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THE SYNTHESIS AND SOME REACTIONS OF PENTAFLUOROETHYL VINYL KETONE

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SUMMARY

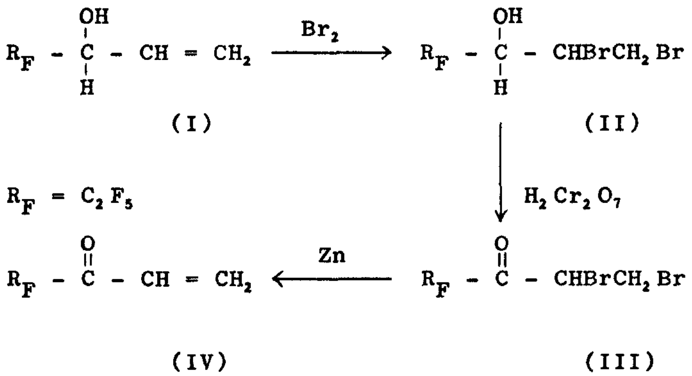
The title compound has been prepared in a four step synthesis starting from acrolein. Both its dimerization, which yields a 3.4-dihydropyranyl derivative, and the uncatalyzed addition of ethanol across the C=C-bond take place at 20°, reflecting the high reactivity of this α,β-unsaturated ketone.

INTRODUCTION

Ketones containing a F-alkyl group and either a propenyl [1] or a styryl [2] group can be obtained from reactions between perfluorocarboxylic acids or their alkali salts and appropriate Grignard reagents. However, related compounds of the type $R_F(CO)CH{=}CH_2$ are not accessible by this method and, to our knowledge, had not yet been reported.

RESULTS AND DISCUSSION

We have now synthesised the first example of these compounds, F-ethyl vinyl ketone, using the reaction sequence outlined in Scheme 1. A similar approach has been successfully employed by Anderson [3] to prepare F-alkyl F-vinyl ketones.

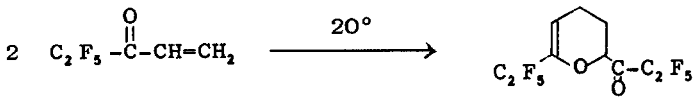


SCHEME 1

The allylic alcohol I was obtained from acrolein and pentafluoroethyl magnesium chloride at -40° [4] . Since several attempts to simply oxidize compound I to the desired ketone IV, by means of chromic acid in acetone (Jones reagent) or water, merely led to the destruction of the C=C-bond, the double bond had first to be protected by addition of bromine. The resulting dibromide II was oxidized with acid dichromate to form the pentanone III. Alternatively it is possible to directly convert the alcohol I into III by oxidative bromination with N-bromosuccinimide; thus, when a solution of I in boiling tetrachloromethane was reacted for eight hours with NBS in a molar ratio of 1 : 2, the dibromoketone was isolated in 45 % yield, together with 15 % of the compound II.

Finally, the debromination of III was effected by using an excess of zinc dust in hot di(n-butyl)ether, in order to remove the vinyl ketone as quickly as possible from the reaction mixture. Even then, ketone IV, a colorless liquid of b. p. 58°, could be obtained in only moderate yield. All attempts to prepare the C_6F_{13} analogue of IV failed due to the rapid polymerization of the product under various dehalogenation conditions. The reagents employed included zinc in dioxan, magnesium in diethyl ether and alkali iodides in acetone.

Pentafluoroethyl vinyl ketone is a very reactive compound. On standing at room temperature, it slowly undergoes a Diels-Alder type dimerization to form a product the spectroscopic data of which (see Table 1) clearly show it should be formulated as the 3.4-dihydropyranyl derivative V.



(IV) (V)

The mass spectrum of V showed the molecular ion at m/e 348. The most intense peak was observed at m/e 201 and corresponds to the F-ethyl dihydropyranyl cation. The rate of the dimerization process was measured by nmr spectroscopy using a neat sample of IV and the half life was found to be 60 hours at 20°. In regard to this reaction, it is noteworthy that acrolein does form a "thermal dimer" [5] , having

Table 1 Spectroscopic Data

Compound	NMR[a] (ppm) ^1H	^{19}F $\delta\ CF_2$	$\delta\ CF_3$	IR[b] (cm^{-1}) ν C=O	ν C=C	UV[c] (mμ) λ max.
II	CHO 4.58dd, CHBr 4.51 t CH_2Br 3.80d, OH 3.03 JCH_2CH = 7.5 Hz	F_A 44.5, F_B 51.3 JAB = 282 Hz JAH = 5 Hz, JBH =22Hz	4.8			
III	CH_ABr 4.98dd, CH_MH_XBr 4.02 t, 3.68 dd, JAM = = JMX = 11.5Hz,JAX =4.5Hz	F_A 38.2, F_B 46.6 JAB = 295 Hz	3.6	1775 vs		
IV	= CH_AH_B 6.78 m, = CH_C 6.12 dd	46.4	5.3	1732 vs	1613 s	222 vs 334 w
V	= CH 5.66m, CHO 5.10 m, 2 CH_2 2.25 m	43.9 44.3	5.1 6.9	1766 vs	1688 s	314 w
VI	3.73 t, 3.45 q, 2.95 t, 1.13 t	45.8	4.5	1758 vs		296 w

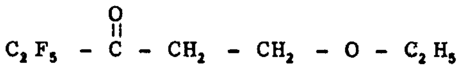
a) Jeol C 60 instrument, CCl_4 solutions, ^1H: δ at 60 MHz, downfield from i-TMS, ^{19}F: δ at 56.45 MHz, upfield from e-CF_3CO_2H.

b) Perkin-Elmer 325 grating spectrophotometer, films on KBr plates.

c) Zeiss PMQ 11 spectrometer, n-hexane solutions.

a structure comparable to that of V, while similar cyclizations were not observed for the F-alkyl propenyl [1a] and F-alkyl F-vinyl [6] ketones.

The C=C double bond of IV readily undergoes nucleophilic attack. Thus, an equimolar mixture of this ketone and ethanol, without the assistance of any catalyst, afforded the expected ether VI over one hour at 20°.



$$C_2F_5 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2 - CH_2 - O - C_2H_5 \qquad \text{(VI)}$$

Compound VI can also be prepared in good yield, if $C_2F_5(CO)CH{=}CH_2$ is generated in situ by the debromination in ethanol of III with potassium iodide.

The relevant spectroscopic data of compounds II - VI are summarized in Table 1. The coupling pattern observed for the olefinic protons of IV resembled that of ethyl vinyl ketone, however, all hydrogen resonances of IV appeared at lower field (0,2 ppm for α-H and 0,5 ppm for the β-H's) due to the high electronegativity of the F-ethyl group.

EXPERIMENTAL

The ractions were carried out under nitrogen using carefully dried solvents. All of the new compounds were colorless liquids and had satisfactory elemental analyses (limits of error: C ± 0,2 %, H ± 0,1 %, Br ± 0,1 %, F ± 0,3 %).

4.4.5.5.5-Pentafluoro-1-penten-3-ol (I)

To a solution of 2,4 mol of ethyl magnesium chloride in 1,6 l of diethylether, cooled to -40°, was slowly added a solution of 492 g (2,0 mol) of pentafluoroethyl iodide in 1 ltr of ether. After the mixture had been stirred for 10 min at -35°, acrolein (145,6 g; 2,6 mol), dissolved in 200 ml of ether, was added with vigorous stirring, while maintaining the temperature below -20°. Stirring was continued for 1 hr at -30° and then the mixture was hydrolysed at 0° with 15 % sulfuric acid. The ethereal layer was separated, dried and distilled to give 239 g of alcohol I (68 % yield based on C_2F_5J, b. p. 98 - 99°, GLC-purity 99,2 %).

1.2-Dibromo-4.4.5.5.5-pentafluoro-3-pentanol (II) (nc)

A solution at 0° of 79,9 g (1,0 mol) of bromine in 100 ml of tetrachloromethane was added dropwise to a stirred solution of 88 g (0,5 mol) of I in 100 ml of tetrachloromethane. The mixture was allowed to stand at room temperature over-night; then it was concentrated under reduced pressure. Distillation afforded 158,1 g (yield 94 %) of II, boiling at 105°/100 Torr.

1.2-Dibromo-4.4.5.5.5-pentafluoro-3-pentanone (III)

250,7 g (0,75 mol) of the dibromide II and 68 ml of concentrated sulfuric acid were placed in a 4 neck flask and a solution composed of sodium dichromate dihydrate (190 g), water (265 ml) and sulfuric acid (112 ml) was slowly added at 50°. The mixture was stirred for 8 hr at 90°. On cooling to 20° and addition of 255 ml of concentrated sulfuric acid, the crude product was distilled off under vacuum (10 Torr). It was dried over magnesium sulfate and fractionated to give 197 g (yield 78,7 %, b. p. 84°/100 Torr) of ketone III.

Pentafluoroethyl vinyl ketone (IV)

A mixture of zinc dust (15 g) and di(n-butyl)ether (100 ml) was heated to 110° in a distillation apparatus, equipped with a short Vigreux column connected to a dry ice-cooled receiver. 33,4 g (0,1 mol) of III was added dropwise with rapid stirring. After the first 3 ml had been added, the temperature rose to 135° and the product started to distill. 4,7 g (yield 27 %) of IV were obtained. The nmr spectrum of this volatile material (b. p. 58-60°) revealed the presence of ca. 3 % of the dimeric species V.

Pentafluoroethyl 2-(6-pentafluoroethyl-3.4-dihydropyranyl) ketone (V)

A small flask containing a 2 g sample of compound IV and 5 mg of hydroquinone, under nitrogen, was kept for 6 weeks at room temperature. Subsequent inspection by nmr indicated a nearly quantitative conversion into the dimer V (b. p. 137°).

Pentafluoroethyl 2-ethoxyethyl ketone (VI) (nc)

A stirred solution of 50 g (0,15 mol) of the dibromoketone III in 200 ml of 90 % ethanol was cooled to 0°, and potassium iodide (99,6 g, 0,6 mol) was added slowly.

Stirring was continued for 2 hr at 20°. The precipitated iodine was removed by adding a concentrated aqueous solution of sodium thiosulfate and the mixture was twice extracted with 100 ml portions of dichloromethane. The combined extracts were dried over sodium sulfate and fractionated to give 27,4 g (yield 83 %) of the ether product boiling at 123°.

The analogous perfluorohexyl compound (b. p. 76°/12 Torr) was prepared in 74 % yield by the same method.

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