

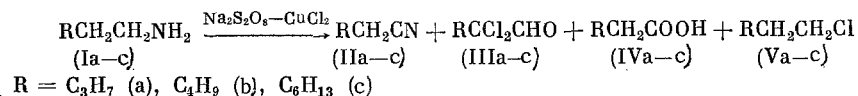
OXIDATIVE SUBSTITUTION OF THE AMINO GROUP IN PRIMARY
ALIPHATIC AMINES

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Primary aliphatic amines are converted into Schiff bases on oxidation with peroxydisulfates in alkaline medium catalyzable by Ag^+ ions [1].

It has been established by us that nitriles (IIa-c), 2,2-dichloroaldehydes (IIIa-c), alkanolic acids (IVa-c), and chloroalkanes (Va-c) are formed from amines $\text{RCH}_2\text{CH}_2\text{NH}_2$ (Ia-c) under the action of the system $\text{Na}_2\text{S}_2\text{O}_8\text{-CuCl}_2$ in water. Amine, conversion %, reaction prod-



uct, yield on amine reacting % were as follows: (Ia), 41, (IIa), 39 (IIIa), 17, (IVa), 12, (Va), 7; (Ib), 32, (IIb), 43, (IIIb), 11, (IVb), 17, (Vb), 8; (Ic), 42, (IIc), 38, (IIIc), 12, (IVc), 19, (Vc), 12.

The conversion of amines into 2,2-dichloroaldehydes (III) and chloroalkanes (V) are new reactions of oxidative substitution of the amino group in primary aliphatic amines. The reaction mechanism evidently includes a one-electron oxidation of (Ia-c) to aminyl radicals $\text{RCH}_2\text{CH}_2\dot{\text{N}}\text{H}$ on deprotonation of which aldimines $\text{RCH}_2\text{CH}=\text{NH}$ are obtained. The latter are oxidized into nitriles (IIa-c) and are also hydrolyzed to aldehydes RCH_2CHO (VIa-c) which are oxidized to acids (IVa-c). It is possible that under the reaction conditions (VIa-c) interact with the initial (Ia-c) with the formation of Schiff bases $\text{RCH}_2\text{CH}=\text{NCH}_2\text{CH}_2\text{R}$ (VIIa-c). On oxidative chlorination and hydrolysis these form (IIIa-c). The proposed mechanism was confirmed by control experiments on the oxidation of $\text{C}_3\text{H}_7\text{CH}_2\text{CH}=\text{NCH}_2\text{CH}_2\text{C}_4\text{H}_9$ (VIIId) to a mixture of (IIIa) (14%) and (Ib) (48%). Similarly (IIIa) was obtained from a mixture of (Ib) and (VIa) in 13% yield from (VIa) at a conversion of (Ib) of 34%. It should be recorded that only (IVa) was obtained from (VIa) under the action of the system $\text{Na}_2\text{S}_2\text{O}_8\text{-CuCl}_2$ and oxidative chlorination with the formation of (IIIa) did not occur.

A solution of $\text{Na}_2\text{S}_2\text{O}_8$ (100 mmole) in water (50 ml) was added at 75-80°C over 1-1.5 h to a mixture of amine (Ia-c) (100 mmole) or Schiff base (VIIId) (100 mmole) or (Ib) (50 mmole) and (VIa) (50 mmole) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (100 mmole) in water (30 ml), the mixture was heated at 80°C for 3.5-4 h, cooled, extracted with ether (3 × 100 ml), the extract dried over MgSO_4 , evaporated, and (IIa-c) and (Va-c) were determined in the residue by GLC. The aqueous layer was basified with NH_4OH , and then with KOH , extracted with ether, the extract dried over MgSO_4 , evaporated, the quantity of unreacted amine (Ia-c) in the residue was determined by GLC, and then isolated preparatively.

The structures of (IIa-c) to (Va-c) were confirmed by comparison with authentic specimens, and by data of IR and chromato-mass spectra. Compounds (IIIa-c) were obtained by an alternative synthesis [2].

LITERATURE CITED

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