The configurations of the amino alcohols have tentatively been assigned on the basis of the synthetic relation to the *cis* and *trans* stilbene oxides, assuming consistent *trans* reactions.

Because of the failure of α-(N-ethyl-N-ethanolamino)-desoxybenzoin and two related tertiary-nitrogen analogs to undergo reduction by aluminum isopropoxide, a cyclic structure for this type is suggested. Dehydration of one of these compounds was brought about by heating at 160°, and the reverse reaction was accomplished by the action of acid.

α-(Ethanolamino)-desoxybenzoin, in which the nitrogen is secondary, is reduced by aluminum isopropoxide and appears to be normal in its properties.

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[CONTRIBUTION FROM THE PURDUE RESEARCH FOUNDATION AND DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Some Fluorinated Derivatives of Propane[1]

BY E. T. MCBEE, ANTHONY TRUCHAN AND R. O. BOLT[2]

This paper is one of a series[3] describing the synthesis of derivatives of fluoroalkanes; it offers an improved synthesis of $CF_3CH_2CF_3$ and describes new chlorofluoropropanes.

Hexachloropropene was subjected to the sequence

$$CCl_3CCl{=}CCl_2 \xrightarrow{SbF_3} CF_3CCl{=}CCl_2{}^4 \xrightarrow{HF/SbCl_5}$$
$$CF_3CHClCClF_2 \xrightarrow{Zn/C_2H_5OH} CF_3CH{=}CF_2 \xrightarrow{HF} CF_3CH_2CF_3{}^5$$

No addition of hydrogen fluoride across the double bond or halide replacement occurred when $CF_3CCl{=}CCl_2$ was heated with anhydrous hydrogen fluoride at 240° in a pressure vessel, but in the presence of antimony(V) halides reaction did occur. Rectification of the product showed that $CF_3CCl{=}CCl_2$, $CF_3CHClCCl_2F$, $CF_3CHClCClF_2$, $CF_3CHClCF_3$, $CF_3CCl_2CCl_2F$ and $CF_3CCl_2CClF_2$ were present in the mixture. Two independent reactions may be viewed as taking place, (a) addition of hydrogen fluoride to the double bond followed by halogen exchange and (b) addition of chlorine (from antimony (V) chlorofluorides) to the double bond followed by halogen exchange. $CF_3CHClCCl_2F$ was formed but it could not be rectified from unreacted $CF_3CCl{=}CCl_2$ because the difference in boiling points is only one degree. For physical constants, $CF_3CHClCCl_2F$ was independently prepared by fluorination of $CF_3CHClCCl_3$, obtained by addition of chlorine to $CF_3CH{=}CCl_2$. The structure of $CF_3CHClCClF_2$ was established by dechlorination to $CF_3CH{=}CF_2$,[4] and dehydrochlorination to $CF_3CCl{=}CF_2$.[3]

The ratio of $CF_3CHClCClF_2$ to $CF_3CHClCF_3$ was controlled by varying the amount of hydrogen fluoride used. The use of a 100% excess of hydrogen fluoride gave high yields of $CF_3CHClCF_3$ with a corresponding decrease in the yield of $CF_3CHClCClF_2$. The amount of $CF_3CCl_2CCl_2F$ and $CF_3CCl_2CClF_2$ varied with the amount of antimony(V) chloride used. Further fluorination of $CF_3CHClCF_3$ with anhydrous hydrogen fluoride and antimony(V) chloride did not take place even at temperatures of 260°. The starting material was recovered.

Bromine was added to $CF_3CH{=}CF_2$ under pressure at 140° to give $CF_3CHBrCBrF_2$. Hydrogen bromide was eliminated readily from the latter compound to give $CF_3CBr{=}CF_2$.

Experimental

Starting Materials and Apparatus.—The $CF_3CCl{=}CCl_2$ used in this work was prepared by the method of Henne and co-workers[4] from hexachloropropene (Hooker Electrochemical Company). J. T. Baker, C. P. antimony(V) chloride and anhydrous hydrogen fluoride (prime commercial grade from Harshaw) were used for the fluorinations.

Fluorination of $CF_3CCl{=}CCl_2$.—A 2-liter, nickel-lined autoclave was assembled, evacuated and then chilled to 0°. $CF_3CCl{=}CCl_2$ (3.25 moles), antimony(V) chloride (0.3 mole) and hydrogen fluoride (18.4 moles) were sucked into the autoclave in the order mentioned through the needle valve. The charged autoclave was heated in a stationary, vertical position for one hundred hours at 250 ± 5°. After cooling to 150°, the contents were released through the needle valve into a recovery train consisting of a gallon bottle three-fourths full of water, drying tower and, finally, a receiver cooled with solid carbon dioxide. No alkali was used in the water scrubber because $CF_3CHClCClF_2$ is easily dehydrochlorinated to $CF_3CCl{=}CF_2$. The organic product was steam distilled, dried and rectified in a suitable column. The products from three similar runs were combined for rectification. Purification of the compounds for chemical analysis and determination of physical properties was accomplished by washing with water, drying and re-rectifying. The recovery of $CF_3CCl{=}CCl_2$ plus an unknown amount of $CF_3CHClCCl_2F$ was 21%. The conversions to $CF_3CHClCF_3$, $CF_3CHClCClF_2$, $CF_3CCl_2CClF_2$ and $CF_3CCl_2CCl_2F$ were 16%, 50%, 2% and 2%, respectively.

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[1] Presented before the Symposium on Fluorine Chemistry as paper 24, Division of Industrial and Engineering Chemistry, 112th Meeting of the American Chemical Society, New York, New York. Taken in part from a doctoral thesis to be submitted by Anthony Truchan to the faculty of Purdue University in partial fulfillment of requirements for the degree of doctor of philosophy.

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[3] E. T. McBee and co-workers, THIS JOURNAL, **62**, 3340–3341 (1940); **69**, 944–947 (1947); *Ind. Eng. Chem.*, **39**, 409, 418, 420 (1947).

[4] A. L. Henne, A. M. Whaley and J. K. Stevenson, THIS JOURNAL, **63**, 3478–3479 (1941).

[5] A. L. Henne and T. P. Waalkes, *ibid.*, **68**, 496–497 (1946).

TABLE I

NEW COMPOUNDS

Compounds	B. p., °C.	t, °C.	d^t_4	$n^{24}D$	Fluorine, % Calcd.	Fluorine, % Found	Chlorine, % Calcd.	Chlorine, % Found	Mol. wt. Calcd.	Mol. wt. Found
$CF_3CHClCCl_3$	125.1	24	1.6757	1.4180	24.1	24.8	60.2	60.3	...	...
$CF_3CHClCCl_2F$	87.0–87.3	23	1.6174	1.3699	34.6	35.4	48.5	48.8	...	...
$CF_3CHClCClF_2$	50.4	22	1.5564	1.3208	46.7	47.7	34.9	35.4	203	199
$CF_3CHClCF_3$	14.5–15.0	4	1.5415	....	61.1	61.4	19.1	20.6	186	183

In another experiment, a 2-liter, monel lined autoclave was charged with $CF_3CCl{=}CCl_2$ (3.3 moles) and anhydrous hydrogen fluoride (12 moles) and heated at 240° for sixty-seven hours. A pressure of 1225 lb./sq. in. was observed. The product was isolated in the usual manner and rectified. Five-hundred and sixty-six grams of the starting material, $CF_3CCl{=}CCl_2$, was recovered, indicating that substantially no fluorination had occurred.

Synthesis of $CF_3CH{=}CF_2$ and $CF_3CH_2CF_3$.—A 5-liter, 3-necked flask was fitted with a dropping funnel, a mercury sealed stirrer and a reflux condenser through which ice water was circulated. A receiver cooled by solid carbon dioxide was connected in series with the condenser. The flask was charged with zinc dust (7 moles) and absolute ethanol (1500 ml.). This mixture was heated to the temperature of refluxing alcohol and $CF_3CHClCClF_2$ (5.8 moles) was added dropwise to the zinc–alcohol suspension over a period of six hours. Upon rectification of the product, 655 g. $CF_3CH{=}CF_2$ (5.0 moles) and 122 g. $CF_3CHClCClF_2$ (0.6 mole) were obtained representing a conversion of 86% and a yield of 96%. $CF_3CH{=}CF_2$ was converted to $CF_3CH_2CF_3$ by addition of hydrogen fluoride.[5]

Synthesis of $CF_3CHClCCl_3$.—A Carius tube was charged with $CF_3CH{=}CCl_2$ (0.4 mole), liquid chlorine (0.75 mole) and antimony(V) chloride (0.04 mole) and the mixture heated at 140° for twenty-four hours. The product was washed with aqueous alkali, dried and purified by rectification. Fifty grams of $CF_3CHClCCl_3$ (0.21 mole) was obtained representing a yield and conversion of 53%.

Synthesis of $CF_3CHClCCl_2F$.—A mixture of $CF_3CHClCCl_3$ (0.18 mole), antimony(III) fluoride (0.13 mole) and antimony(V) chloride (0.06 mole) was refluxed for one hour. The product was steam distilled and purified by rectification. Twenty-three grams (0.10 mole) of $CF_3CHClCCl_2F$ was obtained representing a yield and conversion of 56%.

Synthesis of $CF_3CHBrCBrF_2$.—Two Carius tubes were charged with $CF_3CH{=}CF_2$ (0.7 mole) and bromine (0.72 mole) and heated at 140° for twenty-four hours. The products were combined, washed free of bromine with aqueous Na_2SO_3, dried and rectified. There was obtained 42 g. of $CF_3CBr{=}CF_2$, b. p. 24.7–25.0°, 216 g. of $CF_3CHBrCBrF_2$, b. p. 88.0°, d^{25}_4 2.1637, $n^{25}D$ 1.3780. Dehydrobromination of $CF_3CHBrCBrF_2$ during washing caused the formation of $CF_3CBr{=}CF_2$.

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Summary

A new series of reactions for the preparation of $CF_3CH_2CF_3$ is described. The fluorination of $CF_3CCl{=}CCl_2$ with anhydrous hydrogen fluoride and antimony(V) chloride gave $CF_3CHClCCl_2F$, $CF_3CHClCClF_2$, $CF_3CHClCF_3$, $CF_3CCl_2CCl_2F$ and $CF_3CCl_2CClF_2$. Several new compounds are reported.

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[CONTRIBUTION FROM THE SLOAN–KETTERING INSTITUTE FOR CANCER RESEARCH, NEW YORK, THE NATIONAL RESEARCH COUNCIL OF CANADA, AND THE STAMFORD RESEARCH LABORATORIES OF THE AMERICAN CYANAMID CO.]

Studies in Steroid Metabolism. IV. The Characterization of Carbonyl and Other Functional Groups in Steroids by Infrared Spectrometry[1]

BY R. NORMAN JONES, V. Z. WILLIAMS, M. J. WHALEN AND KONRAD DOBRINER

Many organic compounds can be identified by the direct comparison of their ultraviolet, visible or infrared absorption spectra with the spectra of known substances measured under comparable experimental conditions. Such a procedure is strictly empirical and involves no premises as to the nature of the processes concerned in the absorption of the radiation. However, much more insight into the molecular structure of the compound can be derived from the spectrometric measurements if the location and the intensities of the absorption bands can be related to specific molecular structure. In the case of a new compound it is only through such correlations that information about the molecular structure can be derived from the spectrometric measurements.

The high specificity of the infrared absorption spectra of organic compounds has recently become generally appreciated,[2,3] and infrared spectrometry is now applied quite extensively for the qualitative and quantitative analysis of organic compounds. Thus infrared spectrometry was used as an aid in the establishment of the identity of synthetic folic acid with that isolated from natural sources,[4] and the application of infrared spectrometry to the analysis of the steroid constituents of human urine has been described in an

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[2] "The Application of Infrared Spectra to Chemical Problems. A General Discussion," *Trans. Faraday Soc.*, **41**, 171 (1945).

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[4] Angier, *et al.*, *Science*, **102**, 227 (1945).