

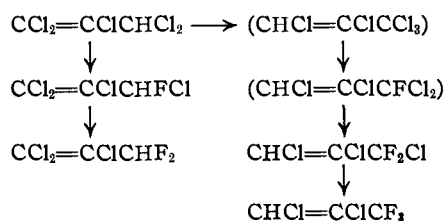
[JOINT CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA AND FROM HALOGEN CHEMICALS INC.]

## Isomerization During Allylic Fluorination

BY A. M. WHALEY AND H. W. DAVIS

In the attempt to prepare  $\text{CCl}_2=\text{CClCHF}_2$  (I) by the allylic fluorination of  $\text{CCl}_2=\text{CClCHCl}_2$  (II) unexpected results were obtained. The fluorination was conducted in the usual way for allylic polychlorides<sup>1</sup> except that some antimony pentachloride was added. This was done to make sure that no material remained in the monofluoride stage. The boiling point of the above difluoride was predicted to be approximately  $112^\circ$ ; however, the entire product distilled at about  $53^\circ$ . This material was found to be  $\text{CHCl}=\text{CClCF}_3$  (III), the formation of which is explained by an allylic rearrangement during fluorination.

In order to determine if the antimony pentachloride was the isomerization agent, a fluorination was carried out using only antimony trifluoride. The product upon fractionation, yielded the following compounds: (III), 26%;  $\text{CHCl}=\text{CClCF}_2\text{Cl}$  (IV), 21%; (I), 24%. There was also a small amount of material boiling at  $150^\circ$ , the predicted boiling point of  $\text{CCl}_2=\text{CClCHFCl}$  (V). The course of the reaction is indicated by the following scheme:



This experiment shows that even in the reaction with antimony trifluoride alone there is partial isomerization. Moreover, this isomerization becomes more complete as the reaction progresses. This was evidenced by the fact that the temperature of the reaction distillate was approximately  $54^\circ$  during the last part of the process.

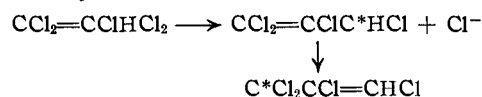
This appears to be a novel case of rearrangement during allylic fluorination. It is of interest to note that it does not occur when compounds containing an allylic  $-\text{CCl}_3$  group are fluorinated. For example,  $\text{CHCl}=\text{CClCCl}_3$  (VI) is known to give (III)<sup>1</sup> and  $\text{CHCl}=\text{C}(\text{CH}_3)\text{CCl}_3$  forms  $\text{CHCl}=\text{C}(\text{CH}_3)\text{CF}_3$ .<sup>2</sup> Hexachloropropene gives  $\text{CCl}_2=\text{CClCF}_3$ ; however, in this case isomerization would not lead to a different product.

To study further the fluorination of allylic  $-\text{CHCl}_2$  groups,  $\text{CHCl}=\text{CClCHCl}_2$  (VII) was prepared by the method of Prins<sup>3</sup> and fluorinated. Only  $\text{CHCl}=\text{CClCHF}_2$  (VIII) was found, but as in the case of hexachloropropene, even if rear-

angement occurred, only one product would be formed.

The fluorination of  $\text{CCl}_2=\text{CHCHCl}_2$  (IX) has been mentioned in the literature<sup>4</sup> with the formation of  $\text{CCl}_2=\text{CHCHF}_2$  (X); however, the tetrachloroolefin actually obtained from the  $\text{CHCl}_2\text{-CHClCHCl}_2$  (XI) used as an intermediate is (VII)<sup>3,5</sup> and not (IX). Therefore, the difluoride reported to be (X) was in reality (VIII). Moreover, fluorination of (IX), if isomerization occurred as it does in the case of (II), would give  $\text{CHCl}=\text{CHCF}_3$ .

The rearrangement herein reported can be clarified by the mechanism



This last then reacts with antimony trifluoride to form (III). The isomerization apparently occurs during the actual process of fluorination since no  $\text{CHCl}=\text{CClCCl}_3$  (VI) was obtained when (II) was refluxed for one hour with antimony pentachloride. Generally, when it is possible for a  $-\text{CF}_3$  group to form, one is obtained. Thus it is possible that the tendency to form the stable  $-\text{CF}_3$  group is the driving force causing this allylic rearrangement. In any event, this isomerization represents a new method of preparation of  $-\text{CF}_3$  groups. In our work at no time was there any evidence of the migration of a fluorine atom.

The physical constants, b.p.  $186.7^\circ$ ,  $n_D^{20}$  1.5333, obtained for our starting material (II), differed somewhat from those reported by Prins,<sup>3</sup> which were  $183^\circ$  and 1.5313, respectively. The structure of (II), however, could hardly be other than  $\text{CCl}_2=\text{CClCHCl}_2$  since we prepared it from  $\text{CHCl}_2\text{CCl}_2\text{CHCl}_2$ , a compound which can only give one pentachloroolefin on dehydrochlorination. The presence of an allylic  $-\text{CHCl}_2$  group was confirmed by the method of Prins,<sup>3</sup> the phenylhydrazone obtained having the same melting point as reported by that author. The above values were again found when (II) was made (a) from  $\text{CCl}_2\text{-CHClCHCl}_2$  formed by condensing  $\text{CHCl}_3$  with  $\text{CHCl}=\text{CCl}_2$  and (b) from the hexachloride fraction obtained in the chlorination of 1,2,3-trichloropropane.

That the properties of the material assumed to be (III) agreed with published values<sup>1</sup> was taken as sufficient proof of structure. Also, exhaustive chlorination in sunlight led to a compound melting at  $109^\circ$ , which agrees with the value reported for

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

(2) Unpublished work, A. M. Whaley.

(3) Prins, *J. prakt. Chem.*, [2] **89**, 421 (1914).

(4) Henne, Alderson and Newman, *THIS JOURNAL*, **67**, 919 (1945).

(5) Gerding, Prins and Rijnders, *Rec. trav. chim.*, **65**, 165-167 (1946).

$\text{CCl}_2\text{CCl}_2\text{CF}_3$ .<sup>6</sup> To prove the structure of (I), it was stirred at room temperature with excess sulfuric acid for six hours and poured in water. During the acid treatment hydrogen fluoride was evolved. An irritating oil was obtained which reacted with phenylhydrazine to give a hydrazone identical with that from (II), melting at 97–98°. The fluorinated material boiling at 97° is without doubt (IV) since its boiling point is 43° higher than that of (III). This is in agreement with the general change in boiling point caused by replacing a chlorine atom by an atom of fluorine in such groups.

### Experimental

**Fluorination of  $\text{CCl}_2=\text{CClCHCl}_2$  (II) with Catalyst.**—Ground antimony trifluoride, 537 g. (3 moles), was placed in a two-liter round-bottom flask surmounted by a 550-mm. air condenser. The top of this tube contained a thermometer and a bent tube connected to a water cooled downward condenser for distillation. A filter flask, containing about 200 ml. of concentrated hydrochloric acid and attached to the condenser with an adapter, served as a receiver. Fifteen milliliters of antimony pentachloride was added as catalyst. Then (II), 500 g. (2.35 moles), was added gradually from a dropping funnel, heat being applied at the same time. The reaction soon started and product distilled smoothly at 54°. Fresh olefin was added at the same rate at which product was removed. The distillate was washed three times with concentrated hydrochloric acid, once with dilute sodium hydroxide solution,

(6) Henne and Whaley, *THIS JOURNAL*, **64**, 1158 (1942).

dried and distilled to give 357 g., 92%, of (III), b. p. 53.7°.

**Fluorination of (II) without Catalyst.**—The apparatus was the same in this case as before. Ground antimony trifluoride, 970 g. (5.4 moles), was placed in the reaction flask, addition of 852 g. (4 moles) of (II) started and heat applied. The reaction was slow to start, rather strong heat being required. The distillate temperature at the start was 140° but it gradually went down, staying for awhile around 110°. During the addition of the last 300 g. of (II) the temperature was in the vicinity of 54°. The product was purified as before and distilled with the following results: 175 g., 26%, of (III), b. p. 53.7°; 157 g., 21%, (IV), b. p. 97°,  $n_D^{20}$  1.4253; 179 g., 24%, (I), b. p. 114.4°,  $n_D^{20}$  1.4452; 44 g. of material boiling from 115 to 180°.

**Fluorination of  $\text{CHCl}=\text{CClCHCl}_2$  (VII).**—Two-hundred forty-eight grams (1.33 moles) of (VII) and 230 g. of ground antimony trifluoride (1.3 moles) reacted without catalyst as described above. The temperature of the distillate during the reaction was 100–110°. Purification gave 160 g., 82%, of (VIII), b. p. 89°,  $n_D^{20}$  1.4150. The use of a small amount of antimony pentachloride as catalyst was found to hasten the reaction. However, when more than about 5 ml. of catalyst was used, the yield was decreased considerably.

### Summary

The fluorination of two allylic polychlorides,  $\text{CCl}_2=\text{CClCHCl}_2$  and  $\text{CHCl}=\text{CClCHCl}_2$ , has been studied. In the case of the first one, an isomerization leading to the formation of a  $-\text{CF}_2$  group was observed. Two new compounds,  $\text{CHCl}=\text{CClCF}_2\text{Cl}$  and  $\text{CCl}_2=\text{CClCHF}_2$ , are reported.

COLUMBIA, S. C.

RECEIVED OCTOBER 8, 1947

[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

## Reactions of Some Highly Chlorinated Unsaturated $\text{C}_5$ Hydrocarbons with Chlorine and Copper<sup>1</sup>

BY R. W. BOST AND J. A. KRYNITSKY<sup>2</sup>

In connection with a study of some highly chlorinated hydrocarbons, it was of interest to investigate some chlorination and coupling reactions of some polychlorinated unsaturated  $\text{C}_5$  hydrocarbons which were used as intermediates in the preparation of hexachlorocyclopentadiene.<sup>3</sup>

Early work by Prins<sup>4</sup> showed that hexachloropropene can be made to add chlorine, in the presence of sunlight, to give almost quantitative yields of the octachloro compound. Later, McBee and co-workers<sup>5,6</sup> reported that the action of chlorine at high temperatures and pressures on polychloropentanes and heptanes results in a chlorinolysis with the formation of carbon tetrachloride, hexa-

chloroethane, and a substance which was later shown to be octachlorocyclopentene. Recently, Prins<sup>7</sup> has reported that hexachlorocyclopentadiene reacts readily with chlorine to form octachlorocyclopentene yet octachloro-1,3-pentadiene (I) does not add the halogen but does give a small amount of hexachloroethane on continual exposure.

In this work, chlorinations of both octachloro-1,3-pentadiene (I) and 1,1,2,3,3,4,5,5,5-nona-chloro-1-pentene (II) were carried out in the presence of direct sunlight. It was found that at temperatures of 100–130°, (I) undergoes a chlorinolysis reaction to form considerable amounts of hexachloroethane and carbon tetrachloride. However, at lower temperatures (36–52°), the extent of reaction was found to be much reduced and only small amounts of the chlorinolysis products were obtained. Experiments with (II) showed that this compound, like (I), is also cleaved through the action of chlorine to form hexachloroethane and s-heptachloropropane. With (II), however, reaction was found to proceed more rapidly than

(1) From a thesis presented by John A. Krynitsky to the Graduate School of the University of North Carolina, June, 1943, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. This work was done under a contract between the Naval Research Laboratory, Washington, D. C., and the University of North Carolina. Publication was delayed for security reasons.

(2) Present address: Naval Research Laboratory, Washington, D. C.

(3) Krynitsky and Bost, *THIS JOURNAL*, **69**, 1918 (1947).

(4) H. J. Prins, *J. prakt. Chem.*, **89**, 414–429 (1914).

(5) McBee, Hass and Pierson, *Ind. Eng. Chem.*, **33**, 181–185 (1941).

(6) McBee, Hass and Bordenca, *ibid.*, **35**, 317–320 (1943).

(7) H. J. Prins, *Rec. trav. chim.*, **65**, 455–467 (1946).