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QUARTERNARY AMMONIUM FLUORIDE. A REAGENT FOR PROTON ABSTRACTION

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Elimination reactions promoted by the halide ion furnish an interesting problem in organic chemistry (1). Scattered reports in preparative works suggest fluoride ion plays a role as a base in some instances (2,3,4).

In this communication, examples of the proton abstraction by fluoride ion are presented. These examples show definitely the potential ability of the ion as a strong base in an aprotic solvent.

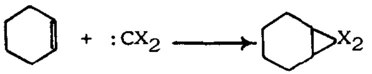
The reagent, tetraethylammonium fluoride (I) was prepared from the bromide $Et_4N{\cdot}Br$ and silver fluoride in aqueous solution. The solution was concentrated in vacuo, acetonitrile was added and removed again in vacuo to eliminate traces of water (5). Recrystallization of the residue from acetonitrile gave pure (I).

Acetonitrile and dimethylsulfoxide were a good solvent for (I). However, DMSO reacted slowly with (I) at slightly elevated temperature. Isolation of hydroxysulfoxide $Ph_2COH{\cdot}CH_2SOCH_3$ from the mixture of (I) and DMSO after treatment with benzophenone proved the formation of methylsulfinyl carbanion (6).

In solution or in solid state, decomposition of (I) took place over 80°C. Ethylene, triethylamine and hydrogen fluoride were the products identifited (4).

Fluoride ion affected the α-elimination of hydrogen halide from haloform producing dihalonorcarane in the presence of cyclohexene. In analogy with the well-established reaction of a conventional base such as potassium alkoxide or alkyl lithium (7), the reaction of fluoride ion could be formulated as follows;

$CHX_3 + F^- \longrightarrow CX_3^- + HF$ (i), $CX_3^- \longrightarrow :CX_2 + X^-$ (ii)



(iii), $HF + F^- \longrightarrow HF_2^-$ $(Et_4N{\cdot}HF_2)$ (iv)

In the typical experiment, (I)(8.4 g. 0.057 mole) in acetonitrile (20 ml.)

was added to cyclohexene (75 ml.). To this suspension chloroform (10 g., 0.084 mole) was added in small portions at room temperature. Stirring was continued overnight and the mixture was poured into water. The work-up in a usual way followed by the separation with preparative gas-chromatography gave 2.8 g. (20%*)) of dichloronorcarane (II)(8). The formation of chloride ion (ca. 80%) was shown by the titrimetric analysis (9) of the water soluble product(s).

The fluoride salt is liable to lose its reactivity if the reaction mixture is contaminated with water. In an attempted preparation of (II) utilizing (I) and chloroform in the presence of about twice-molar equivalent of water to (I), chloride ion (8%)*) and (II)(trace) were produced in greatly diminished yields.

Bromoform reacted with (I) in the presence of cyclohexene giving dibromonorcarane (16--20%)*) and bromide ion (80%)*). The α-elimination from p-nitrobenzenesulfonoxy urethane was affected by (I) giving insertion products of nitrene.

Fluoride ion promoted β-elimination also took place, styrene was produced in an excellent yield (over 90%) by the reaction of β-phenylethyl bromide with (I) at room temperature.

Detailed studies of the fluoride ion promoted eliminations as well as of the onium fluoride chemistry are in progress. The result will be reported later.

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*) Yields (from (I)) were calculated according to the scheme presented.

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