GENERATION OF CARBANIONS OF WEAK CH ACIDS UNDER THE INFLUENCE OF FLUORIDE ANION

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In anhydrous aprotic solvents the fluoride ion is a powerful proton acceptor with respect to such weak

CH acids as indene and fluorene (pK_a 18.5 and 20.5). A much weaker acid, namely triphenylmethane (pK_a 28.8), no longer forms the corresponding carbanion under the influence of fluorides [1].

It was interesting to estimate the ability of the fluoride ion to cleave a proton from those CH acids whose pK_a value ranges from 20 to 28. With this in mind we studied the reaction of tetraethylammonium fluoride (TEAF) with phenylacetylene (pK_a 23.2) and acetonitrile (pK_a 25) [2, 3]. The TEAF was obtained by the reaction of excess anhydrous HF with tetraethylammonium iodide and subsequent neutralization of the formed polyfluorohydrate. The fluoride obtained in this manner retains water tenaciously, and long drying in vacuo over P_2O_5 leads only to the TEAF dihydrate. Attempts to remove the water by heating the (C_2H_5)₄ · NF · 2H₂O proved unsuccessful, since here the salt begins to undergo a rapid Hofmann decomposition with the formation of ethylene, triethylamine, and TEAF fluorohydrate. Previously [4] the formation of ethylene and triethylamine fluorohydrate was observed on heating (C_2H_5)₄NF.

The formation of the carbanions of weak CH acids under the influence of TEAF dihydrate was recorded by reaction with carbonyl compounds. Thus, phenylacetylene when treated with a 1 M solution of TEAF $2H_2O$ in CH_3CN forms the phenylacetylene anion. The addition of acetone to this solution gave 2methyl-1-phenyl-3-butyn-2-ol (I)

As a result, in a 1 M solution of TEAF \cdot 2H₂O in anhydrous CH₃CN the solvation of the fluoride ion by water does not completely suppress the reaction of cleaving a proton from phenylacetylene (pK_a 23.2). Besides this, under these conditions the F^{\odot} also reacts directly with the CH₃CN, which is a much weaker acid (pK_a 25)

$$CH_{3}CN + 2(C_{2}H_{5})_{4} \overset{\oplus}{N}F^{\circ} \rightleftharpoons (C_{2}H_{5})_{4} \overset{\oplus}{N}C\overset{\oplus}{H}_{2}CN + (C_{2}H_{5})_{4} \overset{\oplus}{N}HF_{2}^{\circ}$$
(1)

The equilibrium character of this reaction finds confirmation in the unexpected absence of the ¹⁹F NMR signal of a saturated solution of TEAF $\cdot 2H_2O$ in CH_3CN (the spectra were studied on a Hitachi H-60 instrument). When alcohol is added to this solution a broad signal of the fluorine appears in the +63 ppm region relative to CF_3COOH (CH_3CN : alcohol, 3:1). Apparently, the specific solvation of the F^{\odot} anion by alcohol suppresses its basicity. Here equilibrium (1) is shifted completely to the left and the exchange processes stop. The formation of HF_2^{\odot} according to Eq. (1) is confirmed by the appearance of an absorption band at 1235 cm⁻¹ in the IR spectrum of a solution of TEAF in CH_3CN (a band at 1230-1235 cm⁻¹ is characteristic for MHF_2 , when M = K, Rb, or Cs [5]). In an aqueous solution of TEAF this absorption band is absent (the F^{\odot} anion is solvated, its basic properties are suppressed, and the formation of HF_2^{\odot} fails to occur). Based on the IR spectroscopy data, the reaction of the less basic Cl° and Br° anions with anhydrous CH_3CN is limited by the formation of a complex with a hydrogen bond of type X° . . . HCH_2CN [6].

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The formation of CH_2CN according to Eq. (1) could be confirmed by the addition of this anion to the carbonyl bond of acetophenone and benzophenone. Here the nitrile of β -hydroxy- β -phenylbutyric acid (II) and the nitrile of β -hydroxy- β , β -diphenylpropionic acid (III) were respectively obtained

 $(C_{2}H_{5})_{4} \overset{\oplus \odot}{\overset{\otimes}{\overset{\otimes}{N}}} CH_{2}CN + C_{6}H_{5}COR \xrightarrow{H_{2}O} C_{6}H_{5} \xrightarrow{-C} CH_{2}CN$ OH $R = CH_{3} (II), C_{6}H_{5} (III)$

EXPERIMENTAL

<u>Tetraethylammonium Fluoride Dihydrate.</u> Under vigorous reflux, 257 g of tetraethylammonium iodide was slowly sifted into 800 ml of anhydrous HF. Then the mixture was heated for 2 h at 60° to remove the excess HF, after which 1 liter of water was added and the whole was neutralized with aqueous NaOH solution. The mixture was filtered, the aqueous solution was evaporated in vacuo at 50°, the residue was extracted several times with anhydrous CH_3CN , and the solvent was removed in vacuo. The product was recrystallized three times from anhydrous CH_3CN at -60° , and then dried over P_2O_5 at 10^{-2} mm for 6 days. We obtained 96 g of TEAF $\cdot 2H_2O$, mp 104–108°. Found: F 10.05; N 7.31%. $C_8H_{24}NFO_2$. Calculated; F 10.27; N 7.57%.

Decomposition of $\text{TEAF} \cdot 2\text{H}_2\text{O}$. Here 1.77 g of $\text{TEAF} \cdot 2\text{H}_2\text{O}$ in a copper thimble was placed in a flask, connected to a vacuum system. The flask was gradually heated in an oil bath at an initial pressure of 4 mm. The evalution of ethylene began at 105° (based on a thermometer immersed in the copper thimble). The amount of evolved ethylene was 55.4% (the calculation was based on the pressure change in the system) after 7 h at 150°. Drops of triethylamine appeared on the flask walls after cooling. The ethylene and triethyl-amine were identified by GLC.

<u>2-Methyl-4-phenyl-3-butyn-2-ol (I)</u>. To 3.06 g of TEAF \cdot 2H₂O in a dry argon stream were added 2 g of phenylacetylene, 1.4 ml of anhydrous acetone and 15 ml of anhydrous CH₃CN. The obtained dark solution (pH 8) was stirred for 4 h at 50°, after which the CH₃CN was vacuum-distilled, water was added to pH 7, and the whole was acidified with conc. HCl and extracted with ether (5 × 5 ml). The extract was washed with water and dried. Evaporation of the ether gave 0.14 g of (I) (16.8%, when based on the TEAF \cdot 2H₂O), mp 47.5° [after sublimation at 100° (12 mm)]; from [7]: mp 53°. The mixed melting point with an authentic sample was not depressed. Infrared spectrum of (I): 3445 cm⁻¹ (OH). The molecular ion with m/e 160 was detected in the mass spectrum of the reaction mass. Phenylacetylene does not react with acetone in the presence of CsF in anhydrous ether or CH₃CN. Phenylacetylene and acetone are formed (based on the GLC data) when (I) is heated in a solution of TEAF \cdot 2H₂O in CH₃CN.

<u>Nitrile of β -Hydroxy- β -phenylbutyric Acid.</u> To 2 g of TEAF · 2H₂O in a dry argon stream were added 10 ml of anhydrous CH₃CN and 1.6 g of acetophenone. The mixture was heated at 50° for 6 h, evaporated in vacuo, water and then hydrochloric acid were added to pH 3, and the whole was extracted with ether (5 × 5 ml). The extract was washed with water, dried over MgSO₄, and evaporated in vacuo. The residue was recrystallized from cyclohexane. We obtained 0.12 g (6.8%) of (II), mp 56.5-58°, cf. [8] [after sublimation at 1.00° (15 mm)]. Infrared spectrum: 2250 (C=N), 3448 (OH) cm⁻¹. NMR spectrum (δ , ppm, CCl₄): singlet 1.65 (CH₃), singlet 2.40 (OH), singlet 2.62 (CH₂), multiplet 7.3 (C₆H₅); relative to HMDS; ratio of signals = 3:1:2:5, cf. [9]. Found: C 74.94; H 6.79; N 8.87%.

<u>Nitrile of β -Hydroxy- β , β -diphenylpropionic Acid.</u> In a similar manner, from 3.1 g of TEAF · 2H₂O and 3.64 g of benzophenone in 20 ml of CH₃CN, after evaporation of the ether extract, we obtained 0.68 g (18.2%) of (III), mp 137.5-138.5° (benzene-hexane); from [10]: mp 144°; from [11]: 140°. Infrared spectrum: 2275 (C=N), 3379 (OH) cm⁻¹. The molecular ion with m/e 223 was detected in the mass spectrum of the reaction mixture. NMR spectrum (δ , ppm, CH₂Cl₂): 2.22 (OH), 3.28 (CH₂), 7.34 (C₆H₅); relative to HMDS. Found: C 80.58; H 5.93; N 6.19%.

CONCLUSIONS

1. A study was made of the reaction of fluoride ion with weak CH acids.

2. The dihydrate of tetraethylammonium fluoride cleaves a proton from phenylacetylene and acetonitrile with the generation of the corresponding carbanions.

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