REACTIONS IN ANHYDROUS HYDROGEN FLUORIDE*
COMMUNICATION 5. FLUOROAMINOMETHYLATION AND FLUOROACYLAMINOMETHYLATION OF HALOOLEFINS†

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As we have shown [1], in the reaction of aromatic hydrocarbons with hexamethylenetetramine in anhydrous hydrogen fluoride at room temperature mainly symmetrically substituted hexahydrotriazines are formed:

Since the ion A is a powerful electrophilic agent, it may be assumed that it will be possible to bring about its reaction with olefins. Aminomethylation in acid media has been effected previously on olefins with a strongly marked nucleophilic character, and it has been described in detail only in the case of α-methylstyrene. With aqueous solutions of formaldehyde and primary amine or ammonium salts, usually substituted 1,3-oxazines [2, 3] are formed together with piperidinols [4]. With secondary amine salts under the same conditions unsaturated tertiary amines are formed [2, 5-7]. In individual cases products of conjugated aminomethylation have been isolated: amino alcohols [5] or amino acetates [6].

For these transformations the authors propose the following schemes (schemes at top of next page), $X^-$ is the anion of the corresponding acid.

It was not found possible to bring about the aminomethylation of less nucleophilic olefins [6].

It was found that in presence of HF hexamethylenetetramine readily condenses with vinylidene chloride, vinylidene fluoride, and trifluoroethylene under extremely mild conditions (5-20°, atmospheric pressure). With tetrafluoroethylene the reaction could be brought about only at 50° under pressure. The main reaction products were the corresponding symmetrical N-(fluoroalkyl)-substituted hexahydrotriazines (Ia)-(Id) and the propylamines (Iia)–(IId):

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(Ib) was obtained as a mixture of crystals and liquid. The liquid product had an IR spectrum which was completely identical to that of the crystalline product, and it was converted into the crystalline form on long standing and also on distillation; on acid hydrolysis both substances gave the hydrochloride of (Iib). The formation of the above-described products can be explained by the following reaction scheme:

We have already established the mechanism of the cleavage of hexamethylenetetramine in anhydrous hydrogen fluoride [1]. The ion A makes an electrophilic attack on the double bond of the olefin. The intermediate ion B formed becomes stabilized by combining with $3F^\ominus$. The hexahydrotriazine formed is partially hydrolyzed by water to the corresponding amine and formaldehyde. It may be supposed that with N-(hydroxymethyl)acetamide in HF conjugated fluoroacetamidomethylation of olefins will occur in a similar way as in the case of hexamethylenetetramine. We have been able to find only one communication in the literature on the reaction of N-(hydroxymethyl)acetamide with olefins: from compounds with an activated multiple bond ($\alpha$-methylstyrene, terpenes) substituted 1,3-oxazines were obtained [8].