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THE DIRECT FLUORINATION OF ACETONE

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SUMMARY

A synthesis for hexafluoroacetone using elemental fluorine is reported. Previously hexafluoroacetone and other ketones have been difficult to prepare using fluorination based syntheses.

INTRODUCTION

Hexafluoroacetone is a moderately toxic, reactive, nonflammable gas. The inductive effect of fluorine causes the carbonyl bond to become highly susceptible to attack by nucleophilic reagents [1]. This reactivity makes hexafluoroacetone a useful reagent in the synthesis of new polymers [2], pharmaceuticals, and agrochemicals [3].

The commercial production of hexafluoroacetone involves a halogen exchange reaction between hexachloroacetone and hydrogen fluoride using a chromium catalyst [4,5]. Other methods for the synthesis of hexafluoroacetone have been explored. The oxidation of perfluoroisobutylene with $KMnO_4$ [6], the oxidation of hexafluoropropylene over fluorinated Al_2O_3 catalyst [7], or isomerization of hexafluoropropylene oxide with cesium fluoride in acetonitrile [8]. Acetone has been subjected to direct fluorination using jet reactor [9], low temperature gradient [10], and porous tube reactor conditions [11] with varying results. The fluorination of acetone has been reexamined here to try to improve the results using the low temperature gradient method.

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EXPERIMENTAL

Acetone was purified by distillation from its sodium iodide adduct. Sodium fluoride was ground to -120 mesh and dried at 150 °C. Fluorine was reagent grade (Air Products).

Acetone (1.00 grams) was mixed with 10 grams of dry sodium fluoride powder. The reactor has been previously described [12]. The starting material mixture was evenly distributed over the copper turnings in the reactor cavity. The reactor was cooled to -50 °C and purged overnight with a 60 cc min^{-1} flow of helium. The reactor was then cooled to -100 °C and the fluorination begun. The fluorination conditions are outlined in Table 1. The glass product trap was kept at -196 °C throughout the reaction.

RESULTS

Upon completion of the fluorination process the trap contents were separated on a vacuum line into -78 °C, -131 °C, and -196 °C fractions with the majority collecting in the -131 °C trap. The contents of the -78 °C trap turned from clear to brown in a short time. Infrared analysis of this material showed a large carbonyl stretch and a C-H stretch, probably due to partially fluorinated acetone and acid fluorides. The -131 °C fraction was transferred to an evacuated steel cylinder. The weight of the crude product was 2.78 grams. The crude product was separated on a Hewlett-Packard 5880A gas chromatograph, using a 1/4 inch by 10 foot stainless steel column packed with 25% OV-101 on 60/80 mesh Chromosorb A. The samples were run at 30 °C isothermal with a helium flow of 45 cc min^{-1}.

Infrared analysis was performed on a Biorad Digilabs FTS-40 Fourier Transform infrared spectrometer. All samples were run in a 10 cm gas cell equipped with KBr windows. Mass spectrometry was performed on a Bell and Howell CEC 21-491.

The product was found to be 39% hexafluoroacetone, identified by comparison with a commercial sample (PCR, Inc.). Two other components were identified by infrared and mass spectral analysis as trifluoroacetyl fluoride and octafluoropropane.

TABLE 1

Fluorination conditions for acetone

He (cm^3 min^{-1})	F_2 (cm^3 min^{-1})	Temperature (°C)	Time (hours)
20	1	-100	18
20	2	-100	18
20	3	-100	24
20	4	-100	24
10	4	-100	24
0	4	-100	24
0	4	-90	18
0	4	-80	18
0	4	-60	18
0	4	-40	18
60	0	25	24

DISCUSSION

The reactor used by Bigelow in the jet fluorination reaction of acetone represents a very vigorous fluorination system. In a typical reaction, acetone and fluorine were introduced into a heated brass reaction zone packed with copper gauze. The reaction zone was heated to 60 °C initially but the temperature would rise considerably as the reaction progressed. The gas volume ratios of fluorine to acetone were varied from 2:1 up to 6:1 with a fluorine flow rate of 1800 cc $hour^{-1}$. Compared to the low temperature gradient fluorination system used in this laboratory, this represents a very energetic reaction system.

Bigelow postulated a radical mechanism to explain the products obtained from the jet fluorination of acetone [9]:

(1) $F_2 \rightarrow 2F\cdot$

(2) $CH_3COCH_3 + F\cdot \rightarrow CH_3COCH_2\cdot + HF$

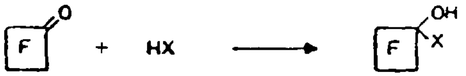
(3) $CH_3COCH_2\cdot + F_2 \rightarrow CH_3COCH_2F + F\cdot$
until CF_3COCF_3 is formed. Then

(4) $CF_3COCF_3 + F\cdot \rightarrow CF_3CO\cdot + CF_4$

He considered the interaction of fluorine with the carbonyl carbon unlikely since no octafluoropropane was observed. Under jet fluorination conditions of high fluorine concentration and high temperature, a radical mechanism would surely dominate. The combination of thermally excited reactant molecules and high concentration of fluorine radicals would be expected to lead to extensive degradation of the reactant molecule and low yield for the reaction.

The difference between Bigelow's reaction system and the low temperature gradient process is immediately obvious. In the Bigelow jet reactor, no attempt is made to control the energetics of the reaction. A large amount of fluorine is mixed with the hydrocarbon and made to react quickly. The energy imparted to the molecules by the replacement of hydrogen by fluorine is not allowed to dissipate before further reaction. The low temperature gradient fluorination system is designed to dissipate the considerable heat of reaction produced by the replacement of hydrogen by F_2. In the case of the low temperature gradient reaction, other processes must be occurring to reduce the amount of hexafluoroacetone produced.

In the low temperature fluorination process, the presence of hydrogen fluoride (m.p. -83.55 °C, b.p. 19.51 °C) by-product must be considered. The addition of HX (X = any of the four halogens) to aldehydes and ketones gives the α-haloalcohol [13,14]. In solution these compounds are unstable and an equilibrium is rapidly established. The only isolated α-halohydrin has been prepared by the addition of HX to perfluorocyclobutanone [15].



X = F,Cl,Br,I

The reaction of fluorine on fluoroalcohols produces fluoroxy fluoroalkanes (hypofluorites) [16]. Further fluorination would lead to the formation of the fluoroalkane while decomposition of the hypofluorite would yield the acid fluoride and CF_4.

$$(R_F)_2CO + HF \longrightarrow (R_F)_2CFOH$$

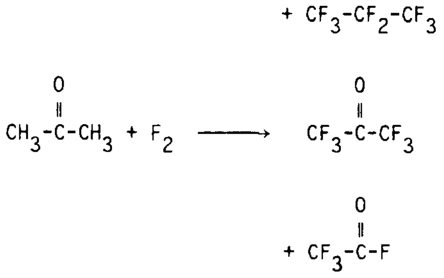
$$(R_F)_2CFOH + F_2 \longrightarrow (R_F)_2CFOF \xrightarrow{F_2} (R_F)_2CF_2$$

$$(R_F)_2CFOF \xrightarrow{\Delta} CF_4 + R_F\text{-}C(O)F$$

The lack of octafluoropropane in the jet fluorination product may be due to the combination of high temperature and high fluorine concentration. The high concentration of fluorine would assure that partial replacement of H for F would occur quickly. Since the basicity of a ketone is significantly reduced as halogen content increases [17,18], the reaction of the ketone with HF would be less likely to occur. The high temperature of the reactor would assure the quick decomposition of any hypofluorite that may be produced.

The addition of sodium fluoride to the low temperature direct fluorination system allows more of the ketone to be gently fluorinated to hexafluoroacetone. Free HF is absorbed to form sodium bifluoride ($NaHF_2$), which would otherwise react with acetone to yield α-halohydrin. Decreasing the acidity of the environment of the reaction appears to reduce the amount of side reactions that can occur, increasing the yield of the desired product.

From the consideration of the products obtained by the different reaction schemes, it appears that the optimum yield of hexafluoroacetone by direct fluorination should be realized in a system which would allow quick initial fluorination of acetone without the high temperatures which lead to carbon-carbon bond cleavage. The good yield of hexafluoroacetone from the direct reaction of elemental fluorine on acetone represents another important development in the field of fluorine chemistry. The conditions listed for the reaction were not optimized to give the maximum yield of hexafluoroacetone. Optimization of the direct fluorination reaction may increase the industrial importance of this method as a direct route to some useful perfluorinated compounds.



$$CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + F_2 \longrightarrow CF_3\text{-}CF_2\text{-}CF_3 + CF_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}CF_3 + CF_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}F$$

ACKNOWLEDGEMENT

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