733. *Organic Fluorides. Part XIII.* The High-temperature Dimerisation of Chlorotrifluoroethylene.*

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Chlorotrifluoroethylene, when passed through a tube packed with Pyrex glass chips at about 700°, is converted into a complex mixture of products, the chief of which is 1 : 2-dichlorohexafluoro*cyclo*butane. This product is formed also when the olefin is heated at 200° under high pressures. By dechlorination, the cyclic dimer is converted into perfluoro*cyclo*butene; this gives the corresponding 1 : 2-dibromo-compound with bromine, and, by oxidation with aqueous permanganate, tetrafluorosuccinic acid.

Part of the programme of work on organic fluoro-compounds in progress in this department a few years ago was a study of fluorinated olefins and the derived polymers. At that time one of the few readily available aliphatic fluoro-derivatives was 1 : 1 : 2-trichloro-1 : 2 : 2-trifluoroethane, which may be prepared by treatment of hexachloroethane with antimony trifluoride (Booth, Mong, and Burchfield, *Ind. Eng. Chem.*, 1932, **24**, 328; Locke, Brode, and Henne, *J. Amer. Chem. Soc.*, 1934, **56**, 1726). It is dechlorinated by zinc dust in boiling ethyl alcohol to give chlorotrifluoroethylene (Booth, Burchfield, Bixby, and McKelvey, *ibid.*, 1933, **55**, 2231; Locke, Brode, and Henne, *loc. cit.*). This olefin may be polymerised to give medium- and long-chain products, as was first reported in patents issued to I. G. Farben. A.-G. (Fr. P. 796,026, B.P. 465,520, G.P. 677,071). The polymers have been studied extensively in the U.S.A. [Miller, Dittman, Ehrenfeld, and Prober, *Ind. Eng. Chem.*, 1947, **39**, 333; Belmore, Ewalt, and Wojcik, *ibid.*, p. 338; for a full report

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of the work by Miller and his many co-workers see the chapter by Miller in " Preparation, Properties, and Technology of Fluorine and Organic Fluoro-compounds " (Editors, Slesser and Schram), McGraw-Hill, New York, 1951, p. 567], and we have carried out similar (unpublished) investigations in collaboration with workers of Imperial Chemical Industries Limited, Dyestuffs Division, Blackley.

In addition to this type of reaction we investigated the possibility of using chlorotrifluoroethylene and trichlorotrifluoroethane for the synthesis of other fluoro-compounds and, since attempts at Wurtz-type reactions were unsuccessful, attention was turned to possible short-chain polymerisations of chlorotrifluoroethylene. It was found that the olefin could be dimerised by heat, a *cyclo*butane derivative being the principal product; this paper describes these investigations.

The first experiments on the thermal dimerisation of chlorotrifluoroethylene were carried out by passing the olefin through an iron tube packed with copper turnings and heated to various temperatures. Variations tried were the use of gold-plated copper turnings, Pyrex glass chips, and nickel chips as packings in Pyrex glass tubes which, though some softening and deformation occurred, could be used with care at about 700°. These early experiments showed that at temperatures below 620° most of the chlorotrifluoroethylene could be recovered unchanged, whereas, at 800° or above, complete decomposition occurred; but between 680° and 730° a mixture of products was formed, most of which had boiling points between 18° and 100°. Of the materials tested, the best packing for the tube appeared to be Pyrex glass chips. Further, it was noticed that during several successive runs through a tube, the surface of the glass packing gradually became etched and that this coincided with a steady increase in the yield of products boiling higher than the starting material. Accordingly, some glass packing was etched by treatment with potassium fluoride and sulphuric acid before use, and, compared with ordinary unetched Pyrex chips, the yield of high-boiling product was considerably increased.

Treatment of the fractions of the pyrolysis product having b. p. 50—100° with zinc dust and ethyl alcohol gave a product, b. p. 0—10°, which could not be purified, but which appeared to be an impure fluoro-olefin.

Since these preliminary experiments indicated that a reaction, probably dimerisation, of chlorotrifluoroethylene was taking place under the influence of heat, a new and improved apparatus was built. Duplicate copper tubes (3′ long × 1″ internal diameter) were mounted in two twin-tube electrical furnaces, each 14″ long, placed end to end, thus enabling gradations of temperature to be achieved. In most of the experiments it was found to be convenient to use the first electric furnace as a preheater at 450—550°, the early experiments having shown that there was little or no reaction at these temperatures. The second furnace provided the reaction zone. The tubes were packed with pre-etched Pyrex glass chips. Experiments were first carried out to establish the optimum reaction temperature; the results are given in Table 1. Because of the complexity of the dimerisation product, complete fractionation was not attempted in these preliminary experiments; instead the fractions, b. p. 50—100°, were treated with zinc dust and ethyl alcohol, to determine the amounts of unsaturated fluorocarbon thus formed (Table 1). The effects of varying the size of the tube packing (Table 2) and of the length of packed section (Table 3) were also investigated. The optimum conditions found for the production of the chlorofluorocarbon intermediate were the use of etched glass chips in a tube graduated from 450—705°, a length of about 14″ being at the latter temperature. Fractionation of the complex pyrolysis product gave few pure compounds. 1 : 2-Dichloro-1 : 2-difluoroethylene and 1 : 1 : 2-trichloro-1 : 2 : 2-trifluoroethane were formed but the chief fraction, b. p. 60°, was a dimer of chlorotrifluoroethylene, later identified as 1 : 2-dichlorohexafluoro*cyclo*butane.

This cyclic chlorofluoro-compound, when refluxed with zinc dust and ethyl alcohol, gave an unsaturated fluorocarbon, b. p. 5—6°, which under ultra-violet irradiation gave a dibromo-addition product. Oxidation of the fluoro-olefin with potassium permanganate solution gave tetrafluorosuccinic acid, m. p. 116°, identified also as the dianilinium salt. By alkaline oxidation of heptafluoroadipic acid (Barbour, Mackenzie, Stacey, and Tatlow, unpublished results) tetrafluorosuccinic acid and its salt were obtained, identical with those

described above. Tetrafluorosuccinic acid has been reported but there is some confusion about the melting point. Henne and Zimmerschied (*J. Amer. Chem. Soc.*, 1947, **69**, 281) reported m. p. 86·4—87·4°, similar values being mentioned by later authors, but Padbury and Kropa (U.S.P. 2,502,478) gave m. p. 116—119°. We found that the acid had m. p. 116° when intensively dried and that it then analysed correctly for the anhydrous acid; if not specially dried the acid had m. p. 87°.

Isolation of tetrafluorosuccinic acid from the oxidation showed that the fluoro-olefin was perfluoro*cyclo*butene, and its precursor the corresponding 1 : 2-dichloro-compound. It was found that this dichlorohexafluoro*cyclo*butane was formed more conveniently from chlorotrifluoroethylene when the latter was heated at about 200° in a rocking autoclave at initial pressures of 50—100 atmospheres. Attempts to polymerise perfluoro*cyclo*butene by aqueous emulsion techniques were unsuccessful, no high-boiling or solid products being formed.

Simultaneously, similar investigations were carried out in the U.S.A. Henne and Ruh (*J. Amer. Chem. Soc.*, 1947, **69**, 279) mentioned briefly the high-pressure dimerisation of chlorotrifluoroethylene to the cyclic dimer, followed by the dechlorination of the latter to perfluoro*cyclo*butene; Harmon (U.S.P. 2,404,374 and 2,436,142) reported a similar series of reactions. The hot-tube reactions of chlorotrifluoroethylene were studied by Miller and his co-workers (*op. cit.*), who used unpacked tubes; below 500° they obtained the cyclic dimer; above 500°, in addition to this, the straight-chain dimer 3 : 4-dichlorohexafluoro-but-1-ene (b. p. 65—66°) and chlorofluoropropenes were formed. We did not isolate a pure fraction corresponding to the straight-chain dimer, but such a product was in fact present. The dechlorinations of the pyrolysis products (b. p. 50—100°) of the preliminary experiments yielded fluoro-olefins containing a small proportion of a more reactive olefin which appeared to be perfluorobutadiene. Small quantities of this diene were isolated in an impure form by dechlorination of the higher-boiling pyrolysis product (b. p. >65°). It appears that formation of the straight-chain dimer is inhibited if the pyrolysis is carried out in glass-packed tubes.

There is now considerable evidence that in fluorinated compounds the *cyclo*butane ring is a fairly stable structure. It is formed quite readily from several fluoro-olefins by self-dimerisation, or by reaction with other olefins [see Coffman, Barrick, Cramer, and Raasch (*J. Amer. Chem. Soc.*, 1949, **71**, 490) for reactions of tetrafluoroethylene in which *cyclo*-butane derivatives are formed].

Experimental

Preparation of Chlorotrifluoroethylene.—Ethyl alcohol (900 c.c.) was stirred in a 2-l. flask fitted with a paddle stirrer and liquid seal, a dropping funnel, and a reflux condenser which was cooled by ice and salt. Zinc dust (540 g.) was slowly added and then, whilst the flask was heated to 70°, 1 : 1 : 2-trichloro-1 : 2 : 2-trifluoroethane (405 g.) was run in during 1½ hours. The crude product which distilled through the cold condenser was redistilled, to give chlorotrifluoro-ethylene (217 g., 86%), b. p. −27°. Booth, Burchfield, *et al.* (*loc. cit.*) gave b. p. −28°.

Pyrolysis of Chlorotrifluoroethylene.—(a) *Apparatus.* The pyrolysis tube was of copper (36″ long × 1″ internal diameter); at the inlet end there was a copper–glass seal to which the vessels containing the chlorotrifluoroethylene were connected through standard ground-glass joints and a glass spiral, whilst at the outlet end a copper–glass ground flange, cooled by a lead spiral through which water was passed, led to a series of traps. The higher-boiling products were condensed in a trap cooled by ice and salt, whilst unchanged chlorotrifluoroethylene was trapped in a vessel cooled by solid carbon dioxide and could then be recycled. A duplicate pyrolysis tube was included alongside the first such that either could be connected to the inlet and the exit train. The pyrolysis tubes were heated by two twin-tube electric furnaces, each 14″ long, arranged end to end so that graded temperatures could be achieved, the temperatures being measured by iron–constantan thermocouples. The pyrolysis tubes were packed with Pyrex glass chips (1/16—1/8″) which had been cleaned with chromic acid, etched with potassium fluoride and sulphuric acid, treated a second time with chromic acid, washed with water, and dried. This treatment, together with standardisation of the size of the chips, was necessary to ensure reproducible results.

Chlorotrifluoroethylene was allowed to vaporise at 2·0—2·5 g./min. and was passed through

the pyrolysis tube. The product which did not condense in a trap cooled by ice–salt contained appreciable quantities of unchanged starting material and was recycled until it appeared that no more high-boiling material was produced. Since the product obtained was a very complex mixture it was not completely fractionated in the preliminary experiments, but the material having b. p. 50—100° was treated with zinc dust and ethyl alcohol, and pyrolysis efficiencies were based upon the yield of fluoro-olefin thus obtained.

(b) *Pyrolysis temperature.* The effect of different temperatures are summarised in Table 1. One electric furnace was used as a preheater and maintained the first half of the

TABLE 1.

Temp.	680°	690°	700°	705°	710°	715°	730°	735°	740°	765°
Monomer input (g.)	150	320	310	320	270	300	315	330	345	225
Crude yield, b. p. 50—100° (g.)	16	58	65	70	60	67	70	69	68	39
Yield of derived fluoro-olefin (g.)	0	4·5	8·0	10·0	8·2	7·9	5·5	5·0	4·3	0·8
Yield of derived fluoro-olefin (%)	0	2·0	3·7	4·5	4·4	3·8	2·5	2·2	1·8	0·5

reaction tube at 560° throughout this series, the reaction took place in the second section of the tube, the temperature of which is recorded in the table. The glass catalyst used all passed through an $\frac{1}{8}$″ mesh, and the input rate of chlorotrifluoroethylene was 2·4 g./min. The products were distilled, and material, b. p. 50—100°, was refluxed for 8 hours with a ten-fold excess of zinc dust and ethyl alcohol. No attempt was made to estimate the amounts of unchanged monomer in these experiments, so that the yields of olefin based on the monomer actually consumed were about twice those given.

(c) *Size of tube-packing.* These experiments were carried out with the preheater at 460° and the reaction zone at 705°. Chlorotrifluoroethylene was introduced at 2·4 g./min. The product having b. p. 50—100° (1 part) was refluxed for 8 hours at 85° with zinc dust (2·5 parts) and ethyl alcohol (4 parts) and from this dechlorinated material the fluoro-olefin, b. p. 6—8°, was isolated by fractional distillation. Details are given in Table 2.

TABLE 2.

Size of glass packing	Monomer input (g.)	Unchanged monomer recovered (g.)	Crude yield (g.) of material of b. p.: >20°	Crude yield (g.) of material of b. p.: 50—100°	Yield of olefin (g.)	Yield of olefin (%)
$<\frac{1}{16}$″	262	120	50	39	7·1	7·2
$\frac{1}{8}$—$\frac{1}{16}$″	277	138	92	66	20·0	20·7
$\frac{1}{4}$—$\frac{1}{8}$″	277	124	97	62	10·4	9·8
$>\frac{1}{4}$″	300	126	132	77	8·7	7·2

(d) *Length of packed heated section of tube.* Three experiments were carried out, the tube being packed with catalyst (size $\frac{1}{16}$—$\frac{1}{8}$″) as follows: (i) the tube was packed completely, and the whole length (28″) was heated to 705°, (ii) the tube was packed completely, 14″ was used as a preheater at 405°, the final 14″ being heated to 705°, and (iii) the final 6″ only of the tube was packed with catalyst, the first 14″ of the tube was heated to 405°, the final 14″ being heated to 705°. The monomer input rate was 2·3 g./min. The results are given in Table 3.

TABLE 3.

Expt. no.	Monomer input (g.)	Unchanged monomer recovered (g.)	Crude yield (g.) of material of b. p.: >20°	Crude yield (g.) of material of b. p.: >50°	Yield of olefin (g.)	Yield of olefin (%)
(i)	255	40	110	46	5	3·3
(ii)	270	135	89	62	19	20·2
(iii)	270	—	15	10	0	0

(e) *Fractionation of the crude pyrolysis product.* The crude product, obtained as in experiment (d) (ii), was fractionated in a 3-ft. vacuum-jacketed column packed with Fenske helices. The mixture was complex; after removal of unchanged chlorotrifluoroethylene (b. p. −27°) several fractions of constant b. p. were isolated (yields are expressed as percentages of the amount of unrecovered monomer). Fraction (i) (3·2%), b. p. 22° (Found: *M*, 139. Calc. for $C_2Cl_2F_2$: *M*, 133), was 1 : 2-dichloro-1 : 2-difluoroethylene for which Booth, Burchfield, *et al.* (*loc. cit.*) gave b. p. 21°; fraction (ii) (3·3%), b. p. 43—44° (Found: *M*, 178), was probably dichloro-

tetrafluoropropene; fraction (iii) (6·9%), b. p. 47·5—48·5°, n_D^{19} 1·3578, was 1 : 1 : 2-trichloro-1 : 2 : 2-trifluoroethane (Booth, Mong, and Burchfield, *loc. cit.*, gave b. p. 46·5—47°, n_D^{23} 1·3530); and fraction (iv) (20%), b. p. 59·5—60°, n_D^{14} 1·336 (Found: C, 20·6; Cl, 30·0; F, 49·0%; *M*, 238. Calc. for $C_4Cl_2F_6$: C, 20·6; Cl, 30·4; F, 48·9%; *M*, 233), was 1 : 2-dichlorohexafluoro-*cyclo*butane, identical with the material mentioned below.

Fraction (iii) (20·0 g.) was refluxed for 8 hours at 80° with zinc dust (60 g.) and ethyl alcohol (100 c.c.), to give chlorotrifluoroethylene (11·2 g., 90%), b. p. −27°.

High-pressure Dimerisation of Chlorotrifluoroethylene.—The olefin (293 g.) was heated at 220° for 12 hours in a rocking autoclave (initial pressure 80 atm.). From the product, there was isolated, by fractionation as before, 1 : 2-dichlorohexafluoro*cyclo*butane (174 g., 59%), b. p. 58·5—59·5°, n_D^{20} 1·3339, identical with the material from the pyrolysis experiments. Harmon (*loc. cit.*) gave b. p. 58—59°, n_D^{20} 1·3339, and Henne and Ruh (*loc. cit.*), b. p. 59·9°, n_D^{20} 1·3340.

In a reaction at 170—175° for 10 hours the olefin (217 g.) gave the cyclic dimer (21·2 g., 29%; olefin recovered 145 g.) whilst at 180—200° for 12 hours the olefin (338 g.) yielded the cyclic dimer (128 g., 57%; olefin recovered 113 g.).

*Hexafluoro*cyclo*butene.*—1 : 2-Dichlorohexafluoro*cyclo*butane (48·0 g.) was refluxed for 2½ hours with zinc dust (120 g.) and ethyl alcohol (225 c.c.). The product which distilled through the reflux condenser was collected and redistilled, to give perfluoro*cyclo*butene (26·7 g., 80%), b. p. 5—6°, m. p. −59°, d_{-35} 1·60 (Found: *M*, 159. Calc. for C_4F_6: *M*, 162). Harmon (*loc. cit.*) gave b. p. 5—6°, and Henne and Ruh (*loc. cit.*) recorded b. p. 1·1°, m. p. −60·4°.

1 : 2-*Dibromohexafluoro*cyclo*butane.*—The cyclic olefin (10·25 g.) and bromine (5 c.c.) were refluxed for 6 hours in a quartz vessel irradiated by ultra-violet light. The product, after being washed with sodium thiosulphate solution and with water, was dried (P_2O_5), filtered, and distilled, to give 1 : 2-dibromohexafluoro*cyclo*butane (10·6 g., 52%), b. p. 96—97°, n_D^{20} 1·3895 (Found: C, 14·9; F, 35·8%; *M*, 327. Calc. for $C_4Br_2F_6$: C, 14·9; F, 35·4%; *M*, 322). Harmon (*loc. cit.*) reported b. p. 96°, n_D^{20} 1·3889, for this compound.

Tetrafluorosuccinic Acid.—Perfluoro*cyclo*butene (15·7 g.), potassium permanganate (70 g.), and water (300 c.c.) were heated at 105° for 14 hours in a rocking autoclave. The mixture was filtered and the filtrate was decolourised with sulphur dioxide, acidified with concentrated sulphuric acid (50 c.c.), and extracted exhaustively with ether. The ethereal extracts were distilled, and the residue was heated at 75°/15 mm., leaving a very hygroscopic white acidic product (17·1 g., 93%), m. p. 87°.

A part of this acid (8·0 g.) was distilled under diminished pressure; the distillate (7·0 g.), after being dried *in vacuo* over phosphoric oxide for 5 hours at 60°, had m. p. 116—116·5° (Found: C, 25·3; H, 1·4; F, 39·6. Calc. for $C_4H_2O_4F_4$: C, 25·3; H, 1·1; F, 40·0%).

A portion of the acid (1·0 g.) in ether (25 c.c.) was treated with aniline until precipitation was complete. The precipitate, recrystallised from ethyl alcohol–chloroform, was *dianilinium tetrafluorosuccinate* (1·4 g.), m. p. 224° [Found: Equiv., 185 (by titration with standard alkali). $C_{16}H_{16}O_4N_2F_4$ requires Equiv., 188]. The acid and salt are identical with specimens prepared by oxidation of heptafluoroadipic acid (Barbour, Mackenzie, Stacey, and Tatlow, forthcoming publication). For the acid, Henne and Zimmerschied (*loc. cit.*) gave m. p. 86·4—87·4°, and Padbury and Kropa (*loc. cit.*) recorded m. p. 116—119°.

*Attempted Polymerisation of Perfluoro*cyclo*butene.*—This olefin was not polymerised when shaken in sealed tubes for 18 hours at 30—60° in an atmosphere of nitrogen with various aqueous systems including ammonium persulphate–sodium metabisulphite, ammonium persulphate–sodium thiosulphate, and ammonium persulphate–sodium hydroxide, with and without the addition of emulsifying agents. With the alkaline media some hydrolysis occurred with liberation of fluoride ion. The olefin was not affected by prolonged irradiation in ultra-violet light.

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