

[CONTRIBUTION NO. 251 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & COMPANY, WILMINGTON, DELAWARE]

Synthesis of Chlorofluoropropanes

BY DONALD D. COFFMAN, RICHARD CRAMER AND G. W. RIGBY

Chloroform or carbon tetrachloride reacts with chloroethylenes in the presence of aluminum chloride to yield chloropropanes.¹ In seeking to extend this addition reaction to fluorinated methanes, Henne and co-workers² were deterred by the replacement of organic fluorine by chlorine from the aluminum chloride catalyst; to prepare the desired chlorofluoropropanes, they treated various chloropropanes with antimony fluoride.^{2b,3}

We have now successfully brought about the aluminum chloride-catalyzed addition of chloromethanes and chlorofluoromethanes to tetrafluoroethylene as shown in Table I. In addition reactions with chlorotrifluoroethylene (see Table II), the yields were smaller and halogen exchange occurred with replacement of organic fluorine by chlorine.

TABLE I

PRODUCTS FROM HALOMETHANES AND TETRAFLUOROETHYLENE

Halomethane	Primary adduct %	Halogen replacement product
CHCl ₃	CHCl ₂ CF ₂ CF ₂ Cl	83
CCl ₄	CCl ₃ CF ₂ CF ₂ Cl	88
CCl ₃ F	CCl ₂ FCF ₂ CF ₂ Cl	55
CHCl ₂ F	CHClFCF ₂ CF ₂ Cl	50
CHClF ₂		C ₃ Cl ₂ F ₃ H (14%)
CHCl ₂ F	CHClFCCl ₂ CCl ₃ ^a	58

^a Adduct from tetrachloroethylene. The authors are indebted to Dr. W. A. Hoffman for this experiment.

TABLE II

PRODUCTS FROM HALOMETHANES AND CHLOROTRIFLUOROETHYLENE

Halomethane	Primary adduct %	Halogen replacement product %
CHCl ₃	CHCl ₂ CF ₂ CFCl ₂	2 CHCl ₂ CF ₂ CCl ₃ 20 ^a
CCl ₄	CCl ₃ CF ₂ CFCl ₂	14 CCl ₃ CF ₂ CCl ₃ 30 C ₃ Cl ₄ F ₄ 18
CCl ₃ F	CCl ₂ FCF ₂ CFCl ₂	30
CHCl ₂ F	CHClFCF ₂ CFCl ₂	28
CHClF ₂		C ₃ Cl ₃ F ₄ H 9

^a The authors are indebted to Dr. T. A. Ford for this experiment.

Formation of the primary adducts without halogen exchange appears dependent on the use of a monofluoromethane. Thus dichlorofluoromethane and trichlorofluoromethane gave only the

(1) (a) Böeseken and Prins, *K. Akad. Wetenschappen, Amsterdam*, **19**, 776 (1911); (b) Prins, *J. prakt. Chem.*, **89**, 414 (1914); (c) Prins, *Rec. trav. chim.*, **81**, 1065 (1932); (d) Prins and Engelhard, *ibid.*, **64**, 307 (1935).

(2) (a) Henne and Newman, *THIS JOURNAL*, **60**, 1697 (1938); (b) Henne and Ladd, *ibid.*, **60**, 2491 (1938).

(3) (a) Henne and Renoll, *ibid.*, **59**, 2434 (1937); (b) Henne and Renoll, *ibid.*, **61**, 2489 (1939); (c) McBee, Henne, Hass and Elmore, *ibid.*, **62**, 3340 (1940); (d) McBee, Truchan and Bolt, *ibid.*, **70**, 2023 (1948).

primary products in reactions with tetrafluoroethylene, chlorotrifluoroethylene or tetrachloroethylene. In a single instance, the replacement of chlorine by fluorine was observed. The product from carbon tetrachloride and chlorotrifluoroethylene contained a fraction C₃Cl₄F₄ which can be accounted for in this way.

The structures assigned in Table III to five of the chlorofluoropropanes are identical with structures previously proposed by Henne and co-workers for chlorofluoropropanes synthesized in a different way and of somewhat different properties. The structures designated in Table III can be inferred from the following facts. The product from carbon tetrachloride and tetrafluoroethylene corresponds in composition to the chlorofluoropropane formed by addition of one chlorine atom and one trichloromethyl group across the ethylenic bond. In reactions involving a chloromethane containing hydrogen or fluorine, the fragments which add must also be chlorine and its complementary halomethyl group, since neither carbon tetrafluoride nor trifluoromethane combines with tetrafluoroethylene and since the carbon-hydrogen bond of chloroform is not broken in Prins type reactions.^{1b}

The synthesis of chlorofluoropropanes from chlorotrifluoroethylene apparently proceeds by a similar mechanism. The chlorine evidently attaches itself to chlorotrifluoroethylene at the carbon atom already bonded to chlorine, since none of the products could be dechlorinated by refluxing with zinc and alcohol. This indicates that adjacent carbon atoms are not chlorinated and therefore the central carbon atom of the propane must be completely fluorinated. This mechanism is similar to that established by Prins^{1b} for the addition of chloromethanes to chloroethylenes.

In selected instances in which fluorine was replaced by chlorine, the halogen exchange *must* have taken place after formation of the chlorofluoropropane, while in other instances the exchange *may* have occurred before the Prins type reaction.

Experimental

Most of the chlorofluoropropanes were synthesized in a silver-lined autoclave under their own pressures at 50–125° with aluminum chloride catalyst present in amounts ranging from 0.5 to 10.0% by weight of combined reactants. The reaction times varied from two to twenty-four hours. The reactants used and the yields and properties of the products are listed in Table III. The aluminum chloride, and halomethane if liquid at room temperature, were placed in the

TABLE III
 SYNTHESIS OF CHLOROFLUOROPROPANES

Reactant/ Methane Ethylene		Probable structure	Yield, ^g %	Products B. p., °C.	<i>n</i> _D ²⁰	<i>d</i> ₄ ²⁰	C	Calcd. Cl	Analyses, %			Found Cl	F
									F	C			
CHCl ₃	C ₂ F ₄	CHCl ₂ CF ₂ CF ₂ Cl ^a	83	91.2	1.3704	1.6115		48.6	34.6			47.4	32.7
CCl ₄	C ₂ F ₄	CCl ₃ CF ₂ CF ₂ Cl ^b	88	114.5	1.3974	1.6927		55.9	29.9			56.1	30.4
CCl ₃ F	C ₂ F ₄	CCl ₂ FCF ₂ CF ₂ Cl	54	72-73	1.3578	1.6429	15.2	44.9		16.1		44.7	
CHCl ₂ F	C ₂ F ₄	CHClFCF ₂ CF ₂ Cl	46	51-53	1.3262	1.5492	17.7	34.9	46.8	18.1		33.8	43.7
CHClF ₂	C ₂ F ₄	C ₃ Cl ₂ F ₆ H	12	52-54			17.7	34.9		17.8		33.1	
CHCl ₂ F	C ₂ Cl ₄	CHClFCCl ₂ CCl ₃	38	209-211	1.5072			79.2				78.5	
CHCl ₃	C ₂ ClF ₃	CHCl ₂ CF ₂ CFCl ₂	2	127	1.4189	1.6704		60.2	24.2			60.8	23.6
		CHCl ₂ CF ₂ CCl ₃ ^c	10	171-172	1.4621	1.7241		70.3	15.1			67.1	14.8
CCl ₄	C ₂ ClF ₃	CCl ₃ CF ₂ CFCl ₂ ^d	3	155.5-157	1.4399	1.7608	13.4	65.6	21.0	13.4		61.8	20.5
		CCl ₃ CF ₂ CCl ₃ ^e	9	196.5-197	1.4777	1.7975	12.5	74.2	13.3	13.1		71.5	13.1
		C ₃ Cl ₄ F ₄	6	114-115.5	1.4081		14.2	55.9	29.9	14.4		54.1	24.7
CCl ₃ F	C ₂ ClF ₃	CCl ₂ FCF ₂ CFCl ₂	24	112.5-115	1.3980	1.7006	14.2	55.9	29.9	14.0		54.0	26.1
CHCl ₂ F	C ₂ ClF ₃	CHFCICF ₂ CFCl ₂	20	90-91	1.3712	1.6162	16.4	48.6	34.6	16.7		46.1	33.1
CHClF ₂	C ₂ ClF ₃	C ₃ Cl ₃ F ₄ H	20	90-93	1.3710	1.6142	16.4	48.6	34.6	16.9		47.3	35.0

^a Henne, *et al.*,^{4c} have assigned this structure to a compound boiling at 91.7-91.9°; *n*_D²⁰ 1.3750; *d*₄²⁰ 1.5877. ^b Henne, *et al.*,^{4c} have described a compound of this structure, b. p. 112-112.5°; *n*_D²⁰ 1.3961; *d*₄²⁰ 1.6992. ^c Henne, *et al.*,^{4a} have described a compound of this structure, b. p. 174°; *n*_D²⁰ 1.46410; *d*₄²⁰ 1.7557. ^d Melts at 55-56°. Henne, *et al.*,^{4a} attribute this structure to a compound melting < -80°; b. p. 152-154°; *n*_D²⁰ 1.43887; *d*₄²⁰ 1.7607. ^e Melts at -5°. Henne, *et al.*,^{4a} have described a compound of this structure, b. p. 194-194.4°; m. p. -15.8°; *n*_D²⁰ 1.48064; *d*₄²⁰ 1.8136. ^f When carbon tetrachloride or chloroform was one of the reactants the mole ratio of methane to olefin was about 2:1. In all other cases the mole ratio was 1:1. ^g Based on olefin used.

autoclave which was closed and chilled in Dry Ice-acetone. The halomethane if gaseous at room temperature and the haloethylene were forced in under pressure. The autoclave was clamped in a reciprocating shaker and heated. Following reaction, the gaseous compounds were bled off and liquified in a trap cooled with Dry Ice-acetone. The condensate was fractionally distilled. The liquid and solid remaining in the autoclave were removed by slurring with ether. The slurry was shaken with hydrochloric acid containing crushed ice, and the ethereal extract was washed with water, dried over Drierite and fractionally distilled.

The reaction of dichlorofluoromethane with tetrachloroethylene was carried out at atmospheric pressure. A glass flask fitted with a reflux condenser and an efficient stirrer was charged with tetrachloroethylene and aluminum chloride at room temperature, and dichlorofluoromethane was distilled in slowly. The reaction was accompanied by the evolution of heat. When the reaction mixture had cooled to room temperature, the product was removed and

washed with hydrochloric acid containing ice. After washing with water, the product was dried over calcium chloride and fractionated.

Acknowledgment.—The authors desire to express their appreciation to Dr. Paul R. Austin and to Dr. R. M. Joyce for helpful suggestions relating to this investigation.

Summary

Chlorofluoropropanes, including several new ones, have been prepared by the reaction of halogenated methanes with haloethylenes in the presence of aluminum chloride.

Reactions of chloroform or carbon tetrachloride with tetrafluoroethylene, of dichlorofluoromethane or trichlorofluoromethane with tetrafluoroethylene or chlorotrifluoroethylene, and of dichlorofluoromethane with tetrachloroethylene, proceeded normally without appreciable replacement of fluorine by chlorine. Halogen replacement occurred in reactions involving chlorodifluoromethane.

WILMINGTON, DELAWARE

RECEIVED JULY 27, 1948