

N-Haloalkylation Reaction in the Presence of Trichloroacetic Acid

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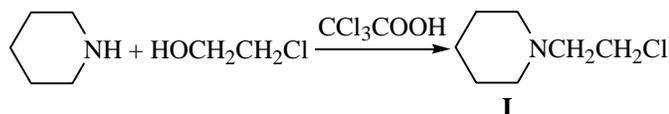
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N-Substituted ureas, thioureas, and related compounds find applications in industry, engineering, agriculture, and medicine, therefore the interest of researchers is still attracted by the synthesis of these substances.

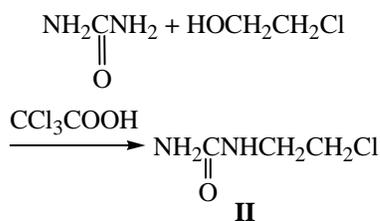
We formerly investigated the nucleophilic substitution of a hydroxy group in alkoxy- and alkylthio-substituted 1,2-chlorohydrins by weak N-nucleophiles, like urea and thiourea, in the presence of trifluoroacetic acid [1, 2] and in a mixture of sulfuric and acetic acids [3]. From these reactions resulted various alkoxy- and alkylthio-substituted carbamides and thiocarbamides.

The practical value of N-alkylation reactions used nowadays is limited by the requirement to perform them in the concentrated mineral acids. The processes of this type in the presence of trichloroacetic acid were not described in the literature.

It turned out that the piperidine, a stronger base than urea, reacted with ethylene chlorohydrin in the presence of trichloroacetic acid affording in a 65% yield *N*-(2-chloroethyl)piperidine (**I**).



With the less nucleophilic urea the reaction occurred at heating to 50–60°C giving *N*-(2-chloro-ethyl)urea (**II**) in a 60% yield.



The reaction progress was monitored by TLC following the disappearance of the initial substrate.

The results of the study show that application of trichloroacetic acid instead of sulfuric acid prevents sulfonation and oxidation processes in the course of the synthesis of N-substituted compounds.

N-(2-Chloroethyl)piperidine (I). A solution of 3.4 g (0.04 mol) of piperidine, and 3.22 g (0.04 mol) of ethylenechlorohydrin in 9 ml of trichloroacetic acid was stirred with a magnetic stirrer at room temperature for 2 h. On completion of the reaction the excess trichloroacetic acid was distilled off in a vacuum, the residue was treated with water and chloroform. The organic phase was washed with water, dried over Na₂SO₄, and the solvent was distilled off. The product was purified by recrystallization from a mixture hexane–ethyl acetate, 3:1. Yield 65%, mp 189–190°C. IR spectrum, ν , cm⁻¹: 690 (C–Cl). ¹H NMR spectrum, δ , ppm: 1.6–1.9 m (6H, 3CH₂), 2.9 m (4H, 2CH₂), 3.2 t (2H, N–CH₂), 3.7 t (2H, CH₂Cl). ¹³C NMR spectrum, δ , ppm: 54.78 (CH₂), 24.56 (CH₂), 23.12 (CH₂), 58.97 (NCH₂), 40.93 (CH₂Cl). Found, %: C 57.01; H 9.52; Cl 24.15; N 9.48. C₇H₁₄ClN. Calculated, %: C 56.94; H 9.49; Cl 24.06; N 9.49.

N-(2-Chloroethyl)urea (II). A solution of 2.4 g (0.04 mol) of urea, and 3.22 g (0.04 mol) of ethylene chlorohydrin in 9 ml of trichloroacetic acid was stirred with a magnetic stirrer at 50–60°C for 6 h. On completion of the reaction the excess trichloroacetic acid was distilled off in a vacuum, the residue was treated with water and chloroform. The organic phase was washed with water, dried over Na₂SO₄, and the solvent was distilled off. The product was purified by recrystallization from a mixture hexane–ethyl acetate, 1:1. Yield 60%, mp 206–207°C.

IR spectrum, ν , cm^{-1} : 3490 (NH_2), 3340 (NH), 1635 ($\text{C}=\text{O}$), 700 ($\text{C}-\text{Cl}$). ^1H NMR spectrum, δ , ppm: 6.85 s (1H, NH), 5.75 s (2H, NH_2), 3.5 t (2H, $\text{N}-\text{CH}_2$), 3.9 t (2H, CH_2-Cl). Found, %: C 29.44; H 5.69; Cl 29.01; N 22.81. $\text{C}_3\text{H}_7\text{ClN}_2\text{O}$. Calculated, %: C 29.38; H 5.71; Cl 28.97; N 22.85.

^1H and ^{13}C NMR spectra from solutions in $\text{DMSO}-d_6$ were registered on spectrometer Bruker-300 (300 MHz) at 25°C . IR spectra were recorded on spectrophotometer Specord 75IR from mulls in mineral oil. The reaction progress was monitored and the purity of compounds obtained was checked by TLC on Silufol UV-254 plates.

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