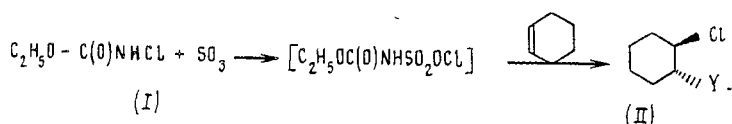


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We have shown that SO₃ inserts at the N-Cl bond of N-chloroalkylamines with the formation of O-chloro-N,N-dialkylsulfamates (R₂NSO₂OCl) [1], which, in turn, readily undergo electrophilic addition with olefins to give rearranged and nonrearranged chlorohydrin N,N-dialkylsulfamates [2, 3].

A new step in the use of the insertion of SO₃ at the N-Cl bond is the extension of this method to N-chlorourethanes. We have found that the treatment of N-chlorourethane (I) with an equivalent amount of SO₃ in CH₂Cl₂ at -50°C and then with cyclohexene at -30°C with gradual warming to 20°C gives N-carboethoxy-O-(trans-2-chlorocyclohexyl)sulfamate (II) in 65% yield according to the following scheme



Sulfamate (II) may be additionally purified by recrystallization from hexane, mp 78-79°C. PMR spectrum in CDCl₃ at 200 MHz (δ, ppm): 8.43 s (1H, NH), 4.75 d. t (1H, HCO, J₁ = J₂ = 9, J₃ = 4.5 Hz), 4.20 q (2H, OCH₂), 3.8 d. t (1H, HCCl, J₁ = J₂ = 9, J₃ = 4.5 Hz), 1.6-2.5 m (8H), 1.36 t (3H, CH₃, J = 7 Hz). Analogous adducts were obtained from 1-hexene and cyclopentene. The structures of these products were demonstrated by ¹H NMR and IR spectroscopy and elemental analysis for C, H, and N. The scope for the use of this new reaction and its synthetic possibilities are under study.

LITERATURE CITED

1. N. S. Zefirov, N. V. Zyk, A. S. Koz'min, et al., Dokl. Akad. Nauk SSSR, 297, No. 4, 863 (1987).
2. N. S. Zefirov, N. V. Zyk, S. I. Kolbasenko, and A. G. Kutateladze, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 959 (1984).
3. N. S. Zefirov, N. V. Zyk, S. I. Kolbasenko, and A. G. Kutateladze, J. Org. Chem., 50, No. 23, 4539 (1985).