CONCLUSIONS

1. A new equilibrium reaction was found involving transformation of perfluoro-4-oxo-2,5-dimethyl-2-(2'-oxa-3'-fluorocarbonylbutyl)-1,3,-dioxolane into perfluoro-4-oxo-2,5-dimethyl-2-fluorocarbonyl-1,3-dioxolane and perfluoro-2-oxo-3,6-dimethyl-1,4-dioxane. A scheme for the process is proposed.

2. A catalytic ionic fragmentation was discovered of some perfluoro-4-oxo-1,3-dioxolanes containing a fluoroanhydride group to give trifluoroacetyl fluoride and carbon monoxide.

LITERTURE CITED

1. S. Selman, Patent 3,475,456, USA, Chem. Abstrs., 72, 2167b.
2. R. Bancs, E. D. Burling, B. A. Dodd, et al., J. Chem. Soc. C., 1706 (1969); R. Bancs and K. Mullen, J. Chem. Soc. C., 2333 (1967).
3. V. S. Yuminov, S. V. Kartsov, V. L. Maksimov, and A. V. Fokin, Izv. Akad. Nauk SSSR, Ser. Khim., 392 (1988).
4. A. Gordon and R. Ford, Chemist's Companion, Wiley-Interscience, New York (1973).
5. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, 2nd edn., Wiley-Interscience, New York (1970).

STUDY OF THE REACTION OF FLUOROALKYL β-KETOESTERS WITH METHYLHYDRAZINE BY ^1H and ^{19}F NMR SPECTROSCOPY

V. I. Saloutin, M. I. Kodess, A. N. Fomin,
S. I. Selivanov, B. A. Ershov, and K. I. Pashkevich

UDC 543.422.25:542.91:547.484'161:547.234.1

β-Ketoesters, including fluoroalkyl ketoesters, form pyrazol-5-ones upon reaction with hydrazines [1, 2]. However, data on the structure of the intermediates of these reactions are limited to [3] in which reaction of acetoacetic ester (AAE) with hydrazine (H_2O, 30°C) was studied by PMR spectroscopy under continuous flow and stopped flow conditions. It was shown that the reaction involves hydrazine addition with formation of an adduct at the carbon β-atom, dehydration to hydrazone, and cyclization of the latter to 3-methylpyrazol-5-one with simultaneous elimination of ethanol [3].

We have studied the reaction of fluoroalkyl β-ketoesters (β-FKE) [(I)-(III), Table 1] methylhydrazine (MH) in CD_3OD from −30 to 30°C by ^1H and ^{19}F NMR spectroscopy. It was found that the reaction includes formation of a salt of the β-FKE with MH (B), and of a 3,5-dioxypyrazolidine intermediate (C) followed by elimination of methanol (C → D) and water (D → E) to form pyrazol-5-one (E) (Scheme 1).

Signal assignments in the PMR spectra of the reaction mixtures were based on the spectra of the starting β-FKEs (I)-(III) and their adducts with methanol [4], the independently prepared salts of β-FKE (II) with diethylamine (IV), 5-hydroxy-2-methyl-3-trifluoromethyl-1,2-pyrazole (V), and data of [5] in which the reaction of β-diketones with MH was studied.

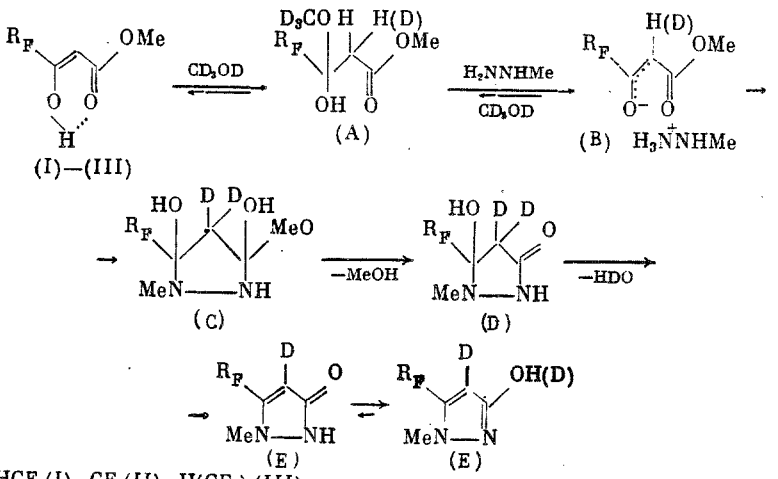
β-FKEs (I)-(III) with methanol give a mixture of β-FKE and hemiketal, which is formed by addition of one alcohol molecule to the β-FKE [4]. In order to explain the stability of the hemiketal under the conditions of reaction of β-FKE with MH the ^{19}F NMR spectra of solutions of β-FKE (II), ($R_F = CF_3$) in methanol in the presence of bases (diethylamine, triethylamine) were recorded. In the ^{19}F NMR spectrum of a methanol solution of the starting β-FKE the CF_3 group signal is present at 81.02 ppm, which corresponds to hemiketal [4]. Upon addition of diethylamine or triethylamine to a solution of β-FKE (II) in methanol this signal disappears and a signal at 88.40 or 87.98 ppm appears, which could be assigned to a diethyl- or triethylammonium salt, respectively. In order to confirm this assumption we

Institute of Chemistry, Ural Branch, Academy of Sciences of the USSR.

Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 399-402, February, 1988. Original article submitted June 18, 1986.

0568-5230/88/3702-0318$12.50

Scheme 1



$R_F = HCF_2(I)$, $CF_3(II)$, $H(CF_2)_4(III)$.

obtained in an isolated state the diethylammonium salt (IV) of β-FKE (II), in the ^{19}F NMR spectrum of which the chemical shift of the CF_3 group is 88.38 ppm. Thus, upon addition of bases to hemiketals (A) obtained by addition of HO-nucleophiles to β-FKEs they decompose to give a salt of the β-FKE with base.

In the PMR spectra of the solutions of β-FKE (I) and (II) in deuteromethanol at −30°C signals of methoxy group protons are present at 3.67-3.68 ppm which correspond to the hemiketal (A) of the β-FKE with methanol. Upon MH addition a signal at 3.58-3.59 ppm appears in the PMR spectra which is characteristic of salts of β-FKEs with amines (IV), and signals appear at 3.71-3.72 and 2.48-2.49 ppm for the OCH_3 and NCH_3 groups of the 3,5-dioxypyrazolidine (C) formed (Table 1).

β-FKE (III), $R_F = H(CF_2)_4$, forms practically no hemiketal [4], therefore it exhibits a PMR signal for the OCH_3 group of the enol form at 3.82 ppm. After MH addition this is transformed into two signals at 3.58 and 3.66 ppm (Table 1) which can be attributed to the methoxy groups of salt (B) and 3,5-dioxypyrazolidine (C), respectively. Also a signal due to the 3,5-dioxypyrazolidine (C) NCH_3 group appears at 2.49 ppm. During the first 20 min after mixing the reagents the signals of salt (B) decrease in intensity and the signals of 3,5-dioxypyrazolidine (C) increase. Then a signal at 3.34 ppm appears due to the eliminated methanol and a signal at 3.01-3.02 ppm due to the NCH_3 group of the 5-oxypyrazoline (D) formed.

Upon increasing the temperature of the reaction mixture to 25°C a PMR signal for the NCH_3 group of the pyrazol-3-one (E) formed appears at 3.49-3.54 ppm, and 1.5 h after the beginning of reaction of a mixture of β-FKE (I)-(III) with MH, PMR signals of a mixture of products (D) and (E) are present.

The absence of methine and methylene proton signals in the PMR spectra of the reaction mixtures of β-FKEs (I)-(III) with MH is explained by isotopic exchange on these products by deuterium, since the reaction proceeds in deuteromethanol.

For confirmation of the suggested scheme of reaction of β-FKEs with MH we have taken ^{19}F NMR spectra of a mixture of β-FKE [(II), $R_F = CF_3$] with MH in methanol solution. The spectrum of the starting compound (II) in methanol solution contains only the hemiketal signal (81.02 ppm) [4], which upon addition of MH to the solution at −30°C decreases and two new signals appear, one at 88.3 ppm assigned to the methylhydrazinium salt of β-FKE (B) and one at 81.30 ppm assigned to the trifluoromethyl group of 3,5-dioxypyrazolidine (C).

After 10 min a ^{19}F NMR signal at 79.70 ppm begins to appear with simultaneous decrease in intensity of the signal at 81.30 ppm, which indicates elimination of methanol and formation of 3-oxypyrazoline (D). During the following 40 min a relative change of intensity of the signals at 81.30 and 79.70 ppm takes place – the first one decreases and the second increases. At 1 h after mixing of the reagents the temperature of the reaction mixture was increased to 30°C and a spectrum was recorded in which a signal at 100.9 ppm appeared, which was assigned to the final reaction product – pyrazol-5-one [assignment was based on the ^{19}F NMR spectrum of a known sample of (V)].

TABLE 1. Proton and ^{19}F Chemical Shifts of Intermediate and Final Products Formed in the Reaction of β-FKEs with MH (CD_3OD)*

R_F	Starting β-FKE (I)-(III)		Adduct with CD_3OD (A)		Salt with MH (B)		3,5-Dioxypyrazolidine (C)			3-Oxopyrazoline (D)		Pyrazol-5-one (E)	
	OCH_3	CF_3	OCH_3	CF_3	OCH_3	CF_3	NCH_3	OCH_3	CF_3	NCH_3	CF_3	NCH_3	CF_3
HCF_2 †	—	—	3,67	—	3,58	—	2,48	3,71	—	3,01	—	3,49	—
CF_3	—	—	3,69	81,02	3,59	88,3	2,49	3,72	81,3	3,01	79,70	3,50	100,9
$H(CF_2)_4$ †	3,82	—	—	—	3,58	—	2,49	3,66	—	3,02	—	3,54	—

*Signals of the CH_2 and CH groups are absent due to deuterium exchange.
†Signals of the HCF_2 and $H(CF_2)_4$ groups are not shown because of the complexity of their interpretation.

Thus, our data showing that upon reaction of β-FKEs with MH, first elimination of methanol from the intermediate occurs (C → D) followed by water (D → E), emphasizes the difference from the reaction of acetoacetic ether [3], where elimination of water takes place first from the adduct of hydrazine at the carbon atom and then cyclization to pyrazol-5-one with simultaneous elimination of alcohol.

EXPERIMENTAL

PMR spectra were recorded on CFT-20 (80 MHz) and Tesla BS-567A (100 MHz) spectrometers, ^{13}C and ^{19}F NMR spectra on a Tesla BS-567A (25.1 MHz, 94.1 MHz) with TMS (^1H and ^{13}C) and hexafluorobenzene (^{19}F) as internal standards.

β-FKEs (I)-(III) were obtained by the method of [6]. Methylhydrazine was obtained by decomposition of methylhydrazine sulfate with diethylenetriamine and dried by distillation above KOH in an Ar flow.

For recording the spectra of the intermediates in the reaction of β-FKEs (I)-(III) with MH the following procedure was used: into the NMR tube 0.5 ml of freshly prepared β-FKE solution in deuteromethanol (1 M) was placed. The solution was cooled to −30 to −35°C and the spectrum of the starting β-FKE was recorded. Then an equimolar amount of MH solution in deuteromethanol, cooled to −30 to −35°C, was added. The tube was shaken and the spectrum was recorded. The spectra were again recorded at −30°C at 3, 5, 15, 30, 40, and 60 min after mixing the reagents by rapid scanning of separate spectral regions. Then the temperature was increased to ~20°C and the signals of the products forming were recorded (1.5 h).

5-Hydroxy-2-methyl-3-trifluoromethyl-1,2-pyrazole (V). To a solution of 5 g (0.03 mole) of 4,4,4-trifluoroacetoacetic ester (II) in 30 ml methanol a solution of 1.7 g (0.035 mole) MH in 10 ml methanol was added dropwise and the mixture was refluxed for 6 h. Solvent was distilled off and the residue was recrystallized from xylene. There was obtained 4.5 g of (V) with mp 164-166°C. Found %: C 36.60; H 3.00; F 34.30; N 16.69. $C_5H_5F_3N_2O$. Calculated, %: C 36.16; H 3.03; F 34.31; N 16.86. PMR (δ, ppm, J, Hz): 3.64 d (3H, NCH_3, J = 0.6), 5.75 q (1H, CH=, J = 0.7), ^{19}F NMR (δ, ppm, J, Hz): 100.9 d.q (CF_3, J_d = 0.7, J_q = 0.6), ^{13}C NMR (δ, ppm, J, Hz): 34.2 (2-CH_3), 85.5 (C^4), 122.7 q (3-CF_3, J = 266.7), 140.4 q (C^3, J = 37.6), 153.7 (C^5).

Methyl-N,N-diethylammonium-3-keto-4,4,4-trifluoro-2-butenoate (IV). To a solution of 6.5 g (0.04 mole) of 4,4,4-trifluoroacetoacetic ether (II) in 40 ml diethyl ether a solution of 2.93 g (0.04 mole) diethylamine in 10 ml diethyl ether was added and the mixture was refluxed for 2 h. The ether was distilled off and the residue recrystallized from hexane. There was obtained 8.1 g of salt (IV) with mp 119-120°C. Found, %: C 44.09; H 6.25; F 23.60; N 5.88. $C_9H_{16}F_3NO_3$. Calculated, %: C 44.44; H 6.63; F 23.43; N 5.79. PMR (δ, ppm): 1.13 t (6H, CH_3), 2.99 q (4H, CH_2), 3.56 (3H, OCH_3), 5.0 (1H, =CH−), 9.3 (2H, $\overset{+}{N}H_2$), ^{19}F NMR (δ, ppm): 88.37 (CF_3).

CONCLUSIONS

By ^1H and ^{19}F NMR spectroscopy it was shown that reaction of fluoroalkyl β-ketoesters with methylhydrazine in deuteromethanol at −30 to 30°C involves intermediate formation of

the β-ketoester salts with methylhydrazine and 3,5-dioxypyrazolidines which successively split off methanol and H_2O with formation of 3-oxypyrazolines and pyrazol-5-ones, respectively.

LITERATURE CITED

1. K. I. Pashkevich and V. I. Saloutin, Usp. Khim., 54, 1997 (1985).
2. V. I. Saloutin, A. N. Fomin, and K. I. Pashkevich, Izv. Akad. Nauk SSSR, Ser. Khim., 144 (1984).
3. M. Cocivera, K. W. Woo, and P. Livant, Can. J. Chem., 56, 473 (1978).
4. A. N. Fomin, V. I. Saloutin, K. I. Pashkevich, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 2626 (1983).
5. S. I. Selivanov, R. A. Bogatkin, and B. A. Ershov, Zh. Org. Khim., 18, 909 (1982).
6. A. L. Henne, M. S. Newman, L. L. Quill, and R. A. Staniforth, J. Am. Chem. Soc., 69, 1819 (1947).

NEW ROUTE TO PERFLUOROTERT-BUTYL IODIDE

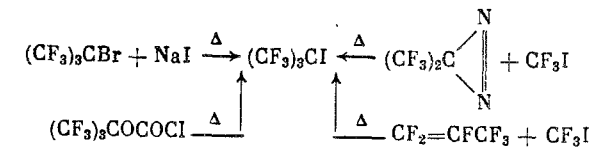
L. E. Deev, T. I. Nazarenko, and K. I. Pashkevich

UDC 542.91:547.226'161:547.413.5'161

Perfluorotert-butyl iodide is a convenient source of the perfluorotert-butyl radical [1].

Preparations of $(CF_3)_3CI$ (I) have included the reaction of hexafluoroethane with tetraiodomethane under electric discharge [2], treatment of $(CF_3)_3CBr$ with iodide using flash CO_2 laser irradiation [3], and iodofluorination of perfluoroisobutylene [1, 4]. However, the complexity of the experimental apparatus and the high toxicity of perfluoroisobutylene do not favor these methods. Our work has concerned a new synthetic method for (I).

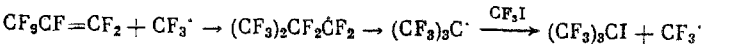
It has been shown that treatment of $(CF_3)_3CBr$ with NaI in aprotic solvents (MeCN, acetone) gave (I) in 5-6% yield. The main product was 2-hydroperfluoroisobutane apparently formed because the highly reactive perfluorotert-butyl anion can remove a proton from the solvent. Treatment of perfluorotert-butyl chloroformate with KI at 180-200°C gave a 30% yield of (I). This reaction probably occurs via formation of an unstable perfluorotert-butyl iodoformate which loses CO_2 on heating.



Heating bis(trifluoromethyl)diazirine with CF_3I to 150-200°C also led to a 10-12% yield of (I).

A high yield of (I) (70-75%) was successfully obtained by co-pyrolysis of hexafluoropropylene with CF_3I in a flow-through reactor at 280-400°C. The ratio of products formed depended upon the temperature, the ratio of reagents, and the reactor material (Table 1).

The proposed formation of (I) can arise by the following scheme:



Apparently the nickel wall of the reactor promotes the isomerization of the perfluoroisobutyl radical to the more stable perfluorotert-butyl as a result of which (I) predominates

Chemistry Institute, Ural Branch, Academy of Sciences of the USSR, Sverdlovsk.

Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 402-404, February, 1988. Original article submitted June 16, 1986.

0568-5230/88/3702-0321$12.50