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Functionalization of the Aliphatic Chain in 4-Nitro-*N*,*N*-diethylaniline: Direct Trifluoroacetylation of the β-Carbon Atom

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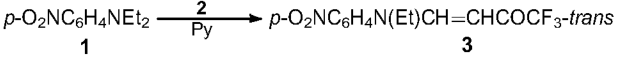
Treatment of 4-nitro-*N*,*N*-diethylaniline **1** with trifluoroacetic anhydride **2** at 120 °C unexpectedly gives *trans*-1,1,1-trifluoro-4-[*N*-ethyl-*N*-(4-nitrophenylamino)]but-3-en-2-one **3** in good yield.

Trifluoroacetylation of *N*,*N*-dialkylanilines proceeds under very mild conditions (Et_2O, 40 °C) to yield 4-trifluoroacetylated derivatives.[1] We supposed that 4-substituted compound **1** could be trifluoroacetylated at position 2 of the aromatic ring under drastic conditions. However, as preliminary experiments showed, the reaction of **1** with **2** does not occur at 40 °C, but instead the total amount of **1** degrades into black tar at 120 °C. Therefore, we performed the process at 120 °C in the presence of pyridine and found that **1** transforms entirely into **3**[†] and that only traces of unidentified by-products were recorded by TLC, reaction (1).



$$p\text{-}O_2NC_6H_4NEt_2 \xrightarrow[\text{Py}]{(CF_3CO)_2O\ \mathbf{2}} p\text{-}O_2NC_6H_4N(Et)CH{=}CHCOCF_3\text{-}\mathit{trans} \quad (1)$$

1 **3**

[†] A solution of **1** (10 mmol), pyridine (25 mmol) and **2** (60 mmol) in benzene (15 cm^3) was heated at 120 °C for 6 h. The reaction mixture was then poured into cold water (200 cm^3) and the benzene layer was washed with water and separated. After the benzene solution was passed through Al_2O_3 (100 cm^3) **3** was obtained (2.1 g, 70 %) as yellow crystals, m.p. 140–141 °C (benzene).

Characterization data for **3**: MS *m*/*z* 288 (M^+, Calc. for $C_{12}H_{11}F_3N_2O_3$ 288). ^1H NMR δ ($CDCl_3$, internal HMDS) 8.12 (d, $J_{\alpha,\beta} = 13.5$ Hz, 1H, =CHN); 5.73 (d, $J_{\beta,\alpha} = 13.5$ Hz, 1H, =$CHCOCF_3$). IR (KBr, ν/cm^{-1}): 1690 (C=O). (Found: C 50.0; H 3.84; F 19.81; N 9.72%. Calc.: C 50.0; H 3.82; F 19.79; N 9.72%).

Trifluoroacetylation of tertiary aliphatic amines in the presence of NaH has been reported.[2] A similar process for trifluoroacetylation of 1,2,3,4-tetrahydrocarbazole at position 1 with subsequent aromatization of an intermediate into 1-trifluoroacetylcarbazole as final product is also known.[3] We assume that both anhydride **2** and ion pairs $(CF_3COPy)^+$ CF_3COO^- can play the role of single electron acceptors. Indeed, a small amount of 4,4′-bipyridine (12%) was obtained from the reaction mixture. Probably, this is a result of dehydrogenation of *N*-acylated derivatives of some hydro-4,4′-bipyridines by excess **2**. The formation of 1,1′-dehydro- and 1,1′,4,4′-tetrahydro-4,4′-bipyridines in the reduction of an acetic anhydride–pyridine mixture with zinc powder at 30–90 °C has already been described.[4] Most likely, a single electron oxidiser promotes an ion-radical process leading to enamine **1a** and then to the final trifluoroacetylated product **3**. The role of the pyridine is probably to form ion pairs $(CF_3COPy)^+$ CF_3COO^- and to deprotonize cation intermediates, reaction (2).

$$\mathbf{1} \xrightarrow{-e} \mathbf{1}^{+\bullet} \longrightarrow \underset{(\mathrm{Ar}\,=\,4\text{-nitrophenyl})}{\mathrm{ArN^{+}(Et)}{=}\mathrm{CHMe}} \xrightarrow{-\mathrm{H}^{+}} \underset{\mathbf{1a}}{\mathrm{ArN(Et)}{=}\mathrm{CH_2}} \xrightarrow{\mathbf{2}} \mathbf{3} \quad (2)$$

Thus, the reaction described appears to be a hitherto unknown example of direct and selective functionalization of the aliphatic chain of a tertiary aromatic amine. We now intend to develop the process into a new synthetic method for preparing unsaturated acids and some heterocycles bearing a CF_3 group.

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