

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.

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## The Action of Elementary Fluorine Upon Organic Compounds. VIII. The Influence of Dilution on the Vapor Phase Fluorination of Ethane<sup>1</sup>

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In a previous paper of this series<sup>2</sup> 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,<sup>2</sup> 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,<sup>2</sup> and the higher boiling constituents divided into a number of empirically chosen cuts, from which pentafluoroethane  $\text{CF}_3\text{CHF}_2$ , *sym*-tetrafluoroethane  $\text{CHF}_2\text{CHF}_2$ , and 1,1,2-trifluoroethane  $\text{CHF}_2\text{CH}_2\text{F}$  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°,<sup>3</sup> 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

(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).

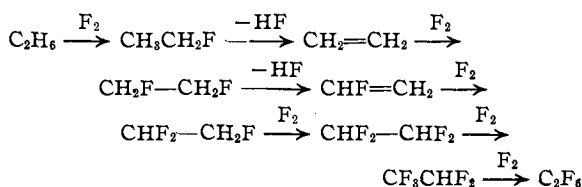
(3) Henne and Midgley, *ibid.*, **58**, 882, 884 (1936).

TABLE I  
 THE PRODUCTS OBTAINED BY RECTIFYING THE FLUORINATED ETHANE

Liquid volume % of material boiling	Gas volume ratio of fluorine to ethane to nitrogen											
	2.3:1:0 <sup>a</sup>	2:1:2	2:1:4	2:1:6	2:1:8	4:1:0 <sup>a</sup>	4:1:4	4:1:8	4:1:12	4:1:16	4:1:40	4:1:80
All < -105° (mostly CF <sub>4</sub> )	10	5	5	5	0	20	Trace	5	5	Trace	0	0
-104° (Azeotrope A <sup>2</sup> )	15	0	0	0	0	20	0	0	0	0	0	0
-96° (Azeotrope B <sup>2</sup> )	50	40	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 to -40°	..	5	10	5	10	..	20	20	25	30	30	30
-40 to -35°	..	5	5	10	5	..	Trace	0	0	0	0	0
-35 to -28°	..	Trace	5	5	..	..	Trace	5	0	0	0	0
-28 to -19°	..	10	10	10	..	..	15	15	40	40	35	20
All > -19°	..	10	15	15	..	..	20	15	25	20	25	30
All > -78°	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 <sup>b</sup>	8 <sup>b</sup>	10

<sup>a</sup> From ref. 2 for comparison. <sup>b</sup> After the removal of SiF<sub>4</sub>.

of ethane may perhaps be represented simply as follows.



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.<sup>4</sup> 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 alone. This was in accord with their free radical, 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<sub>3</sub>CHF<sub>2</sub>, or even of CH<sub>3</sub>CF<sub>3</sub>, 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, sublimates 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 -50 to -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

