

No. 9 from $\text{CCl}_2=\text{CFCF}_3$ to $\text{CClF}=\text{CFCClF}_2$ or possibly $\text{CCl}_2\text{FCF}=\text{CF}_2$
 No. 10 from $\text{CCl}_2\text{BrCFBrCF}_3$ to CClFBrCFBrCClF_2 or possibly $\text{CCl}_2\text{FCFBrCF}_2\text{Br}$

Summary

A corrected representation of the stepwise ac-

tion of antimony trifluoride on $\text{CHCl}_2\text{CCl}_2\text{CCl}_3$ is $\text{CHCl}_2\text{CCl}_2\text{CCl}_2\text{F} \rightarrow \text{CHCl}_2\text{CCl}_2\text{CClF}_2 \rightarrow \text{CHCl}_2\text{-CClFCClF}_2 \rightarrow \text{CHClFCClFCClF}_2$.

Physical properties of CHClFCClFCClF_2 , $\text{CCl}_2\text{-FCClFCClF}_2$, and $\text{CCl}_3\text{CClFCF}_3$ are tabulated.

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

A New Method of Synthesizing Organic 1,1,1-Trifluorides

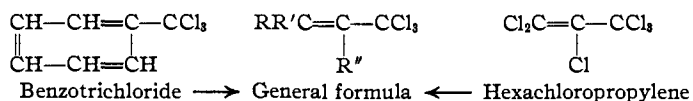
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The origin of the present work is the discovery that hexachloropropylene, $\text{CCl}_2=\text{CClCCl}_3$, heated with antimony trifluoride without the usual salt of pentavalent antimony as a "fluorine carrier," is easily and completely transformed into $\text{CCl}_2=\text{CClCF}_3$. The novel features of this reaction are: (1) substitution proceeds smoothly and rapidly; (2) no salt of pentavalent antimony is needed or wanted as a "fluorine carrier"; (3) a $-\text{CF}_3$ group is generated where antimony fluoride was expected to substitute only two halogen atoms and to create a $-\text{CClF}_2$ group. It is concluded that substitution of fluorine for chlorine is facilitated and made more complete because the three replaceable halogen atoms are linked to a carbon atom once removed from a double bond, and can therefore be regarded as "allylic" in nature.

In order to establish the generality of the method as well as its limitations, the following additional experiments were performed: (1) $\text{CF}_2=\text{CClCClF}_2$ was transformed into $\text{CF}_2=\text{CClCF}_3$, (2) $\text{CHCl}=\text{CClCCl}_3$ into $\text{CHCl}=\text{CClCF}_3$, (3) $\text{CCl}_2=\text{CFCCl}_3$ into $\text{CCl}_2=\text{CFCF}_3$, (4) $\text{CCl}_2=\text{CHCCl}_3$ into $\text{CCl}_2=\text{CHCF}_3$. In contrast, it was found impossible to replace the chlorine by fluorine in $\text{CH}_2=\text{CHCCl}_3$ and the reagents were recovered unaffected. In the case of $\text{CH}_2=\text{CHCH}_2\text{-Cl}$, extensive decomposition occurred and no reaction product was obtained. These experiments were interpreted as an indication that the doubly linked carbon atoms must bear some halogen atoms.

There is a strong experimental resemblance between the synthesis of $\text{CCl}_2=\text{CClCF}_3$ from $\text{CCl}_2=\text{CClCCl}_3$ and that of $\text{C}_6\text{H}_5\text{CF}_3$ from $\text{C}_6\text{H}_5\text{CCl}_3$. Both occur very fast and take place by heating the organic chloride with antimony trifluoride to 125–140°. The only difference is that the first

reaction occurs almost quantitatively, while the second one gives only 60% yields and is accompanied by extensive decomposition. The structure resemblance of the reagents is best illustrated by their developed formulas.



The olefinic compounds prepared, together with such of their dichlorides as are new, are listed in Table I. The compound $\text{CF}_2=\text{CClCF}_3$, which was too volatile to be handled conveniently, was immediately transformed into its dichloride, $\text{CF}_2\text{-ClCCl}_2\text{CF}_3$. The compound $\text{CCl}_2=\text{CFCF}_3$ was transformed into its dichloride at once, lest the small amount prepared be lost during its purification. The compound $\text{CCl}_2=\text{CHCF}_3$ was prepared on a very small scale. All dichlorides were thoroughly purified and analyzed.

In Table I, MR_D is the molecular refraction calculated by means of the Lorentz-Lorenz formula. AR_F is the atomic refraction for fluorine, obtained by subtracting from MR the generally accepted increments for C (2.418), H (1.100), Cl (5.967) and double bond (1.733).

Chlorine analyses are reported for all compounds which could be handled conveniently; when this was impractical, the chlorine analysis of their dichlorides is given. Fluorine analyses, which are difficult and tedious, were performed at crucial points only. In general, the analytical results have a tendency to be slightly low, and this is attributed to the great difficulty of obtaining a complete decomposition of these extremely stable compounds. The results are listed in Table II.

The position in which the fluorine atoms enter the molecule is demonstrated by the fact that identical samples of $\text{CCl}_3\text{CCl}_2\text{CF}_3$ were obtained

TABLE I

PHYSICAL PROPERTIES						
Name	F. p., °C.	B. p., °C.	d_{20}^{20}	n_D^{20}	M_{RD}	A_{RF}
$CCl_2=CClCCl_2F$	Glass	170.2	1.7041	1.5050	40.43	1.60
$CCl_2=CClCClF_2$	-103.0	128.0	1.6598	1.4573	35.43	1.29
$CCl_2=CClCF_3$	-114.7	88.3	1.6188	1.4095	30.48	1.20
$CCl_3CCl_2CF_3$	+109.1	153.1
$CF_2=CClCF_2Cl$	-121.2	44.7	1.5406	1.3484	25.45	1.13
$CF_2=CClCF_3$	-130.4	6.8
$CF_2CClCCl_2CF_3$	- 4.30	72.0	1.6681	1.3519	30.77	1.12
$CCl_2=CFCF_3$..	46.0	(approximate)	
$CCl_3CClFCF_3$	+ 12.1	112.4	1.7254	1.4002	35.69	1.14
$CHCl=CClCF_3$	-109.23	53.7	1.4653	1.3670	25.27	1.08
$CCl_2=CHCF_3$..	54.5	..	1.3688

TABLE II

ANALYSES					
Name	% Chlorine		% Fluorine		
	Calcd.	Found	Calcd.	Found	
$CCl_2=CClCCl_2F$	76.3	75.6			
$CCl_2=CClCClF_2$	65.7	65.5			
$CCl_2=CClCF_3$	53.3	53.3	28.6	28.3	
$CCl_3CCl_2CF_3$	65.7	65.6			
$CF_2=CClCF_2Cl$	38.8	38.7			
$CF_2CClCCl_2CF_3$	44.8	44.4	40.0	40.0	
$CCl_3CClFCF_3$	55.9	55.5	29.9	29.1	
$CHCl=CClCF_3$	43.0	42.6			

by two different sequences of reaction, thus: (1) $CCl_2=CClCCl_3 \rightarrow CCl_2=CClCF_3 \rightarrow CCl_3CCl_2CF_3$ and (2) $CH_3CH_2CCl_3 \rightarrow CH_3CH_2CF_3 \rightarrow CCl_3CCl_2CF_3$.¹ Samples of $CF_2CClCCl_2CF_3$ prepared in two different ways were also found to be identical: (1) $CF_2=CClCF_2Cl \rightarrow CF_2=CClCF_3 \rightarrow CF_2CClCCl_2CF_3$ and (2) $CH_3CH_2CF_3 \rightarrow CCl_3CCl_2CF_3 \rightarrow CF_2CClCCl_2CF_3$.²

Experimental

The substitutions of fluorine for chlorine were performed by experiments analogous to the following.

Preparation of $CCl_2=CClCF_3$.—Four moles of $CCl_2=CClCCl_3$ and six moles of finely ground antimony trifluoride were placed in a metal container surmounted by a one meter length of pipe to act as dephlegmator. The top of the pipe was fitted with a thermometer well, and delivered into a metal, water-cooled downward condenser. The container was placed in an oil-bath which had been heated to 150°. The purpose of this was to carry out the reaction as quickly as possible, because this procedure minimizes decomposition. The reaction started promptly, and the reaction product distilled rapidly at 90–105°. When the distillation slowed down, the oil-bath was removed, and the reaction vessel heated with a free flame until all the organic material had been removed. The distillate was steam distilled, dried, and rectified to give 43%

of $CCl_2=CClCF_3$ (b. p. 88°), 28% of $CCl_2=CClCCl_2F$ (b. p. 128°), 13% of $CCl_2=CClCCl_2F$ (b. p. 170°), and 10% of recovered $CCl_2=CClCCl_3$.

Preparation of $CF_2=CClCF_3$.—The starting material, $CF_2=CClCF_2Cl$, was obtained quantitatively by a treatment of $CF_2CClCCl_2CF_2Cl$ with zinc in absolute alcohol. One-half a mole of this material was placed in a steel container together with 0.3 mole of ground antimony fluoride. The container was surmounted by a metal pipe bearing a pressure gage and a releasing needle valve. The whole equipment was tested beforehand to withstand a working pressure of forty atmospheres. The reaction vessel was heated to 200° in an oil-bath. The pressure rose progressively to 18 atmospheres, then rapidly to about 23 atmospheres. The oil-bath was removed and the reaction vessel allowed to cool to room temperature. The needle valve was opened and the $CF_2=CClCF_3$ (b. p. 7°) was allowed to distill into a receiver cooled with dry-ice. The valve was closed, the vessel heated again to 200° and tapped intermittently until the pressure no longer rose. At this point, the unreacted material was allowed to distill to be recovered. The yields of repurified product were 47% of $CF_2=CClCF_3$ (b. p. 7°), and 15% of recovered $CF_2=CClCF_2Cl$ (b. p. 45°). Handling losses were relatively large on account of the small amount of material used, its low boiling point, and the high temperature prevailing in the laboratory during the operations.

Preparation of $CF_2CClCCl_2CF_3$.— $CF_2=CClCF_3$ was placed in a flask surmounted by a dry-ice reflux condenser. Chlorine was bubbled through the liquid, part of it adding readily. An excess of chlorine was introduced into the liquid, and the mixture was allowed to reflux in strong sunlight for two hours. After removal of the excess of chlorine, $CF_2CClCCl_2CF_3$ (b. p. 72°) was obtained quantitatively.

Summary

A $-CCl_3$ group once removed from a double bond is rapidly and quantitatively transformed into a $-CCl_2F$, $-CClF_2$ or $-CF_3$ group by halogen interchange with antimony trifluoride, in the absence of the usual catalyst.

COLUMBUS, OHIO

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(1) A. M. Whaley, Dissertation, The Ohio State University, 1941

(2) James K. Stevenson, M.S. Thesis, The Ohio State University, 1942.

(3) Henne and Renoll, THIS JOURNAL, 61, 2489 (1939).