Organic Chemistry

Reaction of methylmagnesium iodide with dibutylcyanamide and dibutylnitrosamine

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The reaction of methylmagnesium iodide with di(*n*-butyl)cyanamide results in dibutylamine, dibutylisopropylamine, and acetonitrile, while the reaction with di(*n*-butyl)nitrosamine affords acetaldehyde dibutylhydrazone. Formaldehyde, acetone, and 2-butanone dibutylhydrazones, as well as acetaldehyde butyl(1-methylbutyl)hydrazone, 2-butanone butyl(1-methylbutyl)hydrazone, 1,1-dibutyl-2,2-dimethylhydrazine, and 1,1-dibutyl-2-ethyl-2-methylhydrazine were also identified in minor amounts. Di(*n*-butyl)nitramine reacts with methylmagnesium iodide to give di(*n*-butyl)nitrosamine.

Key words: di(*n*-butyl)cyanamide; di(*n*-butyl)nitrosamine; methylmagnesium iodide; formaldehyde dibutylhydrazone; 2-butanone dibutylhydrazone; acetaldehyde butyl(1-methylbutyl)hydrazone; 2-butanone butyl(1-methylbutyl)hydrazone; 1,1-dibutyl-2,2-dimethylhydrazine; 1,1-dibutyl-2-ethyl-2-methylhydrazine; di(*n*-butyl)nitramine.

As we found earlier,[1,2] reactions of RMgX with substrates containing C—element σ-bonds can result in heterolytic cleavage of these bonds, along with the known addition, enolization, and reduction reactions. We also demonstrated the possibility of homolytic cleavage of C—element σ-bonds in thiocyanates, nitriles, and α-substituted β-diketonates.[3,4]

In order to determine the range of substrates able to undergo homolysis by the action of RMgX we performed a chromato-mass-spectrometric study of the reactions of MeMgI with an aminoalkyl analog of thiocyanates, *viz*., dibutylcyanamide, and its nitroso and nitro analogs, *viz*., di(*n*-butyl)nitrosamine and di(*n*-butyl)nitramine.

Data on the reactions of RMgX with dialkylcyanamides are scarce. The main products are amidines, and nitriles RCN are formed in parallel.[5]

Dibutylcyanamide does not react with MeMgI when boiled in ether. A reaction occurs only when it is boiled in decane, and gives three main products.

$$\mathrm{Bu_2NCN + MeMgI \longrightarrow Bu_2NH + Bu_2N{-}Pr\text{-}\mathit{i} + MeCN + Mg(CN)I}$$

The presence of CN^- ions was revealed by the forma-

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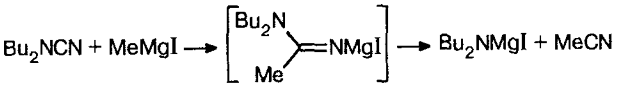
tion of Berlin blue.

$$CN^- + Fe^{2+} + Fe^{3+} \rightarrow Fe_3[Fe(CN)_6]_2$$

One of the possible directions of the reaction is the nucleophilic cleavage of the C—N σ-bond of the substrate.



An alternative route is the homolysis of the C—N σ-bond.

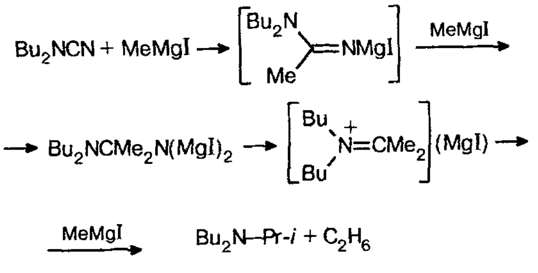
$$Bu_2NCN + MeMgI \rightarrow [Bu_2NCN^{-\cdot}MeMgI^{+\cdot}] \rightarrow$$
$$\rightarrow Bu_2N^{\cdot} + CN^- + Me^{\cdot} + MgI^+$$

$$Bu_2N^{\cdot} + HSolv \rightarrow Bu_2NH$$

(HSolv is the solvent molecule)

The presence of a minor amount of MeCN and a noticeable amount of the cyanide ion (judging from the formation of Berlin blue) in the reaction mixture indicates that homolysis is the preferable route.

The presence of dibutylisopropylamine in the reaction products may indicate that dibutylamine is formed after the addition of the cryptobase of a Grignard reagent to cyanamide. In fact, the formation of azomethine is followed by the addition of a second methyl group at the C=N bond. Under drastic conditions, the resulting compound is transformed into dibutylisopropylidene ammonium, which is subsequently reduced by a third MeMgI molecule.



The presence of the cyanide ion in the reaction mixture and the absence of dibutylmethylamine indicates that homolytic cleavage of the C—N σ-bond occurs.

Thus, cyanamides are homolytically cleaved by the Grignard reagent at the C—N σ-bond only under drastic conditions.

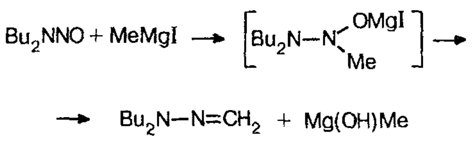
It was also found that the addition of EtMgI to diethylnitrosamine results in acetaldehyde diethylhydrazone.[6] Aromatic Grignard reagents react with analogous nitrosamines to give 2-aryl-1,1-diethylhydrazines and 1-(1-aryl)ethyl-1-ethyl-2-phenylhydrazines.[7] We showed that the reaction of dibutylnitrosamine with MeMgI at 20 °C in ether results in a number of products, with acetaldehyde dibutylhydrazone as the main product.

$$Bu_2NNO + MeMgI \rightarrow \underset{(78\ \%)}{Bu_2N{-}N{=}CHMe}$$

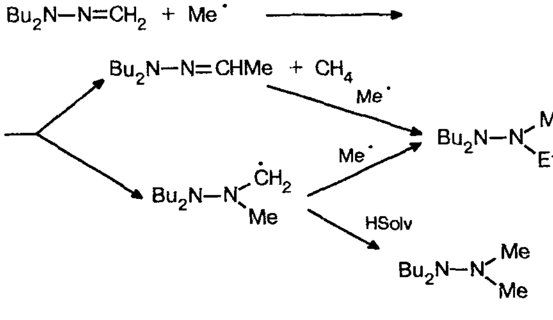
Earlier,[8] it was found that aldehyde hydrazones have a *syn* configuration. The structure of the above hydrazone was confirmed by mass spectral, ^1H NMR, and IR spectral data. The mass spectrum of the hydrazone contains an intense molecular ion peak characteristic of compounds of this class,[9] peaks of $[M-Pr]^+$, $[M-Pr-MeCHCN]^+$, $[M-Pr-C_4H_8]^+$, and $[M-Pr-PrCHNBu]^+$ ions, as well as low-intensity peaks of $[M-C_3H_6]^{+\cdot}$ and $[M-C_4H_8]^{+\cdot}$ ions.

The ^1H NMR spectrum contains signals for the CH=N group at δ 6.90 (q, J = 5.1 Hz) and the CH_3 group at δ 1.95 (d, 3 H) typical of aldehyde dialkylhydrazones.[10] The IR spectrum of the hydrazone displays an absorption band at 1673 cm^{-1} corresponding to the stretching vibrations of the C=N bond (*cf.* Ref. 11).

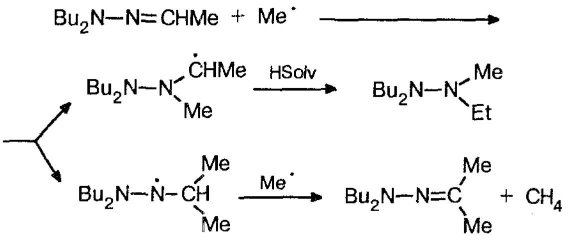
Minor amounts of formaldehyde, acetone, and butanone dibutylhydrazones, as well as 1,1-dibutyl-2,2-dimethylhydrazine and 1,1-dibutyl-2-ethyl-2-methylhydrazine, were also detected in the reaction mixture. Evidently, as in the case of dibutylcyanamide, the addition of a methyl cryptobase at the nitroso group occurs at the first reaction step. Subsequent abstraction of hydroxymagnesium iodide results in formaldehyde hydrazone.



The resulting formaldehyde hydrazone further reacts with the next MeMgI molecule by a free radical mechanism. The attack can involve both the nitrogen atom (N-addition) and the carbon atom (C-addition) of the azomethine group.



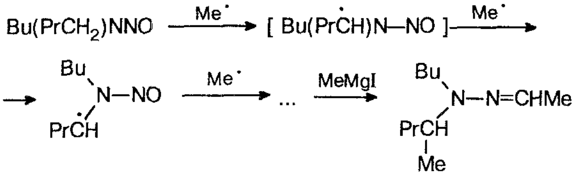
Acetaldehyde hydrazone can also be attacked by the methyl radical at the N and C atoms of the azomethine bond.



The structures of the hydrazones and tetraalkyl-substituted hydrazines were established from the mass spectra by the fragmentation typical of these types of compounds.[9]

Thus, the addition of a methyl group at the N atom of the nitroso group is likely to occur initially. The hydrazone formed after the abstraction of hydroxymagnesium iodide subsequently reacts with the excess methylmagnesium iodide.

Acetaldehyde butyl(1-methylbutyl)hydrazone and 2-butanone butyl(1-methylbutyl)hydrazone were also detected in the reaction mixture. Hence, yet another reaction center appears during the reaction. No data on the mobility of the α-hydrogen atoms are available for hydrazones (*cf.* Ref. 12), but such mobility was observed for nitrosamines.[13] This suggests that the replacement of the H atom occurs at the step of the formation of nitrosamine.

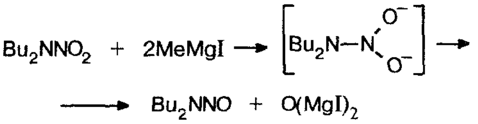


The structures of the hydrazones with α-methyl substituents in the butyl radical were confirmed by mass spectra.

The main product of the reaction of di(*n*-butyl)nitramine with MeMgI is di(*n*-butyl)nitrosamine. Products of reactions of the nitrosamine with MeMgI were also formed in minor amounts.

$$Bu_2NNO_2 + MeMgI \longrightarrow \underset{(86\ \%)}{Bu_2NNO}$$

In our opinion, the reduction of the nitro group of the substrate into the nitroso group occurs at this point.



The nitrosamine subsequently formed reacts with the Grignard reagent to give the above products.

Thus, the one-electron transfer reactions of dibutylcyanamide, dibutylnitrosamine, and dibutylnitramine in the presence of excess MeMgI occur in different ways. Dibutylcyanamide undergoes homolysis at the C—N σ-bond and addition at the CN group. Dibutylnitrosamine not only adds a methyl group at the N atom of the nitroso group, but also replaces an α-H atom in the butyl group. In the case of dibutylnitramine, the Grignard reagent reacts as a typical reducing agent.

Experimental

Mass spectra were obtained on a Kratos 25 RF chromato-mass-spectrometer with a DS-90 data processing system (energy of ionizing electrons 70 eV, ion source temperature 260 °C) using a capillary column (25 m) with the SE-30 stationary liquid phase. The temperature was programmed at 5 °C/min in the 30—150 °C range and 10 °C/min in the 150—300 °C range. IR spectra were recorded on a Bruker IF-48 spectrophotometer in films or in CCl_4. ^1H NMR spectra were recorded on a Bruker 250 spectrometer (250 MHz) in $CDCl_3$.

Dibutylcyanamide was synthesized according to a procedure in Ref. 14. B.p. 143—145 °C (32 Torr). MS, *m/z* (I_{rel} (%)): 154 $[M]^{+\cdot}$ (12), 139 $[M-Me]^{+\cdot}$ (5), 125 $[M-Et]^{+\cdot}$ (8), 111 $[M-Pr]^{+\cdot}$ (30), 97 $[M-Bu]^{+\cdot}$ (7), 84 $[M-Pr-HCN]^{+\cdot}$ (6), 69 $[PrCN]^{+\cdot}$ (100), 57 $[Bu]^{+\cdot}$ (45), 55 (80), 44 (20), 41 (70).

Dibutylnitrosamine was synthesized according to a procedure in Ref. 15. B.p. 235—237 °C. MS, *m/z* (I_{rel} (%)): 158 $[M]^{+\cdot}$ (15), 141 $[M-OH]^{+\cdot}$ (10), 116 $[M-C_3H_6]^{+\cdot}$ (20), 115 $[M-Pr]^{+\cdot}$ (15), 103 $[M-C_4H_8]^{+\cdot}$ (3), 99 $[M-NO-C_2H_5]^{+\cdot}$ (20), 84 $[C_4H_9NCH]^{+\cdot}$ (100), 57 $[Bu]^{+\cdot}$ (97), 42 (60), 43 (60), 41 (95), 30 $[NO]^{+\cdot}$ (55).

Dibutylnitramine was synthesized according to a procedure in Ref. 16. B.p. 129—130 °C. MS, *m/z* (I_{rel} (%)): 157 $[M-OH]^{+\cdot}$ (1), 131 $[M-Pr]^{+\cdot}$ (25), 128 $[M-NO_2]^{+\cdot}$ (12), 89 $[M-Pr-C_3H_6]^{+\cdot}$ (12), 84 $[C_4H_9NCH]^{+\cdot}$ (100), 57 $[Bu]^{+\cdot}$ (25), 43 $[Pr]^{+\cdot}$ (50).

Reactions of dibutylcyanamide, dibutylnitrosamine, and dibutylnitramine with MeMgI (general procedure). MeMgI (1 mol) in ether was added to a solution of the substrate (0.1 mol) in abs. ether. The mixture was stirred for 1 h and decomposed with aqueous NH_4Cl. The ethereal layer was separated and dried with $CaCl_2$. An aliquot of the solution was studied by chromato-mass-spectrometry. The solvent was distilled off, and the residue was chromatographed on Silpearl SiO_2 and eluted with benzene to isolate acetaldehyde 1,1-dibutylhydrazone.

A. In the case of dibutylcyanamide, chromato-mass-spectrometry revealed two products.

Dibutylamine. MS, *m/z* (I_{rel} (%)): 129 $[M]^{+\cdot}$ (10), 86 $[M-Pr]^{+\cdot}$ (80), 57 $[Bu]^{+\cdot}$ (18), 44 $[M-Pr-C_3H_6]^{+\cdot}$ (100), 41 (28), 30 $[CH_2NH_2]^{+\cdot}$ (70).

Dibutylisopropylamine. MS, *m/z* (I_{rel} (%)): 171 $[M]^{+\cdot}$ (3), 156 $[M-Me]^{+\cdot}$ (5), 128 $[M-Pr]^{+\cdot}$ (18), 114 $[M-Bu]^{+\cdot}$ (5), 100 (10), 86 $[M-Pr-C_3H_6]^{+\cdot}$ (100), 72 $[M-Pr-C_4H_8]^{+\cdot}$ (5), 57 $[Bu]^{+\cdot}$ (8), 44 $[CH_3NCH_3]^{+\cdot}$ (58), 43 $[Pr]^{+\cdot}$ (95).

B. In the case of dibutylnitrosamine, eight products were identified.

Acetaldehyde dibutylhydrazone. M.p. 65 °C. Found (%): C, 70.37; H, 13.23. $C_{10}H_{22}N_2$. Calculated (%): C, 70.53; H, 13.02. ^{1}H NMR, δ: 0.98 (t, 6 H); 1.53 (m, 8 H); 1.95 (d, 3 H); 3.05 (t, 4 H); 6.90 (q, 1 H). MS, *m/z* (I_{rel} (%)): 170 $[M]^{+\cdot}$ (28), 127 $[M-Pr]^{+\cdot}$ (100), 85 $[M-Pr-C_3H_6]^{+\cdot}$ (70), 71 $[M-Pr-C_4H_8]^{+\cdot}$(52), 57 $[Bu]^{+\cdot}$ (20), 43 (10), 42 $[CH_2NCH_2]^{+\cdot}$ (20), 41 (30).

Formaldehyde dibutylhydrazone. MS, *m/z* (I_{rel} (%)): 156 $[M]^{+\cdot}$ (15), 113 $[M-Pr]^{+\cdot}$ (65), 71 $[M-Pr-C_3H_6]^{+\cdot}$ (70), 57 $[M-Pr-C_4H_8]^{+\cdot}$(100), 43 (15), 42 $[CH_2NCH_2]^{+\cdot}$ (20), 41 (45).

Acetone dibutylhydrazone. MS, *m/z* (I_{rel} (%)): 184 $[M]^{+\cdot}$ (13), 141 $[M-Pr]^{+\cdot}$ (100), 127 $[M-Pr-CH_2]^{+\cdot}$ (2), 113 $[M-Pr-C_2H_4]^{+\cdot}$ (3), 99 $[M-Pr-C_3H_6]^{+\cdot}$ (45), 85 $[M-Pr-C_4H_8]^{+\cdot}$ (20), 57 $[Bu]^{+\cdot}$ (20), 44 (10), 43 (12), 42 $[CH_2NCH_2]^{+\cdot}$ (10), 41 (30).

2-Butanone dibutylhydrazone. MS, *m/z* (I_{rel} (%)): 198 $[M]^{+\cdot}$ (20), 155 $[M-Pr]^{+\cdot}$ (100), 141 $[M-Bu]^{+\cdot}$ (2), 127 $[M-Pr-C_2H_4]^{+\cdot}$ (3), 113 $[M-Pr-C_3H_6]^{+\cdot}$ (50), 99 $[M-Pr-C_4H_8]^{+\cdot}$(20), 70 (10), 57 $[Bu]^{+\cdot}$ (20), 44 (10), 43 (12), 42 $[CH_2NCH_2]^{+\cdot}$ (10), 41 (30).

1,1-Dibutyl-2,2-dimethylhydrazine. MS, *m/z* (I_{rel} (%)): 172 $[M]^{+\cdot}$ (30), 157 $[M-Me]^{+\cdot}$ (5), 129 $[M-Pr]^{+\cdot}$ (40), 115 $[M-Bu]^{+\cdot}$ (100), 87 $[M-Bu-C_2H_4]^{+\cdot}$ (10), 73 $[M-Bu-C_3H_6]^{+\cdot}$(45), 59 $[M-Bu-C_4H_8]^{+\cdot}$ (20), 44 (55), 43 (15), 42 $[CH_2NCH_2]^{+\cdot}$ (20), 42 (15).

1,1-Dibutyl-2-ethyl-2-methylhydrazine. MS, *m/z* (I_{rel} (%)): 186 $[M]^{+\cdot}$ (30), 171 $[M-Me]^{+\cdot}$ (3), 143 $[M-Pr]^{+\cdot}$ (35), 129 $[M-Bu]^{+\cdot}$ (100), 101 $[M-Bu-C_2H_4]^{+\cdot}$ (10), 87 $[M-Bu-C_3H_6]^{+\cdot}$ (35), 71 $[M-Bu-C_4H_8]^{+\cdot}$ (23), 44 (55), 43 (15), 42 $[CH_2NCH_2]^{+\cdot}$ (20), 42 (15).

Acetaldehyde butyl-(1-methylbutyl)hydrazone. MS, *m/z* (I_{rel} (%)): 184 $[M]^{+\cdot}$ (10), 169 $[M-Me]^{+\cdot}$ (5), 141 $[M-Pr]^{+\cdot}$ (100), 126 $[M-Pr-CH_2]^{+\cdot}$ (3), 113 $[M-Pr-C_2H_4]^{+\cdot}$ (5), 99 $[M-Pr-C_3H_6]^{+\cdot}$ (10), 85 $[M-Pr-C_4H_8]^{+\cdot}$ (40), 71 $[M-Pr-C_5H_{10}]^{+\cdot}$ (52), 57 $[Bu]^{+\cdot}$ (20), 44 (20), 43 (30), 42 $[CH_2NCH_2]^{+\cdot}$ (20), 41 (30).

2-Butanone butyl-(1-methylbutyl)hydrazone. MS, *m/z* (I_{rel} (%)): 212 $[M]^{+\cdot}$ (10), 197 $[M-Me]^{+\cdot}$ (5), 183 $[M-Et]^{+\cdot}$ (2), 169 $[M-Pr]^{+\cdot}$ (100), 155 $[M-Bu]^{+\cdot}$ (3), 141 $[M-Pr-C_2H_4]^{+\cdot}$ (3), 127 $[M-Pr-C_3H_6]^{+\cdot}$ (5), 113 $[M-Pr-C_4H_8]^{+\cdot}$ (20), 99 $[M-Pr-C_5H_{10}]^{+\cdot}$ (42), 84 (3), 70 (10), 57 $[Bu]^{+\cdot}$ (15), 44 (20), 43 (30), 42 $[CH_2NCH_2]^{+\cdot}$ (10), 41 (30).

C. Dibutylnitrozamine (yield 86 %, judging by GLC data) and the abovementioned products of its transformation were detected in the case of dibutylnitramine.

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