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According to [1], perfluoro-2-methyl-2-pentene oxide (I) when treated with alkali-metal fluorides is easily isomerized to perfluoro-2-methyl-3-pentanone (II). In the present paper it was shown that (I) when treated with NaCl and NaBr in diglyme respectively gives the α -chloro- (III) and α -bromoperfluoro-2-methyl-3-pentanones (IV) in good yields:



Besides this, in order to obtain (III) and (IV) we studied the reaction of 2-H-perfluoro-2-methyl-3-pentanone (V) [2] with PCl₅ and PBr₅. In the reaction with PCl₅ the hydrogen is replaced at 200°C by a chlorine atom:



However, with PBr₅, even under more drastic conditions $(300^{\circ}, 5 \text{ h})$, (IV) is not formed, apparently due to the larger size of the PBr₅ molecule when compared with PCl₅, which hinders attack on the α -C atom.

It seemed of interest to compare the chemical behavior of ketones (II)-(V) when treated with an aqueous solution of alkali and alkali-metal fluorides.

It is known that poly- and perfluroalkyl perfluoroisopropyl ketones in reactions with primary and secondary amines undergo haloform cleavage to give amides and 2-hydroperfluoropropane, in which connection, depending on the type of fluoroalkyl substituent, the direction of the reaction changes from haloform decomposition to reduction [3, 4]. In [5] it was shown that perfluoroalkoxy ketones when treated with bases undergo haloform cleavage, predominantly with a rupture of the bond between the carbonyl and the secondary C atoms of the fluoroalkyl substituent.

We established that ketone (II) at $\sim 20^{\circ}$ reacts vigorously with aqueous alkali solution, and here it is hydrolyzed to give 2-H-perfluoropropane and pentafluoropropionic acid.

The reactivity of ketones (III) and (IV) decreases when the α -fluoro atom of the perfluoroisopropyl group is replaced by Cl or Br, and, consequently, the alkaline hydrolysis requires more drastic conditions (refluxing for 1 h). The hydrolysis of (III) and (IV) is accompanied by the formation of 2-chloro(bromo)-2-hydroperfluoropropanes and pentafluoropropionic acid:

$$(CF_3)_2 CXCC_2 F_5 \xrightarrow{MOH, H_2O} (CF_3)_2 CXH + C_2 F_5 COOM \xrightarrow{H_2SO_4} C_2 F_5 COOH$$

X = F, C1, Br. M = K, Na.

As a result, the direction of the haloform decomposition is the same for ketones (II)-(IV).

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The alkali-metal fluorides are highly basic [6]. However, cleavage using anhydrous CsF was observed only for ketone (II) when refluxed vigorously. Hexafluoropropylene (HFP) and perfluoropropionyl fluoride were isolated as a reaction result.

Ketones (III) and (IV) do not react with CsF even after long refluxing. However, when a mixture of (III) and CsF in diglyme is refluxed, the Cl atom is replaced by F to give (II) and the subsequent haloform decomposition of (II) to HFP and perfluoropropionyl fluoride:

(III) $\xrightarrow{\text{CsF, diglyme}}$ (II) + CF₃CF=CF₂ + CF₃CF₂COF

In the given series of ketones a special position is occupied by (V), which is stable to aqueous alkali and alkali-metal fluorides. This can be explained by the deprotonation of (V) by the base to give a stable mesomeric anion, which prevents the haloform cleavage.

EXPERIMENTAL

The ¹⁹F NMR spectra were taken on Perkin-Elmer R-32 and Tesla BS-487 instruments (84.6 and 80 MHz, respectively). The IR spectra were obtained on a UR-20 spectrometer for CCl₄ solutions. The decomposition products were analyzed by GLC on an LKhM-72 chromatograph equipped with a katharometer, and using helium as the carrier gas and a 6 m × 4 mm column packed with 5% SKTF-100 deposited on Chromosorb G.

 $\frac{2-\text{Chloroperfluoro-2-methyl-3-pentanone (III).}}{(I) \text{ and } 6 \text{ g of NaCl in } 20 \text{ ml of diglyme was refluxed for } 20 \text{ h.}} Subsequent distillation gave 5.6 g (35%) of (II) and 9.5 g (55.8%) of (III), bp 76-76.5°. ¹⁹F NMR spectrum (from external CF₃COOH, <math>\delta$, ppm): -7.3 t (6F, (CF₃)₂, J = 10.1 Hz); 5.6 s (3F, CF₃); 38.6 sept (2F, CF₂, J = 10.1 Hz). Infrared spectrum (ν , cm⁻¹): 1770 (C=0). Found: C 21.51; C1 10.72; F 62.71%. C₆ClF₁₁O. Calculated: C 21.65; C1 10.68; F 62.85%.

b) A mixture of 20 g (0.067 mole) of (V) and 17 g (0.081 mole) of PCl₅ was charged into a 50-ml steel autoclave and shaken for 3 h at 200°. Then the autoclave was cooled to 0°, the gas was scoured, and the residue was treated with water. The lower layer was separated and dried over MgSO₄. Based on the GLC data, the obtained liquid (19 g) was a mixture of 20% of (V) and 80% of (III). Fractional distillation gave (III) with bp 76-77°.

<u>2-Bromoperfluoro-2-methyl-3-pentanone (IV).</u> With stirring, a mixture of 25 g of oxide (I) and 10 g of NaBr in 30 ml of monoglyme was refluxed for 24 h. Fractional distillation gave 16 g (53.7%) of (IV), bp 96-97°. ¹⁹F NMR spectrum (from internal C₆H₆, δ , ppm): -94.0 t (6F (CF₃)₂, J = 6.0 Hz); -78.5 s (3F. CH₃); -48.3 sept (3F, CF₃, J = 6.0 Hz). Infrared spectrum (v, cm⁻¹): 1760 (C=0). Found: C 19.23; Br 21.38; F 55.32%. C₆BrF₁₁0. Calculated: C 19.10; Br 21.22; F 55.43%.

<u>2-H-Perfluoro-2-methyl-3-pentanone (V)</u>. With stirring, 83 ml of conc. H_2SO_4 was added dropwise to a mixture of 45 g (0.15 mole) of 2,3-dihydroperfluoro-2-methyl-3-pentanol (VI) [7] and 50 g (0.225 mole) of $K_2Cr_2O_7$ in 70 ml of H_2O , the mixture was refluxed for 2 h, and the ketone was distilled off. The yield of (V) was 26 g (58%), bp 60-61° [2].

Haloform Decomposition of Perfluoro-2-methyl-3-pentanone (III). a) A solution of 1.6 g (0.04 mole) of NaOH in 2.2 ml of H_2O was added dropwise to 10 g (0.032 mole) of (I). The low-boiling product was collected in a trap, and the residue was distilled over conc. H_2SO_4 to give 4.9 g (92%) of $(CF_3)_2CFH$ (identified by comparing with an authentic specimen via GLC) and 4.4 g (85%) of C_2F_5COOH with bp 96-98°, n_d^{20} 1.2842 [8].

b) A mixture of 33.2 g (0.1 mole) of (II) and 15.2 g (0.1 mole) of CsF was heated in a Wood's metal bath for 2 h at 250°. Here 10.2 g (68%) of HFP was collected in the trap, while C_2F_5COF was isolated from the residue.

Haloform Decomposition of 2-Chloroperfluoro-2-methyl-3-pentanone (III). a) A solution of 1 g (0.025 mole) of NaOH in 1.5 ml of H₂O was added dropwise to 7 g (0.021 mole) of (III) and the stirred mixture was refluxed for 40 min, after which the product with bp 15-18° was distilled off. The residue was distilled over conc. H₂SO₄ to give 2.0 g (51%) of (CF₃)₂CC1H and 2.1 g (43%) of C₂F₅COOH with bp 96-98°, np²⁰ 1.2839 [8].

b) A mixture of 8 g (0.024 mole) of (III) and 8 g (0.052 mole) of CsF in 2 ml of diglyme was refluxed for 1 h, with periodic removal of the product distilling below 50° . The low-boiling products were collected in a trap. We obtained 2.9 g (38%) of (II) and 1 g of a mixture of HFP and C₂F₅COF.

<u>Haloform Decomposition of 2-Bromoperfluoro-2-methyl-3-pentanone (IV)</u>. The reaction of 10 g (0.026 mole) of (I) with 1.2 g (0.03 mole) of NaOH in 2 ml of H₂O was run in a similar manner. We obtained 4.5 g (73.5%) of $(CF_3)_2CBrH$ with bp 32-33° and 3.1 g (71.2%) of $C_2F_5CO_2H$, bp 96-99°, $n_D^{2^\circ}$ 1.2840 [8].

CONCLUSIONS

1. Some 2-X-perfluoro-2-methyl-3-pentanones (X = Cl, Br) were obtained by reacting perfluoro-2-methyl-2-pentene oxide with NaCl or NaBr in diglyme. 2-Chloroperfluoro-2-methyl-3-pentanone was also obtained by reacting 2-H-perfluoro-2-methyl-3-pentanone with PCl₅.

2. In the 2-X-perfluoro-2-methyl-3-pentanone series (X = F, Cl, Br) the haloform decomposition using aqueous alkali and alkali-metal fluorides is most easily accomplished when X = F.

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FLUORINATED β -HYDROXY- β -CARBOMETHOXY ACIDS AND PHOTOREDUCTION

OF THEIR COPPER SALTS

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 β -Hydroxy- β , β -bis(trifluoromethyl)propionic acid is formed in 96% yield when hexafluoroacetone is passed through a solution of malonic acid in pyridine at -78° C and the reaction mass is then held for \sim 12 h [1]. The reaction of hexafluoropropylene α -oxide with acetone in water leads to 2-hydroxy-2-carboxy-1,1,1-trifluoro-4-pentanone, which is obtained by the condensation of the intermediately formed trifluoropyruvic acid with acetone [2]. Other reactions of the fluorinated α -keto acids and their derivatives with CH acids are unknown at the present time.

In the present paper we studied the reaction of the methyl esters of the polyfluorinated α -keto acids (I)-(V) with malonic acid in pyridine, and the formation of the copper salts from the products of this condensation and their photoreduction by alcohols in the presence of UV light.

 $\begin{array}{c} X(CF_2)_n COCOOMe + CH_2(CO_2H)_2 \xrightarrow{Py} X(CF_2)_n CCH_2COOH \\ & OH \\ (I)-(V) & (VI)-(X) \\ X = F, \ n = 1 \ (I), \ (VI); \ X = H, \ n = 2 \ (II), \ (VII); \ X = F, \ n = 2 \ (III), \ (VIII); \ X = H, \\ n = 4 \ (IV), \ (IX); \ X = F, \ n = 4 \ (V), \ (X). \end{array}$

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