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REACTION OF 2,2-DICHLOROTRIFLUORO-1-IODOETHANE WITH ZINC*

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SUMMARY

The zinc coupling reaction of a pure sample of 2,2-Dichlorotrifluoro-1-iodoethane (I) in acetic anhydride-methylene chloride has been investigated. The coupled product $C_4F_6Cl_4$ was found to be a single isomer by ^{19}F NMR and had the structure $CFCl_2CF_2CF_2CFCl_2$ (II). The probable modes of formation of by-products such as $C_6F_9Cl_5$ and $C_8F_{12}Cl_6$ are discussed.

INTRODUCTION

This work was carried out in continuation of an earlier study on the reaction of 1,2-dichlorotrifluoroiodoethane (Ia) with zinc in acetic anhydride-methylene chloride [1]. In the earlier work, a sample of Ia contaminated by the isomeric 2,2-dichlorotrifluoro-1-iodoethane (I) was inadvertently used leading to erroneous conclusions on the isomeric purity of the primary product and the mode of formation of secondary products [2]. Other workers [3,4] have also studied the zinc-coupling reaction of Ia which was prepared by the addition of ICl to chlorotrifluoroethylene. The apparent assumption was that their starting iodide was a single isomer, Ia. There was no reference to the possible presence of isomer I in the starting iodide or to the isomeric purity of the coupled product, $C_4F_6Cl_4$.

The addition of ICl to chlorotrifluoroethylene was reported to give Ia as the exclusive ICl adduct [5]. A later publication,

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however, reported that the addition was bidirectional leading to both 1,2-dichlorotrifluoroiodoethane (Ia) and 2,2-dichlorotrifluoro-1-iodoethane (I) [6]. Reaction in glass at low temperatures was reported to give predominantly Ia while addition at higher temperatures in presence of Fe or $FeCl_3$ gave predominantly I. Experimental methods involving treatment of the mixture of isomers with chlorosulfonic acid were used to isolate pure I, while pure Ia was isolated by preparative chromatography [6].

In the absence of sufficient amounts of pure Ia to repeat the work carried out in this laboratory [1,2], attention was directed at the isomer I. Like Ia, this isomer also has iodine and chlorine atoms on adjacent carbon atoms that could be eliminated as ICl to give chlorotrifluoroethylene. A pure sample of I was prepared in sufficient amounts using the procedure reported [6]. Its purity was established by ^{19}F NMR, and it was then subjected to reaction with zinc in acetic anhydride-methylene chloride. The results are presented here.

RESULTS AND DISCUSSION

The zinc coupling reaction of 2,2-dichlorotrifluoro-1-iodoethane (I) was studied under conditions that were identical to those used for the reaction of Ia [1]. The reaction was exothermic, but appeared milder than that of Ia, and no external cooling was necessary to maintain the temperature below 35°C. A gaseous product was formed during the reaction as observed in the Zn coupling of Ia, and this was identified as chlorotrifluoroethylene by comparison of its IR spectrum with that of an authentic sample. Obviously, elimination of ICl from I occurs under these experimental conditions as was observed for Ia. The liquid product isolated, on GC/MS analysis, was found to be a mixture of $C_4F_6Cl_4$, $C_6F_9Cl_5$ and $C_8F_{12}Cl_6$ in the approximate ratio of 78:20:2.

The major product in this coupling reaction, $C_4F_6Cl_4$ was isolated by distillation in 40% yield. Its ^{19}F NMR spectrum indicated that it was a pure isomer and had the expected structure $CFCl_2CF_2$-CF_2CFCl_2 (II). One of the secondary products

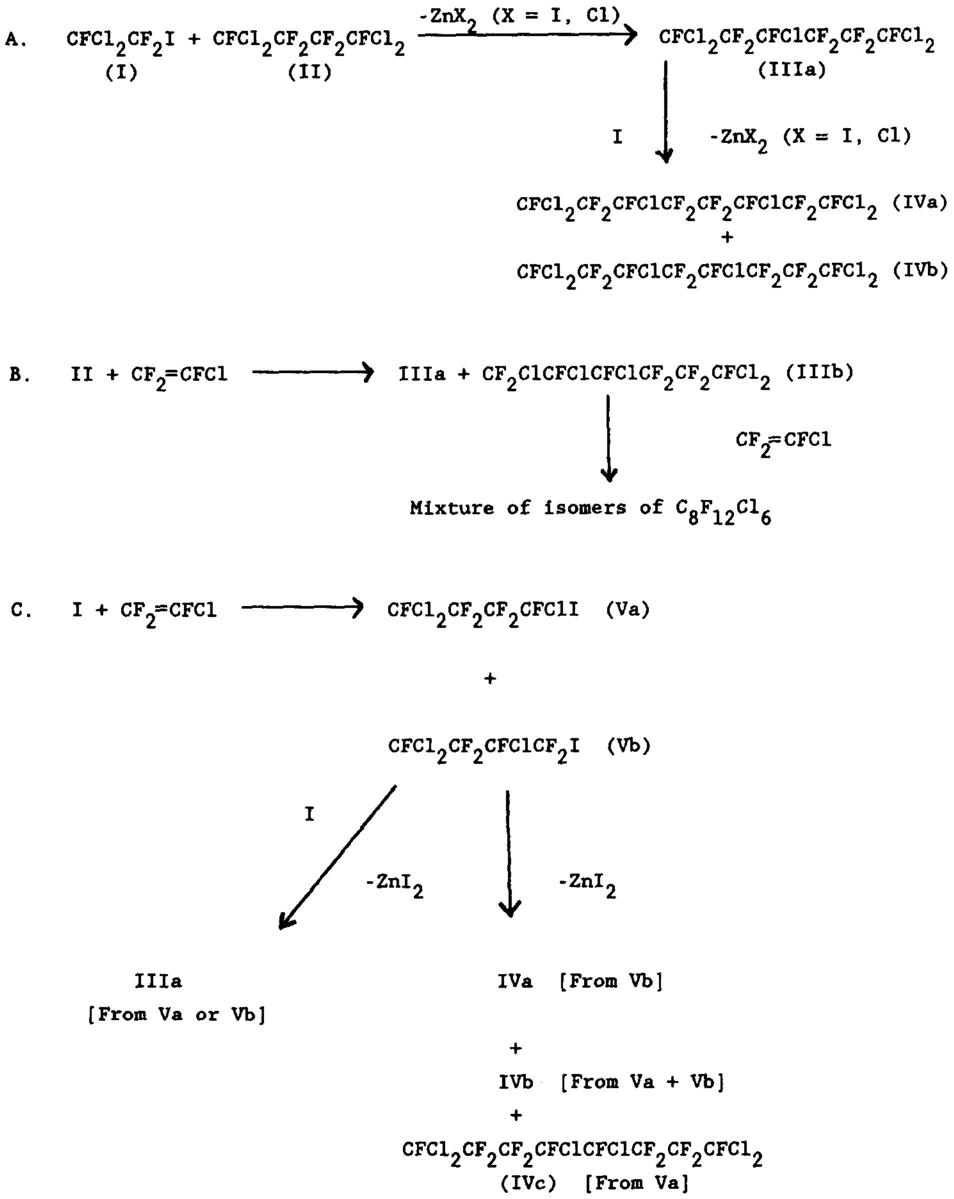
$C_6F_9Cl_5$ was also isolated by semi-preparative gas chromatography. ^{19}F NMR studies suggested that it was also a single positional isomer and the data confirmed the structure $CFCl_2CF_2CF_2CFClCF_2CFCl_2$ (IIIa).

The isomeric (positional) purity of the primary product II as well as one of the secondary products (IIIa) clearly rules out telomerization of chlorotrifluoroethylene involving initiation and chain transfer by chlorine as a side reaction, as was believed during the study on the coupling of Ia [1]. Bidirectional linking of the monomers in such a process would lead to three positional isomers for even $C_4F_6Cl_4$.

Other possible modes of formation of $C_6F_9Cl_5$ and $C_8F_{12}Cl_6$ that may be considered are: (A) coupling of I with the primary coupled product II as was suggested [4], (B) addition of II to one or more molecules of chlorotrifluoroethylene and (C) addition of the starting iodide (I) to chlorotrifluoroethylene followed by coupling. These possibilities are shown in Scheme 1. It may be remarked that the addition product of I can involve more than one molecule of chlorotrifluoroethylene leading to telomeric iodides before coupling. Such a process may not be easily distinguishable from 'C' shown in Scheme 1.

Considering 'A' (Scheme 1), this secondary reaction should give a single positional isomer of $C_6F_9Cl_5$ (IIIa) and two positional isomers of $C_8F_{12}Cl_6$ (IVa and IVb). The verification of this process by the specific reactants I and II would be complicated by the fact that chlorotrifluoroethylene would be formed from I under the influence of zinc; and in the presence of I, the reaction can also follow the course indicated in "C" of Scheme 1. However, if instead of I, an iodide without a chlorine on the adjacent carbon atom is selected, the formation of an olefin and subsequent addition can be avoided. Thus, the reaction of n-C_3F_7I with II was attempted in acetic anhydride-methylene chloride in the presence of zinc at 30-35°C. The only product detected was C_6F_{14}. No cross-coupling product was formed.

The possibility of the secondary reaction following route 'B' of Scheme 1 was also explored. Since zinc halides would be formed in the primary coupling process and also during elimination of ICl from I, these salts were used to verify route "B."


A.
$CFCl_2CF_2I$ + $CFCl_2CF_2CF_2CFCl_2$
(I)
(II)
$-ZnX_2$ (X = I, Cl)
$CFCl_2CF_2CFClCF_2CF_2CFCl_2$
(IIIa)
I
$-ZnX_2$ (X = I, Cl)
$CFCl_2CF_2CFClCF_2CF_2CFClCF_2CFCl_2$ (IVa)
+
$CFCl_2CF_2CFClCF_2CFClCF_2CF_2CFCl_2$ (IVb)
B.
II + CF_2=CFCl
IIIa + $CF_2ClCFClCFClCF_2CF_2CFCl_2$ (IIIb)
CF_2=CFCl
Mixture of isomers of $C_8F_{12}Cl_6$
C.
I + CF_2=CFCl
$CFCl_2CF_2CF_2CFClI$ (Va)
+
$CFCl_2CF_2CFClCF_2I$ (Vb)
I
$-ZnI_2$
$-ZnI_2$
IIIa
[From Va or Vb]
IVa [From Vb]
+
IVb [From Va + Vb]
+
$CFCl_2CF_2CF_2CFClCFClCF_2CF_2CFCl_2$
(IVc) [From Va]

Scheme 1.

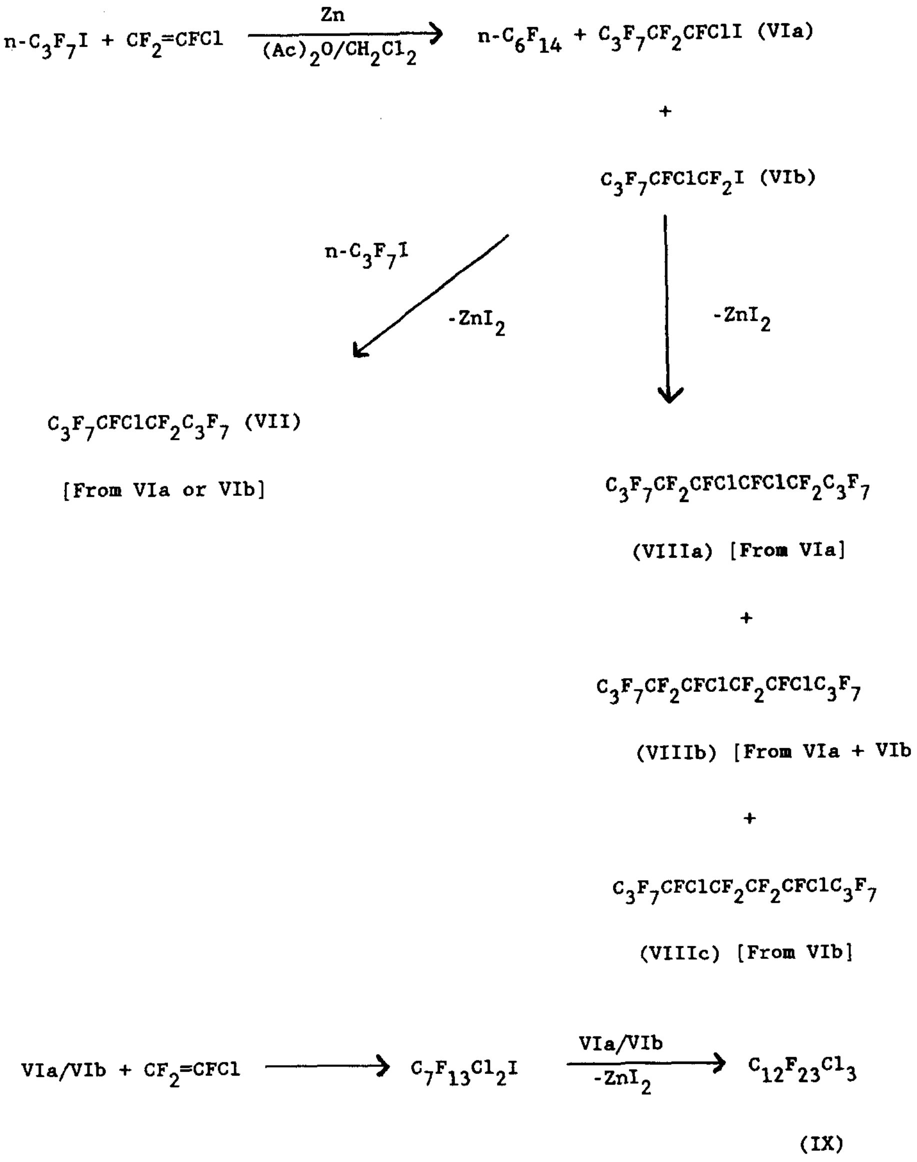
Into a mixture of Zn, ZnI_2, $ZnCl_2$, and II in acetic anhydride-methylene chloride, $CF_2=CFCl$ was bubbled at ca. 30°C. No addition products corresponding to $C_6F_9Cl_5$ or $C_8F_{12}Cl_6$ were formed, indicating that the secondary products are not formed by reaction 'B' of Scheme 1.

In order to investigate the possibility of addition of the starting iodide to chlorotrifluoroethylene ('C' in Scheme 1), use was made of a model reaction between C_3F_7I and $CF_2=CFCl$. The products that can be formed in this reaction are indicated in Scheme 2. Among the various products possible, C_6F_{14}, VII, VIII (a-c) and IX were identified by GC/MS. Compound VII, $C_8F_{17}Cl$ was isolated by distillation and ^{19}F NMR confirmed that it was a single positional isomer, 4-chloro-n-perfluorooctane. Compound VIII (a-c), $C_{10}F_{20}Cl_2$ was isolated by semi-preparative GC. Its ^{19}F NMR spectrum showed the presence of more than one isomer. Due to the presence of 2 asymmetric carbon atoms in the molecule, leading to four optical isomers, and the non-first order nature of the spectrum with all CF_2 and CFCl peaks close together, it was not possible to distinguish with certainty the different isomers present.

The above studies would suggest that of the different modes possible for the formation of by-products such as $C_6F_9Cl_5$ and $C_8F_{12}Cl_6$ in the reaction of I with zinc in acetic anhydride-methylene chloride solvent, the most probable would involve addition of $CFCl_2CF_2I$ to $CF_2=CFCl$ followed by coupling (route 'C', Scheme 1). A similar process can account for the formation of by-products in the reaction of the isomeric iodide, $CF_2ClCFClI$, with zinc.

EXPERIMENTAL

All reactions were carried out under an atmosphere of dry nitrogen. The zinc metal used (20 mesh) was from Mallinckrodt. Methylene chloride was dried and freshly distilled along with freshly distilled acetic anhydride. Chlorotrifluoroethylene was passed through a silica column just before use. All boiling points are uncorrected. Gas chromatographic analyses were carried out on Perkin-Elmer Sigma 1 or Sigma 2B instruments using


$n\text{-}C_3F_7I + CF_2{=}CFCl \xrightarrow[(Ac)_2O/CH_2Cl_2]{Zn} n\text{-}C_6F_{14} + C_3F_7CF_2CFClI$ (VIa)
+
$C_3F_7CFClCF_2I$ (VIb)
$n\text{-}C_3F_7I$
$-ZnI_2$
$-ZnI_2$
$C_3F_7CFClCF_2C_3F_7$ (VII)
[From VIa or VIb]
$C_3F_7CF_2CFClCFClCF_2C_3F_7$
(VIIIa) [From VIa]
+
$C_3F_7CF_2CFClCF_2CFClC_3F_7$
(VIIIb) [From VIa + VIb
+
$C_3F_7CFClCF_2CF_2CFClC_3F_7$
(VIIIc) [From VIb]
$VIa/VIb + CF_2{=}CFCl \longrightarrow C_7F_{13}Cl_2I \xrightarrow[-ZnI_2]{VIa/VIb} C_{12}F_{23}Cl_3$
(IX)

Scheme 2.

6' x 1/4" stainless steel columns packed with 10% SE-30 on Chromosorb W. A 6' x 1/8" carbowax 20M column was used to separate the isomeric dichlorotrifluoroiodoethanes. Mass spectra were obtained on a DuPont Type 21-491B mass spectrometer using chemical ionization or electron impact. ^{19}F NMR spectra were obtained in $CDCl_3$ on an NT-300 spectrophotometer at 282.3 MHz using $CFCl_3$ as internal standard and the chemical shifts are reported as ppm. Infrared spectra were taken on a Beckman Microlab 600 instrument.

Preparation of Pure 2,2-dichlorotrifluoro-1-iodoethane (I)

The preparation and purification were carried out as described by Hauptschein *et al.* [6] by passing chlorotrifluoroethylene (101 g, 0.87 mole) into a flask containing ICl (100 g, 0.62 mole) and a catalytic amount of anhydrous $FeCl_3$ at 35-45°C during a period of 6 h. The product was decolorized with aqueous sodium bisulfite, dried and distilled to obtain 65.2 g of a mixture of $CFCl_2CF_2I$ (I) (53%) and $CF_2ClCFClI$ (Ia) (47%). The two isomers could be separated on a 6' x 1/8" carbowax 20M GC column.

This mixture of isomers (62 g) was treated with approximately 4.5 molar excess of chlorosulfonic acid for 9 h. at 40°C followed by 4 h. at 50°C to preferentially remove all of the $CF_2ClCFClI$ by conversion to its chlorosulfate. The reaction was stopped by careful addition to ice, and the lower layer decolorized with sodium bisulfite and washed with water. This crude mixture of $CFCl_2CF_2I$ and $CF_2ClCFClOSO_2Cl$ was stirred with 10% aqueous NaOH for 18 h. to convert the chlorosulfate to water soluble $CF_2ClCOONa$. After washing the lower layer with water and drying on molecular sieves, its IR spectrum (liquid) showed no absorption at 6.9 μ due to chlorosulfate. The crude $CFCl_2CF_2I$ was distilled on a spinning band column. The purest fraction weighed 14.7 g. It is a colorless liquid boiling at 101°C (lit [6] 101°C). Its ^{19}F NMR spectrum had the following chemical shifts ($CFCl_3$); δ - 55.2 (d, 14.2 Hz; CF_2I) and -67.6 (t, 13.9 Hz; $CFCl_2$) (absorption ratios as expected). It was free from the isomer $CF_2ClCFClI$. MS (EI) 282, 280, 278 $(M)^+$, 245, 243 $(M-Cl)^+$, 195, 193 $(CFClI)^+$, 177 $(CF_2I)^+$, 155, 153, 151 $(C_2F_3Cl_2)^+$, 127

$(I)^+$, 118, 116 $(C_2F_3Cl)^+$, 105, 103, 101 $(CFCl_2)^+$, 87, 85 $(CF_2Cl)^+$.

This sample was used for the coupling reaction.

Reaction of $CFCl_2CF_2I$ with Zinc

Reaction of this iodide with zinc was carried out under identical conditions to that reported for the impure sample of $CF_2ClCFClI$ [1].

Granulated zinc (2.91 g; 0.0445 mole), freshly distilled acetic anhydride (7 ml) and methylene chloride (7 ml) were placed in a round-bottom flask fitted with a thermometer, addition funnel and a reflux condenser backed by a dry-ice trap. The contents were stirred at ambient temperature while passing a slow stream of N_2 through the flask and 2,2-dichlorotrifluoro-1-iodoethane (12.4 g; 0.0445 mole) was added in one lot. A mild exotherm was noticed; but unlike the reaction of $CF_2ClCFClI$, no external cooling was necessary to control the temperature below 35°C. A volatile compound collected in the dry-ice trap which was found, by comparison of its IR spectrum with that of an authentic sample, to be $CF_2{=}CFCl$ contaminated with CH_2Cl_2. After 3 h. the unreacted zinc was removed by decantation, and the liquid containing suspended zinc salts was treated with diluted H_2SO_4 while being cooled in an ice bath. The lower layer was separated, treated with aqueous sodium bicarbonate, washed with water and dried. Analysis by GC on a 6' SE-30 (10%) column showed essentially three new compounds identified by GC/MS as $C_4F_6Cl_4$ (78%), $C_6F_9Cl_5$ (20%) and $C_8F_{12}Cl_6$ (2%). This mixture was distilled to obtain 2.7 g (40% yield) of pure $CFCl_2CF_2CF_2CFCl_2$ (II) as a colorless liquid boiling at 127-8°C. Its ^{19}F NMR spectrum showed the following absorptions ($CFCl_3$): δ - 72.35 (pentet, 9.0 Hz) and -111.85 (d, 9.0 Hz and additional unresolved splitting) in the expected ratio for the structure. No other isomers were detected. MS (CI) of $C_4F_6Cl_4$: 289, 287, 285, 283 $[M-F]^+$, 273, 271, 269, 267 $[M-Cl]^+$, 105, 103, 101 $[CFCl_2]^+$, 87, 85 $[CF_2Cl]^+$. Anal. Calc'd. for $C_4F_6Cl_4$: C, 15.80; Cl, 46.68%. Found: C, 15.50; Cl, 46.50%.

From the pot residue obtained after distillation, a small amount of $C_6F_9Cl_5$ was isolated as a colorless liquid by semi-preparative gas chromatography. Its NMR spectrum (^{19}F, $CFCl_3$) showed the following absorptions: δ - 68.1 and -72.0 (m, $CFCl_2$), -108.1 and -111.8 (m, CF_2), two sets of doublets by ~260 Hz, each multiplets at -109.9, -110.9 and -113.4 and -114.3 (F in CF_2 next to CFCl) and -130.9 (m, CFCl) in the expected relative ratios suggesting that the spectrum is reasonably consistent with the structure $CFCl_2CF_2CF_2CFClCF_2CFCl_2$ (IIIa) (nc). More extensive studies employing two-dimensional ^{19}F NMR confirmed structure IIIa. MS (CI), 407, 405, 403, 401, 399 $(M-F)^+$, 389, 387, 385, 383 $(M-Cl)^+$, 155, 153, 151 $(C_2F_3Cl_2)^+$, 105, 103, 101 $(CFCl_2)^+$, 87, 85 $(CF_2Cl)^+$.

For $C_8F_{12}Cl_6$, mass spectral data alone (by GC/MS) is available. MS (CI) 503, 501, 499 $(M-Cl)^+$, 431, 429 $(C_8F_{12}Cl_3)^+$, 315, 313 $(C_6F_9Cl_2)^+$, 87, 85 $(CF_2Cl)^+$.

Attempted Reaction of $CFCl_2CF_2CF_2CFCl_2$ (II) with $n-C_3F_7I$

The attempt to cross-couple II and $n-C_3F_7I$ was carried out as follows: Metallic zinc (0.15 g; 0.0023 mole) was taken in a mixture of acetic anhydride (2 ml) and methylene chloride (2 ml) under a N_2 atmosphere. The flask containing this mixture was fitted with a water condenser, backed by a -78°C trap, and, while stirring, a mixture of II (0.61 g; .002 mole) and $n-C_3F_7I$ (0.59 g; .002 mole) was added in about 10 minutes. An exotherm was observed, and in about 1 h. a white solid began to appear. A volatile product was seen condensing in the -78°C trap which was probably $n-C_6F_{14}$. This was not analyzed. The flask's contents were stirred at ambient temperature for a total of 4 h. The solution was decanted off by washing with a small amount of methylene chloride. This was cooled in ice and hydrolyzed with dil. H_2SO_4. The organic layer on GC/MS analysis showed only CH_2Cl_2, II and C_6F_{14}. No cross-coupling products were detected.

A similar reaction carried out with $CF_2ClCFClCFClCF_2Cl$ and $n-C_3F_7I$ did not give any cross-coupling products, suggesting that the side products in the reaction of Ia with Zn are not formed by such cross-coupling.

Attempted Reaction of $CFCl_2CF_2CF_2CFCl_2$ (II) with $CF_2{=}CFCl$

Under a N_2 atmosphere, a mixture of zinc (0.065 g), anhydrous $ZnCl_2$ (0.068 g) and ZnI_2 (0.16 g) dry acetic anhydride (1 ml) and dry CH_2Cl_2 (1 ml) was added to a flask fitted with an efficient water condenser, backed by a -78°C trap, thermometer and a gas inlet. To this, $CFCl_2CF_2CF_2CFCl_2$ (0.30 g) was added. After stopping the nitrogen flow, a stream of gaseous chlorotrifluoroethylene (~12 g) was bubbled through this mixture at ambient temperature and atmospheric pressure for 2 h. The liquid part was carefully decanted and hydrolyzed with dil. H_2SO_4, while cooling, and the lower layer analyzed by GC. Only II and methylene chloride could be detected, suggesting that there had been no addition of II to $CF_2{=}CFCl$ nor any telomerization of the olefin under these conditions.

Reaction of $n\text{-}C_3F_7I$ and $CF_2{=}CFCl$

Granulated zinc (3.27 g; 0.05 g atom) acetic anhydride (8 ml) and methylene chloride (8 ml) were placed under a N_2 atmosphere in a round-bottom flask fitted with a thermometer, addition funnel and a reflux condenser backed by a dry-ice trap. The contents were stirred and the flask cooled in an ice-water bath to about 10°C. While bubbling a stream of $CF_2{=}CFCl$ through the reaction mixture, $n\text{-}C_3F_7I$ (14.8 g; 0.05 mole) was added dropwise. An exotherm was observed and the temperature was controlled below 20°C. Addition of the iodide took about 1 h. during which time about 15 g of chlorotrifluoroethylene (CTFE) had been bubbled through. The reaction was followed by GC analysis of hydrolyzed samples. At the end of 1 h., CTFE addition was stopped, N_2 admitted and the contents stirred below 20°C for 3 h. At the end of this period, products were observed, but the starting iodide was still present. The ice-water bath was then removed, and the contents allowed to warm up to ambient temperature. Stirring was continued for another 2 h. while an additional 10 g of CTFE was bubbled through the reaction mixture. The iodide had almost completely disappeared by this time and there were considerable amounts of white solid in the reaction flask. The liquid and the suspended salts were decanted from unreacted zinc, transferred to another flask, and, whilst being

cooled in an ice-bath, hydrolyzed with dil. H_2SO_4. The organic layer which separated showed two layers. The upper layer on GC analysis was found to be essentially CH_2Cl_2 with small amounts of n-C_3F_7I. The lower layer (3.5 g) was found to be a mixture of C_6F_{14} (9.7%), unreacted C_3F_7I (2.0%), $C_8F_{17}Cl$ (VII) (73%), $C_{10}F_{20}Cl_2$ (VIII a-c) (14%) and $C_{12}F_{23}Cl_3$ (IX) (1.3%), as determined by GC/MS data and GC area percent. From this VII and VIII were isolated by semi-preparative gas chromatography.
$C_8F_{17}Cl$ (VII) boiled at 115-7°C. ^{19}F NMR: ($CFCl_3$) δ - 81.7 (two overlapping triplets due to 2 CF_3), -112 to -128 (series of five AB patterns each corresponding to a $-CF_2-$ group in which the two fluorines are non-equivalent; 5 CF_2) and -136 ppm (broad singlet;CFCl) which indicated that the compound was a pure positional isomer of the structure $CF_3(CF_2)_2CFCl(CF_2)_3CF_3$ (nc). MS (CI): 437, 435 $(M-F)^+$, 419 $(M-Cl)^+$, 349, 347 $(C_7F_{12}Cl)^+$, 287, 285 $(C_5F_{10}Cl)^+$, 249, 247 $(C_5F_8Cl)^+$, 237, 235 $(C_4F_8Cl)^+$, 219 $(C_4F_9)^+$, 199, 197 $(C_4F_6Cl)^+$, 169 $(C_3F_7)^+$, 149, 147 $(C_3F_4Cl)^+$, 131 $(C_3F_5)^+$, 119 $(C_2F_5)^+$, 87, 85 $(CF_2Cl)^+$, 69 (CF_3). Anal. Calc'd. for $C_8F_{17}Cl$: C, 21.12; F, 71.07; Cl, 7.8%. Found: C, 21.34; F, 68.69; Cl, 7.65%.

$C_{10}F_{20}Cl_2$ (VIII a-c)

Colorless liquid. ^{19}F NMR ($CFCl_3$): δ - 81.6 (triplet, 10 Hz; CF_3), -109 to -115 (two overlapping AB patterns, CF_2 next to CFCl), -118 to -122 (probably an AB pattern overlapping a singlet; CF_2) and -125 to -128 (multiplet, CF_2 next to CF_3, plus CFCl). These four sets of peaks showed the relative area of 6:4:4:6, respectively. Due to the non-first-order nature of the spectrum, with all CF_2 and CFCl peaks close together, it was not possible to distinguish between the three possible positional isomers (VIIIa, b and c, Scheme 2). Perhaps all the possible isomers were present. MS (CI): 555, 553 $(M-F)^+$, 537, 535 $(M-Cl)^+$, 481 $(C_{10}F_{19})^+$, 449, 447 $(C_9F_{16}Cl)^+$, 355, 353, 351 $(C_6F_{11}Cl_2)^+$ 337, 335 $(C_6F_{12}Cl)^+$, 317, 315, 313 $(C_7F_9Cl_2)^+$, 287, 285 $(C_5F_{10}Cl)^+$, 269 $(C_5F_{11})^+$, 249, 247 $(C_5F_8Cl)^+$, 237, 235 $(C_4F_8Cl)^+$, 219 $(C_4F_9)^+$, 199, 197 $(C_4F_6Cl)^+$, 169 $(C_3F_7)^+$, 149, 147 (C_3F_4Cl), 119 $(C_2F_5)^+$, 87, 85 $(CF_2Cl)^+$, 69 $(CF_3)^+$. Anal. Calc'd.

for $C_{10}F_{20}Cl_2$: C, 21.02; Cl, 12.42. Found: C, 21.02; Cl, 12.10%.

$C_{12}F_{23}Cl_3$ (IX)

For this material only MS data are available. MS (CI): 669, 667 $(M-F)^+$, 651 $(M-Cl)^+$, 599, 597 $(C_{12}F_{22}Cl)^+$, 405, 403, 401 $(C_7F_{13}Cl_2)^+$, 355, 353, 351 $(C_6F_{11}Cl_2)^+$, 337, 335 $(C_6F_{12}Cl)^+$, 305, 303, 301 $(C_5F_9Cl_2)^+$, 287, 285 $(C_5F_{10}Cl)^+$, 249, 247 $(C_5F_8Cl)^+$, 169 $(C_3F_7)^+$, 149, 147 $(C_3F_4Cl)^+$, 119 $(C_2F_5)^+$, 87, 85 $(CF_2Cl)^+$, 69 $(CF_3)^+$.

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