further chlorination **A** gave only $CH_3CF_2CCl_2CH_3$ and $CH_3CF_2CHClCH_2Cl$, while **B** gave $CH_3CF_2CH_2CHCl_2$, then $CH_3CF_2CH_2CCl_3$ almost exclusively. These results show that the chlorination is directed away from an alpha CH_3 group, and tends to accumulate the chlorine atoms on the same carbon atoms. The failure of $CH_2ClCF_2CH_2CH_3$ to be chlorinated to $CHCl_2CF_2CH_2CH_3$ confirms the direction away from a terminal group alpha to a CF_2 group.

Chlorine reactivity tests show that alpha chlorine atoms are immobilized and that beta chlorine atoms are repressed, while gamma chlorine atoms seem to be unaffected.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

The Synthesis and Directed Chlorination of 1,1,1,-Trifluorobutane

BY ALBERT L. HENNE AND JAMES B. HINKAMP

To find out how far a CF_3 group would extend its influence, trifluorobutane, $CF_3CH_2CH_2CH_3$, was synthesized and subjected to the action of chlorine. The synthesis problem consisted in devising a practical method for obtaining an intermediate compound, $CCl_2{=}CHCH_2CH_3$, from which the desired $CF_3CH_2CH_2CH_3$ was made by variations of the procedures previously used to synthesize $CF_3CH_2CH_3$.[1] The chlorination as well as the isolation and identification of the chlorinated compounds were performed in a manner previously described.[1,2]

Synthesis of $CCl_2{=}CHCH_2CH_3$

The sequence $CHOCH_2CH_2CH_3$, to $CHCl_2CH_2CH_2CH_3$, to $CHCl{=}CHCH_2CH_3$, to $CHCl_2CHClCH_2CH_3$, to $CCl_2{=}CHCH_2CH_3$, was first tried. The transformation of butyraldehyde into its dichloride by means of phosphorus pentachloride gave only a 23% yield, which was finally brought up to 39% by a series of time-consuming improvements. Since these improvements called for hydrolysis of the reaction product at 0°, the risk of handling an incompletely hydrolyzed material prevented their application to larger quantities. The dehydrohalogenation to $CHCl{=}CHCH_2CH_3$ required a saturated solution of potassium hydroxide in boiling butanol, and gave 64% of olefin together with 29% of recovered dichloride.

For large quantities it was deemed safer and more economical to start from technical $CH_2ClCHClCH_2CH_3$. Dehydrohalogenation occurred easily with a 30% solution of sodium hydroxide in denatured alcohol and formed only two of the possible three olefins. The reaction was sufficiently exothermic to maintain itself and it yielded 27% of $CH_2{=}CClCH_2CH_3$, 46% of the desired $CHCl{=}CHCH_2CH_3$ and 16% of recovered dichloride. Since $CH_2{=}CClCH_2CH_3$ was easily transformed into $CH_3CF_2CH_2CH_3$ used in the preceding study,[2] this procedure proved to be very satisfactory. The addition of chlorine which synthesizes $CHCl_2CHClCH_2CH_3$ was performed in the dark to prevent substitution. Pilot tests showed that water would greatly accelerate the rate of addition, but at the expense of increased substitution. When time matters little, it is best to operate without water, at about 10°, and with a slight excess of olefin, for a net yield of 70–75%. In the presence of water, the reaction proceeds nearly four times faster, but the net yield drops to approximately 55%.

The dehydrohalogenation of $CHCl_2CHClCH_2CH_3$ proceeded very easily with either aqueous or alcoholic sodium hydroxide, and gave 96% of the desired $CCl_2{=}CHCH_2CH_3$.

Synthesis of $CF_3CH_2CH_2CH_3$

At room temperature, $CCl_2{=}CHCH_2CH_3$ does not react with hydrogen fluoride. When the temperature is raised, addition takes place to form $CFCl_2CH_2CH_2CH_3$, then substitution occurs to yield $CF_2ClCH_2CH_2CH_3$. With longer reaction periods, higher temperatures, and a greater excess of hydrogen fluoride, the formation of $CF_2ClCH_2CH_2CH_3$ is progressively enhanced.

A three mole quantity of $CCl_2{=}CHCH_2CH_3$ was mixed with 24 moles of hydrogen fluoride in a steel container surmounted by a one meter length of half-inch steel pipe bearing a pressure gage and a releasing needle valve. The top twenty centimeters of the pipe were surrounded by a jacket which could be filled with Dry Ice. The reaction was started by putting the cylinder in a hot water bath, its progress being shown by an increase in pressure due to the formation of hydrogen chloride. With Dry Ice in its container to ensure an efficient dephlegmation, the hydrogen chloride was slowly released into a water absorber by operating the needle valve so as to maintain the pressure between 17 and 20 atmospheres. When the pressure no longer increased, the reaction vessel was cooled in Dry Ice, and its contents were poured onto cracked ice, then worked up by

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(1) Henne and Whaley, THIS JOURNAL, 64, 1157 (1942).

(2) Henne and Hinkamp, *ibid.*, 67, 1194 (1945).

steam distillation followed by fractional distillation. Comparative data are:

Reaction temperature, °C.	65	100
Time in hours	18	6
$CF_2ClCH_2CH_2CH_3$ formed, %	5.3	49.6
$CFCl_2CH_2CH_2CH_3$ formed, %	33.0	10.3
Recovered dichloride, %	38.0	5.3
Tar, %	10.6	19.4
Material accounted for, %	90	87

The dehydrohalogenation of $CF_2ClCH_2CH_2CH_3$ to $CF_2{=}CHCH_2CH_3$ took place with ease but required precise experimental conditions to ensure good yields, because of the low boiling points of the reagent and of the reaction product.

In a three-liter, three-necked flask equipped with a mercury-sealed stirrer, a dropping funnel and a twelve-bulb reflux condenser, 180 g. (3.2 moles) of potassium hydroxide was stirred with 340 ml. of gently boiling absolute ethanol. This is more than enough hydroxide to make a saturated solution. Over a period of three hours, 196 g. (1.52 moles) of $CF_2ClCH_2CH_2CH_3$ was added dropwise. The operating skill consists in adding the halide at exactly the rate at which $CF_2{=}CHCH_2CH_3$ is produced and removed through the reflux condenser to be liquefied in a Dry Ice cooled receiver. When the halide is added too rapidly, it accumulates and automatically lowers the temperature of the reaction to the boiling point of the azeotropic mixture of the halide with ethanol. At this lower temperature dehydrohalogenation is exceedingly slow. The yield obtained was 83.3% of pure difluoroolefin, and in addition 6% of unreacted reagent was recovered.

The hydrofluorination of $CF_2{=}CHCH_2CH_3$ to $CF_3CH_2CH_2CH_3$ is a quantitative, highly exothermic reaction. One mole of the olefin was mixed with four moles of hydrogen fluoride at −80° in a steel container. The container was sealed, then allowed to warm up to room temperature. The reaction started spontaneously and proceded to completion within a few seconds, causing the pressure to rise temporarily to 16 atmospheres. The reaction mixture was left to cool spontaneously to room temperature, after which it was placed in a water-bath held at 40°. The reaction products were then released through a water washer followed by an alkali washer, dried over calcium chloride and condensed in an ice-cooled receiver protected against losses by a trap held at −80°. The yields were from 96 to 99% of pure $CF_3CH_2CH_2CH_3$.

Additional quantities of $CF_2ClCH_2CH_2CH_3$ were obtained by working up the intermediate $CFCl_2CH_2CH_2CH_3$. The latter was dehydrohalogenated in 90% yield to $CFCl{=}CHCH_2CH_3$ by means of a saturated solution of potassium hydroxide in boiling ethanol. To obtain $CF_2ClCH_2CH_2CH_3$, the hydrofluorination of the olefin was carried out substantially as above, except that heating at 65° for eight hours was needed to complete the addition. This is a detail of much practical importance because the olefin and its hydrofluorinated product boil only 1.6° apart and their separation from an incompletely reacted mixture is exceedingly impractical.

In the various hydrofluorinations, it was assumed that addition took place in strict accordance with the rule of Markownikow. This assumption was verified by subjecting both $CFCl_2CH_2CH_2CH_3$ and $CF_2ClCH_2CH_2CH_3$ to halogen exchange with mercuric fluoride in the manner previously described.[3] The resulting trifluoride proved to be identical with the sample prepared by hydrogen fluoride addition to a double bond.

Chlorination

In sunlight and in the presence of water, $CF_3CH_2CH_2CH_3$ gave only two of the possible three monochlorides. $CF_3CH_2CHClCH_3$ and $CF_3CH_2CH_2CH_2Cl$ were formed in a ratio of 4:5, while $CF_3CHClCH_2CH_3$ was completely absent. As in previous cases[1,2] the group alpha to the fluorinated cluster resisted chlorination; the beta and gamma groups were affected in a manner which deviated but slightly from random chlorination, in favor of the beta group.

Illustrating again the previously observed tendency of the chlorine atoms to accumulate on the same carbon, further chlorination of $CF_3CH_2CHClCH_3$ yielded 8 parts of $CF_3CH_2CCl_2CH_3$ to 6 parts of $CF_3CH_2CHClCH_2Cl$ while further chlorination of $CF_3CH_2CH_2CH_2Cl$ gave 2 parts of $CF_3CH_2CH_2CHCl_2$ to 1 part of $CF_3CH_2CHClCH_2Cl$. When $CF_3CH_2CH_2CHCl_2$ was chlorinated, the product far predominant was found to be $CF_3CH_2CH_2CCl_3$.

Identifications

While the experimental work was in progress, the identities of the chlorides were postulated from the agreement between the observed boiling points and those predicted by analogies with propane derivatives previously studied. As boiling points of isomers differ markedly (see table of physical constants) and can be predicted within one or two degrees, the method is of considerable help. The formulas were, however, verified as follows:

Fluorination of the compound thought to be $CF_3CH_2CCl_2CH_3$ yielded a pentafluoride which proved identical with that obtained previously from $CCl_3CH_2CF_2CH_3$[2] and therefore had to be $CF_3CH_2CF_2CH_3$. The position of both chlorine atoms in the starting material had thus been correctly postulated.

The monochloride from which $CF_3CH_2CCl_2CH_3$ was obtained must perforce have been $CF_3CH_2CHClCH_3$. Its isomer must have been $CF_3CH_2CH_2CH_2Cl$ because it boiled higher, and also because it proved different from $CF_3CHClCH_2CH_3$ which was synthesized for the purpose of identification, as follows. Chlorine was added to $CF_2{=}CH_2CH_2CH_3$ to yield $CF_2ClCHClCH_2CH_3$. The latter was fluorinated with mercuric fluoride.

(3) Henne and Flanagan, THIS JOURNAL, 65, 2362 (1943).

TABLE I

PHYSICAL CONSTANTS

The analyses were performed by Dr. W. M. MacNevin and Mr. Joseph Varner, by the procedure described in Mr. Varner's Master's thesis, The Ohio State University, 1943.

	Freezing range	F. p., °C.	B. p. (760 mm.), °C.	d^{20}_4	n^{20}_D	*MR*	AR_F	Chlorine, % Found	Chlorine, % Calcd.	Fluorine, % Found	Fluorine, % Calcd.
$CFCl_2CH_2CH_2CH_3$	0.1	−112.4	95.3	1.1578	1.4007	30.41	1.10	48.9	49.0	13.1	13.2
$CF_2ClCH_2CH_2CH_3$	.004	−119.39	56.03	1.0754	1.3462	25.47	1.07				
$CFCl{=}CHCH_2CH_3$	.1	−144.9	54.4	1.0216	1.3851	24.90	0.93	32.7	32.7	17.2	17.5
$CF_2{=}CHCH_2CH_3$	.1	−164.95	3.71	0.9284 (0°)	1.3253 (0°)	19.97	0.99				
$CF_3CH_2CH_2CH_3$	.02	−114.79	16.74	1.0144	1.2921	20.51	1.05	..	..	50.7	50.8
$CF_2ClCHClCH_2CH_3$		Below −100	96.98	1.2715	1.3878	30.24	1.02				
$CF_3CHClCH_2CH_3$		Below −100	58.3	1.196$_7$	1.336$_9$	25.4	1.0$_7$	24.2	24.2	38.6	38.9
$CF_3CH_2CHClCH_3$	.1	− 79.2$_4$	65.6$_3$	1.2133	1.3433	25.54	1.10	24.0	24.2	38.7	38.9
$CF_3CH_2CH_2CH_2Cl$	.02	− 67.25	86.60	1.2425	1.3505	25.41	1.06	24.4	24.2	39.2	38.9
$CF_3CH_2CCl_2CH_3$		*Ca.* −48	89.90	1.374	1.355	30.6	1.1$_4$	39.3	39.2	31.3	31.5
$CF_3CH_2CF_2CH_3$	.01	− 35.01	40.14	1.2666	1.2824	20.67	1.10	..	..	63.8	64.1
$CF_3CH_2CHClCH_2Cl$			115	1.390							
$CF_3CH_2CH_2CHCl_2$			110	1.382							

in hydrogen fluoride as a solvent, a process which is known to fluorinate a halogen cluster in preference to a single halogen atom.[1,3] The resulting $CF_3CHClCH_2CH_3$ proved different from both the isomers formed in the chlorination of CF_3CH_2-CH_2CH_3.

The structure of $CF_3CH_2CHClCH_2Cl$ was derived from the fact that it was obtained from both $CF_3CH_2CH_2CH_2Cl$ and $CF_3CH_2CHClCH_3$.

Purification and Physical Constants.—The purification procedure and the physical measurements were carried out as indicated in the preceding paper,[2] and with the degree of accuracy shown in the table.

Reactivity Tests.—Tested with a boiling solution of silver nitrate in alcohol,[2] CF_3CHCl-CH_2CH_3 and $CF_3CH_2CHClCH_3$ gave negative results while $CF_3CH_2CH_2CH_2Cl$ gave a faint turbidity. The interpretation was that both the alpha and the beta chlorine atoms were immobilized by the CF_3 group, while the gamma chlorine atom was only repressed. The influence of a CF_3 group extends, therefore, further than that of a $—CF_2—$ group.[2]

Treated with alcoholic alkali, $CF_3CHClCH_2CH_3$ did not react; $CF_3CH_2CHClCH_3$ gave $CF_3CH{=}CHCH_3$; and $CF_3CH_2CH_2CH_2Cl$ gave an ether $CF_3CH_2CH_2CH_2—O—R$. The first two results are similar to those recorded in the preceding paper[2] for the monochloro derivatives of CH_3CF_2·CH_2CH_3. The formation of an ether in gamma position shows that the chlorine atom is too far from the CF_3 group to be affected by it and behaves like that of butyl chloride, which also gives an ether when so treated.

Summary

$CF_3CH_2CH_2CH_3$ was synthesized by the action of hydrogen fluoride on $CCl_2{=}CHCH_2CH_3$, which yields $CF_2ClCH_2CH_2CH_3$, followed by hydrogen chloride removal to $CF_2{:}CHCH_2CH_3$ then hydrogen addition to $CF_3CH_2CH_2CH_3$. Chlorination did not affect the alpha CH_2, but only the beta CH_2 (4 parts) and the gamma CH_3 (5 parts). Further chlorination tended to accumulate on the carbon atoms already affected. The CF_3 group immobilized alpha and beta chlorine atoms and repressed a gamma chlorine atom, thus proving more effective in this respect than a CF_2 group; it also accentuated the acid character of the alpha hydrogen atoms.

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[4] This manuscript was originally received on October 11, 1943, and after examination by the editorial board was accepted for publication in THIS JOURNAL. It was, however, referred to the National Defense Research Committee and at their request was withheld from publication, in a confidential file, until clearance was granted on May 5, 1945.