FORMATION OF ALKYL PERCHLORATES IN THE DEAMINATION OF ALKYLAMINES IN THE PRESENCE OF PERCHLORATE ANION SOURCES

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We have discovered a new nucleophilic substitution reaction for aliphatic diazo compounds, in which the entering nucleophilic group is the perchlorate anion. We were led to study this reaction by our previous discovery of the competitive binding of the superweak ClO_4^- nucleophile in the final step of electrophilic addition [1]. In order to extend this effect for other carbonium processes (see our previous work [2]), we studied the deamination of C_4-C_9 aliphatic amines by sodium nitrite and $HClO_4$, AcOH, or HCl in various solvents (AcOEt, Et_2O, and H_2O) in the presence of 2-16 eq. $LiClO_4$ at 25°C. For example, the reaction of n-heptylamine with sodium nitrite and acetic acid in diethyl ether in the presence of 3 eq. $LiClO_4$ with stirring for 1 h and subsequent washing with aq. $NaHCO_3$ and separation on a silica gel column (40/100 μ, hexane eluent) yields 27% n-heptyl perchlorate and 38% n-heptyl alcohol as well as traces ($\leq$4%) of n-heptyl acetate. In all cases, thin-layer chromatography, gas–liquid chromatography, and PMR spectroscopy showed that the reaction mixture contained the corresponding alkyl perchlorates (I) (which were the predominant products when the amount of $LiClO_4$ was increased at 16 eq) in addition to alkanols and, when the reactions were run in acetic acid, alkyl acetates

$$RCH_2NH_2 + HNO_2 \xrightarrow{ClO_4^-} \underset{(I)}{RCH_2OClO_3}$$

$R = C_nH_{2n+1}$, $n = 3 \div 9$

Alkyl perchlorates (I) were isolated by chromatography on silica gel columns in 15-40% yield. Their structures were confirmed by comparison with authentic samples [3]. We should note that we were also able to detect the formation of alkyl perchlorates upon deamination in the presence of $HClO_4$ by previously reported methods [4]; the perchlorates decompose upon continuation of the treatment described in the literature.

Thus, this reaction, in addition to its novelty, may serve as a new, safe, and simple method for the synthesis of alkyl perchlorates.

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