

374. Fluorination of 1 : 2 : 3 : 4-Tetrachlorobutadiene with Chlorine Fluorides.

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Tetrachlorohexafluoro-, pentachloropentafluoro-, and hexachlorotetrafluoro-butanes have been prepared by the reaction of 1 : 2 : 3 : 4-tetrachlorobutadiene with chlorine fluorides. The yields of the individual chlorofluorobutanes depended on the conditions and the fluorinating agent used. Dechlorination of the butanes by zinc gave the appropriate perfluoro- and chlorofluoro-butadienes.

VERY little work has been done on the fluorination of organic compounds with chlorine fluorides. Ellis and Musgrave¹ reported the fluorination of aromatic hydrocarbons to products with low halogen contents and there are patents covering the preparation of chlorofluorocarbon oils.²

This paper describes work on the preparation of chlorofluorobutanes and the evaluation of chlorine mono- and tri-fluoride as fluorinating agents for organic compounds. The work involved liquid-phase reactions of 1 : 2 : 3 : 4-tetrachlorobutadiene with chlorine mono- and tri-fluoride under conditions which ensure dissipation of the energy released in the highly exothermic reactions. This requirement was satisfied by using a relatively large charge in a nickel vessel in which the chlorine fluoride feed-line was placed $\frac{1}{4}$ in. below the centre of a high speed vaned-disc stirrer, the arrangement providing good dispersion of the reagent throughout the whole charge. The fluorinating agent was diluted with nitrogen in the early stages of the reaction.

For determination of their structures the products were dechlorinated to dienes which in turn were brominated and/or chlorinated by established methods.

EXPERIMENTAL

1 : 2 : 3 : 4-Tetrachlorobutadiene was separated from the by-products obtained in manufacture of trichloroethylene. It was purified by fractional distillation through a still with an efficiency of 15 theoretical plates. The tetrachlorobutane used in the fluorinations was a mixture of the liquid and the solid stereoisomer, identified by their physical properties.³ The solid isomer was separated by cooling the mixture and filtering it off at -20° . It was purified by recrystallisation from ethyl alcohol.

The liquid isomer had b. p. 188° , n_D^{20} 1.557 (Found: C, 24.1; H, 1.1; Cl, 75.1%; M , 193. Calc. for $C_4H_2Cl_4$: C, 25; H, 1.05; Cl, 73.95%; M , 192). The solid isomer had b. p. 189° , m. p. 49.5° (Found: C, 24.2; H, 1.0; Cl, 75.2%; M , 197).

Reaction of 1 : 2 : 3 : 4-Tetrachlorobutadiene with Chlorine Trifluoride.—The reaction was carried out in a 4 l. nickel vessel under a water-cooled condenser. Gaseous chlorine trifluoride, initially diluted with 5 volumes of nitrogen, was passed through vigorously stirred tetrachlorobutadiene (3800 g.), the temperature of which was gradually raised from 20° to 150° . The flow-rate of chlorine trifluoride was gradually increased from 10 to 40 l./hr., and dilution by nitrogen was reduced to 1 : 1 during 10 hr.; nitrogen was cut off completely after 20 hr.

The reaction was stopped when the refractive index of the charge remained practically constant at n_D^{20} 1.449 ± 0.001 , a total of 3800 g. of chlorine trifluoride having been passed. During the run samples of the charge were withdrawn and analysed.

Fractional distillation of the final product (6030 g.) showed that it consisted of: (i) 1 : 2 : 3 : 4-tetrachloro-1 : 1 : 2 : 3 : 4-hexafluorobutane (3%), n_D^{20} 1.385, b. p. 135° (Found: C, 15.6; Cl, 47.8; F, 36.1. Calc. for $C_4Cl_4F_6$: C, 15.8; Cl, 46.7; F, 37.5%) (Miller⁴ gives b. p. 134.5° , n_D^{20} 1.385); (ii) a product $C_4Cl_5F_5$ (20%), n_D^{20} 1.423, b. p. 172° (Found: C, 15.0; Cl, 56.9;

¹ Ellis and Musgrave, *J.*, 1950, 3608; 1953, 1063.

² B.P. 633,678, 676,374, 695,811, 738,289, 774,737; Canad. P. 556,636.

³ Huntress, "The Preparation, Properties, Chemical Behaviour, and Identification of Organic Compounds," J. Wiley and Sons, Inc., New York, 1948.

⁴ Miller, Nat. Nuclear Energy Series Div. VII, Vol. I, "Preparation, Properties and Technology of Fluorine and Organic Fluorine Compounds," 1951, pp. 567—685.

F, 28.2. Calc. for $C_4Cl_5F_5$: C, 15.0; Cl, 55.4; F, 29.6% (Miller ⁴ gives b. p. 104.5°/100 mm., n_D^{20} 1.420); (iii) 1 : 1 : 2 : 3 : 4 : 4-hexachloro-1 : 2 : 3 : 4-tetrafluorobutane (50%), n_D^{20} 1.455, b. p. 209° (Found: C, 14.2; Cl, 63.5; F, 22.2. Calc. for $C_4Cl_6F_4$: C, 14.2; Cl, 63.2; F, 22.6%) (Miller ⁴ gives b. p. 134°/100 mm., n_D^{20} 1.457); and (iv) material, $C_4Cl_7F_3$, n_D^{20} 1.488, b. p. 245°/760 mm., 92°/20 mm. (Found: C, 13.7; Cl, 70.3; F, 16.2. Calc. for $C_4Cl_7F_3$: C, 13.6; Cl, 70.3; F, 16.1%) (Miller ⁴ gives b. p. 125°/25 mm., n_D^{20} 1.491). The rest of the product was in intermediate fractions.

Reaction of 1 : 2 : 3 : 4-Tetrachlorobutadiene with Chlorine Monofluoride.—The reaction was carried out in a vessel similar to that recorded above but of 1 l. capacity. Chlorine monofluoride was prepared by reaction of chlorine trifluoride with chlorine at 360° and was used directly. The gas, initially diluted with 3 volumes of nitrogen, was passed through tetrachlorobutadiene (382 g.) at the rate of 18 l./hr. at 20° increasing gradually to 120°. The flow of nitrogen was gradually decreased so that the fluorinating agent was undiluted after 15 hr. The reaction was stopped when the refractive index remained practically constant at 1.418. Samples were withdrawn during the reaction and analysed.

Fractional distillation of the final product (428 g.) gave 15% of the tetrachlorohexafluorobutane, b. p. 135°, n_D^{20} 1.385, 50% of the pentachloropentafluorobutane, b. p. 172°, n_D^{20} 1.423, and about 25% of a mixture of hexachlorotetrafluorobutane and hydrogen-containing chlorofluorobutanes.

Reaction of Chlorofluorobutanes with Chlorine Monofluoride.—The reaction was carried out in the 1 l. vessel, but the condenser was replaced with a still head so that the product distilled off as it was formed. Undiluted chlorine monofluoride was passed through a mixture of chlorofluorobutanes (n_D^{20} 1.449; 542 g.), at 150–155°, previously obtained in the reaction of 1 : 2 : 3 : 4-tetrachlorobutadiene with chlorine trifluoride. The product (440 g.) consisted of 70% of tetrachlorotetrafluoro- (b. p. 135°, n_D^{20} 1.385) and 10% of pentachloropentafluorobutane (b. p. 172°, n_D^{20} 1.423), the rest being chlorofluorocarbons of less than 4 carbon atoms and $C_4Cl_6F_4$.

Dechlorination of 1 : 2 : 3 : 4-Tetrachloro-1 : 1 : 2 : 3 : 4 : 4-hexafluorobutane.—The chlorofluorobutane was added dropwise to the stirred mixture of zinc dust (about 400 g.), butyl alcohol (1.2 l.), and acetic acid (5 ml.) at 85–95°; in no run were more than 2 g. of the chlorofluorobutane used per g. of zinc dust. The product passed through a fractionating column kept at 10° and was collected in traps at 0° and –80°.

The product was refluxed for 3 hr. over phosphoric oxide and fractionally distilled in a low-temperature still with an efficiency of 20 theoretical plates. Practically all the product boiled at 5.5° and had a molecular weight of 159.5 ± 0.5 (65% yield). Miller ⁴ and Haszeldine ⁵ reported 6° and 5.8° respectively for the b. p. of perfluorobutadiene.

Dechlorination of Pentachloropentafluorobutane.—The dechlorination was carried out as above except that the fractionating column was at room temperature instead of 10°. The product, after refluxing over phosphoric oxide, was distilled first at atmospheric pressure, then at 80 mm. in the low-temperature still. The final product (60% yield) boiled at 38°/760 mm. and –11.5°/80 mm. and had n_D^{20} 1.3385 ± 0.0005 (Found: M , 178.5 ± 0.5). Miller ⁶ prepared $CF_2\text{CCl}\cdot CF\text{CF}_2$, b. p. 37°.

Dechlorination of 1 : 1 : 2 : 3 : 4 : 4-Hexachloro-1 : 2 : 3 : 4-tetrafluorobutane.—Dechlorination was carried out as above with the fractionating column at 60°. The crude product distilled at 75–80° at atmospheric pressure. The distillate was refluxed over phosphoric oxide, then fractionated at 55 mm.; most of it then boiled at $11^\circ \pm 1^\circ$ and had M , 195 ± 1 . A fraction of b. p. 12–14°, having M , 194 ± 2 , was also obtained. It is possible that both fractions were isomers of dichlorotetrafluorobutadiene. The mixed fractions (48% yield) had b. p. $79^\circ \pm 1^\circ$, n_D^{20} 1.404. Miller ^{4,6} gives for $CClF\text{CF}\cdot CF\text{CClF}$ b. p. 78°, n_D^{20} 1.402, and for $CF_2\text{CCl}\cdot CCl\text{CF}_2$ b. p. 69–70°, n_D^{20} 1.3832. Haszeldine and Osborne ⁷ give for $CCl\text{CF}\cdot CF\text{CClF}$ b. p. 79°, n_D^{20} 1.403.

Derivatives of Perfluoro- and Chlorofluoro-butadienes.—Addition of bromine to perfluorobutadiene was carried out at 0° rising to 105°, and to monochloropentafluoro- and dichlorotetrafluorobutadiene at 20–150°. In each case the product consisted of a single fraction of constant b. p. and n . Addition of chlorine to dibromohexafluorobutene obtained in the addition of bromine to perfluorobutadiene occurred only at 120° in light of 5300–4500 Å.

⁵ Haszeldine, *J.*, 1952, 4423.

⁶ Miller, U.S.P. 2,668,182.

The products were: Dibromohexafluorobutene, b. p. 102° , n_D^{20} 1.396 (Found: C, 14.6; Br, 50.1; F, 35.1. Calc. for $C_4Br_2F_6$: C, 14.0; Br, 49.7; F, 35.4%) (Haszeldine⁵ gives b. p. 99—100°, n_D^{20} 1.394). Dibromodichlorohexafluorobutane (from $C_4Br_2F_6$) (Found: C, 12.5; Br, 42.2; Cl, 19; F, 25.8%; M , 394 ± 1 . Calc. for $C_4Cl_2Br_2F_6$: C, 12.2; Br, 40.7; Cl, 18.1; F, 29.0%; M , 393). Dibromochlorotrifluorobutane (from C_4ClF_5), b. p. 137° , n_D^{20} 1.4325 (Found: C, 14.3; Br, 47.0; Cl, 10.9; F, 27.9. Calc. for $C_4ClBr_2F_5$: C, 14.2; Br, 47.3; Cl, 10.5; F, 28.0%). Dibromodichlorotetrafluorobutane (from $C_4Cl_2F_4$), b. p. $80^{\circ}/10$ mm., n_D^{20} 1.477 (Found: C, 13.7; Br, 43.6; Cl, 21.2; F, 20.6. Calc. for $C_4Cl_2Br_2F_4$: C, 13.5; Br, 45.1; Cl, 20.0; F, 21.4%). Miller⁴ and Haszeldine⁵ obtained $C_4Br_2F_6$ in the bromination of perfluorobutadiene at 120° in ultraviolet light (*i.e.*, under more vigorous conditions).

DISCUSSION

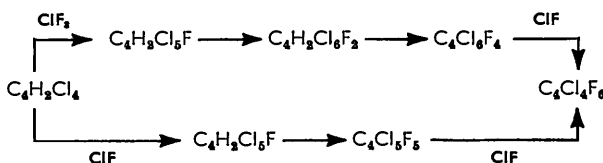
The results show that the yields of the individual chlorofluorobutanes, $C_4Cl_4F_6$, $C_4Cl_5F_5$, $C_4Cl_6F_4$, and $C_4Cl_2F_4$, depend on the reaction conditions, the fluorinating agent, and the extent to which the reactions are carried out (as indicated by the refractive index).

The hexachlorotetrafluorobutane is best prepared by reaction of tetrachlorobutadiene with chlorine trifluoride carried out to n 1.448 ± 0.001 . Good yields of the pentachloropentafluoro-compound are obtained by reaction of the hexachlorotetrafluorobutane with chlorine monofluoride until n drops to 1.418 ± 0.003 . More than 80% of hexachlorotetrafluoro- and/or pentachloropentafluoro-butane is converted into the tetrachlorohexafluorobutane by chlorine monofluoride at 150° if the product, boiling at 135° , is distilled off as it is made.

Only perfluorobutadiene was obtained on dechlorination of the tetrachlorohexafluoro-product; this butadiene, with bromine and then chlorine gave a quantitative yield of dibromodichlorohexafluorobutane; so the chlorofluorobutane must have been $CClF_2 \cdot CClF \cdot CClF \cdot CClF_2$ and the product of dechlorination perfluorobutadiene.

Structures of the products $C_4Cl_5F_5$ and $C_4Cl_6F_4$ cannot be assigned with certainty but the exclusive formation of C_4ClF_5 and $C_4Cl_2F_4$ in their dechlorination indicates that at least one chlorine atom must have been attached to each carbon atom present. Agreement between the boiling points and refractive index of the butadiene derived from $C_4Cl_6F_4$ with that reported^{4,7} for $CClF \cdot CF \cdot CF \cdot CClF$ suggests the structure of $CCl_2F \cdot CClF \cdot CClF \cdot CCl_2F$ although $CClF_2 \cdot CCl_2 \cdot CClF \cdot CCl_2F$ and $CClF_2 \cdot CClF \cdot CCl_2 \cdot CCl_2F$ are not excluded. No reference could be found in the literature to the physical properties of these compounds or to $CF_2 \cdot CCl \cdot CF \cdot CClF$ and $CF_2 \cdot CF \cdot CCl \cdot CClF$, which can be derived from them by dechlorination.

The compositions of samples taken during the fluorinations indicate the annexed reactions.



Since similar observations were made for the reactions of hexachlorobutadiene, chlorinated ethylenes, and chlorinated aromatic compounds with the chlorine fluorides, the following generalisations can be made: (a) Chlorine trifluoride is more vigorous and efficient than the monofluoride in chlorofluorination of unsaturated chlorinated hydrocarbons. It is particularly useful for saturation of double bonds and replacement of hydrogen by halogen. (b) Chlorine monofluoride is a useful reagent for replacement of chlorine by fluorine in chlorofluorocarbons containing more chlorine than fluorine. It does not saturate double bonds or replace hydrogen by halogen as readily as does chlorine trifluoride.

The more vigorous nature of the reactions with chlorine trifluoride than of those with

⁷ Haszeldine and Osborne, *J.*, 1955, 3880.

chlorine monofluoride probably results from easier initiation of the reaction, thought to involve a radical mechanism. Chlorine trifluoride can be considered as very similar to fluorine because of the low heat of dissociation,⁸ $\text{ClF}_3 \rightleftharpoons \text{F}_2 + \text{ClF}$, $\Delta H = 26.5$ kcal./mole. Less energy is required in the dissociation of ClF_3 than in breaking the F-F bond in fluorine or the Cl-F bond in chlorine monofluoride, the respective bond dissociation energies being 36.6 (ref. 9) and 60.3 kcal./mole (ref. 10). The suggestion that the reactions of tetrachlorobutadiene with chlorine fluorides involve free radicals is supported by the results obtained in more recent, unpublished work in which tetrachloroethylene and chlorinated aromatic compounds were treated with a mixture of chlorine trifluoride and oxygen.

The author thanks his colleagues, Mrs. F. Dickinson for low-temperature fractionation of the halogenobutadienes and determinations of the molecular weight of some of the materials, Messrs. M. L. Jones and J. Parle for assistance in the experimental work, Mr. F. P. Johnson for analyses, and Mr. H. R. Leech for valuable discussions.

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[Received, November 14th, 1958.]

⁸ Schäfer and Wicke, *Z. Elektrochem.*, 1948, **25**, 205.

⁹ Nat. Bur. Standards, "Selected Values of Chemical Thermodynamic Properties."

¹⁰ Schmitz and Schumacher, *Z. Naturforsch.*, 1947, **20**, 258.
