Liquid-phase fluorination and dehydrochlorination of 1,1,1-trichloroethane

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Abstract

During the liquid-phase fluorination of 1,1,1-trichloroethane with $SbCl_5 \cdot HF$, 1,1-dichloroethene is formed. This reacts to give linear and branched oligomers. The hydrolysis of these by-products affords 3,4-dichlorophenol, 6-methyl-4-chloro-2-pyran-2-one and 2-methyl-5,7-dichlorochromone whose source is the acid-catalyzed reaction of water with the trimer and pentamer of 1,1-dichloroethene.

Introduction

The fluorination of 1,1,1-trichloroethane is usually carried out in liquid HF, with or without catalysts [1–3]. In the former case, $SbCl_5$ is widely used [4–6] but other Lewis acids are also effective: for example, the use of chlorinated alumina has been recently reported [7]. This reaction provides chlorofluoroalkanes with a very good selectivity, but some by-products are also formed as shown by the purple colour of the crude reaction mixture. Some dehydrochlorination also occurs during this reaction, as indicated by the presence of $H_2C{=}CCl_2$ in the reaction mixture [8]. In the acidic medium employed, this olefin oligomerizes [9]. As a result, the purple material is presumably a partially dehydrochlorinated oligomer [10]. The average composition $[CH_{2-x}{-}CCl_{2-x}]_n$, x being in the range 0.4–0.7, has recently been suggested by Winfield *et al.* [7] for the purple material they obtained when reacting CH_3CCl_3 with chlorinated alumina.

We have reasoned that the hydrolysis of these by-product should give some information about their structure and/or would produce organic compounds whose preparation by other means is not simple.

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Experimental

Fluorination

Fluorination was carried out using an antimony mixed halide [8] according to a procedure previously described. To a stainless-steel autoclave (500 ml) was added 2.35×10^{-2} mol of $SbCl_5$ followed by liquid HF in such an amount that the molar ratio of HF to $SbCl_5$ was approximately equal to 25:1.

After heating at 60 °C for 1 h, the excess HF was vented with a stream of dry nitrogen. This was followed by the addition of 1 mol (133 g) of CH_3CCl_3. After 1 h at 60 °C and 10 bar pressure, 100 ml of 6 N H_2SO_4 was added and the purple organic layer which formed was decanted, washed with water and dried over $MgSO_4$.

Analysis of the residue

The purple residue (2.4 g) was recovered after rotary evaporation of CH_3CCl_3 (F104a), CH_3CCl_2F (F141b) and CH_3CClF_2 (F142b). It was analyzed using flash chromatography on silica employing CH_2Cl_2/CH_3OH mixtures of increasing polarity (CH_3OH (%) = 0, 0.5, 5, 10). About 40 fractions were collected, which were analyzed by thin layer chromatography. The fractions whose composition was similar were combined, evaporated to dryness and their homogeneity checked thin layer chromatography.

This procedure provided three compounds which were identified by mass spectrometry, ^1H and ^{13}C NMR spectroscopy.

Results

The reaction of $SbCl_5$ and HF at 60 °C and 1 MPa pressure affords an antimony mixed halide whose empirical formula is $SbClF_4 \cdot 4HF$ [8]. This compound may be used for the stoichiometric fluorination of CH_3CCl_3, the results being given in Table 1.

The inorganic fluorine was recovered quantitatively in the chlorofluoro compounds F141b and F142b. Fluorine was not detected in the residue and Sb^V was found to have been partially reduced to Sb^{III} [8].

TABLE 1

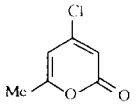
Fluorination of CH_3CCl_3 with $SbClF_4$–4HF[a]

Products (mol%)	Selectivity (%)
F140a	9.9[b]
F141b	39.5
F142b	57.5
F143a	3.0

[a]Temp. = 60 °C; pressure = 1 MPa; $[Sb^V] = 2.35 \times 10^{-2}$ mol; [F140a] = 1 mol.
[b]Relates to percentage conversion of original starting material F140a.

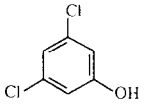
Three compounds were isolated from the crude purple residue. The yield from flash chromatography is given in Table 2. The following structures were assigned according to spectroscopic data. The ^{13}C chemical shifts were identical with those of published structures [11] as were the various mass spectra.

6-Methyl-4-chloro-2-pyran-2-one (**1**):



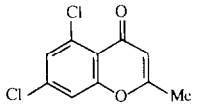
^1H NMR δ: 2.26 (CH_3); 6.06 (3CH); 6.24 (5CH) ppm. ^{13}C NMR δ: 19.5 (CH_3); 105.9 (5CH); 110.6 (3CH); 151.6 (4CCl); 160.8 (2C=O); 162.5 (6C−CH_3) ppm. MS *m/e* (% abundance): 144 (M^+, 83); ($C_5H_2ClO_2^+$, 88); 73 ($C_3H_2Cl^+$, 100).

3,5-Dichlorophenol (**2**):



^1H NMR δ: 6.80 (2CH); 6.86 (4CH) ppm. ^{13}C NMR δ: 114.6 (2CH); 120.2 (4CH); 135 (3CCl); 157.8 (C−OH) ppm. MS *m/e* (% abundance): 162 (M^+, 100); 134 ($C_5H_3Cl_2^+$, 20); 99 ($C_5H_3Cl^+$, 70).

2-Methyl-5,7-dichlorochromone (**3**):



^1H NMR δ: 2.34 (CH_3); 6.10 (3CH); 7.28 (6CH); 7.28 (8CH) ppm. ^{13}C NMR δ: 19.92 (CH_3); 112 (3CH); 117.4 (8CH); 119.,7 (C_a); 128 (6CH); 134.5 (5C); 138.2 (7C); 157.8 (C_b); 164.5 (2C); 176 (4C=O) ppm. MS *m/e* (% abundance): 228 (M^+, 100); 200 ($C_9H_6ClO_2^+$, 60); 188 ($C_7H_2ClO_2^+$, 30); 160 ($C_6H_2ClO^+$, 40).

TABLE 2

Flash chromatographic yield of three compounds isolated

Compound	Yield (g)[a]
1	1.19
2	0.20
3	0.08

[a]Total wt. of initial crude product = 2.4 g; overall yield of compounds = 61%.

Discussion

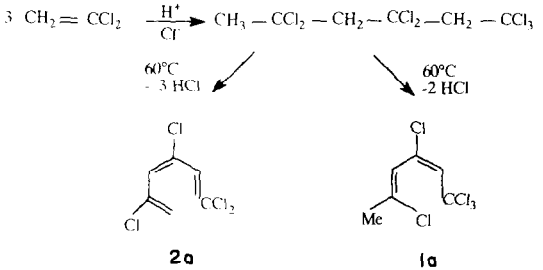
In addition to the substitution of chlorine for fluorine in 1,1,1-trichloroethane during its reaction with HF, there is also competitive dehydrochlorination of CH_3CCl_3 giving $H_2C{=}CCl_2$ [8]. In the presence of Sb^V and HCl, this compound oligomerizes according to a well-known acid-catalyzed reaction [9, 10].

$$n H_2C{=}CCl_2 \xrightarrow{H^+} CH_3CCl_2(CH_2CCl_2)_{n-2}CH_2CCl_3$$

It is also possible that some branching occurs during this reaction.

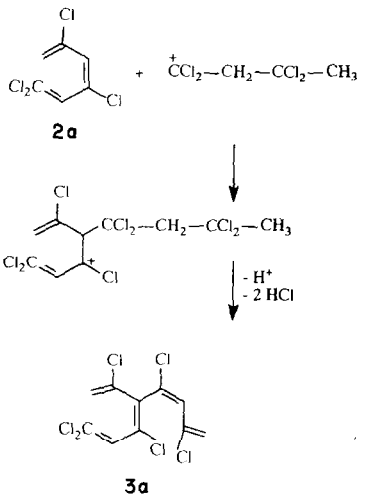
At 60 °C these oligomers are dehydrochlorinated and unsaturated chloropolymers are obtained whose hydrolysis yields the above-mentioned phenol, lactone and chromone. The structures of these compounds indicate that the trimer and pentamer of $H_2C{=}CCl_2$ are formed. The tetramers are also probably formed but their derivatives could not be isolated.

According to our results a head-to-tail oligomerization occurs:



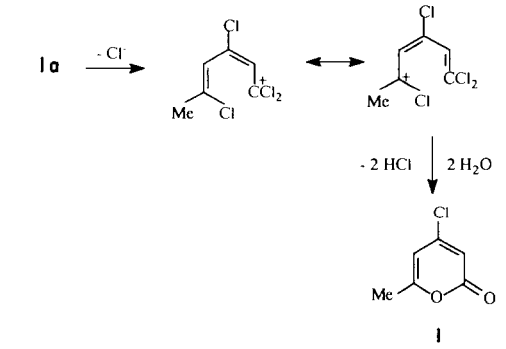
2a **1a**

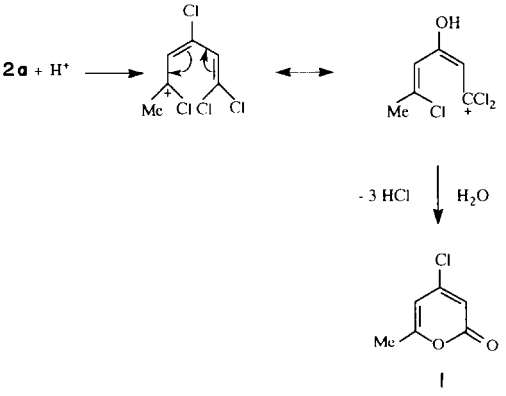
Some branching may occur by attack of a carbocation on a dehydrochlorinated oligomer:

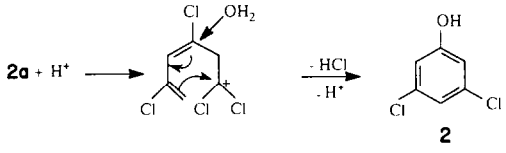


3a

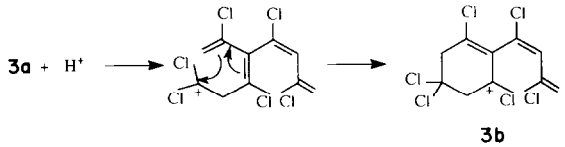
The hydrolysis of **1a**, **2a** and **3a** affords the oxygenated compounds **1**, **2** and **3**:

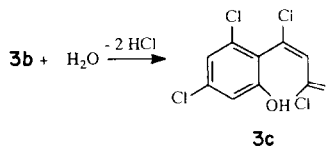


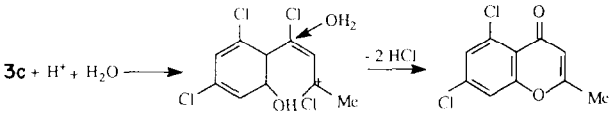




The formation of chromone 3 results from cyclization and hydrolysis of the carbocations derived from **3a**. For example:







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For clarity, this hydrolysis is shown as a stepwise process although it is probable that it is simultaneous.

Our results account for the tri- and pentamerization of $H_2C{=}CCl_2$; it is likely that other polymers such as the tetramer and hexamers must be formed, but we could not isolate the products of their hydrolysis in sufficient amount to enable their identification.

It is worth mentioning that the three products which were identified are not very easy to synthesize since the substituents are in the *meta* position.

Conclusions

The dehydrochlorination of 1,1,1-trichlorethane, which occurs as a side-reaction during the fluorination of this chloroalkane, produces $H_2C{=}CCl_2$ which oligomerizes to dehydrochlorinated polymers. Three of these polymers were identified by analysis of their hydrolysis products.

Our results indicate that if each of these oligomers could be prepared selectively they would provide excellent starting materials for the very simple preparation of these oxygenated compounds.

Acknowledgment

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