Reactions of 2-diazo-1,1,1-trifluoro-3-nitropropane or 1-trifluoromethyl-2-nitroethenes with amines and amino alcohols afforded β-nitro amines, which were used to obtain a number of trifluoromethyl-containing 1,2-diamines, amino alcohols, and β-amino acids.

Key words: diazo compounds, nitroalkenes, organofluorine compounds, amines, amino alcohols, β-amino acids, X-ray diffraction analysis.

Results and Discussion

For the synthesis of N-substituted β-nitro amines, we used 2-diazo-1,1,1-trifluoro-3-nitropropene (1) (prepared by reduction of 2-amino-3,3,3-trifluoro-1-nitropropene with NaBH₄ followed by diazotization of the resulting saturated compound) or fluorene-containing nitroalkenes 2a,b prepared as individual stereoisomers in good yields by dehydration of appropriate nitro alcohols in the presence of P₂O₁₀. For example, the coupling constant J₁H,F = 2.1 Hz in its ¹H NMR spectrum. The ¹H, ¹⁹F, and ¹³C NMR spectra of nitroalkene 2b contain only one set of signals (see Experimental). The signal for the Me group in the ¹H NMR spectrum of compound 2b appears as a quartet of doublets with J₁H,F = 2.0 Hz and J₁H,H = 1.2 Hz. The ¹⁹F NMR spectrum shows a signal for the CF₃ group at δF = 102.92. In the literature, δF = 103.8 and 99.8 and δ₁H,F = 2.1 and 2.0 Hz have been reported for the Z- and E-isomers of 2-methyl-3-trifluoromethylpent-2-enedinitrile, respec-
tively. However, all the above data are insufficient for unambiguous conclusion about the configuration of compound 2b (Z or E).

**Scheme 1**

Reactions of diazo compound 1 (procedure A) or nitroalkene 2a (procedure B) with amines in benzene gives β-nitro amines 4 in moderate to high yields (Scheme 2). Selected physicochemical characteristics of β-nitro amines 4 are given in Table 1. Nitroalkene 2a reacts with compounds 3a–j at ~20 °C, while diazoalkane 1 reacts with less nucleophilic aromatic amines 3d–j at 60 °C.

**Scheme 2**

Under the conditions of procedure B, reactions of nitroalkene 2b with amines 3c, d, g, i proceed nonselectively to give ~1 : 1 mixtures of the R*,S* - and R*,R* -isomers of compounds 5c–f. The major products from cyclic amines 3a, b are nitro amines 5a, b with the R*,S* -configuration (Scheme 3, Table 2). When a mixture of stereoisomers 5a (30% R*,R*-isomer) was kept at ~20 °C for 14 days or distilled in vacuo, the R*,S* -isomer was obtained, which suggests its higher thermodynamic stability. Isolation of all diastereomers 5 in the individual state was beyond the scope of the present work.

**Scheme 3**

Unlike documented18 fluorine-free β-nitro amines, compounds 4 and 5 form no stable hydrochlorides: when treated with dry HCl, their solutions in benzene decompose into the salt of the corresponding amine HNR1R2·HCl (6) and nitroalkenes 2a, b. Partial deamination occurs during distillation of nitro amines 4c–e and 5c–f in vacuo.

To determine the exact configuration of β-nitro amines 5a–f, we examined individual crystals of the most stable isomer of nitro amine 5a by X-ray diffraction. This isomer proved to have the R*,S* -configuration. Structure 5a is in the hindered conformation in which the H atoms at the C(2) and C(3) atoms are antiperiplanar to each other and the trifluoromethyl substituent is antiperiplanar with respect to the nitro group (Fig. 1). The torsion angles C(1)—C(2)—C(3)—C(4) and N(1)—C(2)—C(3)—N(2) are 66.1° and 58.0°, respectively. The piperidine ring (in the chair conformation) and the nitro group are in the synclinal arrangement.

An analysis of the 1H NMR spectra of isomeric mixtures of compounds 5a–f revealed differences between the signals for each pair of diastereomers (see Table 2).

![Fig. 1. General view of the structure of R*,S* -isomer 5a.](image-url)