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figuration had been maintained throughout all esterifications and saponifications. The linkage between the oxygen and carbon of the alcohol had been maintained at all times and the mechanism of the reaction is the same regardless of the strength of the acid.

Experimental

The neopentyl alcohol was prepared by the Grignard reaction from *t*-butyl chloride and formaldehyde gas. The latter was prepared by heating paraformaldehyde dried *in vacuo* over concentrated sulfuric acid for five days. Satisfactory yields of the acetates were obtained by standard methods.

The esters were hydrolyzed by 25% potassium hydroxide. The alcohol produced in each case was dried and the *p*-nitrobenzoate and the 3,5-dinitrobenzoate were made. No depressions in mixed melting point determinations were found, indicating that the alcohol obtained upon saponification was in each case neopentyl alcohol.

Table I and Fig. 1 summarize the experimental data obtained.

Summary

Neopentyl acetate, chloroacetate, dichloroacetate and trichloroacetate have been prepared, hydrolyzed and the resulting alcohol identified as neopentyl alcohol. No evidence of any rearrangement of the neopentyl group was obtained.

The refractive index, specific gravity at three temperatures, and boiling points at four pressures have been determined for each of the esters prepared.

The melting points of the 3,5-dinitrobenzoate and the p-nitrobenzoate of neopentyl alcohol are reported.

The conclusions are drawn (1) that in the esterification of alcohols by carboxylic acids varying in strength from that of glacial acetic to that of trichloroacetic, the water removed is composed of the hydrogen from the alcohol and the hydroxyl from the acid; (2) that in the hydrolysis of these esters the rupture of the carbon-oxygen linkage occurs between the oxygen of the alcohol residue and the carbon of the acid group.

Emory University, Georgia

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

The Action of Elementary Fluorine Upon Organic Compounds. VIII. The Influence of Dilution on the Vapor Phase Fluorination of Ethane¹

By DeWalt S. Young, Nobukazu Fukuhara and Lucius A. Bigelow

In a previous paper of this series² we have described the vapor phase fluorination of ethane, using the pure gases in progressively varying proportions. The chief products were carbon tetrafluoride and hexafluoroethane, together with some higher boiling, partially fluorinated material, the liquid volume of which never exceeded 30% of the total condensate. This paper presents the results obtained when the fluorine was diluted progressively with nitrogen. They showed that the yield of the desired fluoroethanes could be raised to 90% of the total condensate under appropriate conditions.

The fluorinations were run in a metal apparatus, over copper gauze, as described before,² except that nitrogen, measured by a flowmeter, was introduced into the fluorine line. Two reaction chambers were used in series at the three highest dilutions, and adequate precautions taken throughout to avoid back pressure. The products were subsequently rectified in a Booth– Podbielniak low temperature fractionating unit,² and the higher boiling constituents divided into a number of empirically chosen cuts, from which pentafluoroethane CF₈CHF₂, *sym*-tetrafluoroethane CHF₂CHF₂, and 1,1,2-trifluoroethane CHF₂CH₂F were later isolated. However, no mono- or difluoroethanes were found, even when the fluorine was highly diluted.

Since it is known that alkyl monofluorides such as ethyl fluoride tend to be unstable, and also that ethylene fluoride decomposes spontaneously at 0° ,³ it seemed possible that these compounds, if formed at all, might have been decomposed immediately over the catalyst at the temperature of the reaction zone. Granting this, the fluorination

(3) Henne and Midgley, *ibid.*, **58**, 882, 884 (1936).

⁽¹⁾ This paper has been constructed in part from portions of Mr. Young's Doctorate Thesis, presented to the Graduate School of Duke University in October, 1939.

⁽²⁾ Calfee, Fukuhara and Bigelow, THIS JOURNAL, 61, 3552 (1939).

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The Products Obtained by Rectifying the Fluorinated Ethane												
Liquid volume % of material boiling	2.3:1:0) ^a 2:1:2	Ga 2:1:4	as volu 2:1:6	me rati 2:1:8	io of flu 4:1:0ª	orine to 4:1:4	ethane t 4:1:8	o nitro; 4:1:12	gen	4:1:40	4:1:80
All $< -105^{\circ}$ (mostly CF ₄)	10	5	5	5	0	20	Trace	5	5	Trace	0	0
-104° (Azeotrope A ²)	15	0	0	0	0	20	0	0	0	0	0	0
- 96° (Azeotrope B ²)	50	4 0	25	15	15	15	5	0	0	0	0	0
— 89° (Ethane)	0	25	25	50	50	0	0	0	0	0	0	0
 78° (Hexafluoroethane) 	5	0	0	0	0	30	25	30	0	0	0	0
$-50 \text{ to } -40^{\circ}$		5	10	5	10		20	20	25	30	30	30
-40 to -35°		5	5	10	5	• •	Trace	0	0	0	0	0
$-35 \text{ to } -28^{\circ}$		Trace	5	5)			Trace	5	0	0	0	0
$-28 \text{ to } -19^{\circ}$	• •	10	10	10 }	30		15	15	4 0	40	35	20
$All > -19^{\circ}$		10	15	15			20	15	25	20	25	30
$A11 > -78^{\circ}$	15	30	45	45	45	15	55	55	90	90	90	80
Total vol. of condensate for 10 hr. in ml.	20	23	23	22	22	14	14	14	12	9_{9}	85	10

TABLE I THE PRODUCTS OPTAINED BY RECTIONING THE RELIGENATED FTUAND

^a From ref. 2 for comparison. ^b After the removal of SiF₄.

of ethane may perhaps be represented simply as follows.

$$C_{2}H_{6} \xrightarrow{F_{2}} CH_{8}CH_{2}F \xrightarrow{-HF} CH_{2} \xrightarrow{F_{2}} CH_{2}F \xrightarrow{-HF} CH_{2} \xrightarrow{F_{2}} CH_{2}F \xrightarrow{-HF} CHF \xrightarrow{F_{2}} CHF_{2} \xrightarrow{F_{2}} CHF_{2} \xrightarrow{-CHF_{2}} \xrightarrow{F_{2}} CHF_{2} \xrightarrow{-CHF_{2}} \xrightarrow{F_{2}} CF_{3}CHF_{2} \xrightarrow{F_{2}} C_{2}F_{6}$$

This formulation, naturally, is to be regarded as subject to further experimental confirmation, but it is supported to some extent by the observations of Hass, McBee and Weber, working with vapor-phase chlorination.⁴ They noted that such thermal decompositions took place to a greater extent in the presence of free chlorine than when the corresponding alkyl halides were heated This was in accord with their free radical, alone. chain mechanism for chlorination, which would seem to apply equally well to fluorination. They also state that in vapor phase chlorinations, there is a tendency against the formation of dihalides with two chlorine atoms attached to the same carbon atom. Correspondingly, the suggested scheme does not predict the formation of the compound CH_3CHF_2 , or even of CH_3CF_3 , and actually neither of these was found.

Table I shows the quantities of the original fractions produced, expressed in liquid volume per cent. of the total condensate in the same run, as compared with the gas volume ratios of the reactants. In order to make the recorded values really significant, the figures have been rounded off to the nearest 5%, but naturally this increased considerably the deviation of the total from one hundred in some cases.

Two series of runs were made, in which the volume ratios of fluorine to ethane were 2:1 and 4:1, respectively. In the first case, the pro-(4) Hass. McBee and Weber, Ind. Eng. Chem., **28**, 333 (1936).

portion of the product boiling higher than hexafluoroethane (-78°) rose progressively to 45%when the ratio of fluorine to nitrogen was 1:2; after which further dilution had but little effect, and much of the ethane was being recovered unchanged. When the figures were recalculated on the basis of the ethane actually fluorinated, this value continued to rise to 95%, when the fluorine to nitrogen ratio was 1:4. In the second series, it should be noted that when the dilution ratio exceeded 1:3, essentially no organic product boiling below -50° was obtained. However, due to the incomplete absorption of hydrogen fluoride under these conditions, the material contained a considerable amount of silicon tetrafluoride. This compound has no liquid range at atmospheric pressure, sublimes at -90° , and was difficult to handle in the still. In this series, in which most of the ethane reacted, the proportion boiling above -78° rose to 90% when the dilution ratio was 1:3, after which there was little further change even when the ratio was increased to 1:20. From these results it was clear that the higher boiling, partially fluorinated ethanes readily could be formed in excellent yield by diluting the fluorine appropriately with nitrogen. It will be seen also that as the dilution was increased, distinct accumulations of material, amounting under favorable conditions to 30-40% of the total condensate were formed in the boiling ranges of -50to -40° , -28 to -19° , and above -19° ; while less and less of the product boiled below -50° , as would be expected. The sudden disappearance of hexafluoroethane, and the corresponding increase in the fraction boiling from -28 to -19° when the dilution ratio was increased above 1:2, are worthy of note. Also, in considering the results it should be recognized that in these experiments no attempt has been made to control either May, 1940

the temperature of the reaction zone or the time required for the gases to pass through it. We hope to make a study of the influence of these important factors later on.

Although a constant boiling fraction (b. p. about -48°) had been observed from the first,⁵ repeated distillation of the product boiling from -50 to -40° at atmospheric pressure failed to separate 'it into pure components. However, on redistillation at elevated pressure, a pure compound was isolated, boiling at -38° at 1200 mm., and -48.5° at atmospheric pressure. It froze sharply at -103° , and had a molecular weight of 119. This was the hitherto unknown pentafluoroethane, CF_3CHF_2 (mol. wt. 120).

Anal. Calcd. for C₂HF₅: F, 79.2. Found: F, 79.0, 79.1.

When the material boiling in the range from -28 to -19° was distilled at reduced pressure, a fraction was isolated, boiling at -46 to -50° at 200 mm., which on redistillation at atmospheric pressure yielded another pure compound boiling from -23.5 to -22.5° with a molecular weight of 101-102. This was sym-tetrafluoroethane (b. p. $-23^{\circ},^{6}$ mol. wt. 102).

Anal. Calcd. for $C_2H_2F_4$: F, 74.5. Found: F, 74.5, 74.2. Most of the product boiling above -19° consisted of a third pure compound, boiling at 3°, and freezing at -84° , with a constant molecular weight of 84. This was undoubtedly 1,1,2-trifluoroethane (b. p. 5°,⁶ mol. wt. 84). Anal. Calcd. for $C_2H_3F_3$: F, 67.8. Found: F, 67.8, 67.9.

(5) Calfee and Bigelow, THIS JOURNAL, 59, 2072 (1937).

(6) Henne and Renoll, ibid., 58, 887, 889 (1936).

In addition to these compounds, a small amount of material was isolated boiling at -56 to -55° , and freezing at -132° , with a molecular weight of 103, but the quantity obtained was insufficient for analysis. Also, a constant boiling mixture, b. p. -19° , mol. wt. 92-98, was obtained, at times in considerable amounts, as well as small quantities of other materials, but these were not separated. No trace of ethyl fluoride (b. p. -38°) was found, even in a special run in which the ratio of fluorine to ethane was 2:6, although in this case over a quarter of the product boiled in the vicinity of 26° with a molecular weight of 70-75.

The writers are glad to express here their appreciation to Mr. Elbert H. Hadley for valuable assistance, and to the Duke University Research Council for a grant.

Summary

A study has been made of the influence of nitrogen dilution on the vapor-phase fluorination of ethane, and it has been found that a mixture of partially fluorinated ethanes can be obtained in excellent yield under suitable conditions.

Pentafluoroethane CF₃CHF₂, sym-tetrafluoroethane CHF₂CHF₂ and 1,1,2-trifluoroethane CHF₂CH₂F have been isolated from the reaction products boiling above -78° . The first of these is a new compound, and the others have not been prepared previously by direct fluorination.

DURHAM, NORTH CAROLINA RECEIVED JANUARY 19, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

The Synthesis of Some New Pyrimidines and Uric Acids fom Cystamine¹

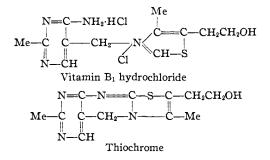
By Edward James Mills, Jr., 2 and Marston Taylor Bogert

Attention recently has been directed increasingly to the important role played by various organic sulfur compounds concerned with vital physiological processes, and the present paper is a contribution in a field whose exploration seems to hold promise of interesting and perhaps useful results.

The great therapeutic value of Vitamin B_1 , and its structural relationship to thiochrome, suggests the possibility of discovering other remedial drugs containing both the pyrimidine and thiazole nuclei, perhaps even when these two cycles have coalesced to a single bicyclic system with two atoms common to each of its constituent rings.

(1) Presented before the Organic Division at the Cincinnati Meeting of the American Chemical Society, April 8, 1940.

(2) E. R. Squibb & Sons Research Fellow at Columbia University, 1937-1939; present address, Department of Anatomy, College of Physicians and Surgeons, Columbia University, New York. Fusion of the pyrimidine and thiazole, or of the purine and thiazole, cycles obviously will result in different structures depending upon the points of attachment of the two rings.



The polycyclic systems with which this communication deals are represented by skeletons (A), (B), (C) and (D):