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USSR TRENDS IN WORK ON ORGANIC FLUORINE COMPOUNDS AND RELATED WORK IN SOME OTHER COUNTRIES

Recent USSR publications indicate that there is a considerable interest in that country in the technical application of fluorocarbons as heat-resistant and fire-resistant lubricants and as chemically inert plastics.(1) The advisability of expanding research that will lead to the production of fluoroorganic plastics has been mentioned in an address dealing with Ukrainian chemical developments and given at the 3d Ukrainian SSR Conference on Organic Chemistry.(2)

The most prominent USSR worker in the field of fluoroorganic compounds is I. L. Knunyants, who in cooperation with members of his group has worked on the polymerization of fluoroolefins.(3) Furthermore, Knunyants has carried out extensive investigations on the interactions of aliphatic oxides with hydrogen fluoride.(4) In the course of this work he developed a method for the synthesis of ethylene fluorohydrin by reacting ethylene oxide with hydrogen fluoride in ether containing 1.5-2% of water. The availability of ethylene fluorohydrin and of its analogs prepared in the same manner made possible the synthesis of many other fluoroorganic compounds.(3, 4, 5,) In the introduction to an article reviewing USSR and foreign work on the addition of hydrogen sulfide and mercaptans to olefins, Knunyants indicates his range of interest in work of this type and the standpoint from which the available information on the subject has been systematized by saying that research in this field leads to physiologically active compounds (e.g., mercaptoamino acids, vitamins, and antibiotics) and that it furthermore is of importance in connection with the study of rubber vulcanization and the synthesis of technically valuable elastomers.(6) One may conclude on the basis of this statement that one of the aims of an extensive series of investigations launched by Knunyants which deal with the addition of alcohols and mercaptans to fluoroolefins (7, 8) is presumably the synthesis of technically useful macromolecular compounds

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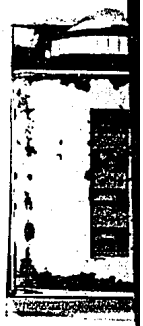

containing fluorine and sulfur, and that Knunyants furthermore must pay close attention to the physiological activity of the compounds synthesized by him in the course of this work. Some of these compounds may be assumed to have toxic properties on the basis of the constitution given by Knunyants. In connection with his prior investigations on the interaction of alkylene oxides with hydrogen fluoride, Knunyants has synthesized toxic and irritant compounds, some of them organophosphorus compounds containing fluorine.(5) In the published account of this work, Knunyants explicitly refers to the toxic and irritant properties of the compounds in question.

The assumption that Knunyants must be interested in polymerizable olefins that contain fluorine and sulfur and that may form a suitable starting material for the production of technically useful macromolecular compounds is born out by his experiments on the dehydrofluorination of corresponding saturated compounds.(7)

Although Knunyants has investigated the addition of thiophenol to perfluorochlorovinyl (7), his work hitherto has been mainly on aliphatic fluorocompounds. L. M. Yagupol'skiy and N. I. Man'ko of the Institute of Organic Chemistry, Academy of Sciences Ukrainian SSR, have published a paper that describes a new method of synthesizing ortho derivatives of trifluoromethylbenzene by introducing a nitrile group converting this group into a carboxylamide group, and then transforming the latter into a carboxyl group or an amino group.(9) A. I. Titov and A. N. Baryshnikova have described the preparation of parafluoroaniline by the reaction of phenylhydroxylamine with anhydrous hydrofluoric acid.(10) Titov points out that prior to that the only known method of introducing a fluorine atom into an aromatic nucleus has been diazotization of an aromatic amine followed by decomposition of the diazonium fluoride or diazonium borofluoride.

It is known on the basis of work done in Germany that introduction of a nitro group into an aromatic compound in the ortho or para position to a fluorine atom makes the fluorine atom more mobile.(11) The effect of the amino group in the compound synthesized by Titov will presumably be opposite to that of a nitro group, i.e., the mobility and reactivity of the fluorine atom in the para position will be reduced. In other words, parafluoroaniline synthesized by Titov's method will be a useful intermediate for the synthesis of compounds containing parafluorophenyl groups.

On the basis of data published by a group of Hungarian investigators, introduction of fluorine atoms into organic compounds by the exchange reaction of chloro derivatives and bromo derivatives with potassium fluoride is effective, at least as far as aliphatic compounds are concerned, when the reaction mixture is irradiated with ultraviolet light. With the use of this method, ethyl chloroformiate has been converted into ethyl fluoroformiate, methyl bromoacetate into methyl fluoroacetate, ethyl chloroacetate into ethyl fluoroacetate, 1, 2-dichloroethane into 1-fluoro-2-chloroethane, 1, 2-dibromoethane into 1-fluoro-2-bromoethane, and diisopropyl chlorophosphate into diisopropyl fluorophosphate. (12, 13) Furthermore, the Hungarian investigators prepared by this method 2-fluoroethanol from ethylene chlorohydrin.(15, 13) They also prepared 2-fluoroethanol by the reduction of methyl fluoroacetate with lithium aluminum hydride. (15, 13) In a subsequent stage of the investigation, they prepared fluoromethanol by reducing ethyl fluoroformiate or formyl fluoride with lithium aluminum hydride.(14, 13)

Except for the use of ultraviolet light, the preparation of 2-fluoroethanol from ethylene chlorohydrin is very similar to a procedure used earlier by

Knunyants, who reacted ethylene chlorohydrin with anhydrous potassium fluoride under pressure and used the ethylene fluorohydrin obtained in this manner to synthesize a great number of other compounds, including the tris-(2-fluoroethyl) ester of phosphorous acid, the mono-(2-fluoroethyl) ester of dichlorophosphoric acid, and the tris-(2-fluoroethyl) ester of phosphoric acid.(5) Some of the other syntheses involving replacement of chlorine or bromine with fluorine had also been carried out before with the use of pressure and in some instances applied industrially. Nevertheless, the new method of carrying out the reactions at atmospheric pressure and at relatively low temperatures represents an improvement.

Similarly to Knunyants and his collaborators, the Hungarians have synthesized compounds which are toxic or can be used as intermediates in the synthesis of toxic compounds. Their research on 1-fluoro-2-chloroethane and 1-fluoro-2-bromoethane is preliminary work leading to an investigation of the possibilities of producing freons with the use of the method proposed by them. They intend to continue prior work dealing with the addition of acid fluorides to carbonyl groups. The synthesis of fluoromethanol was carried out by them with the purpose of developing a simple method for its preparation, so that it will be possible to use this compound in industrial fluoromethylations.(13) The Hungarian investigators have actually prepared benzyl fluoride by reacting benzene with fluoromethanol.(14) They furthermore fluoromethylated benzene with paraformaldehyde and hydrogen fluoride, but were unable to isolate benzyl fluoride under the experimental conditions used, because only diphenylmethane derivatives and resinous polymerization products had formed By condensing monofluorobenzene with fluoromethanol, they prepared p-fluorobenzylfluoride. (16) On the basis of this description of the experimental work, one may assume that the great reactivity of the fluoromethyl group can possibly be used to advantage in preparing high polymers containing fluorinated aromatic nuclei.

While the research done by the Hungarian group, just as the work of Knunyants which it parallels in many respects, leads to both toxic and nontoxic substances, a German investigation on trifluoromethyl arsines (17) deals with a class of substances which are strictly toxic.

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