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SHORT COMMUNICATION

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Observations on 'Trichloro' Material Obtained by Fluorination of Perchlorocyclopentadiene with Cobalt Trifluoride

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Fluorination of perchlorocyclopentadiene with cobalt trifluoride yields a complex mixture of chlorofluorocarbons which has not been analysed in detail but simply used as a source of precursors of perfluorocyclopentadiene and related compounds [1-4]. Initially [1], fluorinations were conducted at ca. 200 °C [5], and the product was distilled to provide multi-component (by g.l.c.) 'trichloro', 'tetrachloro', and 'pentachloro' fractions; on a chemical basis, *viz.* the identities of major dechlorination products, these were judged to contain cyclopentanes (I), (II), and (III) plus (IV), respectively.

Only two products were noticed when 'trichloro' material was subjected to dechlorination with zinc in boiling dioxan (b.p. 101.5 °C): perfluorocyclopentadiene (9% yield) and impure (by <sup>19</sup>F n.m.r.) 4-chloroheptafluorocyclopentene (V) (50%); oxidation (KMnO<sub>4</sub>) of the latter gave acidic material assumed to be essentially β-chloropentafluoroglutaric acid, and characterised by preparation and elemental analysis of standard derivatives [2]. Further information on this dechlorination is now available thanks to a search amongst samples from our previous studies in fluorocarbon chemistry for polyfluorinated glutaric acids (or their precursors) required to extend the discovery [6] that perfluoroglutaric acid can be converted into perfluorocyclopropane *via* the route: HO<sub>2</sub>C(CF<sub>2</sub>)<sub>3</sub>CO<sub>2</sub>H → AgO<sub>2</sub>C(CF<sub>2</sub>)<sub>3</sub>CO<sub>2</sub>Ag → I(CF<sub>2</sub>)<sub>3</sub>I (Hunsdiecker sequence) → cyclo-C<sub>3</sub>F<sub>6</sub> (Hg/u.v.-promoted cyclisation).

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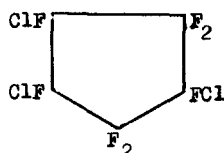
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Since the initial work [1] on the synthesis of perfluorocyclopentadiene was completed,  $\text{CoF}_3$ -fluorination of perchlorocyclopentadiene has been carried out at higher temperatures (ca. 250 °C) in reactors of improved design [7], with re-cycling of 'pentachloro' material, in order to increase the yield of the 'tetrachloro' fraction; also, the efficiency of the synthesis has been greatly improved at the dechlorination stage by using diglyme (b.p. 161 °C), not dioxan, as the reaction medium [8]. 'Trichloro' material obtained as a by-product through over-fluorination of perchlorocyclopentadiene during this later preparative work was dechlorinated using the improved technique and found (by g.l.c.) to give at least six products, including perfluorocyclopentadiene (some of which dimerized [2]), perfluoropenta-2,3-diene (VI), and 4-chloroheptafluorocyclopentene (V). Oxidation ( $\text{KMnO}_4$ ) of an impure sample of the cyclopentene, isolated by distillation, provided *prima facie* evidence that it contained its 3-chloro-isomer (VII) because the product was shown by  $^{19}\text{F}$  n.m.r. spectroscopy to be a ca. 3:1 mixture of  $\beta$ - and  $\alpha$ -chloropentafluoroglutamic acid; since both g.l.c. and n.m.r. analysis indicated that the impurity in the 4-chloroheptafluorocyclopentene amounted to only ca. 10%, easy detection of the  $\alpha$ -chloro-acid in the oxidation product is ascribed to an enrichment effect operative during the formation and/or isolation of the mixture of acids.

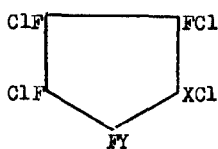
Subjection of the 'trichloro' material to preparative g.l.c. provided not only trichloroheptafluorocyclopentane, assumed, on the evidence just summarised, to contain both 1,2,4-trichloroheptafluorocyclopentane (I) and its 1,2,3-trichloro-isomer (VIII), but also trichlorononafluoropentane which was shown by  $^{19}\text{F}$  n.m.r. spectroscopy to be mainly the 2,3,4-trichloro isomer (IX). The presence of the last compound, which is a ring-opened analogue of (VIII) [9], accounts for production of the allene (VI) under the vigorous dechlorination conditions applied to the 'trichloro' material. No detailed structural information could be obtained by study of the extremely complex  $^{19}\text{F}$  n.m.r. spectrum of the trichloroheptafluorocyclopentane mixture; the spectrum of the impure 2,3,4-trichlorononafluoropentane also defied analysis but indicated the presence of at least three types of  $\text{CF}_3$  group (both *meso*-isomers\* appeared to be present) and six types of  $\text{CFCl}$ .

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\* 2,3,4-Trichlorononafluoropentane contains a pseudoasymmetric atom (C-3), so there are two *meso*-forms ( $\text{AA'BX}_2\text{X}'_3$  systems) and one pair of enantiomers ( $\text{AECX}_3\text{Y}_3$  system).



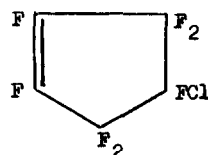
(I)



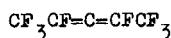
(II) X = Y = F

(III) X = F, Y = Cl

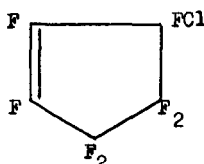
(IV) X = Cl, Y = F



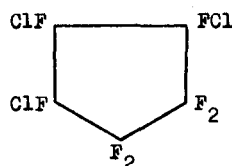
(V)



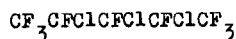
(VI)



(VII)



(VIII)



(IX)

## EXPERIMENTAL

$^{19}\text{F}$  N.m.r. spectra were obtained with a Perkin-Elmer R10 spectrometer operating at 56.46 MHz; chemical shifts were measured relative to external trifluoroacetic acid, absorptions to high field being assigned negative values. Molecular weights were determined using Regnault's method.

Isolation of Trichloroheptafluorocyclopentane and Trichlorononafluoropentane

Material (ca. 3 kg; b.p.  $< 145^\circ\text{C}$ ) obtained by distillation of the product from  $\text{CoF}_3$ -fluorination of perchlorocyclopentadiene at  $240\text{--}270^\circ\text{C}$  [7] through a  $33 \times 1.0$  cm adiabatic Vigreux column was fractionated using first an adiabatic packed column ( $52 \times 1.5$  cm; Hastelloy-B  $0.3 \times 0.2 \times 0.1$  cm wire coils) then a Haage spinning-band column ( $100 \times 0.8$  cm) to give a fraction (199 g) with b.r.  $116\text{--}118^\circ\text{C}$ ; this gave only two g.l.c. peaks (area ratio ca. 1:4) when examined using a 2 m silicone MS550 oil-Celite column at  $83^\circ\text{C}$ . A sample was separated, using a preparative column (6 m at  $65^\circ\text{C}$ ), into slightly impure (by  $^{19}\text{F}$  n.m.r.) 2,3,4-trichlorononafluoropentane

(Found: C, 17.5; F, 50.0%;  $\underline{M}$ , 340. Calc. for  $C_5Cl_3F_9$ : C, 17.8; F, 50.7%;  $\underline{M}$ , 337.5), b.p. 116 °C (Siwoloboff),  $\lambda_{\max}$  (vapour) 7.82m, 8.05vs, and 8.13s (C-F str.)  $\mu\text{m}$  (no absorption below 7.4  $\mu\text{m}$ ),  $\delta_F$  (neat liq.) +2.6 ( $CF_3$ ; complex, showing two distinct groups of absorptions at +2.9 and +2.3 of relative intensity approx. 1:3) and -40 to -50 ( $CFCl$ ; six apparently distinct complex band systems centred at -41.2, -43.6, -44.8, -46.6, -48.2, and -48.5) p.p.m. (rel. int. ca. 2:1), and trichloroheptafluorocyclopentane (Found: C, 20.0%;  $\underline{M}$ , 300. Calc. for  $C_5Cl_3F_7$ : C, 20.0%;  $\underline{M}$ , 299.5), b.p. 120 °C (Siwoloboff),  $\lambda_{\max}$  (vapour) 7.64m (sh.), 7.88s, 8.08vs (br.), 8.91m, and 8.99m (sh.) (C-F str.)  $\mu\text{m}$  (no absorption below 7.4  $\mu\text{m}$ ),  $\delta_F$  (neat liq.) +18 to +57 p.p.m. (extremely complex spectrum comprising more than 20 band systems which could not be analysed), which gave two peaks of almost equal size when subjected to g.l.c. analysis with a 50 m silicone oil-coated capillary column at 50 °C.

#### Dechlorination of the $C_5Cl_3F_9$ - $C_5Cl_3F_7$ Mixture

Zinc dust was activated by treatment with 5M-hydrochloric acid (stirred together for 5 min.) then washed several times, first with distilled water (until the aqueous suspension was neutral to litmus) then with acetone. Finally, it was dried thoroughly in a continuously-evacuated desiccator.

A sample (208 g) of the 'trichloro' material, b.r. 116-118 °C, was added slowly (2 h) to a stirred suspension of activated zinc dust (ca. 250 g) in boiling diglyme (700  $\text{cm}^3$ ; Na-dried) in a vessel swept continuously with dry nitrogen; the mixture was then heated under reflux for 2 h. Volatile product which condensed in two cold traps (-72 °C) attached to the exit from the water-cooled condenser was distilled (30x1.0 cm column packed with Fenske 2 mm glass rings; stillhead cooled with methanol-Drikold) to provide material, b.r. -5 to 30 °C, which gave four g.l.c. peaks (4 m Kel-F oil no. 10-Celite at 20 °C; area ratios 5:1:5:1, in order of increasing retention time). Samples of the two main components were collected and found, respectively, to be perfluoropenta-2,3-diene (Found: C, 27.4; F, 71.2%;  $\underline{M}$ , 210. Calc. for  $C_5F_8$ : C, 28.3; F, 71.7%;  $\underline{M}$ , 210),  $\lambda_{\max}$  (vapour) 4.93  $\mu\text{m}$  (asym. C=C=C str.; lit. [10], 4.94  $\mu\text{m}$ ),  $\delta_F$  (neat liq.) +3.8 ( $CF_3$ ; complex) and -44.7 ( $CF=C=CF$ , complex) p.p.m. (rel. int. 3:1; the spectrum was typical of an  $X_2AA'X_2'$  system in which  $XX'$  coupling is negligible),  $\underline{m/e}$  212 ( $C_5F_8^+$ , 5%) and 93 ( $C_3F_3^+$ , 100%), and perfluorocyclopentadiene (Found:  $\underline{M}$ , 176. Calc. for  $C_5F_6$ :  $\underline{M}$ , 174) which possessed correct spectroscopic characteristics (i.r. and  $^{19}F$  n.m.r.).

The stillpot residue (51 g) was shown by g.l.c. (4 m Kel-F No. 10 oil-Celite) and i.r. and  $^{19}\text{F}$  n.m.r. analysis to be essentially a ca. 7:3 mixture of chloroheptafluorocyclopentene and perfluorocyclopentadiene dimer.

Distillation of the product (35.4 g) from a similar dechlorination (involving 95 g of 'trichloro' material and 150 g of activated Zn dust) gave a fraction (14.3 g) (Found: C, 26.3%. Calc. for  $\text{C}_5\text{ClF}_7$ : C, 26.3%), b.r. 54-56 °C, which gave two g.l.c. peaks of area ratio ca. 9:1 (2 m DNP-Celite at 48 °C) and possessed spectral (i.r.,  $^{19}\text{F}$  n.m.r.) characteristics virtually identical to those reported for impure 4-chloroheptafluorocyclopentene [2].

### Oxidation of the Impure 4-Chloroheptafluorocyclopentene

Impure 4-chloroheptafluorocyclopentene (26.4 g), prepared as described above, was added dropwise to a cold (0 °C) stirred solution of potassium permanganate (37 g) in acetone (1.5 l). The resulting brown solution was allowed to warm to room temperature then mixed with water (1.5 l); the aqueous mixture was evaporated at reduced pressure to remove acetone and the residue was acidified ( $\text{H}_2\text{SO}_4$ ), decolorized with sulphur dioxide, evaporated to a volume of ca. 400  $\text{cm}^3$ , then extracted continuously with ether overnight. Evaporation of the ether extract, followed by storage of the residue in vacuo at 100 °C for several hours to ensure complete removal of solvent and water, provided a pale-brown viscid acid (16.3 g, 55%),  $\lambda_{\text{max}}$ . (film) 5.66 (v br.; C=O str.)  $\mu\text{m}$ , which was converted using standard techniques (via reaction with  $\text{Ag}_2\text{CO}_3$ ) into a disilver salt (76% yield) (Found: C, 13.0; F, 20.2%. Calc. for  $\text{C}_5\text{Ag}_2\text{ClF}_5\text{O}_4$ : C, 12.75; F, 20.2%),  $\lambda_{\text{max}}$ . (mull) 6.10m, 6.22s (br. d; C=O str.)  $\mu\text{m}$ .  $^{19}\text{F}$  N.m.r. analysis of the crude acid (ca. 20% soln. in  $\text{H}_2\text{O}$ ) showed it to be a ca. 3:1 mixture of  $\beta$ -chloropentafluoroglutaric acid [ $\delta_{\text{F}}$  -35.0 ( $\text{CF}_2\text{CFClCF}_2$ ; centre of a ca. 270 Hz AB-type pattern, each component of which showed further splitting) and -56.8 ( $\text{CFCl}$ ; 'quintet') p.p.m. (rel. int. 4:1)] and  $\alpha$ -chloropentafluoroglutaric acid [ $\delta_{\text{F}}$  ca. -39.5 ( $\text{CF}_2\text{CFCl}$ ; centre of a ca. 290 Hz AB-system, the high-field components of which appeared as doublets), -39.0 ( $\text{CF}_2\text{CF}_2\text{CFCl}$ ; s), and -50.6 ( $\text{CFCl}$ ; mult.) p.p.m. (rel. int. 2:2:1)].

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- 4 R. E. Banks, M. Bridge, R. N. Haszeldine, D. W. Roberts, and N. I. Tucker, *J.Chem.Soc. (C)*, (1970) 2531.
- 5 Temperature ranges of 200–220 °C (fixed bed) and 150–220 °C (stirred bed) were used, according to reactor type.
- 6 R. E. Banks and J. V. Latham, unpublished results. U.v.-irradiation for 48 h of a vibrating silica tube (250 cm<sup>2</sup>) containing mercury (ca. 6 g) and perfluoro-1,3-di-iodopropane (4.98 g) yields perfluorocyclopropane (40%), tetrafluoroethylene, and poly(difluoromethylene).
- 7 R. E. Banks, A. C. Harrison, and B. Rigby, unpublished work.
- 8 R. E. Banks, M. Bridge, and R. N. Haszeldine, *J.Chem.Soc.(C)*, (1970) 48.
- 9 Unfortunately, the perchlorocyclopentadiene used in the fluorination work (aimed solely at the preparation of 'tetrachloro' material as a precursor of perfluorocyclopentadiene [7]) was not examined for impurities, particularly acyclic ones. Thus, the expected ring-cleavage of cyclic C<sub>5</sub> chlorofluorocarbon material during the high-temperature CoF<sub>3</sub>-C<sub>5</sub>Cl<sub>6</sub> reaction may not have been the sole source of (IX).
- 10 W. T. Miller, W. Frass, and P. R. Resnick, *J.Amer.Chem.Soc.*, 83 (1961) 1767. These authors found the b.p. of (VI) to be 17 °C.