Journal of Fluorine Chemistry, *35* (1987) 421–424

Received: October 9, 1986; accepted: October 29, 1986

PRELIMINARY NOTE

Reaction of 1,2-Dichloroiodotrifluoroethane With Zinc

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SUMMARY

The zinc coupling reaction of 1,2-dichloroiodotrifluoroethane (I) in acetic anhydride-methylene chloride has been reinvestigated in more detail than its original disclosure. The expected coupling product $C_4F_6Cl_4$ was shown to be an isomeric mixture of three components, $CF_2ClCFClCFClCF_2Cl$ (II, 80%), $CFCl_2CF_2CF_2CFCl_2$ (IIa, 15%) and $CF_2ClCFClCF_2CFCl_2$ (IIb, 5%). In addition, other products e.g. $CF_2{=}CFCl$, $C_6F_9Cl_5$ and $C_8F_{12}Cl_6$ were formed in minor quantities. A probable mode of formation of the various byproducts via initial formation of $CF_2{=}CFCl$ and subsequent telomerization is presented.

The reaction of 1,2-dichloroiodotrifluoroethane (I) with zinc in acetic anhydride-methylene chloride was reported by Henne and Postelneck [1] to yield the coupled product 1,2,3,4-tetrachlorohexafluorobutane (II). While no other products were reported by these authors, a similar study by Keller and Tarrant [2] gave, in addition to II, 1,2,3,5,6-pentachlorononafluorohexane (III) and a gaseous product presumed to be chlorotrifluoroethylene. Reactions carried out in ethyl acetate-methylene chloride gave similar results (see eqn. 1).

$$\underset{(I)}{CF_2ClCFClI} \xrightarrow[Ac_2O/CH_2Cl_2]{Zn} \underset{(II)}{(CF_2ClCFCl)_2} + \underset{(III)}{CF_2ClCFClCF_2CFClCFClCF_2Cl} \qquad (1)$$

$$I + \underset{(IV)}{CF_2ClCFClCF_2CFClI} \xrightarrow[Ac_2O/CH_2Cl_2]{Zn} II\ (14\%) + III\ (46\%) \qquad (2)$$

$$+ \underset{(V)}{(CF_2ClCFClCF_2CFCl)_2}\ (40\%)$$

0022-1139/87/$3.50

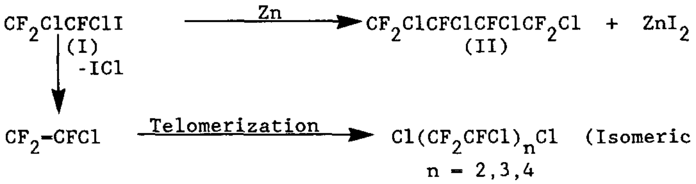
$$\text{I} + \text{II} \xrightarrow[Ac_2O/CH_2Cl_2]{Zn} \text{III} + \text{Polymer} \qquad (3)$$

The identity of III was established by these authors (see eqn. 2) by preparing it in 46 percent yield along with II and V through a cross-coupling reaction between I and IV. A comparison of IR and mass spectra of III obtained by these two different routes showed them to be identical. Furthermore, formation of III in small amounts along with a polymer when I and II were treated with zinc in acetic anhydride-methylene chloride (eqn. 3) led to the suggestion that iodides can be made to couple with chlorides under suitable conditions.

We were interested in obtaining pure 1,2,3,4-tetrachlorohexafluorobutane (II) for use as a model compound in other studies and attempted its preparation by the procedure of Henne and Postelneck [1] with minor modifications. It was found that a gaseous product was indeed formed during the reaction, as observed by Keller and Tarrant [2] and this was identified as chlorotrifluoroethylene by comparison of its IR spectrum with that of an authentic sample. The liquid product isolated on GC/MS analysis showed $C_4F_6Cl_4$, $C_6F_9Cl_5$ and $C_8F_{12}Cl_6$ in the approximate ratio of 91:8:1. The GC retention times of these components were compared with those of a telomer mixture prepared from chlorotrifluoroethylene and sulfuryl chloride under radical initiation, and were found to be identical. Analysis of the product from the Zn coupling reaction, on a capillary column clearly showed multiple peaks, some partially separated, for each of the compound represented by $C_4F_6Cl_4$, $C_6F_9Cl_5$ and $C_8F_{12}Cl_6$, as was also observed with the telomer mixture prepared from chlorotrifluoroethylene. This would suggest that these compounds may be isomeric mixtures rather than pure compounds.

In order to determine the nature of these isomers, $C_4F_6Cl_4$, the major product in the coupling reaction was isolated by fractionation. Its ^{19}F NMR spectrum (282.3 MHz.) indicated that it was a mixture of approximately 80 percent of $CF_2ClCFClCFClCF_2Cl$ (II), 15 percent of $CFCl_2CF_2CF_2CFCl_2$ (IIa) and five percent of $CF_2ClCFClCF_2CFCl_2$ (IIb). Similar analysis of a sample of $C_4F_6Cl_4$ from chlorotrifluoroethylene telomerization showed the presence of approximately 85 percent of IIb and 15 percent of IIa.

These observations lead us to believe that along with the major coupling reaction taking place during treatment of I with Zn (eqn. 1), side reactions occur involving intramolecular elimination of ICl from I leading to chlorotrifluoroethylene which apparently undergoes telomerization under the conditions used (eqns. 4 and 5). The chlorine abstracted to terminate the chain may come from ICl or the CH_2Cl_2 solvent. The process may be represented as shown in the following equations.



$$\begin{tikzcd} \underset{(I)}{CF_2ClCFClI} \arrow[r, "Zn"] \arrow[d, "-ICl"] & \underset{(II)}{CF_2ClCFClCFClCF_2Cl} + ZnI_2 \quad (4) \\ CF_2{=}CFCl \arrow[r, "Telomerization"] & \underset{n = 2,3,4}{Cl(CF_2CFCl)_nCl} \text{ (Isomeric mixtures)} \quad (5) \end{tikzcd}$$

It would appear reasonable to assume that such intramolecular elimination of ICl would occur most readily from fluoroalkyl iodides containing a β-chlorine atom.

An alternate possibility of chlorine migration towards the ends of a chain in II, under the influence of Zn salts acting as Lewis acids, cannot be completely ruled out in the absence of further evidence. Anhydrous aluminum salts are known to bring about such isomerization [3]. Though such isomerization would explain the formation of IIa and IIb and further coupling of an iodide and a chloride [2] would explain the formation of III as well as higher oligomers, we are inclined to consider it as less probable in view of the formation of free chlorotrifluoroethylene during the reaction.

The coupling reaction using Zn was carried out as follows: Freshly distilled acetic anhydride (8 ml), methylene chloride (8 ml), and granulated zinc (3.27 g) were placed in a round-bottom flask equipped with a thermometer, addition funnel and a reflux condensor backed by a Dry-Ice-cooled trap. The contents were stirred at ambient temperature while passing a slow stream of nitrogen through the flask and 1,2-dichloroiodotrifluoroethane (14.0 g) was added in one lot. An exothermic reaction started which was controlled to <35°C by intermittent cooling in an ice bath. After three hours the unreacted zinc was removed by decantation and the liquid containing suspended zinc salts was treated with dil. 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 (12' x 1/4" o.d. column containing OV-1 (three percent) on Supelcoport) showed three new compounds which were identified by GC/MS as $C_4F_6Cl_4$, $C_6F_9Cl_5$ and $C_8F_{12}Cl_6$ in the approximate ratio 91:8:1. Analysis of this product on a 60 m x 0.32 mm. i.d. fused silica capillary column containing Supelcowax 10 as stationary phase, showed multiple peaks for each of the compounds represented by $C_4F_6Cl_4$, $C_6F_9Cl_5$ and $C_8F_{12}Cl_6$. This product mixture was distilled to obtain 4.34 g (57 percent yield) of $C_4F_6Cl_4$ boiling at 133°C (lit. [1] B. P. 133-5°C). The pot residue contained $C_6F_9Cl_5$ and $C_8F_{12}Cl_6$. The highly volatile fraction collected in the Dry-Ice trap was identified as chlorotrifluoroethylene by comparison of its IR spectrum with that of an authentic sample. The NMR spectrum of $C_4F_6Cl_4$ (^{19}F,

$CFCl_3$ as internal standard) gave the following absorptions: δ-61.3, -61.7 (two overlapping AB patterns assigned to 2 CF_2Cl due to chiral forms of II), -63.9 (m, $-CF_2Cl$ of IIb), -65.5 (m, $CFCl_2$ of IIb), -72.3 (m, 2 $CFCl_2$ of IIa), -107.8 (AB pattern, CF_2 of IIb), -111.8 (d, 2 CF_2 of IIa), -120.7, -121.0 (two multiplets, 2 CFCl due to chiral forms of II), -126.5 (m, CFCl of IIb). From the relative intensities of these peaks, ratio of isomers were obtained. A detailed NMR spectroscopic study of these and related chlorofluoro compounds will be published later. MS(CI) of $C_4F_6Cl_4$: 291, 289, 287, 285, 283 $[M-F]^+$, 273, 271, 269, 267 $[M-Cl]^+$, 217, 215, 213 $[C_4F_5Cl_2]^+$, 199, 197 $[C_4F_6Cl]^+$, 185, 183, 181, 179 $[C_3F_2Cl_3]^+$, 155, 153, 151 $[C_2F_3Cl_2]^+$, 105, 103, 101 $[CFCl_2]^+$, 87, 85 $[CF_2Cl]^+$.

We thank Prof. Wallace S. Brey, Jr., of the University of Florida for NMR data and interpretation and Dr. Chi K. Yu of Technical Services Group for mass spectral data.

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