

THE FIRST SUCCESSFUL DIRECT AZOCOUPLING OF NITROAROMATIC ANION-RADICAL

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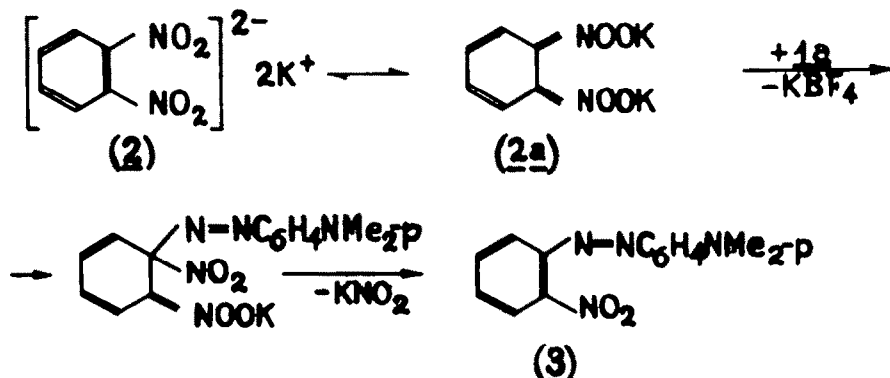
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Abstract - o-Dinitrobenzene dianion reacts with p-N,N-dimethylaminobenzenediazonium cation, forming 2-nitro-4'-N,N-dimethylaminoazobenzene. o-Dinitrobenzene anion-radical, interacting with benzenediazonium cations that contain N,N-dimethylamino or nitro group in para-position, yields 3-nitro-4'-hydroxy-4'-N,N-dimethylaminoazobenzene and 3,4'-dinitro-4'-hydroxyazobenzene, respectively. The above compounds are formed in media promoting the stability of ion pairs between o-dinitrobenzene dianions or anions-radicals and potassium cations. With the dissociation of ion pairs, only the electron-transfer reaction products are observed.

o-Dinitrobenzene (o-DNB) by itself is incapable of entering into the azo-coupling reaction. This reaction has been found to occur when o-DNB is converted into anion-radical or dianion forms. The interaction will proceed differently depending on the substrate ionic form. Used as the reagent were diazosalts with the general formula: p-RC₆H₄N₂BF₄ (1, a R=Me₂N, b R=NO₂).

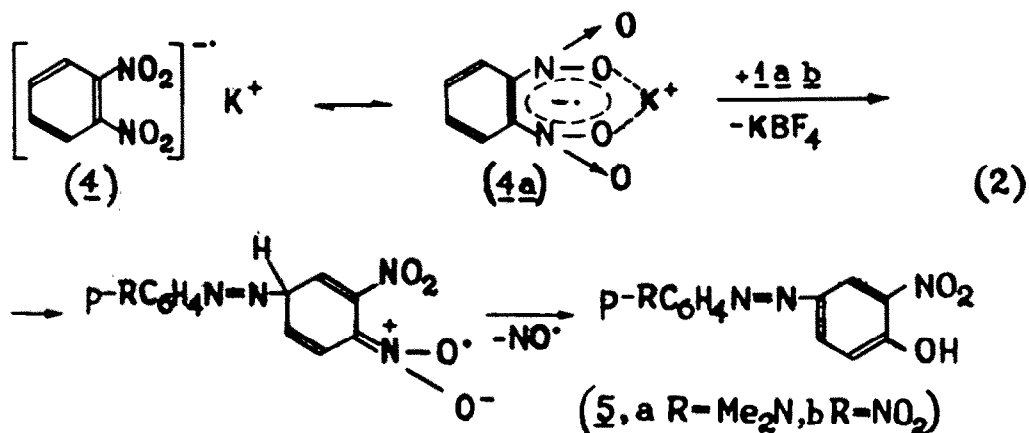
In the case of o-DNB dianion (2) ipso-coupling occurs followed by NO₂⁻ elimination so that o-nitroazocompound (3) is formed, Scheme 1.



Reaction 1 is accompanied by the dianion oxidation followed by the formation of o-DNB, N₂, and dimethylaniline. In THF (E = 7.4) the nitro group substitution by the arylazo group proceeds concurrently the redox process, whereas in MeCN

($\epsilon = 36.5$) only the redox reaction takes place, see Table 1. The above difference is caused, in our opinion, by the ion-pair stabilization in poorly dissociating THF and their decay in the strongly dissociating MeCN.

When o-DNB anion radical potassium salt (4) reacts with diazo cation in DMSO ($\epsilon = 49$) only electron transfer happens. In THF, however, azocoupling occurs. Observed here is not ipso-substitution, as in the case of dianion (2), but the arylazo fragment enters in the p-position of the benzene ring. At the same time, the para-nitro group is converted into a hydroxy group. This is accompanied by the NO^\bullet radical loss; nitrogen monoxide was detected by the gas phase IR analysis. The observed series of conversions is shown in Scheme 2 and has been confirmed by check experiments: the exposure of salt (4) to air or water treatment didn't lead to the replacement of substrate nitro group by the hydroxy group and the addition of H_2^{18}O after the mixing of reagents didn't result in the labelled OH group in product (5). No changes associated with the presence of ^{18}O isotope in the amount exceeding its natural percentage have been observed in the mass spectrum.



Anion-radical (4), interacting with diazo cations (1a, 1b), takes part both in azocoupling and in electron transfer reactions (Table 1).

Table 1

Interaction of o-DNB anionic forms with diazo cations (equimolar ratio)

| Reagent | Substrate | Solvent | N_2 | Yield of products, % of theor. (R in brackets) | | |
|-----------|-----------|---------------------|--------------|---|-------|-----------------|
| | | | | RC_6H_5 | o-DNB | Azo compound |
| <u>1a</u> | <u>2</u> | THF | 72 | 60 (NMe_2) | 83 | <u>2</u> , 13 |
| <u>1a</u> | <u>2</u> | MeCN | 92 | 81 (NMe_2) | 90 | 0 |
| <u>1a</u> | <u>4</u> | THF | 12 | 13 (NMe_2) | 71 | <u>5a</u> , 46* |
| <u>1b</u> | <u>4</u> | THF | 26** | 27 (NO_2) | 63 | <u>5b</u> , 58* |
| <u>1a</u> | <u>4</u> | THF + 18-crown-6*** | 88 | 95 (NMe_2) | 89 | 0 |
| <u>1b</u> | <u>4</u> | THF + 18-crown-6*** | 94 | 95 (NO_2) | 94 | 0 |
| <u>1a</u> | <u>4</u> | DMSO | 91 | 83 (NMe_2) | 90 | 0 |
| <u>1b</u> | <u>4</u> | DMSO | 93 | 81 (NO_2) | 95 | 0 |

* Reagent : substrate, 1 : 2

** NO was also found

*** 18-Crown-6 in equimolar quantity with respect to (4)

Redox reaction is the only one in DMSO; in THF the yields of electron transfer products and the products of azocoupling are comparable. Azocoupling is also completely suppressed in THF by 18-crown-6 ether addition. Therefore, in the case of reaction 2, the ion pair decay prevents the substitution as well.

The difference in the reactivity of substrates (2) and (4) coupled with potassium cations (see Schemes 1 and 2), seems to be caused by the difference in their electronic structure. Dianion (2) has a quinoid structure (2 a)¹, whereas anion-radical (4) retains its aromaticity (even a mesomeric structure corresponding to bicyclic compound (4 a) is possible²). The formation of such aromatic structure is resulted from the ortho-arrangement of the two nitro groups.

From this point of view, it was of interest to ascertain the route of diazo cation interaction with p-nitrobenzene anion-radical potassium salt (6).

In media with a low ionizing power the potassium cation in salt (6) is known² to be coordinated at only one of the two nitro groups, on which most of the spin density is concentrated, i.e. salt (6) is similar to nitrobenzene anion-radical potassium salt (7). We have found salts (6) and (7) to react with aromatic compounds in THF only by the one-electron transfer route (no azocoupling takes place), the replacement of THF by DMSO not changing the reaction direction.

The first successful direct azocoupling for anion-radical (4) has thus been accomplished. Possible mechanisms of this reaction, alternative to Scheme 2, should be considered. Firstly, it is the diazenium radical attack on neutral o-DNB immediately after the electron transfer from the substrate to the reagent (without leaving the solvent cage for the volume). Secondly, it is the recombination of the diazenium radical, resulting from one-electron reduction of the diazonium cation by the substrate, with the other molecule of (4). The reaction of the first type does not seem to be realized. Otherwise, a mixture of two azocompounds isomeric with respect to the position of the azo group (ortho or para) would be obtained. Actually only one isomer is produced (Tables 2, 3).

The reaction of the second type implies a particularly high stability of the diazenium radical. Only upon the emergence of the radical from the solvent cage, its encounter with the other molecule (4) and the azocoupling would be possible. As seen from experimental data (Table 1), the main route of diazenium radical transformation is the dinitrogen elimination when aryl radicals are formed which yield the corresponding benzene derivatives after the hydrogen atom abstraction from the solvent molecule.

Table 2

Melting points and elemental analysis results for azo compounds obtained.

| Compound | M.p., °C (solvent) | Ref. | General formula | % Found (Calculated) | | |
|----------|-----------------------|------|---|----------------------|-------------|---------------|
| | | | | C | H | N |
| 3 | 132 (benzene) | 3 | C ₁₄ H ₁₄ N ₄ O ₂ | 62.22 (62.22) | 4.91 (5.18) | 20.67 (20.75) |
| 2 a | 196 (benzene) | | C ₁₄ H ₁₄ N ₄ O ₃ | 58.52 (58.74) | 4.91 (4.89) | 19.51 (19.58) |
| 2 b | 212 (benzene) | 4 | C ₁₂ H ₈ N ₄ O ₅ | 49.86 (50.00) | 2.80 (2.77) | 19.42 (19.44) |

Table 3

Spectral characteristics of azo compounds obtained

| Compounds | Mass spectrum (m/z) | IR spectrum (ν , cm^{-1}) | PMR spectrum (δ , p.p.m.) |
|--|--|--|---|
| 2-Nitro-4'-N,N-dimethyl- aminoazo- benzene (3) | 270 M^+ , 148 ($\text{M}-\text{C}_6\text{H}_4\text{NO}_2$) $^+$, 120 ($\text{M}-\text{C}_6\text{H}_4\text{N}_2\text{O}-\text{H}_2$) $^+$ | 1150 s (C-N), 1372 s (NO_2) $_g$, 1540 m (NO_2) $_{as}$, 1610 s (N=N) | 7.95-7.55 m (4H, $\text{C}_6\text{H}_4\text{NO}_2$), 7.81 (2H, $\text{H}^{2'}-\text{H}^{6'}$, J 9 Hz), 6.86 (2H, $\text{H}^{3'}-\text{H}^{5'}$, J 9 Hz), 3.12 (6H, NMe_2). |
| 3-Nitro-4'-N,N-di- methyl- aminoazo- benzene (5 a) | 286 M^+ , 128 ($\text{M}-\text{C}_6\text{H}_3(\text{OH})\text{NO}_2$) $^+$, 120 ($\text{M}-\text{C}_6\text{H}_3(\text{OH})\text{NO}_2-\text{H}_2$) $^+$ | 1145 s and 1170 s (C-N), 1320 s and 1360 s (NO_2) $_g$, 1530 m (NO_2) $_{as}$, 1605 s (N=N) | 10.62 s (1H, OH), 8.50 d (1H, H^2 , J_{2-6} 2.5 Hz), 8.12 dd (1H, H^6), 7.87 (2H, $\text{H}^{2'}-\text{H}^{6'}$, J 9 Hz), 7.37 d (1H, H^5 , J_{5-6} 9 Hz), 6.87 (2H, $\text{H}^{3'}-\text{H}^{5'}$, J 9 Hz). |
| 3,4'-Di- nitro-4'- hydroxy- azoben- zene (5 b) | 288 M^+ , 166 ($\text{M}-\text{C}_6\text{H}_4\text{NO}_2$) $^+$, 150 ($\text{M}-\text{C}_6\text{H}_3(\text{OH})\text{NO}_2$) $^+$, 138 ($\text{M}-\text{C}_6\text{H}_3\text{NO}_2-\text{H}_2$) $^+$, 122 ($\text{M}-\text{C}_6\text{H}_3(\text{OH})\text{NO}_2-\text{H}_2$) $^+$ | 1320 s and 1342 s (NO_2) $_g$, 1540 m (NO_2) $_{as}$, 1628 s (N=N) | 8.74 d (1H, H^2 , J_{2-6} 2.5 Hz), 8.47 (2H, $\text{H}^{3'}-\text{H}^{5'}$, J 9 Hz), 8.34 dd (1H, H^6), 8.18 (2H, $\text{H}^{2'}-\text{H}^{6'}$, J 9 Hz), 7.45 d (1H, H^5 , J_{5-6} 9 Hz). |

Thus, the reaction, having no analogues, of the azocoupling of o-DNB pre-converted into the anion-radical form has been found. Accomplished on models this reaction can in all probability be applied to more complex systems as well, in particular, in the synthesis of technically valuable dyes.

EXPERIMENTAL

Chromatographic determinations were performed on Chrom chromatograph-4 (carrier gas nitrogen, stainless steel column 3 x 3700 mm with Carbowax 20 M on silanized chromatone N-AW, 40-60 mesh) or on Tsvet-101 chromatograph (carrier gas nitrogen, glass column 3 x 2000 mm with 5 % SE-20 on chromatone N-AW-DMCS 60-80 mesh).

Magnetic susceptibility was measured on magnetic balance by the Faraday method at -196° and 20° and field intensities from 500 to 3500 Oe.

Mass spectra were obtained on ABI MS-30 instrument with DS-50 automatic data collection system at ionization voltage of 70 V. The system of direct introduction of sample into the ion source was heated to a temperature not exceeding the m.p. of the investigated compound.

IR spectra of ions were obtained on UR-20 instrument in KBr pellets (compacted in argon, fast scanning); the gaseous phase formed over the reaction mixture was collected in an evacuated cuvette with KBr windows after preliminary separation in a trap with a glass filter at -70° .

PMR spectra (at 25°) were recorded on Bruker WP-200 instrument, internal standard TMS, solvent $(\text{CD}_3)_2\text{CO}$.

The substrate was converted into anion-radical or dianion with cyclooctatetraenepotassium used as the electron donor by the procedure described in ⁵. The precipitates obtained were filtered off on a glass filter under small argon pressure, washed twice with cold THF and dried in vacuo. From 1.68 g of o-dinitrobenzene (o-DNB) 2.06 g of o-DNB dianion dipotassium salt (2) (yield 96 % of theor.) was obtained. According to the magnetic susceptibility data, the solid salt contains no paramagnetic particles. In the solid salt IR-spectrum there are no characteristic nitro group absorption bands in the 1330 and 1530 cm^{-1} regions, but intense bands are observed at 1060, 1200, 1390 and 1420 cm^{-1} (cf ⁶).

From 1.68 g of o-DNB 2.17 g of o-DNB anion-radical potassium salt (4), 95 % of theor., was obtained. According to the analysis of the solid salt magnetic susceptibility the content of paramagnetic particles in this sample was 95 %. When salt (4) suspension in THF or its solution in DMSO were treated with dry air or air-free water the initial o-DNB recovery ensued (92-95 %).

Interaction of the ionic forms of nitrocompounds with diazo salts

Suspension of anion-radical or dianion potassium salts of the corresponding nitrocompound (0.01 mol) in 50 ml of THF was mixed with dry diazonium boron fluoride. In some cases (see Table 1) MeCN or DMSO was used instead of THF. The compounds were mixed at -30° in a thoroughly sealed flask filled with argon at normal pressure, and then kept there for 1 hour. After gas-phase determination of nitrogen (volumetric analysis) or nitrogen monoxide (absorption at 1960 cm^{-1} , cf ⁷), as well as RC_6H_5 in liquid (GLC), the solution was filtered. The filtrate was evaporated, and the residue separated on a 22 x 600 mm column (silica gel, a mixture of hexane with ether or ethyl acetate, 3:1 as eluent). The characteristics of the substances obtained are given in Tables 2, 3.

Interaction of p-dinitrobenzene anion-radical potassium salt (6) with p-methoxyphenyldiazonium boron fluoride

Suspension (0.01 mol) of freshly prepared salt (6) in 30 ml of THF was mixed at -30° for 10 min with suspension of $\text{MeOC}_6\text{H}_4\text{N}_2\text{BF}_4$ (0.01 mol) in 20 ml of THF. 123 cm^3 of nitrogen (55 %) evolved. The reaction mixture was stirred for 10 min at -30° and then allowed to warm up to 25° . A red solution over a dark precipitate was obtained, the latter filtered out to give 0.89 g (40 %) of unreacted diazo compound and 0.72 g (57 %) of KBP_4 (IR and luminescent analyses). The filtrate was evaporated, the residue was separated on a thin layer of Al_2O_3 (hexane - ethyl acetate, 2:1). 0.92 g of p-dinitrobenzene, 0.16 g of anisole, and 0.35 g of 4-nitro-4'-methoxy-N,N-diphenylamine, $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_3$, orange crystals with m.p. 153° (ethyl alcohol)⁸ were obtained.

Pound, %: C 63.96 H 4.88 N 11.50. $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_3$.

Calculated, %: C 63.93 H 4.92 N 11.47.

Mass spectrum (m/z): 244 M^+ , 229 $(M-CH_3)^+$, 214 $(M-CH_2O)^+$,
182 $(M-CH_2O-2(O))^+$.

PMR spectrum: (δ , p.p.m.): 4.10 s (3 H, OCH_3), 6.42 s (1 H, NH),
7-8.5 m (8 H, 2 C_6H_4).

IR spectrum (ν , cm^{-1}): 1325 s (NO_2)_g, 1520 s (NO_2)_{as}, 3330 s (NH).

Interaction of nitrobenzene anion-radical potassium salt (I) with
p-methoxyphenyldiazonium boron fluoride

Suspension of 0.01 mol (2.22 g) of $MeOC_6H_4N_2BF_4$ in 20 ml of THF was added during 10 min under intensive stirring to the suspension of 0.01 mol of freshly prepared salt (I) in 30 ml of THF; in other experiments the mixtures were stored at temperatures from -40 to 25° for 20 min. Vigorous nitrogen evolution (210-215 cm^3 or 95 %) was observed, the mixture turned dark red, and a yellowish deposit precipitated (KBF_4 , yield 96 %). The filtrate was evaporated, the residue separated on a 22 x 600 mm silica gel column (hexane - ethyl acetate, 3:1). 1.17 g (95 %) of nitrobenzene and 0.97 g (90 %) of anizole were obtained. In DMSO the same substances are obtained (anizole yield drops to 80 %).

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