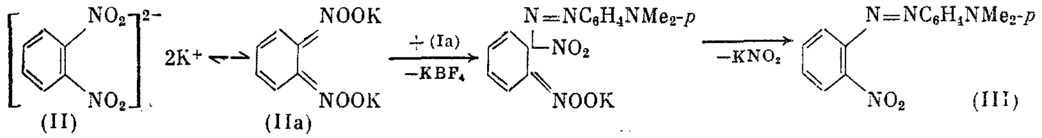
AZOCOUPLING OF o-DINITROBENZENE: REACTIONS OF THE DIANION AND ANION-RADICAL WITH ARYLDIAZOCATIONS

Z. V. Todres, G. Ts. Ovsepyan,
E. A. Ionina, A. Yu. Kosnikov,
S. V. Lindeman, and Yu. T. Struchkov

UDC 542.958.6:547.546:547.556.7-128.4

o-Dinitrobenzene (o-DNB) does not itself undergo azocoupling. We have however found that this reaction becomes possible when the o-DNB is converted into its anion-radical or dianion. The reaction follows different courses, depending on the ionic form of the substrate. The reagents used were diazo-salts of general formula p-RC$_6$H$_4$N$_2$BF$_4$ (I), in which R = Me$_2$N (a), OMe (b), and NO$_2$ (c).

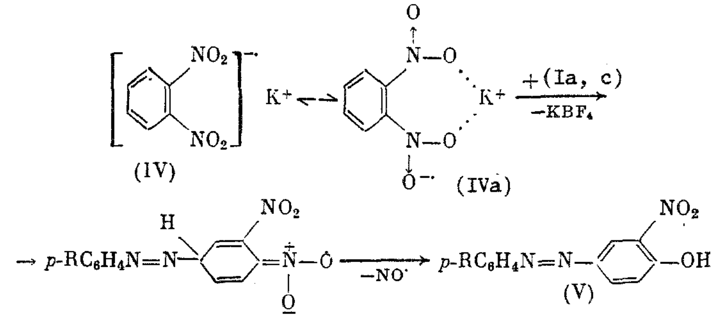
With o-DNB dianion (II), ipso-coupling occurs, followed by expulsion of NO$_2^-$ with the formation of the o-nitroazo compound (III):



(1)

Concurrently with reaction (1), oxidation of the dianion (II) takes place to give o-DNB, N$_2$, and dimethylaniline. Although in THF (ε 7.4) replacement of the nitro-group by the arylazo group competes with the redox reaction, in acetonitrile (ε 36.5) only oxidation–reduction occurs (Table 1). We believe that the different effects of the solvents are due to stabilization of the ion pairs in the weakly polar THF, and their breakdown in acetonitrile, a strongly polar solvent.

In the case of the potassium salt of the o-DNB anion-radical (IV), the reaction with diazo-cations takes place in DMSO (ε 49) only with electron transfer, whereas in THF azocoupling occurs. In the latter case, ipso-substitution, as with the dianion (II), does not occur, but rather entry of the arylazo moiety into the p-position of the benzene ring, with simultaneous conversion of the p-nitro group into hydroxyl. The NO$^\bullet$ radical is lost, nitric oxide being detected by IR examination of the gas phase. The reaction sequence found is depicted in diagram (2), and was confirmed by control experiments, namely treatment of the salt (IV) with air or water, which does not result in conversion of the nitro-group to hydroxyl, and the addition of H$_2{}^{18}$O after mixing the reagents, which does not result in the appearance of the label in the OH group of the product (V).* In the case of the diazo-salt (Ib), the reaction with the anion-radical salt (IV) is more complex, the end-product being 4-methoxy-3'-(2"-nitrobenzene-α-azoxy)-4'-hydroxyazobenzene (VI). The structure of the latter is shown in Fig. 1.



(2)

R = Me$_2$N (a), R = NO$_2$ (c).

---

*There were no changes in the mass spectrum due to the presence of the ^{18}O isotope above the naturally occurring levels.

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1845-1852, August, 1988. Original article submitted April 20, 1987.

0568-5230/88/3708-1651$12.50

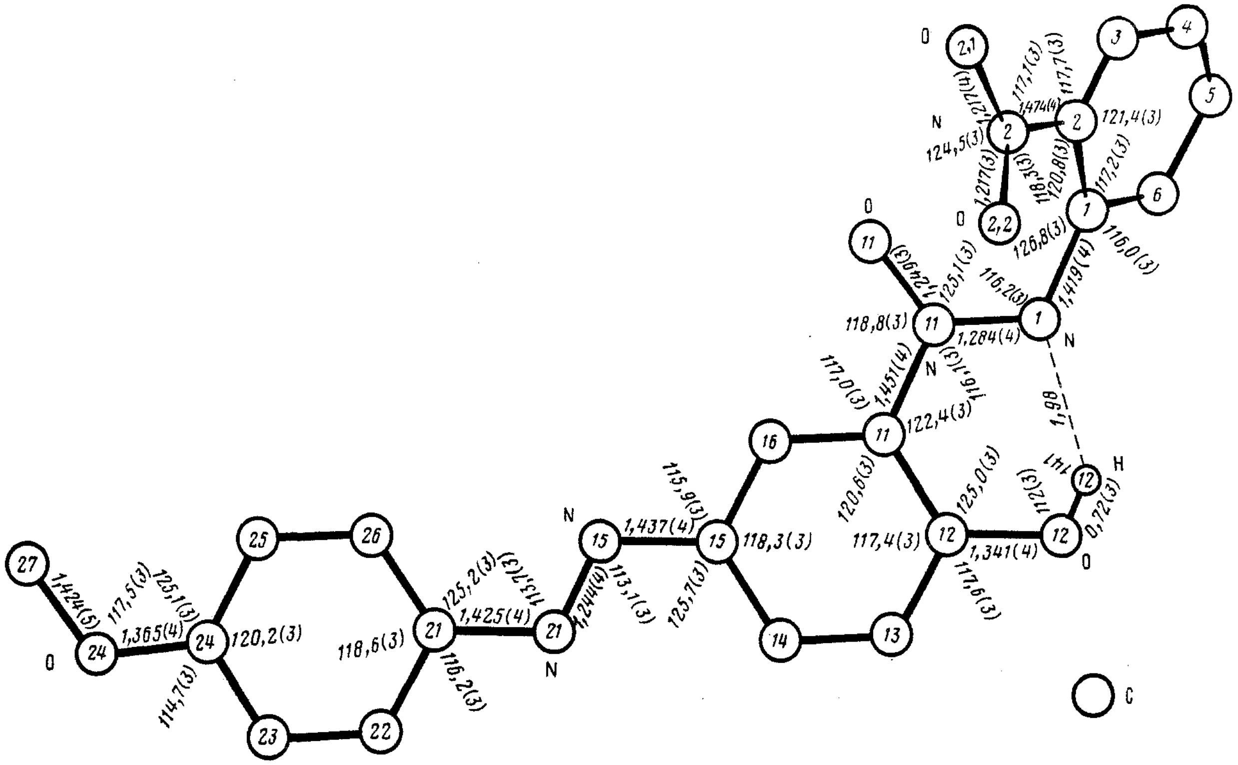


Fig. 1. Structure of 4-methoxy-3'-(2"-nitrobenzene-α-azoxy)-4'-hydroxyazobenzene. The valence angles and bond lengths are given with their errors (the values in brackets are the first and third decimal points respectively).

TABLE 1. Reaction of Ionic Forms of o-DNB with Equimolar Amounts of Diazocations

Reactant	Substrate	Solvent	Yields of products, %			
			nitrogen	RC_6H_5 (R)	o-DNB	azo-compound
(Ia)	(II)	THF	72	60 (NMe_2)	83	13, (III)
(Ia)	(II)	MeCN	92	81 (NMe_2)	90	0
(Ia)	(IV)	THF	12	13 (NMe_2)	71	46[a] (Va)
(Ib)	(IV)	THF	18	20 (OMe)	65	42[b] (VI)
(Ic)	(IV)	THF	26[c]	27 (NO_2)	63	58[a] (Vc)
(Ia)	(IV)	THF+18-crown-6[d]	88	95 (NMe_2)	89	0
(Ib)	(IV)	THF+18-crown-6[d]	92	93 (OMe)	92	0
(Ic)	(IV)	THF+18-crown-6[d]	94	95 (NO_2)	94	0
(Ia)	(IV)	DMSO	91	83 (NMe_2)	90	0
(Ib)	(IV)	DMSO	94	82 (OMe)	94	0
(Ic)	(IV)	DMSO	93	81 (NO_2)	95	0

---

[a] Reagent:substrate ratio = 1:2.

[b] Reagent:substrate ratio = 1:3.

[c] NO also measured.

[d] The crown ether was used in amounts equimolar to (IV).

On reaction of the anion-radical (IV) with diazo-cations (Ia-c), in addition to azo-coupling, electron transfer takes place (Table 1). Redox reactions, only, occur in DMSO, whereas in THF the yields of electron transfer and azo-coupling reactions are comparable. In THF, azo-coupling is also totally suppressed by the presence of 18-crown-6 ether. Consequently in reaction (2) breakdown of the ion pairs prevents substitution.

The difference in the reactivity of substrates (II) and (IV), stabilized as pairs with potassium cations (reactions (1) and (2)), appears to be due to differences in their electronic sructures, the dianion (II) having the quinonoid structure (IIa), while the anion-

TABLE 2. Azo-Compounds (III), (V), and (VI)

Compound	Mp, °C (solvent)	Literature	Empirical formula	Found/Calculated, %		
				C	H	N
(III)	132 (benzene)	[3]	$C_{14}H_{14}N_4O_2$	62,22/62,22	4,91/5,18	20,67/20,75
(Va)	196 (benzene)		$C_{14}H_{14}N_4O_3$	58,52/58,74	4,91/4,89	19,51/19,58
(Vc)	212 (benzene)	[4]	$C_{12}H_8N_4O_5$	49,86/50,00	2,80/2,77	19,42/19,44
(VI)	172 (ethyl acetate)		$C_{19}H_{15}N_5O_5$	58,06/58,02	3,82/3,88	17,80/17,79

TABLE 3. Spectral Characteristics of Azo-Compounds (III), (V), and (VI)

Compound	Mass spectrum (m/z)	IR spectrum (ν, cm^{-1})	PMR spectrum (δ, ppm, Hz)
(III)	M^+ 270, $(M-C_6H_4NO_2)^+$ 148, $(M-C_6H_4N_2O-N_2)^+$ 120	1150 s (C–N), 1372 s $(NO_2)_s$ 1540 m $(NO_2)_{as}$ 1610 s (N=N)	7,55–7,95 m (4H, $C_6H_4NO_2$) 7.81 (2H, $H^{2'}-H^{6'}$, $J_{2',6'}=9$) 6.86 (2H, $H^{3'}-H^{5'}$, $J_{3',5'}=9$) 3,12 (6H, $N(CH_3)_2$)
(Va)	M^+ 286, $(M-C_6H_3(OH)NO_2)^+$ 128, $(M-C_6H_3(OH)NO_2-N_2)^+$ 120	1145 s and 1170 s (C–N), 1320 s and 1360 s $(NO_2)_s$ 1530 m $(NO_2)_{as}$ 1605 s (N=N)	10,62 s (1H, OH), 8,50 d (1H, H^2, $J_{2,6}=9$), 8,12 dd (1H, H^6), 7,87 (2H, $H^{2'}-H^{6'}$, $J_{2',6'}=9$) 7,37 d (1H, H^5, $J_{5,6}=9$) 6,87 (2H, $H^{3'}-H^{5'}$, $J_{3',5'}=9$)
(Vв)	M^+ 288, $(M-C_6H_4NO_2)^+$ 166, $(M-C_6H_3(OH)NO_2)^+$ 150, $(M-C_6H_3NO_2-N_2)^+$ 138, $(M-C_6H_3(OH)NO_2-N_2)^+$ 122	1320 s and 1342 s $(NO_2)_s$ 1540 m $(NO_2)_{as}$ 1628 s (N=N)	8,74 d (1H, H^2, $J_{2,6}=2,5$) 8,47 (2H, $H^{3'}-H^{5'}$, $J_{3',5'}=9$) 8,34 dd (1H, H^6), 8,18 (2H, $H^{2'}-H^{6'}$, $J_{2',6'}=9$) 7,45 d (1H, H^5, $J_{5,6}=9$)
(VI)	M^+ 393, $(M-O_2)^+$ 345, $(M-2(O)-C_6H_4OCH_3)^+$ 238, $(M-O_2-C_6H_4OCH_3-N_2)^+$ 210, $(M-C_6H_4NO_2-N_2-O-C_6H_3OH)^+$ 135, $(M-C_6H_4NO_2-N_2-O-C_6H_3OH-N_2)^+$ 107	1330 s and 1350 s $(NO_2)_s$ 1510 s and 1520 s $(NO_2)_{as}$ 1260 s (C–O–C)	11,76 s (1H, OH) 7–9 m (11H, $2C_6H_4$ and C_6H_3) 4,13 s (3H, OCH_3)

radical (IV) retains its aromaticity (a mesomeric structure corresponding to the bicyclic compound (IVa) is also possible [2]). The ortho orientation of the two nitro groups plays a dominant part in the construction of such a bicyclic aromatic structure.

It was of great interest in this connection to examine the reactions of diazocations with the potassium salt of the anion-radical of p-dinitrobenzene (VII).

It is known [2] that in solvents of low ionizing capacity the potassium cation in (VII) is coordinated with one of the two nitro-groups only, and most of the spin density is concentrated thereon, i.e. salt (VII) is analogous to the potassium salt of the nitrobenzene anion-radical (VIII). We have found that in THF, salts (VII) and (VIII) react with aromatic diazo-compounds by one-electron transfer only (no azo-coupling occurs), replacement of the THF by DMSO having no effect on the course of the reaction.

The first successful direct azo-coupling was effected in this way for the anion-radical (IV). Possible mechanisms for this reaction, alternatives to route (2), may include attack of the diazenium radical on neutral o-DNB immediately following electron transfer from the substrate to the reactant (without movement out of the solvent cell into the bulk of the solution), or recombination of the diazenium radicals formed by one-electron reduction of the diazonium cation by the substrate, with a second molecule of (IV). Reactions of the first type clearly do not occur, since otherwise mixtures of two azo-compounds would be obtained, isomeric in the positions of the azo-groups (ortho- or para-). In practice, a single isomer is obtained (Tables 2 and 3). Reactions of the second type require high stability in the diazenium radical, since only then would it be possible for this radical to leave the solvent cell, encounter another molecule of (IV), and finally undergo azo-coupling The experimental findings (Table 1) show that the main course of reaction of diazenium radicals is elimination of molecular nitrogen with the formation of aryl radicals, which then give the corresponding benzene derivatives by removal of a hydrogen atom from the solvent.

The azo-coupling of o-DNB, following conversion into the anion-radical state which has been observed, has no analogs. Carried out with simple molecules, it appears to the authors that this reaction could also be applied to more complex systems, specifically for the synthesis of dyestuffs of technical value.

EXPERIMENTAL

Chromatographic measurements were carried out on a Khrom-4 chromatograph (carrier gas nitrogen, 3 × 3700 mm stainless steel column with 10% PÉT-20M on Chromatone N-Aw, silanized, 40-60 mesh), or on a Tsvet-101 chromatograph (carrier gas nitrogen, 3 × 2000 mm glass column with 5% SE-20 on Chromatone N-Aw-DMCS, silanized, 20-25 mesh).

X-ray crystallographic analyses were carried out on a Hilger-Watts Y/290 four-circle automatic diffractometer at 25°C (λMoK_α), graphite monochromator, $\theta/2\theta$ scanning, 1431 reflections with $I > 2.5$, ($\sin\theta/\lambda_{max} = 0.703$).

The crystals of 4-methoxy-3'-(2"-nitrobenzene-α-azoxy)-4'hydroxyazobenzene (VI) were triclinic, with $a = 7.5880(8)$, $b = 7.9628(8)$, $c = 16.989(1)$ Å, $\alpha = 83.871(6)$, $\beta = 79.619(6)$, $\gamma = 64.215(8)°$, $V = 908.7(1)$ Å^3, $M = 393$, $d_{calc} = 1.438$ g·cm^{-3}, $Z = 2$, space group $P\bar{1}$.

The structure was calculated directly using the MULTAN program, and refined by the least squares block diagonal method in anisotropic approximation for the nonhydrogen atoms. The H atom of the OH group was located in the difference Fourier synthesis, and refined in isotropic approximation. The remaining H atoms were not refined, but their contributions to the F_{calc} values were taken into account. The final values of the divergence factors were $R = 0.037$ and $R = 0.033$.

All calculations were carried out on an Eclipse S/200 computer using the INEXTL programs [5].

The conformation of the molecule of (VI) in the crystal is planar except for the considerable rotation (56.6°) of the o-nitro-substituted benzene ring relative to the remainder of the molecule (Fig. 1). The rotation of the NO_2 group relative to the plane of the benzene ring to which it is attached was 27.2°. This molecular conformation of (VI) is due to electronic conjugation between all the fragments, destroyed in the case of the o-nitrobenzene ring by steric hindrance (repulsion of the ortho-substituents). A similar conformation is shown in particular by o-nitroperbenzoic acid [6].

The lengths of the N$\overset{...}{-}$O bonds in the nitro-group in (VI) have the usual values (1.217 Å). The difference in the $N^1{=}N^{11}$ (1.284 Å) and $N^{15}{=}N^{21}$(1.244 Å) bond lengths is due to a decrease in electron density at the first of these resulting from the donor-acceptor $N^{11}{-}O^{11}$ bond (1.249 Å).

The hydroxy group in (VI) forms an intramolecular hydrogen bond with the N^1 nitrogen, closing the virtually planar ring $\underline{O^{12}H^{12}\ldots\ldots\ldots N^1N^{11}C^{11}C^{12}}$. The geometry of this bond ($O^{12}\ldots N^1$ 2.583 Å, $H\ldots\ldots N^1$ 1.98 Å, $O^1H^{12}N^1$ 141°) is usual for O–H...N hydrogen bonds closing six-membered rings [7]. The bond lengths and valence angles of (VI) are given in Fig. 1, and the atom coordinates in Table 4.

The magnetic susceptibility was measured on a magnetic balance by Faraday's method at −196 and 20°C, field strength 500-3500 Oe.

Mass spectra were obtained on an AEI MS-300 with a DS-50 automatic data collection system, ionizing voltage 70 V. The direct sample introduction system into the ion source was heated to temperatures no greater than the mp of the compound under examination.

The IR spectra of the ions were obtained on a UR-20 apparatus in KBr disks (compressed under argon, and scanned rapidly). The gas phase formed above the reaction mixture was collected in an evacuated cell with KBr windows, following separation in a trap with a glass filter at −70°C.

TABLE 4. 4-Methoxy-3'-(2"-nitrobenzene-α-azoxy)-4'-hydroxyazobenzene (VI): Atom Coordinates ($\cdot 10^4$, for H atoms $\cdot 10^3$)*

Atom	*X*	*Y*	*Z*
C^1	1832(5)	3222(4)	723(2)
C^2	2025(5)	1750(4)	281(2)
C^3	2802(5)	1599(5)	−517(2)
C^4	3374(5)	2928(5)	−899(2)
C^5	3153(5)	4407(5)	−481(2)
C^6	2403(5)	4548(5)	316(2)
C^{11}	1101(5)	2637(4)	2884(2)
C^{12}	−470(5)	4322(5)	3138(2)
C^{13}	−1029(5)	4567(5)	3964(2)
C^{14}	−88(5)	3214(5)	4498(2)
C^{15}	1459(5)	1533(5)	4244(2)
C^{16}	2035(5)	1268(5)	3436(2)
C^{21}	3200(5)	−1079(5)	5990(2)
C^{22}	2826(5)	−702(5)	6796(2)
C^{23}	3760(5)	−2027(5)	7343(2)
C^{24}	5121(5)	−3786(5)	7089(2)
C^{25}	5490(5)	−4202(5)	6289(2)
C^{26}	4548(6)	−2857(5)	5745(2)
C^{27}	7386(6)	−6835(5)	7463(3)
$O^{2.1}$	2080(4)	−1173(3)	352(2)
$O^{2.2}$	−35(4)	817(4)	1209(2)
O^{11}	3281(4)	716(3)	1864(1)
O^{12}	−1478(4)	5719(3)	2650(1)
O^{24}	6013(4)	−4989(3)	7681(1)
N^1	1018(4)	3555(3)	1542(2)
N^2	1317(4)	352(4)	651(2)
N^{11}	1864(4)	2250(4)	2044(2)
N^{15}	2547(4)	16(4)	4757(2)
N^{21}	2136(4)	417(4)	5475(2)
H^{12}	−106(5)	554(4)	224(2)

---

*The values of the thermal factors may be obtained from the authors.

PMR spectra (at 25°C) were recorded on a Bruker WP-200, internal standard TMS, solvent $(CD_3)_2CO$.

The conversion of the substrate into the anion-radical or the dianion was carried out using cyclooctatetraenedipotassium as electron donor, as described in [8].

Precipitates were filtered through a glass filter for 2 h under slight pressure of argon, washed twice with cold THF, and dried in vacuo. From 1.68 g of o-dinitrobenzene (o-DNB) there was obtained 2.06 g of the dipotassium salt of o-DNB dianion (II) (96%). Measurement of the magnetic susceptibility showed that the solid salt did not contain paramagnetic species. The IR spectrum of the solid salt showed no absorption for the nitro-group at 1330 or 1530 cm^{-1}, but strong absorption was seen at 1060, 1200, 1390, and 1420 cm^{-1}, similar to absorption for the amino-group [9].

From 1.68 g of o-DNB there was obtained 2.17 g of the potassium salt of o-DNB anion-radical (IV) (95%). Measurement of the magnetic susceptibility of the salt showed it to contain 95% of paramagnetic species. Treatment of a suspension of the salt (IV) in THF or a solution in DMSO with dry air or with air-free water resulted in regeneration of the o-DNB (92-95% recovery).

Reaction of Ionic Forms of the Nitro-Compound with Diazo-Salts. A suspension of the potassium salt of the anion-radical or the dianion of the nitro-compound (0.01 mole) in 50 ml of THF was mixed with the dry diazonium fluoroborate. In some instances (Table 1), acetonitrile or dimethyl sulfoxide (DMSO) was used in place of THF. Mixing was carried out at −30°C, and the mixture kept at −30°C for 1 h in a totally sealed vessel filled with argon at normal pressure. After determination of the nitrogen (volumetric analysis) or nitric oxide (absorption at 1960 cm^{-1} [10]) in the gas phase, and of RC_6H_5 (GLC) in the liquid phase), the mixture was filtered. The filtrate was evaporated, and the residue separated on a column (22 × 600 mm, silica gel, eluant – a mixture of hexane with ether or ethyl acetate, 3:1). The properties of the products are shown in Tables 2 and 3.

Reaction of p-Dinitrobenzene Anion-Radical Potassium Salt (VII) with p-Methoxyphenyldiazonium Fluoroborate (Ib). A suspension of 0.01 mole of the freshly-prepared salt (VII) in 30 ml of THF, prepared at −30°C was mixed over 10 min with a suspension of $MeOC_6H_4N_2BF_4$ (0.01 mole) in 20 ml of THF. Nitrogen (123 cm^3, 55%) was liberated. The mixture was stirred for 10 min at −30°C, then allowed to warm up to 25°C, to give a red solution over a dark-colored solid. The solid was found to contain 0.89 g (40%) of unreacted diazo-compound and 0.72 g (57%) of KBF_4 (IR and luminescence analysis). The filtrate from the solid was evaporated, and the residue separated on a thin layer of alumina (hexane—ethyl acetate, 2:1), to give 0.92 g of p-dinitrobenzene, 0.16 g of anisole, and 0.35 g of 4-nitro-4'-methoxy-N,N-diphenylamine, $C_{13}H_{12}N_2O_3$ as orange crystals, mp 153°C (ethanol) [11]. Found: C 63.96; H 4.88; N 11.50%. $C_{13}H_{12}N_2O_3$. Calculated: C 63.93; H 4.92; N 11.47%. Mass spectrum (m/z): M^+ 244, $(M-CH_3)^+$ 229, $(M-CH_2O)^+$ 214, $(M-CH_2O-2(O))^+$ 182. PMR spectrum (δ, ppm): 4.10 s (3H, OCH_3), 6.42 s (1H, NH), 7-8.5 m (8H, $2C_6H_4$). IR spectrum (ν, cm^{-1}): 1325 s $(NO_2)_s$, 1520 s $(NO_2)_{as}$, 3330 s (NH).

Reaction of Nitrobenzene Anion-Radical Potassium Salt (VIII) with p-Methoxyphenyldiazonium Fluoroborate (Ib). To a suspension of 0.01 mole of freshly-prepared salt (VIII) in 30 ml of THF was added over 10 min with vigorous stirring a suspension of 0.01 mole (2.22 g) of $MeOC_6H_4N_2BF_4$ in 20 ml of THF, the temperature being kept from −40 to 25°C in different experiments, for 20 min. Vigorous evolution of nitrogen occurred (210-215 cm^3, 95%), and the mixture became dark red in color with separation of a yellow solid. The solid was KBF_4, yield 96%. The filtrate was evaporated, and the residue separated on a column (22 × 600 mm, silica gel, hexane—ethyl acetate (3:1)). There were obtained 1.17 g (95%) of nitrobenzene and 0.97 g (90%) of anisole. When the reaction was carried out in DMSO, the same compounds were obtained (the yield of anisole fell to 80%).

CONCLUSIONS

1. o-Dinitrobenzene dianion reacts with p-dimethylaminobenzenediazonium cation to give 2-nitro-4'-dimethylaminoazobenzene.

2. o-Dinitrobenzene anion-radical reacts with benzenediazonium cations bearing a dimethylamino- or nitro-group in the para-position, to give 3-nitro-4-hydroxy-4'-dimethylaminoazobenzene and 3,4'-dinitro-4-hydroxyazobenzene respectively.

3. In the case of the 4-methoxybenzenediazonium cation, reaction with the o-dinitrobenzene anion-radical affords 4-methoxy-3'-(2"-nitrophenyl-α-azoxy)-4'-hydroxyazobenzene, the structure of which has been established by x-ray diffraction analysis.

4. These azo-compounds are formed in solvents which favor the stability of ion pairs of the dianion or anion-radical of o-dinitrobenzene with potassium cations. Dissociation of the ion pairs results in the occurrence of electron transfer only.

LITERATURE CITED

1. I. Q. Chambers and R. N. Adams, J. Electroanal. Chem., 9, 400 (1965).
2. C. Y. Ling and J. Gendell, J. Chem. Phys., 47, 3475 (1967).
3. S. N. Chakrabarty and S. Dulls, J. Indian Chem. Soc., 5, 555 (1928).
4. J. T. Hewitt and H. V. Mitchell, J. Chem. Soc., 87, 225 (1905).
5. R. G. Gerr, A. I. Yanovskii, and Yu. T. Struchkov, Kristallografiya, 28, 1029 (1983).
6. M. Sax, P. Beurskens, and S. Chu, Acta Crystallogr., 18, 252 (1965).
7. S. V. Lindeman, V. E. Shklover, Yu. T. Struchkov, et al., Cryst. Struct. Communs., 11, 43 (1982).
8. Z. V. Todres, Izv. Akad. Nauk SSSR, Ser. Khim., No. 8, 1749 (1970).
9. É. S. Lipina, N. D. Stepanov, I. L. Bagal, et al., Zh. Org. Khim., 16, 2404 (1980).
10. B. I. Buryak, Yu. P. Koval', and T. P. Kudinova, Problems in Increasing the Precision of Gas Analytical Measurements [in Russian], Kiev (1984), p. 80; Ref. Zh. Khim., No. 15, G179 (1985).
11. K. Hirauchi and T. Amano, Chem. Pharm. Bull., 27, 1120 (1979).