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Peculiarities of the interaction of dinitrobenzenes with *t*-BuNHMgBr and *t*-BuNHLi

E. T. Apasov,* B. A. Dzhetigenov, E. V. Shepelev, Yu. A. Strelenko, and A. V. Kalinin

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117913 Moscow, Russian Federation. Fax: +7 (095) 135 5328

Reactions of *m*- and *p*-dinitrobenzenes with *t*-BuNHMgBr and *t*-BuNHLi were studied. The reactions afford azo- and azoxy-derivatives and products of nucleophilic substitution.

Key words: dinitrobenzene, alkylaromatic diazenes, alkylaromatic diazeneoxides, azoxybenzene.

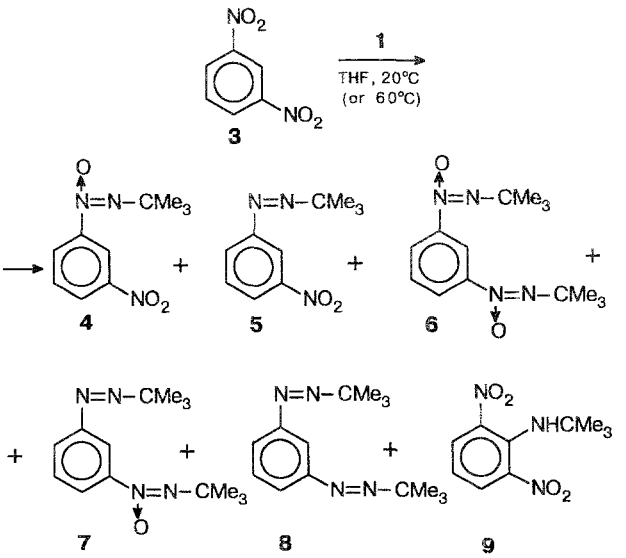
Previously we proposed a method for the synthesis of azoxyarylalkanes from nitroaromatic compounds.[1,2] It has been demonstrated for the example of the interaction of $PhNO_2$ with *t*-BuNHMgBr (**1**) and *t*-BuNLi (**2**) that **2** is more active and selective than **1** in the conversion of the nitro group into an azoxy fragment.[2] The use of **1** results in the formation of an azo-derivative as a by-product through the reduction of a portion of $PhNO_2$ to PhNO followed by condensation of the latter with **1**.[1]

In this work the interaction of **1** and **2** with dinitrobenzenes was studied and several peculiarities due to the presence of two electron-acceptor substituents in the original substrates were found.

The reaction of **1** with 1,3-dinitrobenzene (**3**) follows mainly the same course as with $PhNO_2$, with both NO_2 groups of **3** being reactive (Scheme 1).

A mixture of products (**4**—**8**) is formed with all possible combinations of nitro, *tert*-butylazoxy, and *tert*-butylazo groups, the latter having the *anti*-configuration (see ref.[1]). Moreover, N-*tert*-butyl-2,6-dinitroaniline (**9**), the product of nucleophilic substitution of hydrogen in the aromatic ring, is found in the reaction mixture

Scheme 1



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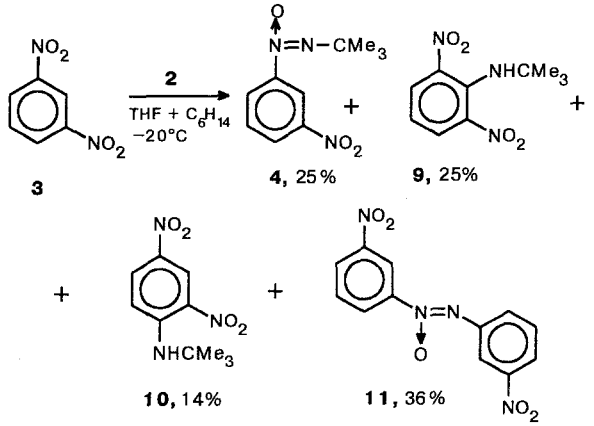
(NMR spectral data are given in Tables 1 and 2). This substitution is favored by the coordinated influence of the acceptor groups in **3**. It seems likely that the coordination of the reagent with the participation of both nitro groups takes place at the first stage of the formation of **9**, so that it is the C(2)-atom that is attacked although the approach to this atom is most sterically hindered.

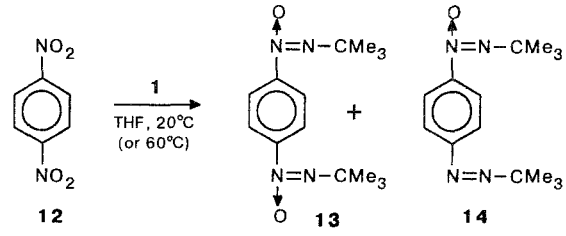
The composition of a reaction mixture depends on the ratio of the reagents and on the reaction conditions. At a ratio **1** : **3** = 4 and when the reaction mixture is boiled for 3 h, the conversion is only 73 % and the product of transformation of only one nitro group is primarily formed (Table 3, run 2). Oxidation-reduction processes resulting in the formation of the azo-fragment occur in parallel. At a threefold excess with respect to one nitro group (**1** : **3** = 6) the substrate conversion increases, with the second nitro group readily entering the reaction. The reduction processes are simultaneously activated, so that compound **7** becomes the main reaction product (Table 3, run 3). At a fivefold excess of the reagent, total transformation of the nitro groups occurs, and the portion of reduction products **7** and **8** increases (Table 3, run 5). If the reaction is carried out at ~20°C, the same influence of reagent ratio on the conversion of the starting compound is observed although it is not so distinct (Table 3, runs 1 and 4).

With compound **2** the total conversion of **3** is achieved under mild conditions even at the ratio **2** : **3** = 3. The use of a Li derivative, as in ref. 2, allows one to avoid the formation of azo-derivatives, although substitution into the nucleus becomes the main direction of the reaction. This is associated with the increase in nucleophilicity of the reagent. In this case, as well as with **1**, the C(2)-atom is predominantly attacked.



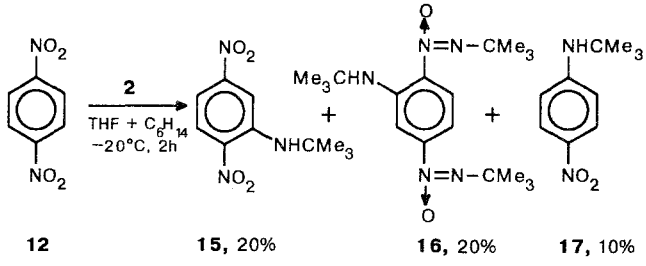
In the course of nucleophilic substitution the replacement of the hydride-ion must take place, therefore it is not surprising that a significant amount of product **11**, which is formed due to partial reduction of **3**, appears in the reaction mixture. A similar process was observed in an investigation of the interaction of lithium piperidide with nitrobenzene.[4]

Upon the action of **1** on 1,4-dinitrobenzene (**12**) both nitro groups react; obviously, the reactivity of the second group increases drastically following the formation of the first azoxy-fragment; therefore, we failed to find a product retaining one nitro group, even at incomplete conversion of the substrate. With a sixfold excess of **1** with respect to **12**, 45 % of the starting substrate **12** remains after 48 h at 20°C, and the yields of **13** and **14** are 25 % and 30 %, respectively. At a fourfold excess of the reagent and with boiling for 3 h, the content of **12**, **13**, and **14** in the reaction mixture comprises 25 %, 25 %, and 49 %, respectively.



As the acceptor groups in **12**, in contrast to **3**, do not act in coordination, the ring becomes less susceptible to nucleophilic attack, and the substitution of hydrogen under the action of **1** was not observed.

Reagent **2** has more pronounced nucleophilic properties than **1**, therefore substitution into the ring with the formation of 2,5-derivatives of N-*tert*-butylaniline **15** and **16** becomes the main direction in the reaction of **2** with **12**.



Upon the action of **2** on **12** not only is the hydrogen in the *o*-position with respect to the nitro and azoxy group replaced, but the nitro group in the *p*-position is also replaced due to the acceptor influence of the second nitro group. Lithium nitrite must be eliminated in the course of this reaction. Apparently, it is lithium nitrite that oxidizes the hydride-ion at the stage of synthesis of **15** and **16**, since, unlike the experiment with **3**, the product of reductive condensation of dinitrobenzene, the corresponding 4,4'-dinitroazoxybenzene, is formed only in trace amounts.

Table 1. ^{13}C NMR of compounds **4—10**, **13—17** ($CDCl_3$, 25°C), δ*

Compound	C(1)**	C(2)	C(3)	C(4)	C(5)	C(6)	azo group		azoxy group		amino group	
							CMe_3	CH_3	CMe_3	CH_3	CMe_3	CH_3
4	149.3	117.9	148.3	125.7	129.6	128.4	—	—	59.6	25.6	—	—
5	152.9	116.5	149.0	124.2	129.7	127.9	68.8	26.8	—	—	—	—
6	148.9	116.7	148.9	124.7	128.8	124.7	—	—	59.4	25.7	—	—
7	152.6	115.6	149.5	125.0	129.0	123.2	68.4	27.0	59.2	25.8	—	—
8	153.1	115.0	153.1	123.5	129.3	123.5	68.0	27.0	—	—	—	—
9	146.3	137.0	129.9	120.8	129.9	137.0	—	—	—	—	59.0	30.0
13	150.2	122.6	122.6	150.2	122.6	122.6	—	—	59.4	25.7	—	—
14	149.2	122.9	122.0	153.7	122.0	122.9	68.4	26.9	59.1	25.8	—	—
15	—	144.5	111.2	—	108.1	129.0	—	—	—	—	52.4	29.5
16	—	141.8	109.0	150.0	107.6	125.6	—	—	59.1, 59.5	25.7, 26.1	51.3	29.7
17	152.3	112.8	126.1	136.9	126.1	112.8	—	—	—	—	51.7	29.3

* The assignment of signals was made taking the additive scheme into account.
** The atoms in the ring were numbered in decreasing order of the substituents in the series: amino, azo, azoxy, nitro group.

Table 2. ^{1}H, ^{15}N, and ^{14}N NMR spectra of compounds **4—10**, **13—17** ($CDCl_3$, 25°C)

Compound	^{1}H NMR, δ*								^{15}N and ^{14}N NMR ($MeNO_2$), δ			
											=$NCMe_3$**	
	H(2)	H(3)	H(4)	H(5)	H(6)	CH_3 azo	CH_3 azoxy	CH_3 amino	NO_2	O←N=	azo	azoxy
4	8.98	—	8.51	7.67	8.39	—	1.49	—	−13.5	−57.8	—	−17.2
5	8.46	—	8.26	7.63	8.06	1.38	—	—	−13.5	—	+177.5	—
6	8.87	—	8.28	7.52	8.28	—	1.48	—	—	56.2	—	−16.9
7	8.37	—	8.16	7.51	7.80	1.35	1.48	—	—	−56.2	+173.2	−18.2
8	7.90	—	7.70	7.53	7.70	1.30	—	—	—	—	+169.0	—
9	—	8.04	7.20	8.04	—	—	—	1.19	−10.7	—	—	—
10	—	9.12	—	8.22	7.15	—	—	1.56	−13.0	—	—	—
13	8.18	8.18	—	8.18	8.18	—	1.47	—	—	−55.3	—	—
14	7.67	8.18	—	8.18	7.67	1.35	1.48	—	—	−53.7	+178.9***	—
15	—	8.26	7.28	—	7.93	—	1.49	—	−12.5	—	—	—
16	—	8.03	7.23	—	7.78	1.40	1.41	1.42	—	−50.1	—	—
17	6.62	8.02	—	8.02	6.62	1.42						

*Multiplicity and integral intensities of the signals correspond to the structure proposed.
**^{15}N NMR (the data were obtained using the INEPT method).
***+124.1 for the Ar—N= fragment (the signals were observed in the ^{14}N NMR spectrum).

Table 3. Reaction conditions and composition of the reaction mixture obtained on the interaction of *t*-BuNHMgBr with *m*-dinitrobenzene over 3 h

Run	Molar ratio **1** : **3**	Reaction temperature (°C)	Compositon of the reaction mixture according to GLC data(%)						
			3	**4**	**5**	**6**	**7**	**8**	**9**
1	4	20	46	29	21	—	—	—	4
2	4	60	27	32	34	1	1	—	5
3	6	60	9	5	16	16	36	13	5
4	10	20	28	32	24	3	4	1	8
5	10	60	—	—	—	15	45	40	—

Experimental

GLC-analysis was carried out with a Biokhrom 1M chromatograph on a glass column (58.5×0.25 mm) with a PEG-40M stationary liquid phase and nitrogen as the carrier gas. NMR spectra were recorded with a Bruker AM-300 spectrometer at working frequencies of 300 MHz for ^{1}H, 75.5 MHz for ^{13}C, 21.7 MHz for ^{14}N, and 30.4 MHz for ^{15}N. The reactions of *t*-BuNHMgBr and *t*-BuNHLi with nitro compounds were carried out according to the previously described procedure.[1,2] All reactions were performed in a dry argon atmosphere using absolute solvents. The products were isolated by column chromatography on SiO_2 and recrystallized from MeOH: **4**, mp 86°C; **6**, mp 82°C; **13**, mp 161°C; **14**, mp 91°C; **15**, mp 112°C; **16**, mp 97°C; **5,6,** and **7** are viscous liquids. The structures of **4—8** and **13—16** were established on the basis of NMR spectral data (see Tables 1 and 2) and elemental analysis. Compounds **9—11** and **17** were identified by comparison with known samples.[4—7]

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Syntheses based on nitrile oxides. 3.* Interaction of aromatic nitrile oxides with bis-trimethylsilylthiodiimide

V. A. Ogurtsov, O. A. Rakitin, Yu. A. Strelenko, N. V. Obruchnikova, and L. I. Khmel'nitskii*

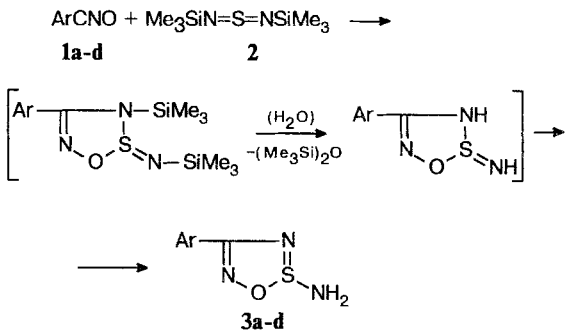
N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117334 Moscow, Russian Federation. Fax: +7 (095) 135 5328

Interaction of aromatic nitrile oxides with bis-trimethylsilylthiodiimide results in 2-amino-4-aryl-1,2,3,5-oxathiadiazoles, the first representatives of a new class of heterocyclic compounds.

Key words: nitrile oxides, thiodiimide, oxathiadiazoles, amidooximes.

Earlier[1] we reported that aromatic nitrile oxides interact with bis-trimethylsilylcarbodiimide to give 5-amino-3-aryl-1,2,4-oxadiazoles.

To continue this work we studied the reaction of aromatic nitrile oxides (**1a—d**) with trimethylsilylthiodiimide (**2**). The main products of this reaction are 2-amino-4-aryl-1,2,3,5-oxathiadiazoles (**3a—f**), the formation of which can be explained by a scheme similar to the formation of 5-amino-3-aryl-1,2,4-oxadiazoles upon interaction of aromatic nitrile oxides with bis-trimethylsilylcarbodiimide:[1]



3a-d

Ar = *m*-$O_2NC_6H_4$ (**a**); *p*-$O_2NC_6H_4$ (**b**); *p*-ClC_6H_4 (**c**); *p*-BrC_6H_4 (**d**).

*For Part 2, see ref. 1.

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