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THE VAPOUR PHASE FLUORINATION OF TRICHLOROETHYLENE WITH COBALT TRIFLUORIDE AND WITH MANGANESE TRIFLUORIDE

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Abstract—Reactions with cobaltic fluoride and with manganic fluoride have been used for the addition of fluorine to trichloroethylene and the ranges of products identified. With manganic fluoride the main one was 1,1,2-trichloro-1,2-difluoroethane. Upon dechlorination this yielded chloro-1,2-difluoroethylene which in some respects did not behave as a typical highly-fluorinated olefin. It was separated into *cis*- and *trans*-isomers and its bromine and iodine chloride adducts converted into bromo- and iodo-chlorodifluoroethylene respectively.

THE controlled addition of fluorine to olefinic double bonds cannot always be accomplished readily. Liquid-phase methods using elementary fluorine yield mixtures, products arising from substitution and dimerization as well as addition.[1,2] In the vapour phase similar effects can occur. Trichloroethylene in the vapour phase with fluorine gave chiefly 1,1,2-trichlorotrifluoroethane and tetrachloro-1,2-difluoroethane.[3] The use of a mixture of lead dioxide and hydrogen fluoride for the addition of two atoms of fluorine to halogeno-olefins has been described;[4] it was assumed that lead tetrafluoride was the fluorinating agent. However, the method is not always easily controlled. A patent claim[5] mentioned the use of cobaltic oxide or of manganese dioxide in place of lead dioxide. Cobaltic fluoride has been used to add fluorine to fluorochloro-olefins,[6] and in this Department, to fluorocyclohex-enes and -dienes.[7] Because 1,3- and 1,4-dienes are readily interconverted under these conditions,[8] complex products were obtained. The work described in this paper was begun some time ago and has been mentioned briefly before.[9] Vapour-phase reactions of trichloroethylene with cobalt trifluoride or manganese trifluoride under mild conditions were studied. A patent on this process has subsequently appeared;[10] treatment of trichloroethylene at 50–100° with cobalt trifluoride was claimed to give 1,1,2-trichloro-1,2-difluoroethane in high (unspecified) yields. No reference was made as to whether other products were formed at the same time. The use of manganese or nickel fluorides as fluorinating agents was also suggested.

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[3] M. Hauptschein and L. A. Bigelow, *J. Amer. Chem. Soc.* **72**, 3423 (1950).

[4] A. L. Henne and T. P. Waalkes, *J. Amer. Chem. Soc.* **67**, 1639 (1945).

[5] A. F. Benning and J. D. Park, U.S.P. 2,437,993/1948.

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[10] A. L. Dittman and J. M. Wrightson, U.S.P. 2,690,459/1954.

TABLE 1

Reagent	Temp	$CHCl{=}CCl_2$ fluorinated	Crude product	$CClF_2{\cdot}CClF_2$ + $CF_3{\cdot}CH_2Cl$ (b.p. 2–8°) I	$C_2HCl_2F_3$ (b.p. 29 –31·5°) II	$CClF_2.CCl_2F$ (b.p. 45·5–48°) III	$CCl_2F{\cdot}CHClF$ (b.p. 72–73°) IV	$CHCl{=}CCl_2$ (b.p. 87°)	$CCl_2F{\cdot}CCl_2F$ (b.p. 91–94°) V	C_2HCl_4F (b.p. 116 –117°) VI
CoF_3	120°	1,450 g[c]	1,471 g	174·2 g (9·2%)	95·1 g (5·6%)	544·8 g (26·3%)	92·5 g (4·9%)	None	234·5 g (10·4%)	—
MnF_3	120°	290 g[d]	302 g	—	10·0 g (3·0%)	23·2 g (5·6%)	86·2 g (23·0%)	35·1 g[a] (12·1%)	—	42·2 g[b] (10·3%)
MnF_3	220°	290 g[e]	322 g	—	8·8 g (2·6%)	18·1 g (4·4%)	150·2 g (40·0%)	None	—	27·0 g (6·6%)

The percentages expressed are the theoretical yields in each case, i.e. the ratio of the weight of carbon in the purified compound to that of starting material expressed as a percentage.

[a] b.p. 75–93°, largely unchanged trichloroethylene

[b] Residue, which decomposed and gave off acid fumes

[c, d, e] Including intermediate fractions, total carbon recovery was 65%; 74%; 81% respectively. The combined weight of all the fractions distilled was 93%; 87·5%; 95% of the crude product respectively.

The action of high-valency transition metal fluorides on organic compounds has been reviewed recently,[9] and the usual technique was followed in the present studies with trichloroethylene. The work was considerably simplified in the later stages by the application of analytical[11] and preparative-scale[12] gas chromatography. The results are summarized in Table 1 and show that from the reaction with manganese trifluoride 1,1,2-trichloro-1,2-difluoroethane (IV) was the main product. With cobalt trifluoride as fluorinating agent, chiefly 1,1,2-trichloro-1,2,2-trifluoroethane (III) was formed. It has previously been shown[13–15] that chlorine atoms are often retained during fluorinations with cobalt trifluoride, and this has been borne out in the present work, although the formation of small quantities of 2-chloro-1,1,1-trifluoroethane (IB), and of *sym*-tetrachlorodifluoroethane (V) under the conditions studied indicated that some rearrangement had occurred. Manganese trifluoride was clearly a much milder fluorinating agent than cobalt trifluoride, in agreement with other observations.[9,16] Under comparable conditions (reaction temp 120°) treatment with manganese trifluoride gave predominantly the trichloro-difluoride (IV) and unchanged trichloroethylene (12 per cent) was present in the products, whereas treatment with cobalt trifluoride afforded largely the trichloro-trifluoride (III), and no unchanged starting material was present.

The products were purified by fractional distillation (Tables 2–4) and their structures were allocated from physical constants, by infra-red and mass spectrometry, and where feasible by the removal of chlorine from adjacent carbon atoms to give olefins.

TABLE 2

Fraction no.	Boiling point (°C)	Weight (g)	Compound
1–4	−26° to −7°	21·3	mixture
5	2–3°	51·0	$CClF_2{\cdot}CClF_2$ (IA) + $CF_3{\cdot}CH_2Cl$ (IB)
6	2–3°	7·2	
7	3–4°	48·0	
8	4–6°	10·0	
9–10	6–8°	58·0	
11	8–24°	14·5	mixture
12–15	29–31·5°	95·1	$CCl_2F{\cdot}CHF_2$ (IIA) $+CClF_2{\cdot}CHClF$ (IIB)
16–19	32–46·8°	35·2	mixture
19–21	45·5–47·9	544·8	$CClF_2{\cdot}CCl_2F$ (III)
22–23	47·9–71·9°	27·0	mixture
24	71·8–72·9°	92·5	$CCl_2F{\cdot}CHClF$ (IV)
25–27	73·9–91	45·2	mixture
28–31	91–93·8	234·5	$CCl_2F{\cdot}CCl_2F$ (V)
32–36	94–150	24·5	mixture
Residue	—	22·0	mixture

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[13] J. C. Tatlow and R. E. Worthington, *J. Chem. Soc.* 1251 (1952).

[14] E. T. McBee, B. W. Hotten, L. R. Evans, A. A. Alberts, Z. D. Welch, W. B. Ligett, R. C. Schreyer and K. W. Krantz, *Ind. Eng. Chem.* **39**, 310 (1947).

[15] M. Couper, F. B. Downing, R. N. Lulek, M. A. Perkins, F. B. Stilmar and W. S. Struve, *Ind. Eng. Chem.* **39**, 346 (1947).

[16] E. J. P. Fear and J. Thrower, *J. Appl. Chem.* **5**, 533 (1955).

TABLE 3

Fraction no.	Boiling point (°C)	Weight (g)	Compound
1	Below 28°	16·6	mixture
2	30–31°	10·0	$CCl_2F{\cdot}CHF_2$ (IIA) $+CClF_2{\cdot}CHClF$ (IIB)
3	31–46·8°	20·4	mixture
4	46·8–48°	23·2	$CClF_2{\cdot}CCl_2F$ (III)
5	48–72°	12·6	mixture
6	72–73°	86·2	$CCl_2F{\cdot}CHClF$ (IV)
7	75–85·2	17·2	mixture
8	85·2–93°	35·1	$CCl_2{=}CHCl$
Residue	—	42·2	$CCl_3{\cdot}CHClF$ (VIA) $+CCl_2F{\cdot}CHCl_2$ (VIB)

TABLE 4

Fraction no.	Boiling point (°C)	Weight (g)	Compound
1	Below 28°	11·8	mixture
2	30–31·5°	8·8	$CCl_2F{\cdot}CHF_2$ (IIA) $+CClF_2{\cdot}CHClF$ (IIB)
3	31·5–47°	33·0	mixture
4	47–48·5°	18·1	$CClF_2{\cdot}CCl_2F$ (III)
5	50–71·9°	13·0	mixture
6	72–73°	150·2	$CCl_2F{\cdot}CHClF$ (IV)
7	73·5–89°	23·0	mixture
8	93–116°	15·6	mixture
9	116–117°	27·0	$CCl_3{\cdot}CHClF$ (VIA) $+CCl_2F{\cdot}CHCl_2$ (VIB)
Residue	—	5·8	mixture

A portion (b.p. 2–3°) of the fraction I which had b.p. 2–8°, when examined by analytical-scale gas chromatography, was found to contain two components in the ratio of 3:1. Separation by preparative-scale gas chromatography gave the pure first component, whose infra-red spectrum was identical with that of 1,2-dichlorotetrafluoroethane (IA).[17] The pure second component had for an infra-red spectrum identical with that of 2-chloro-1,1,1-trifluoroethane (IB);[18] its identity was confirmed by its mass spectrum.

When the fraction (II), which had b.p. 30–30·5°, was examined by analytical gas chromatography, two peaks were present, in the ratio of 1:4, but only partly resolved. The mixture was then separated by preparative-scale gas chromatography. The first component had an unrecorded infra-red spectrum; it was identified as 1,1-dichloro-1,2,2-trifluoroethane (IIA) by its mass spectrum. The infra-red spectrum of the major component was identical with that of 1,2-dichloro-1,1,2-trifluoroethane (IIB) prepared[19] from the addition of chlorine to trifluoroethylene in the presence of active carbon impregnated with ferric chloride. The structure of this 1,2-dichloride (IIB)

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[17] D. Simpson and E. K. Plyler, *J. Res. Nat. Bur. Stand.* **50**, 223 (1953).

[18] J. R. Nielsen, C. Y. Liang and D. C. Smith, *J. Chem. Phys.* **21**, 1060 (1953).

[19] J. D. Park, W. R. Lycan and J. R. Lacher, *J. Amer. Chem. Soc.* **73**, 711 (1951).

was confirmed by its mass spectrum. The third possible isomer, 2,2-dichloro-1,1,1-trifluoroethane (VII) was shown to be absent from a study of its infra-red spectrum.[18] Subsequently, further quantities of 1,2-dichloro-1,1,2-trifluoroethane (IIB) were required for assessment of the compound as a possible anaesthetic.[20] A reported route involved addition of hydrogen chloride to chlorotrifluoroethylene, catalysed by either anhydrous aluminium chloride[21a] or by active carbon.[21b] However, with aluminium chloride we were unable to effect any addition unless appreciable quantities were used, when the product was 2,2-dichloro-1,1,1-trifluoroethane (VII), and not IIB, tetrachloroethylene and hexachloroethane being formed as well. Further, IIB was isomerized by aluminium chloride to give VII which, having a CF_3-group, is probably more stable. It is well-known[22] that chlorofluoro-compounds undergo rearrangement and also replacement of fluorine by chlorine when treated with aluminium chloride. In contrast, we found that the simple addition of hydrogen chloride to give IIB could be done in reasonable yield in a flow system with an active carbon catalyst. To confirm the identity of the IIB, attempts were made to dechlorinate it to trifluoroethylene with zinc dust, a reaction reported before.[21a] Under normal conditions no olefin was formed, though the analogous hydrogen bromide adduct gave trifluoroethylene readily. It seems that 1,2-dichloro-1,1,2-trifluoroethane (IIB) resembles 1,2-dichlorotetrafluoroethane (IA) in being unusually resistant to dechlorination with zinc.

The major product of the fluorination reaction with cobalt trifluoride was the fraction (III) which had b.p. 47°. An infra-red spectrum of the fraction was identical with that given for 1,1,2-trichlorotrifluoroethane, and no bands due to the isomeric 1,1,1-trichlorotrifluoroethane were shown.

The trichlorodifluoroethane (IV), which had b.p. 72°, was the major product from the fluorination reaction with manganese trifluoride; it was dechlorinated readily with zinc to give chloro-1,2-difluoroethylene (VIII); the latter was distinguished from the isomeric chloro-1,1-difluoroethylene (IX) by its infra-red spectrum, by its reactions, and by its separation into two geometrical isomers (see later). Compound IV was therefore 1,1,2-trichloro-1,2-difluoroethane. It has been mentioned before[23,24] that dechlorination of this gave chloro-1,2-difluoroethylene (VIII).

The tetrachlorodifluoroethane (V) was the symmetrical isomer, since it gave, upon dechlorination, 1,2-dichloro-1,2-difluoroethylene (X). This olefin was distinguished by infra-red measurements from the other possible product, the isomeric 1,1-dichloro-2,2-difluoroethylene, which would have resulted from a 1,1,1,2-tetrachloride. Dehydrochlorination of 1,1,2-trichloro-1,2-difluoroethane (product IV) with alkali also afforded symmetrical dichlorodifluoroethylene (X), which was characterized further as its dibromide.

A fraction (VI) which had b.p. 116° was isolated from the reaction of trichloroethylene with manganese trifluoride. This was identified from its physical constants and mass spectrum as a mixture of the isomers 1,1,1,2-tetrachloro-2-fluoroethane (VIA) and 1,1,2,2-tetrachloro-1-fluoroethane (VIB).

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[20] J. H. Burn, H. G. Epstein and P. J. Goodford, *Brit. J. Anaesthesia* **31**, 518 (1959).

[21] [a] R. N. Haszeldine, *J. Chem. Soc.* 4259 (1952): [b] A. F. Benning, F. B Downing and R J. Plunkett, U.S.P. 2,365,516/1944.

[22] W. T. Miller, E. W. Fager and P. H. Griswold, *J. Amer. Chem. Soc.* **72**, 705 (1950).

[23] A. L. Henne and E. C. Ladd, *J. Amer. Chem. Soc.* **58**, 402 (1936).

[24] R. P. Ruh and M. R. Rector, U.S.P. 2,716,109/1955.

Chloro-1,2-difluoroethylene (VIII) did not show the characteristic cyclo-dimerization reactions of highly fluorinated olefins. Heating under pressure (conditions which cause cyclo-dimerization of chlorotrifluoroethylene) gave only small quantities of a high polymer. Attempts to add methanol and ammonia under a wide range of conditions of temperature and pressure were also unsuccessful. This is in contrast with the reactivity of the isomeric chloro-1,1-difluoroethylene (IX) towards nucleophilic reagents. It parallels other known cases in which symmetrical isomers are less reactive than the unsymmetrical ones. In connection with the attempted formation of a cyclobutane derivative, it is of interest that all the successful examples of this homo-cyclization reaction of fluoro-olefins so far reported in the literature appear to have involved compounds with two fluorine atoms on an ethylenic carbon ($CF_2:CXY$).

By contrast, the addition of bromine and of iodine mono-chloride to chloro-1,2-difluoroethylene (VIII) proceeded readily at room temperature. The dibromo-addition-compound (XI) was a stable, colourless liquid which reacted readily with alkali to give the olefin 1-bromo-2-chloro-1,2-difluoroethylene (XII), by the elimination of hydrogen bromide. Iodine monochloride added to the olefin (VIII) to give 1,1-dichloro-1,2-difluoro-2-iodoethane (XIII) since treatment with dilute aqueous alkali removed hydrogen chloride, but only traces of iodide, to give 1-chloro-1,2-difluoro-2-iodoethylene (XIV). Both the iodine monochloride addition-compound (XIII) and this olefin (XIV) were somewhat light-sensitive, slowly becoming pink. It has been shown[25] that, as would be expected, when a fluorochloroiodo-compound (with both chlorine and iodine atoms attached to the same carbon atom and adjacent to one carrying hydrogen) is treated with alkali, iodide is removed preferentially.

The direction of addition of iodine monochloride indicates the expected polarization ($\overset{\delta+}{\mathrm{CClF}}=\overset{\delta-}{\mathrm{CHF}}$) in chloro-1,2-difluoroethylene (VIII), due to the chlorine atom, though this olefin obviously differs in some respects from typical highly fluorinated olefins. Further, under normal conditions its dibromide (XI) and its iodine chloride adduct (XIII) did not undergo chain length doubling with zinc and acetic anhydride[26] or zinc and dioxan,[27] nor did the iodine chloride adduct undergo photochemical dimerization in the presence of mercury.[27] These latter reactions are perhaps inhibited by the presence of a hydrogen atom on the carbon carrying the iodine.

When chloro-1,2-difluoroethylene (VIII) was examined by analytical gas chromatography there were shown one small peak (referred to as the impurity), followed by two partly-resolved major peaks present in equal amounts. The trichloro-precursor (IV) could have been a mixture of three possible isomers; (a) 1,1,2-trichloro-1,2-difluoroethane, (b) 1,1,1-trichloro-2,2-difluoroethane, and (c) 1,1,2-trichloro-2,2-difluoroethane. Without rearrangements, (b) would not give a chlorodifluoro-olefin and (c) would give chloro-1,1-difluoroethylene (IX), of which there are no stereoisomers, whilst olefin (VIII) from ethane (a) should exist in *cis*- and *trans*-forms.

The impurity present in the dechlorination product was separated by preparative-scale gas chromatography and was identified as chloro-1,1-difluoroethylene (IX) from its infra-red spectrum. Chlorination of (IX) gave 1,1-difluorotetrachloroethane (XV). Infra-red and gas chromatographic analysis of the original dechlorination product indicated that about 5 per cent of chloro-1,1-difluoroethylene was present, but both

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[25] R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.* 1199 (1953).

[26] A. L. Henne and W. Postelnek, *J. Amer. Chem. Soc.* **77**, 2334 (1955); A. L. Henne, *Ibid.* **75**, 5750 (1953).

[27] R. N. Haszeldine, *J. Chem. Soc.* 4423 (1952).

of these estimations were made on vapour samples of the dechlorination product. Since chloro-1,1-difluoroethylene has a lower boiling point (−17·7°[28]) than chloro-1,2-difluoroethylene (VIII), the dechlorination product from the trichlorodifluoride (IV) probably contained not more than 1–2 per cent of the impurity; all the reactions of the 1,2-difluoro-olefin (VIII) outlined above were carried out on material of this purity. Obviously, therefore, the trichlorodifluoroethane from the fluorination reactions, whilst mainly the 1,1,2-trichloro-1,2-difluoro-isomer (IV) did contain ca. 2 per cent of 1,1,2-trichloro-2,2-difluoroethane.

The two major components of the dechlorination product (VIII) from the trichlorodifluoride (IV) were then separated by preparative-scale gas chromatography. Since the separation was a difficult one, appropriate chromatographic cuts were collected which corresponded to pure first component and to pure second component. When sufficient material had been obtained, its purity was assessed by infra-red spectroscopy. The spectra of both components were consistent with those of geometrical isomers of the same olefin. The vapour pressure of each of the two pure components was measured between −17° and −79°, and their boiling points (−9° and −6° respectively) were estimated from the vapour pressure curves. Each component, when treated with chlorine, gave the same trichloro-difluoride (IV). This provided the final proof of structure of the two major components of the dechlorination reaction of (IV) as geometrical isomers of chloro-1,2-difluoroethylene (VIII). The use of preparative-scale gas chromatography for the separation of geometrical isomers of 2,3-dichlorohexafluorobut-2-ene has been mentioned elsewhere.[29]

EXPERIMENTAL

General. The manganic fluoride reactor was constructed of nickel (3·5′ long, 3·5″ diameter) and resembled a type used before.[9] It was charged originally with manganous fluoride (3 Kg) which was converted into the trifluoride by treatment with fluorine at 200–220°. Manganic fluoride is a mild fluorinating agent and high reaction temp may be needed. Accordingly, in the present design, the stirrer shaft bearings were placed some way from the end of the vessel. Each bearing housing was located 6″ from the end plate, being mounted at the end of a length of tube of bore slightly greater than the diameter of the shaft. Between each bearing and the end plate was a gas-tight bush of "Fluon". The bearing housings were water-cooled. The temp along the reactor were measured by a coaxial thermocouple probe which moved inside the horizontal tubular stirrer shaft The input of trichloro ethylene was maintained by lowering a piston at a constant rate (controlled by a synchronous motor) into a hollow cylinder containing the liquid, the overflow being fed to the inlet tower *via* a capillary dropper. Products were condensed from the exit gas streams in traps cooled by crushed solid carbon dioxide. They were then quickly washed with water and with sodium bicarbonate solution, and dried with anhydrous magnesium sulphate. The products were examined by analytical scale gas chromatography (6′ column, tricresyl phosphate–kieselguhr (1:3), temp 100°, nitrogen flow-rate 1·0 l./hr: this packing gave a good separation of the range of products).

Reaction of trichloroethylene with cobaltic fluoride

The copper reactor[30] was maintained at 120°, except the heater nearest to the exit, which was at 140°. Trichloroethylene (100 cc) was added at 50 cc/hr and then a slow stream of nitrogen was passed for 3 hr while the temp of the reactor was slowly raised to 200°. After 300 cc of trichloroethylene had been passed, the reactor was refluorinated. The bright-yellow fuming liquid obtained was washed and the colourless products (1,471 g) from the treatment of 1,000 cc of trichloroethylene were then fractionally distilled through a 3′ column packed with nickel gauzes. The column was surmounted by

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[28] A. L. Henne and R. P. Ruh, *J. Amer. Chem. Soc.* **70**, 1025 (1948).

[29] F. Dickinson, R. Hill and J. Muray, *J. Chem. Soc.* 1441 (1958).

[30] R. P. Smith and J. C. Tatlow, *J. Chem. Soc.* 2505 (1957).

a water condenser and a condenser cooled by solid carbon dioxide–ethanol, connected to a trap also at −78°. The receiver on the take-off head was cooled by carbon dioxide–ethanol. A low-temp pentane thermometer was used in the distillation until the boiling point of the distillate rose to 29°. During this period, the distillation flask was heated by a constant temp water-bath, which was subsequently replaced by a heating mantle. The fractions obtained with boiling point below room temp were transferred *in vacuo* into weighed glass ampoules, which were then sealed and stored (combined weight 1,330 g, 93% of crude product). The results are given in Table 2.

When the fluorination was conducted at 95° with a nitrogen gas stream (50 l./hr), yields obtained were (III), 17%; (IV), 29%; (V), 7%.

Reaction of trichloroethylene with manganic fluoride

(a) *Fluorination at* 120°. Trichloroethylene (200 cc) was introduced into the fully fluorinated reactor at 50 cc/hr. At the end of the addition, a slow stream of nitrogen was passed through the reactor while the temp was gradually raised to 250°. The products (302 g), when examined by analytical gas chromatography, revealed the presence of some unchanged starting material. Fractional distillation was carried out through a 1′ column surmounted by a water condenser connected to a trap cooled by carbon dioxide–ethanol (combined weight 263·5 g, 87·5% of crude). The results are shown in Table 3.

(b) *Fluorination at* 220°. Trichloroethylene (200 cc) was treated as in the preceding experiment, except that the reactor was at 220°. The washed, dried products (322 g) were fractionally distilled (combined weight 306 g, 95% based on crude). The results are given in Table 4.

Identification of products.

Physical properties and infra-red spectra of fractions obtained in cobalt trifluoride reaction were identical with the corresponding fractions from the manganese trifluoride reaction.

Analytical gas chromatography was carried out in columns 2 m long × 4 mm diameter packed with dinonyl phthalate–kieselguhr (1:2). In preparative-scale work the column used was 488 cm long × 30 mm diameter and was similarly packed. After preparative separations each fraction obtained was distilled from the trap *in vacuo*.

Infra-red measurements were made in the vapour state in a 10·1 cm cell over the range 650–3500 cm^{-1} with a Perkin-Elmer double-beam spectrometer with rock-salt prisms.

Mass spectrometric measurements were made on a Metropolitan-Vickers M.S.2 instrument.

Isolation of 1,2-*dichlorotetrafluoroethane* (IA) *and* 2-*Chloro*-1,1,1-*trifluoroethane* (IB)

The fraction (b.p. 2–3°), from the cobalt trifluoride reaction, by gas chromatography (temp 31°, N_2 flow-rate 1·0 l./hr) showed the presence of two components (ratio 3:1). Separation (6·5 g) in the preparative-scale column (temp 28°, N_2 flow-rate 8·2 l./hr) gave (IA) 1,2-dichlorotetrafluoroethane (2·8 g) and (IB) 2-chloro-1,1,1-trifluoroethane (1·0 g). B.p's cited are respectively (°C) (IA) 3·8,[31] 3·6,[32] 4;[33] (IB) 6·1,[34] 6·9.[28] The infra-red spectra recorded in the literature for 1,2-dichlorotetrafluoroethane[17] and for 2-chloro-1,1,1-trifluoroethane [18] were identical with those of components (IA) and (IB), respectively. A mass spectrum of 2-chloro-1,1,1-trifluoroethane (IB) gave the following mass peaks: 118 (CF_3CH_2Cl); 83 (CF_3CH_2); 69 (CF_3); 49 (CH_2Cl).

Isolation of 1,1-*dichloro*-1,2,2-*trifluoroethane* (IIA) *and* 1,2-*dichloro*-1,1,2-*trifluoroethane* (IIB)

This fraction (b.p. 30–30·5°), n_D^{21} 1·3354, when examined by gas chromatography (temp 26°, N_2 flow-rate 1·0 l./hr) showed the presence of 2 partly-resolved components (ratio of peak heights 1:3·2). Separation (2·2 g) in the preparative-scale column (temp 35°, N_2 flow-rate 8·2 l./hr) gave (IIA) 1,1-dichloro-1,2,2-trifluoroethane (0·15 g); an intermediate cut containing a mixture of both components (0·62 g); (IIB) 1,2-dichloro-1,1,2-trifluoroethane (1·1 g). The infra-red spectrum of the 1,1-dichloro-isomer (IIA) does not appear to have been recorded previously. Its mass spectrum had peaks at 152 ($C_2HF_3Cl_2$) and 101 (CCl_2F). The infra-red spectrum of the 1,2-dichloro-isomer (IIB)

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[31] E. G. Locke, W. R. Brode and A. L. Henne, *J. Amer. Chem. Soc.* **56**, 1726 (1934).

[32] E. E. Aynsley and R. H. Watson, *J. Chem. Soc.* 576 (1955).

[33] M. Iwasaki, S. Nagase and R. Kojima, *J. Chem. Phys.* **22**, 959 (1954).

[34] A. L. Henne and M. W. Renoll, *J. Amer. Chem. Soc.* **58**, 887 (1936).

was identical to that recorded.[19] The mass spectrum gave mass peaks at 152 ($C_2HF_3Cl_2$); 85 (CF_2Cl); and 67 (CHFCl). Constants cited for the 1,2-dichloride (IIB) were b.p. 28°,[23] b.p. 28·2°, n_D^{15} 1·3371;[19] for the 1,1-dichloride (IIA), b.p. 30·2°.[38]

Characterization of the trichlorotrifluoroethane (III)

The trichlorotrifluoride (b.p. 47·1–47·9°, n_D^{21} 1·3588) (Found: C, 12·8. Calc. for $C_2Cl_3F_3$: C, 12·8%) had an infra-red spectrum identical with that of 1,1,2-trichlorotrifluoroethane[35] but different from that of 1,1,1-trichlorotrifluoroethane.[35] Previously cited were b.p. 46·5–47·0°, n_D^{23} 1·3530.[36]

Dechlorination of 1,1,2-*trichloro*-1,2-*difluoroethane* (IV) *to chloro*-1,2-*difluoroethylene* (VIII)

Compound (IV) had b.p. 71·8–72·9°, n_D^{20} 1·3943 (Found: C, 14·5; H, 0·6. Calc. for $C_2HCl_3F_2$: C, 14·2; H, 0·6%); values cited[23] b.p. 72·5°, n_D^{20} 1·3942. Compound IV (184 g) was added dropwise to a vigorously stirred suspension of zinc dust (300 g) in ethanol (600 cc) at 72–75°. Reaction occurred almost immediately, to yield a volatile product, distillation of which gave a colourless liquid, b.p. −6 to −4° (92·7 g). The infra-red spectrum of this (chloro-1,2-difluoroethylene) was different from that of the isomeric chloro-1,1-difluoroethylene (IX)[37] for which b.p. −17·7° was given.[28] In previous references,[24,39] b.p. −15° was cited for chloro-1,2-difluoroethylene.

Characterization of the tetrachlorodifluoroethane (V)

This compound (12·0 g), b.p. 91–91·4°, m.p. 24·5–25° (Found: C, 11·5; F, 19·3. Calc. for $C_2Cl_4F_2$: C, 11·8; F, 18·6%) in ethanol (10 cc) was added slowly to a stirred suspension of zinc dust (20 g) in ethanol (60 cc) at 70–75°. Fractional distillation of the product gave 1,2-dichloro-1,2-difluoroethylene (X. 5·9 g), b.p. 21·2–22·0°. This readily absorbed bromine to yield a solid dibromo-compound, m.p. 31–31·5°. Constants cited[31] were, respectively, b.p. 92·8°, m.p. 24·7°, (V); b.p. 21·0–22·0° (X); m.p. 32·5° (dibromide).

Dehydrochlorination of 1,1,2-*trichloro*-1,2-*difluoroethane* (IV)

This compound (15·0 g) was added slowly to a stirred solution of sodium hydroxide (4·0 g) in 50% aqueous ethanol (40 cc) at 60°. Fractional distillation of the product gave 1,2-dichloro-1,2-difluoroethylene (X; 6·42 g), b.p. 21·8–22·0°. The infra-red spectrum of this olefin was different from that of 1,1-dichloro-2,2-difluoroethylene.[37] The aqueous residue of the original reaction contained much chloride ion but only a trace of fluoride ion. Addition of bromine to the olefin readily afforded the dibromide, b.p. 136–138°, m.p. 30–31°.

Identification of 1,1,1,2-*tetrachloro*-2-*fluoroethane* (VIA) *and* 1,1,2,2-*tetrachloro*-1-*fluoroethane* (VIB)

This fraction (b.p. 116–117°, n_D^{20} 1·4490) (Found: C, 12·9; H, 0·6. Calc. for C_2HCl_4F: C, 12·9; H, 0·5%) showed only one peak when examined by analytical gas chromatography (6′ column, tricresyl phosphate-kieselguhr (1:3), temp 128°, nitrogen flow-rate 1·2 l/hr). A mass spectrum showed that the fraction consisted of a mixture of 1,1,1,2-tetrachloro-2-fluoroethane (VIA) and 1,1,2,2-tetrachloro-1-fluoroethane (VIB). In the absence of pure reference spectra, it was not possible to assess the relative amounts of the two isomers present. Previously cited,[23] b.p. 117°, n_D^{20} 1·4525 (VIA) and b.p. 116·6°, n_D^{20} 1·4487 (VIB).

Addition of hydrogen chloride to chlorotrifluoroethylene

(a) *Catalysed by aluminium chloride.* The olefin (164 g) was heated with anhydrous hydrogen chloride (37 g) and anhydrous aluminium chloride (60 g) at 180° for 23 hr in a rocking autoclave. The product was washed with ice-water and with sodium hydrogen carbonate solution. Distillation through a 1′ column packed with Dixon gauzes gave 2,2-dichloro-1,1,1-trifluoroethane (VII; 25 g), b.p. 27°/748 mm, n_D^{14} 1·3332 with an infra-red spectrum identical with that published.[18] From the residual liquid there was isolated tetrachloroethylene (18 g) and hexachloroethane (6 g).

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[35] J. R. Lacher, J. J. McKinley, C. Walden, K. Lea and J. D. Park, *J. Amer. Chem. Soc.* **71**, 1334 (1949).

[36] H. S. Booth, W. L. Mong and P. E. Burchfield, *Ind. Eng. Chem.* **24**, 328 (1932).

[37] J. R. Nielsen, C. Y. Liang and D. C. Smith, *J. Chem. Phys.* **20**, 1090 (1952).

[38] R. N. Haszeldine and J. C. Young, *J. Chem. Soc.* 4503 (1960).

[39] J. M. Birchall, R. N. Haszeldine and A. R. Parkinson, *J. Chem. Soc.* 2204 (1961).

Similar reactions using less aluminium chloride (ca. 2 g) gave unchanged olefin at lower temperatures or dichlorohexafluorocyclobutane at high temperatures.

(b) *Catalysed by carbon.* A Pyrex glass tube (64 cm × 3·6 cm diam) was packed with activated carbon (ca. 270 g; Sutcliffe, Speakman & Co., Type 206B Mesh 14–25) and swept with nitrogen at 160° till no more steam was evolved. Hydrogen chloride was passed through (ca. 14 g/hr) and also chlorotrifluoroethylene (30 g/hr; 264 g in all). After sweeping out the tube with nitrogen, unchanged olefin was distilled from the product which was then washed (sodium hydrogen carbonate), dried ($MgSO_4$) and distilled through a 1′ column to give 1,2-dichloro-1,1,2-trifluoroethane (IIB; 130 g) with a correct infra-red spectrum. Olefin (80 g) was recovered.

1,2-Dichloro-1,1,2-trifluoroethane (IIB; 17 g) and anhydrous aluminium chloride (8·5 g) were heated at 100° for 35 min in a shaken sealed tube. The product, after being washed, was distilled to give 2,2-dichloro-1,1,1-trifluoroethane (VII; 5·4 g), identified by its infra-red spectrum, and a higher-boiling residue.

When 1,2-dichloro-1,1,2-trifluoroethane (IIB; 121 g) was refluxed in a stirred suspension of zinc dust (300 g) in ethanol (600 cc), there was no reaction (cf. ref 40), though additions of small amounts of 1,1,2-trifluorotrichloroethane and of 1-bromo-2-chloro-1,1,2-trifluoroethane gave the appropriate olefin.

*Addition of bromine to chloro-*1,2-*difluoroethylene* (VIII)

Chloro-1,2-difluoroethylene (12·9 g) was cooled to −25° and stirred whilst bromine (slight excess) was added dropwise. Intermittent removal of the cooling bath permitted solidified bromine to melt and react with the olefin. Absorption was rapid at first, but gradually slackened. The liquid was dried (P_2O_5) and distilled to give 1,2-*dibromo*-1-*chloro*-1,2-*difluoroethane* (XI; 28·2 g), b.p. 118–120°, n_D^{20} 1·4650 (Found: C, 9·6; H, 0·4; F, 14·7. $C_2HBr_2ClF_2$ requires: C, 9·3; H, 0·4; F, 14·7%).

Dehydrobromination of 1,2-*dibromo*-1-*chloro*-1,2-*difluoroethane* (XI)

The dibromo compound (10·0 g) was stirred with aqueous 3·3 N sodium hydroxide solution (15 cc) at 80°. The volatile product (b.p. 47–50°) was redistilled to give 1-*bromo*-2-*chloro*-1,2-*difluoroethylene* (XII; 5·34 g), b.p. 46·5–47·5°, n_D^{21} 1·4085 (Found: F, 21·7. C_2BrClF_2 requires: F, 21·4%).

Addition of iodine monochloride to chloro-1,2-*difluoroethylene* (VIII)

The olefin (10·9 g) was cooled to −25° and iodine monochloride (supercooled, 6 cc) was added dropwise. A vigorous reaction occurred at once and, when this had subsided, the mixture was warmed at 50° for 10 min, water (10 cc) was added, and resulting iodine (0·97 g) was filtered off. The organic layer was separated, decolourized ($NaHCO_3$), dried (P_2O_5), and distilled *in vacuo* to give 1,1-*dichloro*-1,2-*difluoro*-2-*iodoethane* (XIII; 19·28 g), b.p. 38–40°/20 mm, 124–126°/760 mm with slight decomposition, n_D^{21} 1·4863 (Found: C, 9·2; H, 0·5. $C_2HCl_2F_2I$ requires: C, 9·2; H, 0·4%). This compound became pink on exposure to light, but could be stored in the dark.

Action of alkali on 1,1-*dichloro*-1,2-*difluoro*-2-*iodoethane* (XIII)

(a) The freshly-distilled iodo-compound (1·9560 g) was shaken for 18 hr at 15–20° with 2 N sodium hydroxide solution (3·25 cc). The aqueous layer was made up to 100 cc, 50 cc was acidified, and treated with an excess of silver nitrate solution followed by dil ammonium hydroxide (a volume equal to that of the solution), to give silver iodide (4% of the amount from a complete elimination). Acidification of the filtrate with dil nitric acid reprecipitated the silver chloride (76%). Further treatment of the organic layer with 2 N sodium hydroxide solution (2 cc) gave silver iodide (0·2%) and silver chloride (16%). The small amount of iodide could have arisen from decomposition or from the presence of a little of the alternative adduct (CClFI·CHClF).

(b) The iodo-compound (XIII; 12·42 g) was shaken with 2 N aqueous sodium hydroxide (32 cc) at 15–20° for 45 hr. The organic layer was washed with water until neutral, dried (P_2O_5), and distilled to give 1-*chloro*-1,2-*difluoro*-2-*iodoethylene* (XIV; 9·60 g), b.p. 82·5–84°, n_D^{23} 1·4721 (Found: C, 11·0. C_2ClF_2I requires: C, 10·7%).

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[40] H. R. Davis and H. S. K. Chiang, U.S.P. 2,774,798/1956.

*Identification of chloro-*1,1*-difluoroethylene and the separation of chloro-*1,2*-difluoroethylene into geometrical isomers*

Chloro-1,2-difluoroethylene was prepared as described previously, but was purified by fractional distillation through a 1′ column packed with nickel gauzes. The product had b.p. −5·5 to −3°, and a sample of the vapour, when examined by analytical gas chromatography (temp 31°, nitrogen flow-rate 0·8 l./hr), showed the presence of three un-resolved components (the ratio of peak heights was 1:3·4:3·4 respectively). Separation was carried out using the preparative-scale chromatography column. The inlet tube was cooled by solid carbon dioxide. The olefin mixture (at −78°) was quickly poured in and introduced into the column. At the end of every run, the contents of each trap were transferred *in vacuo* into the appropriate tube cooled in liquid air, and stored on a vacuum line until sufficient material had been accumulated.

Under the column conditions employed (temp 30°, nitrogen flow-rate 5·8 l./hr) the olefin mixture (2 g) was separated into the pure first component and an un-resolved mixture of second and third components. After several runs, sufficient of the first component (0·2 g) had been accumulated for identification. Analytical gas chromatography (temp 34°, nitrogen flow-rate 0·9 l./hr) showed only one peak. The infra-red spectrum was identical with that of chloro-1,1-difluoroethylene (IX).[37]

This olefin (0·15 g) was sealed in a hard glass tube with chlorine (1·0 g) and allowed to stand at room temp overnight. The tube was irradiated with U.V. light for 3 hr. The contents were washed ($NaHCO_3$) to remove excess of chlorine. The colourless organic liquid (0·32 g) solidified to a colourless glass with an infra-red spectrum identical with that of tetrachloro-1,1-difluoroethane.[18]

Further separation was carried out (temp 36°, nitrogen flow-rate 6·0 l./hr) in 7 portions of ca. 1 g. The first small peak due to chloro-1,1-difluoroethylene (IX) was rejected in each run. Pure samples of the major components A (2·3 g) and B (2·0 g) were obtained by collecting the first and final chromatographic cuts respectively in each run. By examination of the infra-red spectra, each component was shown to be pure with respect to the other.

The vapour pressures of A and B were determined on a vacuum line using a mercury manometer. The sample was frozen in liquid air, the line evacuated, the sample degassed and then surrounded by the appropriate low temp bath, until the vapour press was at equilibrium. The sample was again cooled to ensure that no air had leaked into the vacuum line during the measurements. The results were as follows:—[respectively, temp (°C), V.P. of A and of B (mm Hg)] −79·5, 16, 13; −77, 19, 16; −64, 51, 38; −27, 341, 299; −17, 577, 513: giving the b.p. of A (first chromatographic fraction) −9°C, and of B (second chromatographic fraction) −6°C.

Addition of chlorine to the geometrical isomers A *and* B *of chloro-*1,2*-difluoroethylene* (VIII)

Olefin A (2·4 g) and chlorine (2·8 g), in a tube surrounded by an ice-bath, were maintained under gentle reflux beneath a condenser cooled by solid carbon dioxide–ethanol. When the vapour was irradiated with U.V. light, a dense white cloud formed beneath the condenser. After 15 min, the light was switched off and the reaction tube was allowed to warm up, the reaction mixture was washed with sodium bicarbonate solution (10%) and the crude, colourless liquid (3·6 g) was distilled from phosphoric oxide. When examined by analytical gas chromatography (temp 74°, nitrogen flow-rate 1·0 l./hr) the distillate showed the presence of one major component, and an impurity (<1%) of very short retention time. Apart from the presence of an additional weak band at 932 cm^{-1}, the infra-red spectrum was the same as that of 1,1,2-trichloro-1,2-difluoroethane (IV) obtained from $CCl_2{=}CHCl$—MnF_3.

Olefin B (2·0 g) was likewise treated with chlorine (3·8 g). Examination of the product (2·57 g) by analytical gas chromatography showed the presence of only one component; its infra-red spectrum was identical with those of IV and of the olefin A-Cl_2 adduct.

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