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REACTION OF 1-(F-ALKYL)-2-iodoethanes WITH AMIDES FOR THE SYNTHESIS OF $R_FCH_2CH_2OH$: A MECHANISTIC STUDY

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Alkylation of formamide or N-methylformamide (NMF) by alkyl halides (RCH_2X) was studied as a mild, non-hydrolytic method for the synthesis of alcohols. Thus, 2-(F-hexyl)-1-iodoethane ($R_FCH_2CH_2I$, 1, $R_F = C_6F_{13}$) with NMF gave 2-(F-hexyl)-1-ethanol (2) and formate ester (3) in a combined yield of 93-99.5 %, which is much higher than in most hydrolytic or substitutive processes with 1. None of the dialkyl ether was formed. Mechanism of reaction involved the rate-determining formation of $HC=NH(Me)-OCH_2R^+ I^-$ (4, HI). This imide salt reacted with nucleophiles, including NMF, to give 2, 3 and $MeNHCH=NHMe^+ I^-$. Similar reaction of 1 with N,N'-dimethylformamide (DMF) and water gave 2 (33 %) and 3 (66 %), and coproduct $Me_2NH_2^+ I^-$. No reaction occurred without water. Accordingly, the imide salt from 1 and DMF is susceptible to attack by a small nucleophile such as water, but not by DMF. These conclusions were confirmed by a study of 1-bromooctane and 1-iodooctane with formamide and with NMF. Rates of formation of products (1-octanol, 1-octene and di-n-octyl ether) and of imide salt were obtained under several reaction conditions. The coproduct amine salt was not $RNH_3^+ X^-$ ($R = Me$ or H) as previously thought, but a methanimidamide salt $HC = NR(NH_2R)^+ X^-$.