The first example of the azo coupling of cyclopropyldiazonium ion under conditions of direct nitrosation of cyclopropylamine

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It is known, that the direct diazotization of aromatic amines gives rise to diazonium salts, which are widely used in the azo coupling reactions. On the contrary, in the case of aliphatic amines, diazonium ions formed are extremely unstable and undergo rapid nitrogen elimination to give carbocations, which undergo further transformations.[1,2]

Previously,[3] we have shown the possibility of generation of cyclopropyldiazonium ion by the alkaline hydrolysis of *N*-cyclopropyl-*N*-nitrosourea and its trapping with some active aromatic compounds, in particular, with naphthalene hydroxy derivatives, to form cyclopropyl azoarenes.

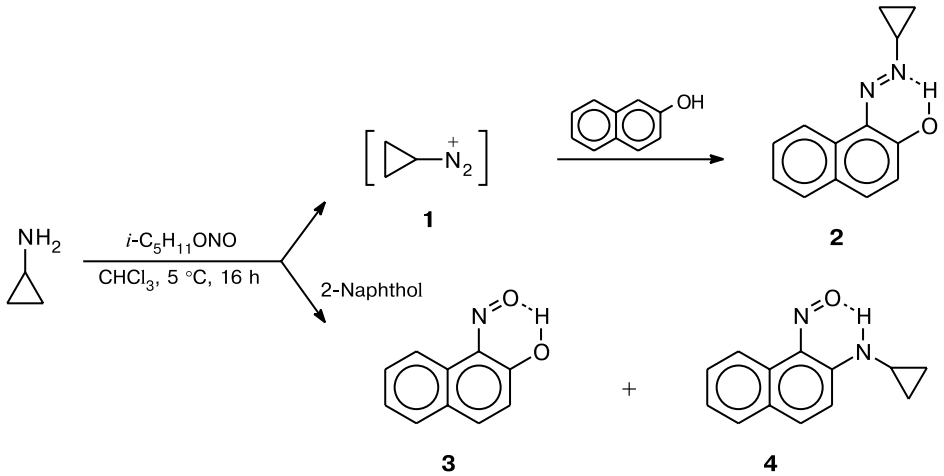
In the present work, for the first time the direct nitrosation of cyclopropylamine by isoamyl nitrite has been investigated. The reaction leads to cyclopropyldiazonium ion (**1**) which can react with 1- and 2-naphthols without nitrogen elimination.

Thus, the reaction of cyclopropylamine, isoamyl nitrite and 2-naphthol in the molar ratio of 1.4 : 1.4 : 1 using $CHCl_3$ as a solvent at 5 °C for 16 hours affords 1-cyclopropyl-2-naphthol (**2**) in up to 60% yield (Scheme 1). According to the TLC, ^1H and ^{13}C NMR data, azo compound **2** is identical to that one we obtained before.[3] At the same time, along with the main product, small amounts (3—4%) of 1-nitroso-2-naphthalene (**3**) and 1-nitroso-2-cyclopropylaminonaphthalene (**4**) were isolated by preparative TCL and characterized by ^1H and ^{13}C NMR spectroscopy. The latter compound was synthesized recently[4] by the heating of 1-nitroso-2-naphthalene with cyclopropylamine in the aqueous medium.

To asses the possibility of alternative formation of azo compound **2** upon nitrosation of 2-naphthol with isoamyl nitrite to afford nitroso compound **3** and the following reaction of the latter with cyclopropylamine, we investigated the possibility of realization of each stage under the same conditions.

It turned out, that the reaction of isoamyl nitrite with 2-naphthol in $CHCl_3$ at 5 °C takes place but the reaction proceeds nonselectively. According to the ^1H NMR spectroscopy, the products does not contain nitroso compound **3,** but 1-nitroso-2-naphthol was identified. At the same time, it was determined, that nitrosonaphthol **3,** preliminary obtained according to the known procedure,[5] reacts with cyclopropylamine in $CHCl_3$ first to give a salt-like compound, which transforms not into azo deriva-

Scheme 1



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tive **2**, but into izomeric compound **4**. On heating in the aqueous medium[4] or in the presence of the excess of nitrosonaphthol, this process accelerates apparently due to the salt destruction and reaction of releasing cyclopropylamine with ketoimine form of nitrosonaphthol.

Similarly to 2-naphthol, the reaction of 1-naphthol with cyclopropylamine and isoamylnitrite under the same conditions leads to 2-(cyclopropylazo)- (**5**), 4-(cyclopropylazo)- (**6**), and 2,4-di(cyclopropylazo)naphthols in a ratio of about 1 : 2.4 : 1 and a total yield of ~55%. The by-products are 2- and 4-nitroso-1-naphthols (~10%), and, as in the previous case, their reaction with cyclopropylamine does not lead to azo compounds **5** and **6**. It should be noted, that direct nitrosation of cyclopropylamine and azo coupling reaction of forming diazonium ion **1** with 1-naphthols lead to the same azo adducts in about the same ratio as upon generation of cyclopropyldiazonium ion **1** from *N*-cyclopropyl-*N*-nitrosourea.[3]

Thus, based on the results obtained, one could consider that, in fact, cyclopropylazonaphthols are formed upon nitrosation of cyclopropylamine with isoamyl nitrite, the former evidently existing as an associate with naphthols, and subsequent reaction of the formed cyclopropyldiazonium ion with naphthols. Besides, side nitrosation of the initial naphthols is probable, but this process is not responsible for the formation of corresponding azo compounds.

Direct generation of cyclopropyldiazonium cation and its azo coupling reaction with 2-naphthol. A solution of isoamylnitrite (0.58 g, 5 mmol) in $CHCl_3$ (5 mL) was added to a stirred solution of 2-naphthol (0.50 g, 3.5 mmol) and cyclopropylamine (0.29 g, 5 mmol) in $CHCl_3$ (10 mL) at 5 °C for 20 min. The reaction mixture was kept at 5 °C for 13—16 h. The solvent and i-$C_5H_{11}OH$ formed were removed *in vacuo*. Reaction products were isolated by preparative TLC (silica gel (Merck), 0.040—0.063 mm, benzene—ether as the eluent, 5 : 1). 1-(Cyclopropylazo)-2-naphthol (**2**) was obtained in a yield of 0.44 g (~60%) (see Ref. 3), R_f 0.75; 1-nitroso-2-naphthol (**3**) was obtained in a yield of 13 mg (~2%), R_f 0.40, and 1-nitroso-2-(cyclopropylamino)naphthalene was obtained as greenish crystals (m.p. 129.5—130.5 °C) in a yield of 10 mg (>1%), R_f 0.35. ^{1}H NMR ($CDCl_3$), δ: for compound **4**: 1.05 and 0.85 (both m, 2×2 H, CH_2CH_2); 2.85 (m, 1 H, CH); 7.40 (d, 1 H, H(3), J = 9.5 Hz); 7.50 (m, 1 H, H(5)); 7.71 (m, 2 H, H(6) and H(7)); 7.85 (d, 1 H, H(4), J = 9.5 Hz); 9.10 (d, 1 H, H(8), J = 8.0 Hz); 14.4 (br.s, 1 H, NH). The partial mass spectrum, m/z (I_{rel} (%)): 212 (70) $[M]^+$, 182 (56), 181 (67), 180 (53), 167 (56), 155 (100), 140 (73).

Analogously, in the reaction with 1-naphthol 0.21 g of the mixture of 2-cyclopropylazo- (**5**) and 2,4-di(cyclopropylazo)-1-naphthols (**7**) in molar ratio of about 1 : 1 (see Ref. 3), R_f 0.85 and 0.22 g (~30%) of 4-cyclopropylazo-1-naphthol (**6**) (see Ref. 3), R_f 0.75, and 43 mg (7%) of 4-nitroso-1-naphthol, R_f 0.35 and 18 mg (~3%) of 2-nitroso-naphthol, R_f 0.30 was isolated.

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