Russian Journal of Organic Chemistry, Vol. 37, No. 3, 2001, pp. 401–403. Translated from Zhurnal Organicheskoi Khimii, Vol. 37, No. 3, 2001, pp. 426–428.

Reactions of Aromatic Nitro Compounds: LXXIV.* Azo Coupling of Anionic Nitroarene σ-Complexes with Aromatic Diazo Compounds. Effect of Reaction Conditions on the Yield of Nitroazobenzenes

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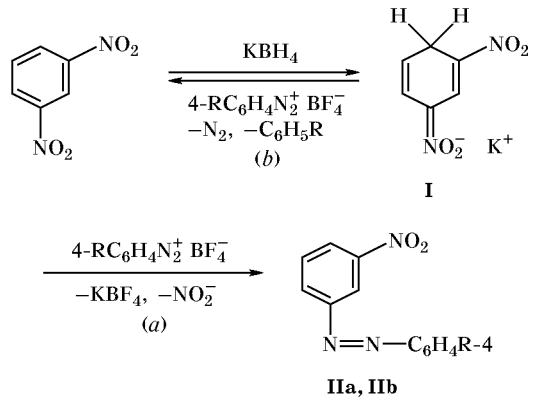
Received December 2, 1999

Abstract—Effect of a number of factors on the yield of nitroazobenzenes in the reaction of 4-nitro- and 4-dimethylaminobenzenediazonium tetrafluoroborates with anionic σ adducts derived from 1,3-dinitrobenzene was studied. Conditions were found which allow nitroazobenzenes to be prepared in 80–90% yield.

Azo coupling reaction remains so far the main method for preparation of aromatic azo compounds [2]. Taking into account the low electrophilicity of diazo compounds, aromatic amines, phenols, and naphthols are generally used as azo component. Direct introduction of the azo group into electron-deficient systems such as nitroarenes is difficult. This obstacle can be circumvented by preliminarily increasing the nucleophilicity of nitroaromatic substrate. We showed in [3–6] that anionic σ-complexes formed by nitrobenzenes, nitronaphthalenes, and nitroanthracenes react with arenediazonium salts through replacement of one nitro group by phenylazo group. As a result, a number of new nitroazo compounds were synthesized. However, the yield of azo compounds in the above reactions was insufficiently high because of concurrent oxidation [3, 4] of the σ-complex to the initial nitro compound with diazonium salt. In the present work we examined the effect of reaction conditions (reactant ratio, temperature, and solvent nature) on the yield of azo compounds. As model reaction we chose the reaction of 1,3-dinitrobenzene σ-complex **I** with 4-nitro- and 4-dimethylaminobenzenediazonium tetrafluoroborates, studied previously in [6] (Scheme 1). These diazonium salts exhibit appreciably different reactivities in both azo coupling and redox processes [7]. The data in Table 1 show

Scheme 1.



R = NO_2 (**a**), $N(CH_3)_2$ (**b**).

Table 1. Effect of the ratio σ-complex–diazonium salt on the yield of 3-nitroazobenzenes **IIa** and **IIb** in a THF–DMF mixture (5:2, by volume)

Molar ratio σ-complex–diazonium salt	Yield, %	
	IIa	**IIb**
1:1	69	72
1:2	81	47
1:3	67	44
1:4	59	44

* For communication LXXIII, see [1].

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Table 2. Effect of the ratio 1,3-dinitrobenzene–KBH_4 on the yield of 3-nitroazobenzenes **IIa** and **IIb** in a THF–DMF mixture (5:2, by volume)

Molar ratio 1,3-DNB–KBH_4	Molar ratio σ-complex–diazonium salt			
	1:1		1:2	
	IIa	**IIb**	**IIa**	**IIb**
1:1	69	72	81	71
1:2	58	72	52	73
1:3	43	82	37	85
1:4	38	89	37	88

Table 3. Effect of the temperature on the yield of 3-nitroazobenzenes **IIa** and **IIb** in a THF–DMF mixture (5:2, by volume)

Temperature, °C	Yield, %	
	IIa	**IIb**
0	81	89
10	68	87
20	64	87
30	42	83
40	24	78

Table 4. Effect of the solvent on the yield of 3-nitroazobenzenes **IIa** and **IIb** (equimolar reactant ratio, 0°C)

Solvent	Yield, %	
	IIa	**IIb**
Dioxane	0	0
THF	0	0
Acetonitrile	28	46
DMF	53	66
DMSO	21	24
Ethanol	28	45
Water	0	0

Table 5. Effect of nonpolar solvents (30 vol %) on the yield of 4-nitroazobenzenes **IIa** and **IIb** in DMF

Nonpolar component	Yield, %	
	IIa	**IIb**
Benzene	52	61
Dioxane	34	49
Pentane	27	38
THF	69	72

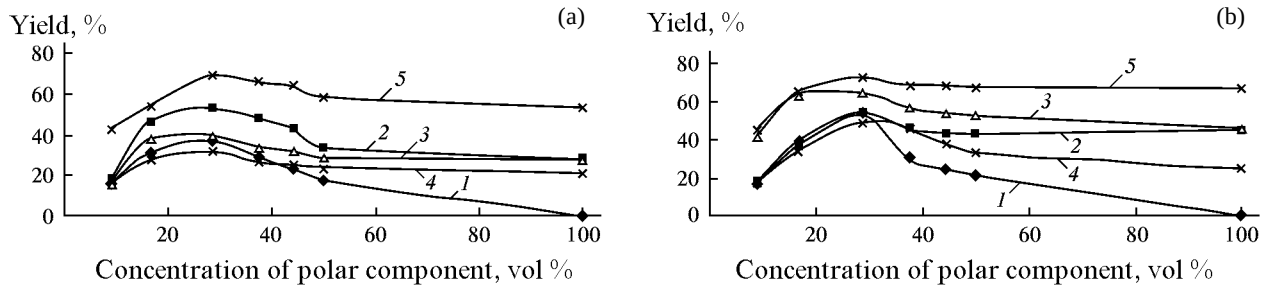
that the yield of azo compounds **IIa** and **IIb** can be increased to 70–80% by variation of the reactant ratio. At an equimolar reactant ratio the yield of 3,4′-dinitroazobenzene (**IIa**) was slightly lower than the yield of 4-dimethylamino-3′-nitroazobenzene (**IIb**). With 2 equiv of *p*-nitrobenzenediazonium tetrafluoroborate, the yield of **IIa** increases to 81%. Further raising the amount of the diazo component leads to reduced yield of **IIa**, presumably because of increasing contribution of the oxidation pathway (pathway *b* in Scheme 1). 4-Dimethylaminobenzenediazonium tetrafluoroborate shows a different relation. In the presence of 2 equiv of the diazo compound the yield of **IIb** falls almost twofold, and further increase in the amount of the diazonium salt does not affect the yield of **IIb**.

As follows from Scheme 1, the process consists of two stages. The first stage, formation of anionic σ-complex, is reversible. It was interesting to estimate the effect of excess reducing agent on the yield of the final product. Experiments were performed without isolation of adduct **I** from the solution to which appropriate diazonium salt was added. By using 4 equiv of KBH_4 with respect to initial 1,3-dinitrobenzene we succeeded in obtaining 89% of azo compound **IIb**. In the case of more active 4-nitrobenzenediazonium tetrafluoroborate the use of excess reducing agent decreased the yield of product **IIa** (Table 2). Obviously, this is the result of side processes, e.g., reduction of the diazo compound with excess potassium tetrahydridoborate.

Insofar as diazonium salts are unstable compounds, the azo coupling is usually carried at low temperature. We have found that mixing of the reactants is accompanied by considerable increase in temperature, i.e., the reaction is exothermic. As might be expected, the optimal reaction temperature is 0°C (Table 3).

The yield of compounds **IIa** and **IIb** strongly depends on the polarity and acid–base properties of the solvent (Table 4). On the whole, more polar solvents (with larger dielectric constant ε) favor formation of the nitroazo compounds. In weakly polar solvents, such as tetrahydrofuran and dioxane, the yield of **IIa** and **IIb** was very poor since salt-like reagents are almost insoluble in these solvents. Water promotes fast protolytic decomposition of the anionic σ-complex to initial 1,3-dinitrobenzene.

We also examined the reactions in binary mixtures of THF with polar solvents (see figure). Initially, the yield of nitroazobenzenes increases as the fraction of polar component rises; the maximal yield is attained at a polar component fraction of 30%. Further rise in the latter results in a slight decrease of the yield, and then it no longer changes up to 100% fraction of the



Effect of polar solvents on the yields of (a) 3,4′-dinitroazobenzene (**IIa**) and (b) 4-dimethylamino-3′-nitroazobenzene (**IIb**) in THF: (*1*) water, (*2*) ethanol, (*3*) acetonitrile, (*4*) DMSO, and (*5*) DMF.

polar component. This pattern can be explained in terms of formation of contact ion pairs by the reagents in weakly ionizing solvents, which decompose in going to more polar medium. Comparison of the data given in Tables 4 and 5 shows that addition of a nonpolar solvent to DMF increases the yield of nitroazo compound only when the nonpolar component is THF.

The result of the present study is that we succeeded in raising the yield of nitroazobenzenes in the reactions of anionic σ-complexes with benzenediazonium tetrafluoroborates to 80–90%. The optimal conditions are as follows: solvent THF–DMF (5:2, by volume), temperature 0°C, and molar reactant ratio 1,3-DNB–KBH_4–4-X-$C_6H_4N_2^+ BF_4^-$ 1:1:2 (X = NO_2) or 1:4:1 (X = NMe_2). The developed procedure extends synthetic potential of the azo coupling reaction, for it provides the possibility of using accessible nitroarenes as azo component and obtaining new nitroazo compounds.

The azo coupling of anionic σ-complexes with benzenediazonium tetrafluoroborates was performed by the procedure described in [6]. The solvents were purified by standard methods [8].

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