b) A 1.9-g portion (0.05 mole) of thiolacetic acid was added cautiously to 3 g (0.022 mole) of dimethylamide (XI); the reaction is exothermal. On the following day, the mixture was evaporated in vacuo, and the residue was distilled. The yield of (X) was 2.5 g (66%), bp 130° C (2 mm), n_{D}^{21} 1.5218.

<u>Reaction of N-Benzyl β -(Acetylthio)butyramide (VI) with SO₂Cl₂. A 0.80-g portion (0.0059 mole) of SO₂Cl₂ in 3 ml of CH₂Cl₂ was added at -18°C to a solution of 2.51 g (0.01 mole) of benzylamide (VI) in 5 ml of CH₂Cl₂. The mixture was held at 20°C for \sim 1.5 h, and the solvent was distilled in vacuo. According to the IR and PMR spectra, the residue obtained was probably a mixture (\sim 1:1) of polymer (XII) and the initial compound (VI).</u>

IR spectrum (ν , cm⁻¹): 1550 (Ar, (VI + (XII)), 1635-1670 (CON, (VI) + (XII)), 1695 (COS, (VI)), 3270 (N-H, (VI)). PMR spectrum (in CH₂Cl₂, δ , ppm): 1.06-1.32 two d. (CH₃ (VI) + (XII), J_{CH₃-CH} = 7.33 Hz); 2.11 s (CH₃COS, (VI)); 2.54-3.84 hump (CH₂, (VI) + (XII)). 3.65-3.88 m (CH, (VI) + (XII)); 4.27-4.50 br. s (NCH₂, (VI) + (XII)); 6.70-7.38 (C₆H₅, (VI) + (XII); NH, (VI)).

CONCLUSIONS

Amides of β -mercapto- or β -(acetylthio)alkanoic acids were obtained by the reaction of β -thiolactones or β -(acetylthio)alkanoic acid chlorides with amines.

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INFLUENCE OF STRUCTURAL FACTORS ON STABILITY OF FLUORINE-

CONTAINING METASTABLE ENOLS

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It has already been shown that perfluoro-2-propenol (I), obtained by heating 2-benzyloxyperfluoropropene with concentrated H_2SO_4 exists as an individual compound, and under the action of basic reagents is converted into a thermodynamically more favorable keto-form (pentafluoroacetone). For example, in the presence of water, this reaction is completed after 15-20 min of boiling, or after 1-2 days at room temperature [1, 2]

In the present work, we tried under similar conditions to obtain enols (II)-(IV) to determine the structural factors which impart the kinetic stability to the fluorine-containing enols

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We found that enol (II) is obtained smoothly as the result of acid hydrolysis of the corresponding benzyl ether (Va)



Like (I), enol (II) can be stored in glassware. However, it is less stable towards basic reagents, and reacts immediately with water at room temperature to form the corresponding ketone (VI)

 $(II) \xrightarrow{H_2O} CF_3CF_2CFHCCF_3$ $(VI) \overset{\parallel}{O}$

Acid hydrolysis of benzyl ether (VII) leads to a mixture containing 30% of enol (III) and 70% of ketone (VIII)

 $CF_{3}CCl = C - CF_{3} \xrightarrow{H_{3}SO_{4}} CF_{3}CCl = C - CF_{3} \xrightarrow{I} CF_{3}CCl = C - CF_{3} + CF_{3}CClHCCF_{3}$ $\downarrow \\ OCH_{2}Ph \qquad OH \qquad O$ $(VII) \qquad (III) \qquad (VIII)$

When the above mixture is held for 16 days in a glass ampule at 20°C, enol (III) converts completely into ketone (VIII). These data show that enol (III) is less stable than enol (II). Enol (IV) could not be obtained. Acid hydrolysis of benzyl ether (IXa) or acidification at 0°C of triethylammonium salt (X), with subsequent removal of the product formed in vacuo, gave only ketone (XI), which shows that enol (IV) has no kinetic stability



It was found that the stability of fluorine-containing enols decreases in the series: (I) > (II) > (III) > (IV).

From the experimental data definite ideas can be obtained on the influence of the substituents in the enol forms of polyfluorine-containing ketones on their kinetic stability. It is known that keto-enol transformations are catalyzed by both acids and bases, and in the absence of bases introduced from outside, the role of the base can be played by the molecules of the compound itself [3]. Therefore, metastable enols can be synthesized and exist in individual state, if they are stable towards both acids and weak bases, for example glass, atmospheric humidity, etc. Substituents with a strong electron-acceptor effect (fluorine and polyfluoroalkyl groups) impart to enols (I), (II) a low affinity to protons, and therefore these compounds cannot be protonated by acids, and spontaneously transform into thermodynamically more favorable keto forms. The Cl atom has a lower electron-acceptor effect than the F atom, and therefore enol (III) is less stable to the action of acids than enol (II).

The stability of metastable enols towards bases is limited by the rate of splitting off the proton or kinetic acidity of the enols. If we assume that the transition state of the proton splitting is structurally close to that of the corresponding mesomeric ion, then the more stable the mesomeric anion, the higher is the kinetic acidity, and the less stable are the metastable enols. Thus, to ensure a fairly high energy barrier for the transition the substituents should destabilize the mesomeric anion. In this process, a decisive role is played by the high positive mesomeric effect of the vinylic F atoms.



The destabilizing effect of two F atoms is naturally higher than the similar effect of one F atom, and therefore enol (II) is less stable to the action of bases than enol (I), while the chlorine-containing enol (III) is less stable than enol (II), since the +M-effect of the Cl atom is smaller than the +M-effect of the F atom [4].

The mesomeric anion corresponding to enol (IV) contains only substituents stabilizing it,* and therefore the kinetic acidity of enol (IV) should be the highest among all the enols under consideration, while its stability towards the action of bases should be lowest. This explains why the enol cannot be recorded even by the NMR method in a glass ampul.

It can be thus concluded that the optimal combination of low affinity to proton and relatively low kinetic acidity ensures that the enol forms of polyfluorine-containing monocarbonyl compounds have a high kinetic stability. This, at first sight contradicting combination is only possible when the substituents have simultaneously -I and +M effects. Because of the -I effects of the substituents, metastable enols are stable towards acids; the +M effects of the substituents cause destabilization of the corresponding mesomeric anions and lead to a decrease in the kinetic acidity of the enol forms up to a level which for these compounds imparts stability towards weakly basic reagents, in particular, glass.

Ethers (Va) and (VII) were obtained by the reaction of the corresponding fluoroolefins with benzyl alcohol in the presence of bases (Et_3N , KOH).

A similar reaction in the case of perfluoro-2-methyl-2-pentene gives a mixture containing 11% of ether (IXa) and 89% of ether (IXb). As the result of treatment of this mixture with CsF in monoglyme, a mixture was obtained containing 60% of (IXa) and 40% of (IXc), which we used in the reaction of acid hydrolysis



EXPERIMENTAL

 $^{19}{\rm F}$ and $^1{\rm H}$ NMR spectra (δ , ppm, J, Hz) were obtained on the Perkin-Elmer R-32 spectrometer (84.6 and 90 MHz, respectively), with CF_3CO_2H and TMS as external standards. The IR spectra were obtained on the UR-20 spectrophotometer. The purity of the compounds was controlled by GLC on the LKhM-8MD (model 3) apparatus, using a column with 20% QF on chromaton. In the purification of the compounds by preparative chromatography, the Perkin-Elmer F-21 apparatus was used: column 5 m \times 20 mm, 20% QF on Chromaton.

<u>Perfluoro-2-penten-2-ol (II).</u> A 2.4-g portion of (Va) and 1.3 ml of a mixture of concentrated H_2SO_4 and P_2O_5 were placed into a quartz distillation apparatus, and the mixture was heated by a burner flame. The fraction distilling up to 70°C was collected. Yield, 0.8 g (45.5%) of (II), bp 64-66°C. Found: C 24.32; H 0.36%. C₅HF₉O. Calculated: C 24.21; H 0.41%. ¹⁹F NMR spectrum: -7.1 d (CF₃¹), 8.7 d. t (CF₃²), 44.5 d. p. (CF₂), 85.7 q.t.q. (F), $J_{CF_31-F} = 22.6$, $J_{CF_32-F} = 5.6$, $J_{CF_2-F} = 11.3$, $J_{CF_2-CF_3} = 1.8$ Hz. PMR spectra: 4.7 s (OH).

*Triethylammonium enolate (X) does not decompose, even on distillation in vacuo [5].

3-Chloroperfluoro-2-buten-2-ol (III) and 3-Chloro-3-hydroperfluoro-butane-3-one (VIII). A 3.1-g portion of (VII) and 0.5 ml of a mixture of concentrated H₂SO₄ and P₂O₅ were placed into a quartz glass distillation apparatus, and the mixture was heated by a burner flame. The fraction distilling up to 80°C was collected. According to ¹⁹F NMR data, it is a mixture consisting of 30% of (III) and 70% of (VIII). After standing for 16 days in the flask, this mixture converts into pure (VIII). By distillation, 1.0 g (46.5%) of (VIII), bp 52-53°C, was obtained. Found: C 22.38; H 0.51; F 53.22, Cl 16.53%. C₄HF₆ClO. Calculated: C 22.38; H 0.47; F 53.15; Cl 16.55%. IR spectrum (v, cm⁻¹): 1790 (C=O). ¹⁹F NMR spectrum (III) cis-isomer (43%): -16.7 q (CF₃⁻¹), -11.1 q (CF₃⁻²), $J_{CF_3} - CF_3^{-2} = 12.2$ Hz; trans-isomer (57%): -13.3 q (CF₃⁻¹), -8.2 q (CF₃⁻²), $J_{CF_3} - CF_3^{-2} = 1.88$ Hz. ¹⁹F NMR spectrum (VIII): -5.9 d. q. (CF₃⁻¹), -0.3 q (CF₃⁻²), $J_{CF_3} - CF_3^{-2} = 1.88$ Hz. PMR spectrum (III): cis and trans isomers 5.5 s (OH). PMR spectrum (VIII): 4.8 q (CH).

<u>E-2-Benzyloxyperfluoro-2-pentene (Va), Z-2-Benzyloxyperfluoro-2-pentene, E-4-Benzyloxy-perfluoro-2-pentene (Vc).</u> A solution of 4.2 g of KOH in 4 ml of water was added slowly, with stirring, to a mixture of 12.5 g of perfluoro-2-pentene [6] and 5.4 g of benzyl alcohol. The temperature was maintained at $\sim 20^{\circ}$ C. The mixture was held for 1 h, and then poured into water. The organic layer was separated, dried over CaCl₂, and distilled. Yield, 10.2 g (60.3%) of a mixture, bp 78-84°C (25 mm), containing, according to the ¹⁹F NMR data, 58% of (Va), 13% of (Vb), and 29% of (Vc). Compound (Va) was isolated by preparative GLC, bp 84-86°C (25 mm). Found: C 40.81%; H 2.26; F 52.02%. C₁₁H₇F₉O. Calculated: C 40.49; H 2.15; F 52.45%. IR spectrum (ν , cm⁻¹): 1700 (C=C). ¹⁹F NMR spectrum of (Va): -11.8 d (CF₃⁻¹), 7.4 d (CF₃⁻²), 42.9 d (CF₂), 68.4 m (F), J_{CF₃-F} = 22.6, J_{CF₂-F} = 9.7, J_{CF₃-F} = 6.7 Hz.



¹⁹F NMR Spectrum of (Vb): -13.6 t.m. (CF_3^1) , 6.4 d.m. (CF_3^2) , 39.8 d.q. (CF_2) , 61.4 m (F), $J_{CF_3^1-CF_2} = 19.8$, $J_{F-CF_2} = 12.2$, $J_{CF_3^1-CF_3^2} = 3.2$, $J_{CF_3^1-F} = 9.0$, $J_{F-CF_3^2} = 7.8$ Hz. ¹⁹F NMR spectrum of (Vc): -8.6 d.d.d. (CF_3^1) , 5.9 m (CF_3^2) , 55.9 d.m. (F^1) , F^2 , F^3 -AB-system: 74.7 q.m. (F^2) and 81.8 d.m. (F^3) , $J_{F2-F_3^2} = 139$, $J_{F1-F_3} = 37.2$, $J_{CF_3^1-F_2} = 21.4$, $J_{CF_3^1-F_3} = 2.7$, $J_{CF_3^2-F_3} = 5.3$, $J_{F1-F_2} = 5.1$, $J_{F2-CF_3^2} = 4.5$ Hz.

<u>3-Hydroperfluoropentane-2-one (VI)</u>. To 1.9 of (II), 10 drops of H₂O was added, while the temperature was maintained at $\sim 20^{\circ}$ C. At the end of the exothermal reaction, 2 ml of concentrated H₂SO₄ was added, and the mixture was distilled. Yield, 1.2 g (63%) of (VI), bp 54-56°C (cf [7]).

<u>2-Benzyloxy-3-chloroperfluoro-2-butene (VII)</u>, A mixture of 11.0 g of benzyl alcohol and 5 g of Et₃N was added slowly, with stirring, to 11.0 g of 2-chloroperfluoro-2-butene [8], cooled to 0°C. The reaction mixture was held for 1 h at 0°C, then heated to $\sim 20°$ C, and poured into water. The organic layer was separated, dried over CaCl₂, and distilled. Yield 10.2 g (67%) of (VII). bp 93-95°C (12 mm). Found: C 44.11; H 2.57; F 36.87%. C₁₁H₇F₆ClO. Calculated: C 45.35; H 2.30; F 37.44. IR spectrum (ν , cm⁻¹): 1640 (C=C). ¹⁹F NMR spectrum (ratio of isomers cis:trans = 1:3); cis isomer: -17.5 q (CF₃¹), -4.5 q (CF₃²), JCF₃1-CF₃2 = 12.3 Hz, trans-isomer: -14.8 q (CF₃¹), -12.9 q (CF₃²), J_{CF₃1-CF₃2 = 1.7 Hz.}

 $\frac{2-\text{Trifluoromethyl-3-benzyloxyperfluoro-2-pentene (IXa), 2-\text{Trifluoro-methyl-3-benzyloxy-perfluoro-1-pentene (IXb), and 2-Trifluoromethyl-2-hydro-3-benzyloxyperfluoropentane (IXc).$ $a) A mixture of 32.0 g of perfluoro-2-methyl-2-pentene [9] and 11.5 g of benzyl alcohol was cooled to 0°C, and, with stirring, a solution of 6.0 g KOH in 30 ml of H₂O was added slowly while the temperature was maintained at 0°C. The mixture was then heated to <math>\sim 20^{\circ}$ C and poured into water. The organic layer was separated, dried over MgSO₄, and distilled. Yield, 10.5 g (42.5% per reacted olefin) of a mixture, bp 58-63°C (3 mm), containing, according to ¹⁹F NMR data, 11% of (IXa) and 89% of (IXb), with 12.9 g of the initial olefin distilled into a trap cooled to -78°C. IR spectrum (ν , cm⁻¹): 1640 (C=C) (IXa), 1720 (C=C) (IXb). ¹⁹F NMR spectrum (IXa): -21.4 t.q.q. (CF₃¹), -18.5 q (CF₃²), 3.33 q (CF₃³), 36.0 q (CF₂), J_{CF₃1-CF₂ = 20.7, J_{CF₃1-CF₃2 = 9.4, J_{CF₃1-CF₃3 = 3.76 Hz. ¹⁹F NMR spectrum (IXb): -20.5 m (CF₃⁻¹), -16.7 m (F¹; F²), 2.22 d (CF₃²), 43.1 m (F³), 47.5 m (CF₂), J_{CF₃2-F³} = 10.3 Hz.}}} b) A 7-ml portion of absolute monoglyme and 0.2 g of calcined CsF were added to 5.3 g of the mixture obtained in experiment a), and the mixture was stirred at $\sim 20^{\circ}$ C for 24 h. The mixture was then poured into water, acidified with HCl, and extracted with ether. The extract was dried over MgSO₄ and distilled. Yield, 2.9 g of a mixture, bp 60-67°C (4 mm), containing, according to ¹⁹F NMR data, 60% of (IXa) and 40% of (IXc). ¹⁹F NMR spectrum (IXc): -16.4 m (CF₃¹, CF₃²), 2.7 d (CF₃³), 45.0 m (CF₂), 48.5 m (F), J_{CF₃³-F} = 12.2 Hz. PMR spectrum (IXc): 6.9 s (Ph), 4.6 s (CH₂), 3.6 hept. d (CH) J_{CF₃¹, CF₃² = 8, J_{H-F} = 2 Hz.}

<u>2-Hydroperfluoro-2-methylpentane-3-one (XI)</u>. a) A 2.9-g portion of a mixture obtained in the preceding experiment b and 30 drops of a mixture of H_2SO_4 and P_2O_5 were placed into a quartz glass distillation apparatus. The mixture was then heated by burner flame, and then fraction distilling up to 70°C was collected. Yield, 1.7 g of (XI), bp 60-62°C (cf. [5]).

b) A 2.6-g portion of perfluoro-2-methyl-2-pentene-3-triethylammonium enolate (X) [5] was added to a mixture of concentrated H_2SO_4 and P_2O_5 at 0°C. The volatile products were removed in vacuo (5 mm) into a trap cooled to -78°C. Yield, 1.4 g of (XI).

CONCLUSIONS

New metastable enols, perfluoro-2-penten-2-ol and 3-chloroperfluoro-2-buten-2-ol, were synthesized. Structural factors were found which impart the kinetic stability to the enol forms of polyfluorine-containing ketones.

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