

Experimental

Preparation of Crotyl Chloride.—Commercial muriatic acid (700 g.) was first concentrated by leading 200 g. of dry hydrogen chloride into it, at ice temperature. This concentrated acid (200 g.) was cooled with an ice-salt mixture, and commercial butadiene (one mole) was distilled from a tank onto it. The bottle was stoppered with a neoprene stopper held in place by a lead screw cap, and rotated around a horizontal shaft for fifteen to twenty hours, to produce a vigorous mixing of the two layers. At the end of this time, any unreacted butadiene had polymerized and gave the aqueous layer a very viscous appearance. The top layer (purple to black) was decanted and distilled. It is not advisable to concentrate the hydrochloric acid to use it more than twice. The mixture invariably contained 65% of primary chloride and 35% of secondary chloride. Yields were computed as 70 to 75% but are actually about 10% higher, because commercial butadiene of mediocre quality was used. Both isomers were affected by one year of storage in a refrigerator; in both cases, the index of refraction rose by 25 to 30 units of the fourth decimal which was regarded as an indication that polymerization rather than isomerization had taken place.

Piperylene Hydrochloride.—Dry hydrogen chloride was passed through crude commercial piperylene, to yield 60 to 70% of addition product. Actual yields were about 15 to 20% higher. The addition took place in the 1,4-position and yielded exclusively 4-chloro-2-pentene. This compound exists only in one form, because its allylic rearrangement gives an identical product.

Diisocrotyl Hydrochloride.—Anhydrous hydrogen chloride was passed through cooled 2,5-dimethyl-2,4-hexadiene ("diisocrotyl") until the proper increase in weight was reached. Unabsorbed gas was removed by suction, after which the product distilled in a 45 to 60° range at fifteen mm. The mixture of isomeric chlorides was stable in the cold, and decomposed little at room temperature but too much to allow a separation by fractional distillation. The 1,4-addition of hydrogen chloride yields 2-chloro-2,5-dimethyl-3-hexene, whose allylic rearrangement generates 4-chloro-2,5-dimethyl-2-hexene.

Condensations.—All the condensations, with Grignard reagents as well as on magnesium, were performed in a copper reaction vessel, externally cooled by a water jacket. A powerful multi-bladed steel stirrer was used, and the condensation products were always stirred overnight to ensure the completion of the reaction. This method permitted a much more efficient control of the temperature than that which prevails in the customary glass devices. In general, 300 to 400 cc. of ether was used per mole of organic halide. This creates a very pasty reaction mass, and makes the use of a powerful stirrer indispensable. Identical results were obtained in glass, copper and steel equipment.

Quantities.—Amounts of hydrocarbon synthesized ranged from one mole to several liters. This made it possible to effect a complete purification in almost every case.

Distilling Columns.—Adiabatic packed columns (glass helices) were used, with total reflux and partial take-off. The reflux ratios were from 50 to 75.

Note.—This work is a part of the American Petroleum Institute Pure Hydrocarbon Program, operated as Project No. 31 of The Ohio State University Research Foundation. It was presented at the Atlantic City meeting of the American Chemical Society, September, 1941.

Summary

Several allylic chlorides have been prepared. They have been condensed with Grignard reagents to synthesize olefins and condensed with themselves or with each other to synthesize diolefins. All products have been described and listed in tables. The proportions of the different products in the reactions have been ascertained. The configurations of the olefins and diolefins have been established.

COLUMBUS, OHIO

RECEIVED JULY 18, 1941

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

Fluorinated Derivatives of Propane. IV*

BY ALBERT L. HENNE AND FRANK W. HAECKL

This article presents the synthesis of two tetrafluorotetrachloropropanes, and uses the new information to correct an error in a previous paper.¹ The previous paper claimed that in the treatment of $\text{CHCl}_2\text{CCl}_2\text{CCl}_3$ with antimony trifluoride, the first three substitution steps were $\text{CHCl}_2\text{CCl}_2\text{CCl}_2\text{F}$, $\text{CHCl}_2\text{CCl}_2\text{CClF}_2$, and $\text{CHCl}_2\text{CClFCClF}_2$. This is correct and has now been verified. The fourth derivative was given incor-

rectly as $\text{CHCl}_2\text{CClF}_2\text{CF}_3$; actually it is CHClFCClFCClF_2 .

The formulas of the monofluoride, $\text{CHCl}_2\text{CCl}_2\text{CCl}_2\text{F}$, and that of the difluoride, $\text{CHCl}_2\text{CCl}_2\text{CClF}_2$, have been demonstrated before.² The formula $\text{CHCl}_2\text{CClFCClF}_2$ was adopted¹ as the most plausible one for the trifluoride. This is here shown to be correct. The trifluoride could only be represented by A, B or C, because it was obtained from the known difluoride, $\text{CHCl}_2\text{CCl}_2$ -

* Original manuscript received January 23, 1941.

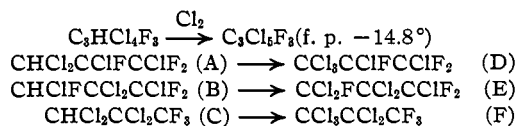
(1) Henne and Renoll, *THIS JOURNAL*, **61**, 2489 (1939).

(2) Henne and Ladd, *ibid.*, **60**, 2491 (1938).

TABLE I

	M. p., °C.	B. p., °C.	d_{20}^4	n_{20}^D	M_{RD}	ARF
(1) CHClFCCIFCCIF_2		90	1.6403	1.3855	30.66	1.09
(2) $\text{CCl}_2\text{FCCIFCCIF}_2$	-58	112.5-112.6	1.7185	1.3960	35.52	1.10
(3) $\text{CCl}_3\text{CCIFCF}_3$	+12.1	112.4-112.6	1.7254	1.4002	35.64	1.14

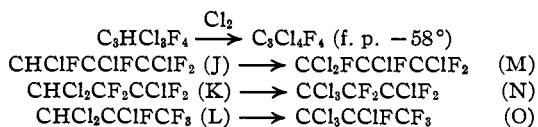
CCl_2F_2 . The replacement of the hydrogen atom by chlorine transformed it into a compound $\text{C}_3\text{Cl}_5\text{F}_3$, which froze at -14.8° and must have been D, E or F.



E is known and freezes at -4.9° .^{1,2} F is described in an accompanying paper³ and melts at $+109^\circ$. It follows that D is the correct formula for the chlorinated product and A is the correct formula for the original trifluoride from which it was derived.

The reason advanced in the previous paper to represent the fourth reaction product as $\text{CHCl}_2\text{CCIFCF}_3$ was that its chlorination product, $\text{C}_3\text{Cl}_4\text{F}_4$, seemed to freeze at about -16° , a very high freezing point for a tetrafluoride. Compounds with a $-\text{CF}_3$ group are generally characterized by such high freezing points, and consequently, it seemed reasonable to adopt $\text{CCl}_3\text{CCIFCF}_3$ as the formula of the chlorinated compound. The reasoning was correct, but the conclusions were based on an experimental error. The true freezing point of the chlorinated product is really -58° , but was masked by high-melting decomposition products in the original experiments. A repetition of the work on a larger scale made it possible to prepare samples of pure $\text{C}_3\text{HCl}_3\text{F}_4$ and of its chlorination product, $\text{C}_3\text{Cl}_4\text{F}_4$. Their physical constants are listed in Table I.

Since it was obtained from the known trifluoride, $\text{CHCl}_2\text{CCIFCCIF}_2$, the tetrafluoride can only be J, K, or L, and its chlorination product must be M, N, or O.



A treatment with zinc in alcohol removed two chlorine atoms from $\text{C}_3\text{HCl}_3\text{F}_4$ as well as from $\text{C}_3\text{Cl}_4\text{F}_4$, and this fact forces the elimination of both K and N as possible formulas. M and O were synthesized as indicated below, and were

(3) Henne, Whaley, and Stevenson, *THIS JOURNAL*, **63**, 3478 (1941).

observed to freeze at -58° and $+12.1^\circ$, respectively. Consequently, M is the correct formula for the chlorinated product, and J the correct formula for the original tetrafluoride.

Synthesis of $\text{CCl}_2\text{FCCIFCCIF}_2$.—One mole of $\text{CCl}_3\text{CCIFCCIF}_2$ was heated in a steel vessel with 0.5 mole of antimony trifluoride with which 0.05 mole of chlorine had been allowed to combine. The vessel was equipped with a vertical pipe acting as a dephlegmator, to permit $\text{C}_3\text{Cl}_4\text{F}_4$ (b. p. 112°) to distill off, while refluxing $\text{C}_3\text{Cl}_5\text{F}_3$ (b. p. 152°) back to the reaction vessel. The temperature was regulated to permit a slow distillation of the tetrafluoride and was raised progressively from 125 to 170° ; finally it was raised considerably to force out the remaining organic material together with a small amount of antimony trichloride (b. p. 225°). The distillate was steamed from a 10% aqueous sodium hydroxide solution. After decantation, rectification gave 70% of pure $\text{CCl}_2\text{FCCIFCCIF}_2$ and 15% of recovered $\text{CCl}_3\text{CCIFCCIF}_2$.

Anal. Calcd. for $\text{C}_3\text{Cl}_4\text{F}_4$: F, 29.94; Cl, 55.87. Found: F, 29.4; Cl, 56.0.

The synthesis depends on the well-established fact that $-\text{CCl}_3$ groups exchange one or two of their chlorines for the fluorine in antimony trifluoride with great ease, in contrast with the other two groups of this molecule.

Synthesis of $\text{CCl}_3\text{CCIFCF}_3$.—The starting material was $\text{CHCl}_2\text{CCIFCCl}_3$ from which alcoholic sodium hydroxide removed hydrogen chloride quantitatively to yield $\text{CCl}_2=\text{CFCCl}_3$. This compound has an "allylic" $-\text{CCl}_3$ group, which is easily transformed into a $-\text{CF}_3$ group by the action of antimony trifluoride without catalyst.³ One mole of $\text{CCl}_2=\text{CFCCl}_3$, and 1.5 moles of antimony trifluoride were heated in the steel apparatus used for the preceding synthesis. The reaction started at 125° and the heating was adjusted to permit $\text{CCl}_2=\text{CFCF}_3$ (b. p. 46° uncor.) to distil, while refluxing $\text{CCl}_2=\text{CFCCIF}_2$ and $\text{CCl}_2=\text{CFCCl}_2\text{F}$ to the reaction vessel. By this reaction, 0.37 mole of $\text{CCl}_2=\text{CFCF}_3$ and 0.27 mole of $\text{CCl}_2=\text{CFCCIF}_2$ were obtained. $\text{CCl}_2=\text{CFCF}_3$ was quantitatively transformed into $\text{CCl}_3\text{CCIFCF}_3$ by the addition of chlorine in bright sunlight.

The final product was analyzed to yield 55.48% chlorine (55.87% Cl calcd.) and 29.1% of fluorine (29.94% F calcd.). If the analyses are computed as the ratio of F atoms to Cl atoms, the value 0.98 is obtained, as compared with the theoretical value of 1.00. The purity of the sample was indicated by its total freezing range of only 0.05° .

Corrections.—The change of formula of the tetrafluorides causes other formulas in the previous paper¹ to be altered.

No. 6 from $\text{CHCl}_2\text{CCIFCF}_3$ to CHClFCCIFCCIF_2

No. 8 from $\text{CCl}_3\text{CCIFCF}_3$ to $\text{CCl}_2\text{FCCIFCCIF}_2$

(4) Pilot work by J. J. Beall, The Ohio State University, 1939.

(5) Henne and Haeckl, *THIS JOURNAL*, **63**, 2692 (1941).

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.

COLUMBUS, OHIO

RECEIVED AUGUST 11, 1941

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

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

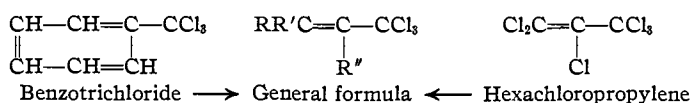
BY ALBERT L. HENNE, ATHERTON M. WHALEY AND JAMES K. STEVENSON

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 $\text{CCl}_2=\text{FCCF}_3$, (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 $\text{CCl}_2=\text{FCCF}_3$ 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