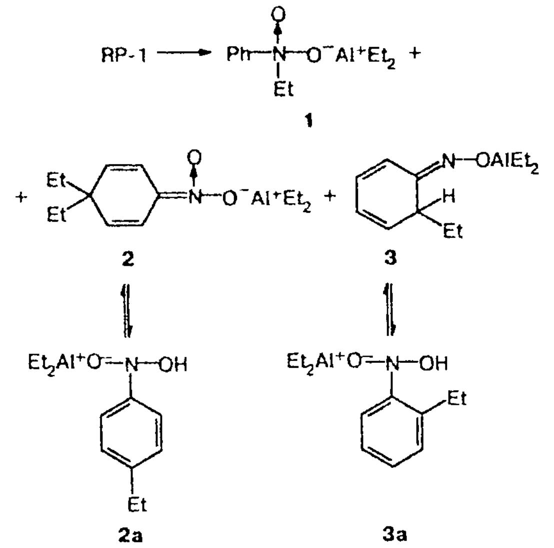
According to the known CIDNP theory,[8] integral nuclei polarization in strong magnetic fields appears in a radical pair with nonequivalent *g*-factors. In our case, the ethyl radical and NB radical anion formed due to the one-electron transfer from the TEA molecule to NB are these radicals (Scheme 1).

Scheme 1



Since all electrons in both molecules were paired before the electron transfer, the radical pair (RP-1) is a singlet. In RP-1, the *g*-factor of the radical anion (g = 2.0044)[9] is higher than that of the ethyl radical (g = 2.0026);[8] due to this, protons and carbon nuclei of radicals in RP-1 gain integral polarization. According to the Kaptein rule,[8,10] in the products of recombination of RP-1, protons of the ethyl radical should have negative polarization (emission, E) and methyl protons should have positive polarization (enhanced absorption, A). The carbon atom of the CH_2 groups gains positive polarization. Recombination of RP-1 is possible at the nitrogen atom to form the salt (**1**) or at the aromatic ring of the radical anion to form compounds **2** and **3** (Scheme 2).

Scheme 2

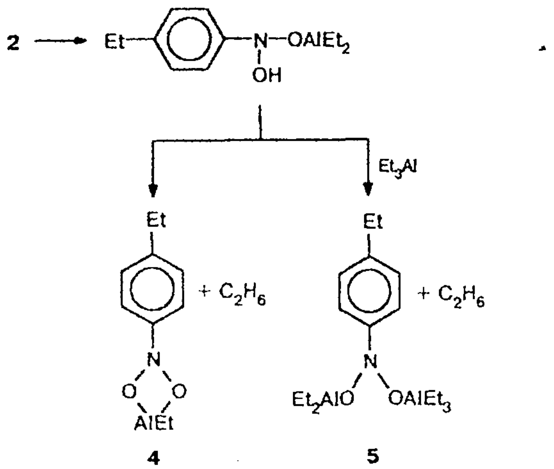


This mechanism has been previously[2] suggested for the reaction of NB with *tert*-butylmagnesium chloride.

The formation of a magnesium salt similar to **1** has been observed previously.[11—13] The corresponding sodium salt with a similar structure was formed during the recombination of the radical anion of *tert*-nitrobutane and of the *tert*-butyl radical when *tert*-nitrobutane is reduced by metallic sodium.[14] Due to two active Al—C bonds, salt **1** can undergo further reduction to hydroxylamine or *N*-ethylaniline, which is observed in the reaction products after hydrolysis. The ^{1}H NMR spectra of the reaction mixture contain a quartet signal of protons of the ethyl group at the N atom with the chemical shift typical of *N*-ethylaniline (3.42 ppm, q). The ^{13}C NMR spectra also exhibit signals, which can be assigned to the ethyl group of *N*-ethylaniline (CH_2, 67.2 ppm; CH_3, 19.2 ppm). All NMR signals mentioned during the reaction should gain integral polarization; however, no polarization was observed. This can be explained by the fact that either this route does not take place at all, *i.e.*, salt **1** is not formed, or the nuclear polarization appearing in RP-1 disappears rapidly due to some reason, for example, at the stage of salt **1** due to the short time of nuclear relaxation.

Compounds **2** and **3** are formed when RP-1 recombines at *ortho*- and *para*-positions of the NB radical anion. This recombination is possible, because the spin density of the unpaired electron is concentrated on the *ortho*- and *para*-carbon atoms of the phenyl ring rather than on the N atom only.[15] Probably, oximes of cyclohexadienones isolated previously[13] from the reactions of 2,4,6-tri-*tert*-butylnitrosobenzene with magnesiumalkyl halides are formed when similar salts are reduced by the Grignard reagent. Compounds **2** and **3** are unstable and undergo further transformations, for example, *via* Scheme 3.

Scheme 3



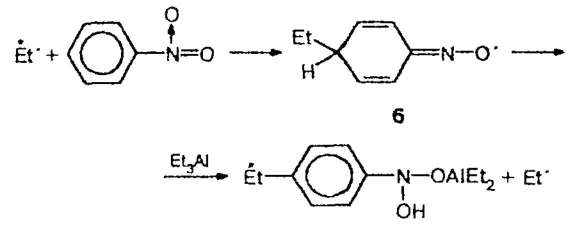
Subsequent transformations of compounds **4** and **5** can lead to the cleavage of the nitrogen—oxygen bonds accompanied by alkylation at the nitrogen atom. Perhaps, diethyl- and triethylaminobenzene are thus formed. In compound **5**, the four remaining aluminum—carbon bonds can react with other molecules of the starting NB; then the structure of ethyl-substituted NB remains until the end of the reaction, and after hydrolysis ethylnitrobenzene is obtained, which was identified in the products. Ethyl groups at the cyclohexadiene ring should be polarized. However, no corresponding signals are observed in the NMR spectra, probably because compounds **2** and **3** are rapidly transformed into **4** and **5** retaining polarization. As a result, we detect CIDNP of the ethyl substituent at the phenyl ring in compounds **4** and **5**. Further processes at the N atom of these intermediates affect slightly the CIDNP effects and chemical shifts of nuclei of the ethyl group. Therefore, only one negatively polarized quartet signal of methylene protons is observed, and the corresponding positively polarized triplet of methyl protons is disguised by intense signals of other components of the reaction mixture.

The radical pair RP-1 can dissociate. The ethyl radical escaping from the cage into the solution can add the H atom and be transformed into polarized ethane, whose emission was observed in the spectrum. Methylene protons of this radical are positively polarized, whereas methyl protons are negatively polarized. In ethane, all protons have the same chemical shift, and the contributions of different signs of polarization are mutually compensated, but the coefficient of negative polarization of methyl protons is somewhat higher, because the HFC constant with protons of the methyl group is higher than that with protons of the methylene group. Therefore, the overall ethane emission is observed in the spectrum.

When the reaction is performed in dioxane, which forms a complex with TEA, the protonic spectra exhibit multiplet polarization of the EA type of methylene protons of the ethyl group in the aromatic ring (see Fig. 1, spectrum *3*). The signals of methyl protons are disguised by more intense lines in the region of 1—2 ppm. The reaction proceeds very slowly at room temperature, because NB should first displace the dioxane molecule from the coordination sphere of TEA to react. When the temperature is increased to 60 °C, the reaction rate increases so that the CIDNP phenomenon can be observed.

Multiplet polarization of ethyl radicals can appear only in radical pairs with equal *g*-factors. In our case, these pairs can be formed only by ethyl radicals. They are randomly met in the solution, hence they are diffusion RP. According to the Kaptein rules,[7] the phase of EA polarization corresponds to radicals leaving the pair. Then the polarized ethyl radical probably attacks the starting NB at the phenyl ring to form paramagnetic intermediate **6**. Subsequent probable transformations of compound **6** occur according to Scheme 4 and then to Scheme 3.

Scheme 4



In other words, further processes can occur as those in a hydrocarbon solvent. The only difference is that the ethyl substituent of the aromatic ring has a multiplet polarization.

Experimental

A solution of commercially available triethylaluminum (1 mol) in cyclohexane, pentane, or dioxane was used for the reactions. Nitrobenzene (reagent grade) was washed with water, dried with P_2O_5, and distilled *in vacuo*. ^{1}H NMR spectra and CIDNP on protons were recorded on Tesla BS-467 (CW, 60 MHz) and Tesla BS-567A (FT, 100 MHz) NMR spectrometers. ^{13}C NMR spectra were obtained on a JEOL FX-90 pulse Fourier spectrometer. ESR spectra were obtained on an SE/X-2543 RADIOPAN spectrometer. To detect CIDNP on protons, a solution of nitrobenzene (0.1—0.2 mL) was injected with a syringe into a 1 *M* solution (0.3 mL) of Et_3Al in cyclohexane-d_{12} or dioxane-d_8 in a 5-mm tube placed directly in the detector of the spectrometer. The maximum CIDNP effects were observed for a 1 : 1 ratio of the reagents. To observe CIDNP on ^{13}C nuclei, the same solutions (1 mL) of the reagents in 10-mm tubes were used.

To identify the products, the reaction of Et_3Al with nitrobenzene was performed as follows. Nitrobenzene (0.9 mL, 9 mmol) in anhydrous pentane (2 mL) was placed in a three-neck flask with a reflux condenser and a magnetic stirrer. A solution (4 mL) of Et_3Al (1.8 mol L^{-1}, 7.2 mmol) in pentane was added dropwise with stirring in an argon atmosphere, and the mixture was stirred for 30 min. The mixture obtained was hydrolyzed by a 20% solution of NaOH at 0 °C. The organic layer was separated, and the aqueous layer was twice extracted with diethyl ether. The extracts were combined. The organic layer was dried with $MgSO_4$, and then a portion of ether and pentane was evaporated. The products identified by LC-MS and their yields are presented in Table 1.

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Received December 29, 1997