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REDUCTIVE DEFLUORINATION OF HEXAFLUOROACETONE AND THE SYNTHESIS

### OF HALOPENTAFLUOROACETONES

S. A. Postovoi, I. M. Vol'pin, E. I. Mysov, UDC 542.944.7:547.446.5'161 Yu. V. Zeifman, and L. S. German

Carbonyl compounds containing halogen atoms other than fluorine in the  $\alpha$ -position readily undergo reductive dehalogenation by the action of metals in aprotic media with the formation of enolates of the corresponding metals. Such dechlorination and debromination is characteristic for monohalo derivatives [1] and for aldehydes and ketones with CHCl<sub>2</sub> [2], CCl<sub>3</sub>, CBr<sub>3</sub> [3], or ClCF<sub>2</sub> groups [4]. The reductive defluorination (RDF) of  $\alpha$ -fluoroacarbonyl compounds is usually achieved only with considerable difficulty and has been observed only under conditions leading to the replacement of fluorine by hydrogen [5, 6]. It has also been reported that hexafluoroacetone (HFA) [7-9], trifluoroacetophenone [10], and methyl trifluoropyruvate [11], in contrast to other  $\alpha$ -halocarbonyl compounds, under pinacolization upon the action of metals.

We have discovered that the reaction of HFA with metals gives RDF with the formation of pentafluoropropenolates (II) and the products of their subsequent transformations in addition to reductive coupling to give perfluoropinacol (I).\* The results of the reaction depends on the nature of the metal and solvent.



Thus, the reaction of HFA with Mg in THF gives not only pinacol, as first reported by Middleton and Lindsey [7], but also hydroketones (III) and (IV) as major products. Chromatomass spectrometry also indicated the formation of (V) and  $C_9$  dihydroxyketones. Magnesium enolate (II) upon formation apparently undergoes condensaton with HFA<sup>+</sup> to give the magnesium

+The pentafluoroenolate generated by the deprotonation of pentafluoroacetone or pentafluoro-2propenol (VI) by bases enters an analogous reaction with fluoroketones [13, 14].

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1173-1176, May, 1989. Original article submitted June 17, 1988.

<sup>\*</sup>For previous communication, see [12].

derivative of hydroxyketone (III), which then under goes RDF by two pathways, leading to (IV) and (V) and the products of the subsequent reaction of (V) with HFA. This reaction sequence was supported experimentally. Independently synthesized (III) is reduced by magnesium in THF to form a mixture of hydroxyketones (IV) and (V). Thus, the reaction of HFA with magnesium in complicated by the combination of reductive dimerization, RDF, and the condensation of the intermediate terminal enolates with HFA.

Pinacolization does not proceed in the reaction of HFA with Zn, Cd, or Sn in THF and also with  $SnCl_2$  in DMF. However, RDF in these reactions is accompanied by condensation and a mixture of hydroxyketones is formed. In the latter case, reduction of the carbonyl group of HFA also occurs, which leads to  $(CF_3)_2$ CHOH.

The greatest synthetic interest is found in the reaction of HFA with aluminum. The reaction in this case, is largely terminated upon the formation of aluminum enolate (II), apparently, due to the more covalent nature of the O-Al bond in comparison with the other metals, which reduces the rate of the condensation of (II) with HFA. On the other hand, Al-enolate (II) may be converted by acid hydrolysis to enol (VI)\* and by halogenation to halopentafluoroacetones (VIIa)-(VIIc).

 $CF_{3} \xrightarrow{I} H_{3}SO_{4} (II) \xrightarrow{X_{2}} X - CF_{2}COCF_{3}$   $(VI) \xrightarrow{(VIIa-c)} X = CI(a), Br(b), I(c).$ 

In addition to bromoketone (VIIb),  $CF_3COCFBrC(OH)(CF_3)_2$  (VIII), which is apparently formed from the Al-enolate precursor of hydroxyketone (IV), was isolated from the mixture of RDF products after bromination.

Products (VI) and (VII) are readily separated from the other products by distillation. This permits us to obtain enol (VI) in about 50% yield and haloacetones (VII) in 40-50% yields. This circumstance in addition to the availability of the starting reagents makes the reaction of HFA with aluminum a convenient preparative method for the synthesis of (VI) and (VII) [14].

The reaction of HFA with Al in monoglyme leads to the same products as in THF but the deflorination with Al (or Mg) is suppressed in solvents such as acetonitrile, DMSO, or DMF. Thus, the reaction of HFA with magnesium in DMF gives pinacol (I) in 80% yield, which is almost free of traces of the RDF products. This method for the synthesis of (I) is more convenient than previously reported procedures [8, 15].

We should note that the transformations of HFA usually feature involvement of the carbonyl group, while the fluorine atoms of the trifluoromethyl groups are not affected [16]. The reaction of HFA with Al, which is a unique example of the selective replacement of an  $\alpha$ -fluorine atom in a perfluoroketone by a halogen (or hydrogen)† expands the synthetic possibilities for this class of organofluorine compounds.

# EXPERIMENTAL

The <sup>19</sup>F NMR spectra were taken on a Bruker WP-200SY spectrometer at 188.3 MHz relative to  $CF_3CO_2H$  as the external standard. The mass spectra were taken on a VG-7070E spectrometer at 70 eV. The m/z and intensity (%) values are given along with the proposed assignment. The analytical and preparative gas-liquid chromatography was carried out on columns packed with FS-1265 on chromosorb W.

<u>Reaction of Hexafluoroacetone with Metals</u>. a) A sample of 10 g HFA was added with stirring over 0.5 h to a mixture of 1 g magnesium filings activated by iodine, 0.2 ml metallic mercury and 30 ml THF distilled over LiAlH<sub>4</sub>, maintaining the temperature at 18-20°C. After 1 h, the reaction mass was poured into a solution of one part conc. hydrochloric acid and five parts water. The precipitated oil was extracted with ether. The solvent was distilled off on a water bath. The residue was distilled over conc. sulfuric acid to give 7.1 g of a fraction

<sup>\*</sup>The formation of small amounts of enol (VI) was also encountered in the reactions of HFA with Zn and Sn.

<sup>+</sup>Enol (VI) is readily converted to pentafluoroacetone by the action of bases [14].

with bp up to 60°C (10 mm), which contained 31% hydroxyketone (III) [13], 28% hydroxyketone (IV), 1.5% hydroxyketone (V), and 32% pinacol (I) as indicated by gas-liquid chromatography. Hydroxyketone (IV) was isolated by preparative gas-liquid chromatography, bp 104°C. Found: C 24.76; H 0.81; F 64.14%. Calculated for  $C_6H_2F_{10}O_2$ : C 24.32; H 0.68; F 64.19%. <sup>19</sup>F NMR spectrum( $\delta$ , ppm, in CDCl<sub>3</sub>): -3.3 m (Fa), -0.2 m (Fc), 131 m (Fb). Mass spectrum: m/z (intensity, %): 257 [M<sup>+</sup>-F-HF](1.9); 227 [M<sup>+</sup>-CF<sub>3</sub>] (18.1); 199 [M<sup>+</sup>-CF<sub>3</sub>CO] (6.0); 179 [M<sup>+</sup>-HF-CF<sub>3</sub>CO] (15.2); 147 C<sub>3</sub>F<sub>5</sub>O (4.0); 129 C<sub>3</sub>HF<sub>4</sub>O (9.4); 119 C<sub>2</sub>F<sub>5</sub> (1.5); 97 CF<sub>3</sub>CO (38.5); 79 HCF<sub>2</sub>CO (1.3); 78 CF<sub>2</sub>CO (3.1); 69 CF<sub>3</sub> (100); 60 CFHCO (13.3); 51 HCF<sub>2</sub> (16.9). The spectral data for (V) are given below.

b) A sample of 0.4 g  $HgCl_2$  was added with stirring to 0.9 g Mg and 30 ml abs. DMF in an argon stream. At the end of the exothermal reaction, 10 g HFA was introduced into the mixture at <20°C. After 1 h, the reaction mass was poured into a solution composed of one part conc. hydrochloric acid and five parts water and extracted with ether. The organic layer was evaporated and distilled over conc. sulfuric acid in vacuum to give 8.4 g (80%) pinacol (I) containing less than 2% (IV) as indicted by gas-liquid chromatography.

c) A mixture of 5 g cadmium filings, 0.8 g  $HgCl_2$ , 20 ml THF, and 10 g HFA was stirred in a sealed ampul for five days at 20°C. Ordinary work-up gave 5.8 g (III) containing 15% (IV) as indicated by gas-liquid chromatography.

<u>Reaction of Hexafluoroacetone with SnCl<sub>2</sub></u>. A mixture of 7.3 g anhydrous SnCl<sub>2</sub>, 15 ml abs. DMF, and 6.5 g HFA was heated in a sealed ampul for 29 hat 95°C and poured into a solution composed of one part conc. hydrochloric acid and five parts water. Ordinary work-up gave 2.7 g of a mixture containing 25% (CF<sub>3</sub>)<sub>2</sub>CHOH, 62% (III), 3% (CF<sub>3</sub>)<sub>2</sub>C(OH)<sub>2</sub>, and 4% (IV).

<u>Reaction of Hydroxyketone (III) with Magnesium</u>. A sample of 7.4 g (III) in 5 ml THF was added with stirring to a mixture of 0.7 g magnesium, 0.4 g HgCl<sub>2</sub>, and 25 ml THF at <20°C. Stirring was continued for 0.5 h. Ordinary work-up and distillation over conc. sulfuric acid gave 4.9 g of a fraction with bp 90-108°C containing 22% (III), 63% (IV), and 14% (V). <sup>19</sup>F NMR spectrum of (V) ( $\delta$ , ppm, in CDCl<sub>3</sub>): -2.2 t (Fc), 38.0 t. hept (Fb), 50.7 d. t (Fa), JFa-Fb = 7, JFb-Fc = 10, JFa-H = 52 Hz. Mass spectrum of (V), m/z (intensity, %): 257 [M<sup>+</sup>-F-HF] (1.5); 245 [M<sup>+</sup>-HCF<sub>2</sub>] (0.7); 227 [M<sup>+</sup>-CF<sub>3</sub>] (0.9); 217 [M<sup>+</sup>-HCF<sub>2</sub>CO] (4.2); 197 [M<sup>+</sup>-HF-HCF<sub>2</sub>CO] (6.1); 179 [M<sup>+</sup>-HF - CF<sub>3</sub>CO] (2.5); 200 C<sub>4</sub>F<sub>8</sub> (16.1); 147 C<sub>3</sub>F<sub>5</sub>O (5.5); 129 C<sub>3</sub>HF<sub>4</sub>O (13.1); 119 C<sub>2</sub>F<sub>5</sub> (7.4); 97 CF<sub>3</sub>CO (37.0); 79 HCF<sub>2</sub>CO (17.3); 78 CF<sub>2</sub>CO (7.0); 60 CF<sub>3</sub> (59.4); 60 HCFCO (7.8); 51 HCF<sub>2</sub> (100).

<u>Pentafluoro-2-propenol</u> (VI). A sample of 0.5 g HgCl<sub>2</sub> was added with stirring to 1.6 g aluminum filings, previously treated with 10% aq. KOH, and 35 ml THF distilled over LiAlH<sub>4</sub>. At the end of the exothermal reaction, 16 g HFA was added to the mixture over 0.5 h at 10-15°C, stirred for 1 h at 20-24°C, and evaporated under vacuum at 3 mm. Then, 30 ml conc. sulfuric acid was added to the residue and 12.7 g of a mixture was obtained upon heating up to 100°C (3 mm). Distillation gave 7.4 g (51.7%) enol (VI), bp 53-55°C, which contains about 3% (CF<sub>3</sub>)<sub>2</sub>CHOH as indicated by <sup>19</sup>F NMR spectroscopy.

<u>Halopentafluoroacetones (VII)</u>. 15 ml abs. acetonitrile and 15 g  $Br_2$  in 10 ml acetonitrile was added to the reaction mixture obtained as in the previous experiment after the removal of THF. The mixture was gradually warmed with stirring and a fraction with bp <80°C was distilled off. Distillation of this mixture over cond. sulfuric acid gave 10.8 g (49%) bromoketone, (VIIb) bp 31-33°C, which was shown to be identical to an authentic sample in its gas-liquid chromatographic and NMR parameters [14]. Analogously, the reaction of Al-enolate (II) with  $Cl_2$  gave chloroketone (VIIa) in 45% yield, while the reaction with ICl gave iodoketone (VIIc) in 40% yield.

The reaction mixture after the removal of (VIIb) was poured into a solution composed of one part conc. hydrochloric acid and five parts water. Preparative gas-liquid chromatography of the organic layer gave (VIII). Found: C 19.46, H 0.30, F 50.41%. Calculated for  $C_6HBrF_{10}O_2$ : C 19.20; H 0.27; F 50.67%. <sup>19</sup>F NMR spectrum ( $\delta$ , ppm, in ether): -7.0 and -6.6 m [(CF<sub>3</sub>)<sub>2</sub>C], -5.5 d. q (CF<sub>3</sub>), 57.6 m (CF, JCF<sub>3</sub>-F = 16.2, JCF<sub>3</sub>-CF<sub>3</sub> = 2 Hz).

# CONCLUSIONS

1. Hexafluoroacetone undergoes reductive defluorination upon the action of metals to form perfluoro-2-propenolates of the metals and the products of their subsequent transformations.

2. A new preparative method was proposed for the synthesis of pentafluoro-2-propenol and halopentafluoroacetones based on the reaction of hexafluoroacetone with aluminum.

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SYNTHESIS OF SUBSTITUTED 1-VINYL-2-PYRIDONES AND A <sup>1</sup>H AND <sup>13</sup>C

NMR STUDY OF THEIR STRUCTURE

M. A. Andriyankov, A. V. Afonin and M. V. Nikitin UDC 542.91:543.422.25:547.823

In previous work [1], we showed that unsubstituted 2-aminopyridine reacts with acetylene in the presence of cadmium acetate as catalyst to form 1-viny1-2-pyridone (I). We undertook to determine the scope of this reaction. For this purpose, 3-, 4-, 5-, and 6-methyl-2-aminopyridines and 5-chloro-2-aminopyridine were used in this reaction. In all cases, the corresponding 1-viny1-2-pyridones (II)-(VI) were obtained.



 $R = 3-CH_3(II), 4-CH_3(III), 5-CH_3(IV), 6-CH_3(V), 5-Cl(VI).$ 

The structure of these products were studied in detail by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The spectral parameters of (II)-(VI) and of 1-viny1-2-pyridone (I) are given in Tables 1 and 2.

The PMR spectra of (II)-(V) have signals for the corresponding vinyl protons (HA, HB, and HX, Table 1), while their <sup>13</sup>C NMR spectra have signals for the vinyl group carbon atoms ( $C_{\alpha}$  and  $C_{\beta}$ , Table 2). The vicinal coupling constants for the vinyl group protons (<sup>3</sup>JAX = 8.3-9.1 Hz and <sup>3</sup>JBX = 15.8-16.1 Hz) indicate the formation of N-vinyl products [2-6]. The <sup>13</sup>C NMR spectra of (II)-(VI) have signals for the carbonyl group carbon atom( $\delta C^2$  159.48-163.23 ppm). Thus these products are N-vinyl-2-pyridone derivatives.

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