white needles, m.p. 261–263° (water); λ_{max}^{EtOH} 226 mμ (ϵ 25,200), 262 mμ (ϵ 4,000), 268 mμ (ϵ 4,700) and 271 mμ (ϵ 3,900).

Anal. Calcd. for $C_{23}H_{24}PBr$: C, 67.2; H, 5.9; P, 7.5; Br, 19.4. Found: C, 67.0; H, 5.8; P, 7.7; Br, 20.1.

Triphenylcyclopentylphosphonium Bromide (VII) from Triphenylphosphoniumcyclopentadienylide (V).—A solution of the phosphinemethylene (V, 0.245 g.) in 30 ml. of water containing 5 ml. of 20% hydrobromic acid was hydrogenated at atmospheric pressure using 109 mg. of PtO_2 catalyst. After 24 hours, a 43-mg. portion of fresh catalyst was added. Two additional portions of fresh catalyst had to be added before reduction was complete; total volume of hydrogen absorbed, 41.7 ml.; calculated, 37.7 ml. Removal of the water and recrystallization of the colorless residue from the minimum amount of water gave a substance, m.p. 259–261°, shown to be identical with authentic triphenylcyclopentylphosphonium bromide (VII) (infrared spectra and mixed m.p.).

The phosphinemethylene (V) was recovered unchanged when thiophene-free benzene solutions were shaken with hydrogen in the presence of PtO_2 catalyst at atmospheric pressure or at 50 pounds pressure.

NEW YORK 27, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF FLORIDA]

A New Synthesis of Simple Fluorocarbon Tertiary Amines[1]

BY RICHARD DRESDNER

RECEIVED JULY 2, 1956

Both $(CF_3)_3N$, tris-(trifluoromethyl)-amine and bis-(trifluoromethyl)-pentafluoroethylamine, have been synthesized by the reaction of $CF_3N{=}CF_2$, perfluoro-2-azapropene, with CF_3SF_5, trifluoromethylsulfur pentafluoride, and $C_2F_5SF_5$, perfluoroethylsulfur pentafluoride, respectively. The preparation of both $C_2F_5SF_5$ and $(C_2F_5)_2SF_4$, bis-(perfluoroethyl)-sulfur tetrafluoride, and their simple physical properties are described. A simple vapor pressure equation, the heat of vaporization, boiling point, freezing point and Trouton's constant for $(CF_3)_3N$ have been measured or calculated.

Introduction

Preparations for both $(CF_3)_3N$[2] and $(CF_3)_2NC_2F_5$[3] are described in the chemical literature. This paper describes their preparation using perfluorinated reactants, namely, $CF_3N{=}CF_2$, perfluoro-2-azapropene[4,5] and CF_3SF_5, trifluoromethylsulfur pentafluoride and $C_2F_5SF_5$, pentafluoroethylsulfur pentafluoride.

The thermal reaction of CF_3SF_5 with the fluorocarbon olefin $CF_3CF{=}CF_2$, perfluoropropene, produced C_4- to C_8-fluorocarbons with the elimination of SF_4.[6] It has been demonstrated in this work that when CF_3SF_5 and $C_2F_5SF_5$ are allowed to react thermally with $CF_3N{=}CF_2$, $(CF_3)_3N$ and $(CF_3)_2NC_2F_5$ result in reasonable yields. Uniquely, the fluorocarbon portions of the fluorocarbon sulfur compounds attach themselves to the nitrogen atom while one atom of fluorine, in each case, adds to the existing ${=}CF_2$ group of $CF_3N{=}CF_2$. Neither reaction occurs appreciably until the decomposition temperatures of the fluorocarbon sulfur compounds are reached or exceeded. For example, CF_3SF_5 decomposes 20% by weight at 500° in a flow system at atmospheric pressure,[6] while $C_2F_5SF_5$ decomposes 100% under the same conditions forming C_4F_{10}, SF_4 and other low boiling sulfur fluorides. In a closed system under pressure, CF_3SF_5 and $C_2F_5SF_5$ decompose completely at 423 and 380°, respectively.

Experimental

Materials.—CF_3SF_5 and $(CF_3)_2SF_4$, bis-(trifluoromethyl)-sulfur tetrafluoride, were prepared electrochemically in an anhydrous HF solution of methyl sulfide.[7,8] The respective yields of the sulfur compounds are 50 and 8% based on the current passed.

$CF_3N{=}CF_2$ (b.p. −33°, mol. wt. 133) was prepared by pyrolysis of $(CF_3)_2NCOF$, bis-(trifluoromethyl)-carbamyl fluoride, at 615°.[5]

$C_2F_5SF_5$ was prepared electrochemically in an anhydrous HF solution of ethyl sulfide. The co-product $(C_2F_5)_2SF_4$ was also isolated in small yields. These two substances are unreported compounds. They were carried over in the gas stream from an electrochemical (Simon's) cell and were trapped in a Dry-Ice cooled condenser after the gas stream from the cell had been passed over lime and bubbled through NaOH solution. An attempt was made to retain the cell solution at a mole ratio of about 0.005 sulfide/HF. About 3 moles of ethyl sulfide was used in preparing 0.84 mole of $C_2F_5SF_5$ and 0.087 mole of $(C_2F_5)_2SF_4$. One hundred and twenty-five grams of other fluorine-containing substances boiling above −54° was collected. No attempt was made to trap products boiling below this.

These two materials were identified by molecular weight and elemental analyses. The elemental analyses were performed similarly to those reported by Silvey and Cady[9] with the exceptions that the fusions were done in a sealed glass tube at 640° and the $S^=$ ion was removed with an exact quantity of Ag^+ before titration for F^-. At least two fusions were made with each compound and three aliquots of each fusion analyzed.

Anal. Calcd. for C_2SF_{10}: F, 77.3; S, 13.0; mol. wt., 246. Found: F, 77.3 ± 0.4; S, 12.8 ± 0.10; mol. wt., 244–247; b.p. 11.3°. Calcd. for C_4SF_{14}: F, 76.9; S, 9.25; mol. wt., 346. Found: F, 76.5 ± 0.3; S, 9.22 ± 0.12; mol. wt., 344–347; b.p. 68.0°; $n^{25}D$ 1.2753; d_{25} 1.878$_5$; MRD 31.81.

It is of interest to note that $(CF_3)_2SF_4$, isomeric with $C_2F_5SF_5$, has a reported b.p. of 20.5°.[5] Also $C_4F_9SF_5$, isomeric with $(C_2F_5)_2SF_4$, has the properties b.p. 70.0°, $n^{25}D$ 1.2710, d_{25} 1.8451 and MRD 31.92.[10]

Reaction of $CF_3N{=}CF_2$ with CF_3SF_5.—The equipment for the reaction between CF_3SF_5 (b.p. −20.5°) and $CF_3N{=}CF_2$ (b.p. −33°) has been described.[1] The reactor was filled

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[1] This work was supported by the Chemistry Branch of the Office of Naval Research and reproduction of all or any part of this paper for purposes of the United States Government is permitted.

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[9] G. A. Silvey and G. H. Cady, THIS JOURNAL, **72**, 3624 (1950).

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with $^1/_8''$ NaF pellets. Twenty-eight grams (0.21 mole) of $CF_3N{=}CF_2$ and 44 g. (0.23 mole) of CF_3SF_5 were run through a nickel tube filled with $^1/_8''$ NaF pellets at 519° and 1 atm. pressure at a mass rate of 0.18 g./min. The materials boiling below −35° and above −12° were removed by fractionation and retained. That boiling between −35 and −12° was further augmented by 9 g. of CF_3SF_5 and passed through the reactor at 540°. The products of both trials were fractionated and were essentially: 8 g. of C_2F_6, 23 g. of SF_4 (and other sulfur fluorides), 4.5 g. of unreacted $CF_3N{=}CF_2$ (from NH_3 evolved on hydrolysis), 10 g. of unreacted CF_3SF_5, 23.5 g. of $(CF_3)_3N$ and 4 g. of unidentified material with a boiling range above 0°. The $(CF_3)_3N$ was obtained from the fractionation at temperatures between −11.3 and −10.7°. The m.p. was −114.7 ± 0.5°. The v.p. curve fits the equation

$$\log_{10} p_{\text{mm.}} = \frac{1250}{T, ^\circ\text{K.}} + 7.61$$

well between −80 and −10°. The calculated b.p. is −10.9°, H_v = 5680 cal./mole and Trouton's constant 21.6. The sharp m.p. indicated that it was a pure compound and not a mixture of isomers. NMR spectrum analysis[11] confirmed the structure as that required for $(CF_3)_3N$. It showed only a single F^{19} resonance component located at $\delta = +0.3$ with respect to benzotrifluoride, $\delta = 10^5(\text{Hr} - \text{Hc})/\text{Hc}$. At a later date this was reconfirmed by a comparison infrared spectrum with material from an independent source.[12]

Attempted Reaction with $(CF_3)_2SF_4$ and $CF_3N{=}CF_2$.—Using the same equipment, 24 g. (0.1 mole) of $(CF_3)_2SF_4$ and 13.5 g. (0.1 mole) of $CF_3N{=}CF_2$ were allowed to react at 520°, one atmosphere pressure and a mass flow rate of 0.15 g./min. Equimolar concentrations were obtained by bubbling the lower boiling reactant, $CF_3N{=}CF_2$, through the higher boiling one at a temperature of about 4° (v.p. 400 mm.) before passing them into the reactor. After the trial, 96% of the $CF_3N{=}CF_2$ was recovered unreacted while 2.0 g. of CF_4, 7.5 g. of C_2F_6, 5.5 g. of SF_4 and 4.5 g. of CF_3SF_3 were found. Almost no $(CF_3)_2SF_4$ was recovered but some material with a greater molecular weight, *viz.*, 253 to 285 was found. From the products recovered and identified, it appeared that the reactions involved were two simultaneous disproportionations as indicated by the equations

$$(CF_3)_2SF_4 \longrightarrow C_2F_6 + SF_4 \ 65\%$$

$$(CF_3)_2SF_4 \longrightarrow CF_3SF_3 + CF_4 \ 35\%$$

Trifluoromethylsulfur trifluoride is a derivative of SF and like it is completely destroyed by aqueous base. It was recovered from fractionation at −6 to −5° (reported −7°).[13]

Anal. Calcd. for CSF_6: F, 72.2; S, 20.3; mol. wt., 158. Found: F, 73.2; S, 18.8; mol. wt., 158.

CF_3SF_3 will attack Pyrex glass slowly at room temperature over a period of months, apparently forming high molecular weight solid silicon fluorides (dec. *circa* 300°).

Reaction of $CF_3N{=}CF_2$ with $C_2F_5SF_5$.—In order to attempt to get greater conversion in this reaction, it was performed in a 500-ml. stainless steel pressure reaction vessel (Hoke) with a pressure gage and valve attached. Thirteen grams (0.1 mole) of $CF_3N{=}CF_2$ and 24.5 g. (0.1 mole) of $C_2F_5SF_5$ were condensed into the vessel, which was heated in a vertical furnace. Temperatures were observed by placing a chromel–alumel thermocouple in the wall of the furnace. Heat was applied slowly, so that the average temperature rise was 2°/min. The slope of the *P vs. T* curve was zero or negative between 372 and 384° indicating a reaction in this temperature range at 12 atm. Above this temperature the pressure rose gradually with temperature and the heating was discontinued. The products were removed from the vessel and examined. In the fractionation, 3.5 g. of C_2F_6, 11.5 g. of SF_4, 5 g. of $CF_3N{=}CF_2$, 6 g. of an azeotrope partly destroyed by dilute aqueous base, b.p. −8 to −6°, mol. wt. 169–172, and 7.5 g. of material boiling at 20.5° identified as $(CF_3)_2NC_2F_5$, mol. wt. 268–272 (calcd. 271) were isolated.[3] Curiously, no C_4F_{10} was detected. Losses and intercuts accounted for the rest of the material. $(CF_3)_2NC_2F_5$ was subjected to NMR spectrum analysis[11] and the resultant lines corresponded to the CF_2, $C{=}CF_3$ and $N(CF_3)_2$ peaks found in pure samples of $(CF_3)_3N$ and $(C_2F_5)_3N$. There was no evidence of any $CF_3NF(C_3F_7)$ isomer present. Again based on the unrecovered amount of $CF_3N{=}CF_2$ the reaction yield to produce $(CF_3)_2NC_2F_5$ was 46%.

Acknowledgments.—The author wishes to thank the Chemistry Branch of the Office of Naval Research for its support of this work. Our thanks are extended to Dr. H. S. Gutowsky and Mr. Apollo Saika for performing and interpreting the Nuclear Magnetic Resonance spectra cited in this work. My profound thanks to my colleague Dr. J. A. Young for his contribution of a sample of perfluoro-2-azapropene and to Dr. T. J. Brice for physical data on perfluorobutylsulfur pentafluoride.

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[11] Analysis and interpretation made by Dr. H. S. Gutowsky and Mr. Apollo Saika, Dept. of Chemistry, Univ. of Illinois, Urbana Ill.; more detailed NMR results to be published by them at a later date.

[12] Sample obtained from Dr. J. A. Young, University of Florida.

[13] E. A. Tyczkowski and L. A. Bigelow, THIS JOURNAL, **75**, 3523 (1953).

GAINESVILLE, FLORIDA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

Effect of Structure on Reactivity. XI. Hydrazinolysis of Ethyl Acetate

BY RICHARD A. FERREN, JOHN G. MILLER AND ALLAN R. DAY

RECEIVED JUNE 28, 1956

The effects of a number of hydroxylated solvents on the hydrazinolysis of ethyl acetate have been determined. In all cases increases in reaction rates were observed.

The reaction of ethyl acetate with hydrazine, as catalyzed by aliphatic alcohols, has been investigated. The effects of these solvents on the rates of hydrazinolysis have been determined and the energies and entropies of activation for the reactions have been calculated. These reactions are similar in many ways to the ammonolyses and aminolyses of esters which have been reported earlier.[1] The previous work showed that the effects of solvents on reaction rates often are quite complex. It was hoped that a quantitative study of the action of certain solvents on the hydrazinolysis of ethyl acetate would produce new and useful information concerning these effects.

In order to study the action of hydroxylated solvents on the rates of hydrazinolysis, the following solutions of reactants and solvents were used:

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