Novel Synthesis of Benzotrihalides: the Pyrolysis of Phenyl Trihalogenoacetates

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Summary Pyrolysis of 4-chlorophenyl trichloroacetate (I) at 500 °C yields 4-chlorobenzotrichloride (II) and some 1,4-dichlorobenzene (III) as by-product; the corresponding trifluoroacetate is converted into 4-chlorobenzotrifluoride.

4-Chlorobenzotrichloride and 2,4-dichlorobenzotrichloride are valuable intermediates for the production of several commercial herbicides.[1] The chlorinated benzotrihalides are prepared from toluene *via* side chain chlorination of either the intermediate chlorinated toluenes[2] or chlorinated toluenesulphonyl chlorides.[3] Both classes of compounds require isomer separations by either distillation or recrystallization. We now report a novel synthesis of benzotrihalides from the pyrolysis of the trihalogenoacetates of the corresponding phenol (equations 1 and 2).

$$\mathrm{ClC_6H_4OH}\text{-}p + \mathrm{Cl_3CC(O)Cl} \rightarrow \underset{\text{(I)}}{\mathrm{ClC_6H_4OC(O)CCl_3}\text{-}p} + \mathrm{HCl} \qquad (1)$$

$$\text{(I)} \xrightarrow{\text{Heat}} \underset{\text{(II)}}{\mathrm{ClC_6H_4CCl_3}\text{-}p} + \underset{\text{(III)}}{\mathrm{ClC_6H_4Cl}\text{-}p} + \mathrm{CO_2} \qquad (2)$$

The results of a typical flow pyrolysis experiment are summarized in the Table. The ester was fed at *ca.* 1 ml min^{-1} (6×10^{-3} mol min^{-1}) through a pre-heater (300 °C) into the reactor [a 1 × 24 in Vycor tube packed with Mallinckrodt anhydrous $CaCl_2$ (4 mesh), 500 °C]. Two moles of nitrogen per mole of ester was used as the carrier gas. The conversion and the ratio of (II) : (III) decrease with time, presumably owing to tar formation on the catalyst. After distillation, (II) and (III) were obtained in 64 and 13·5% yields, respectively.

Table. Pyrolysis of 4-chlorophenyl trichloracetate (I).

Time/h	(II)/%	(III)/%	Other products/ %	Conversion/ %	$ArCCl_3 : ArCl$
0·75	62	9·5	4·5	76	6·5 : 1
2·0	55	8·5	4·0	69	6·0 : 1
3·0	52	8·0	4·0	65	5·7 : 1

Inorganic salts, *e.g.*, $BaCl_2$, $SrCl_2$, $LaCl_3$, and $MgCl_2$ on activated charcoal as well as $Ca_3(PO_4)_2$ and $SrNiPO_4$ were tested as catalysts for the reaction. None gave as good conversion and selectivity as the anhydrous $CaCl_2$.† Pyrolysis of 2,4-dichlorophenyl trichloroacetate gave an 80% conversion at 505 °C with a trichloride : chlorobenzene selectivity of 0·66 : 1. At 480 °C the conversion decreased to 70% and the selectivity increased to 1·50 : 1. At 460 °C the conversion was 60% and selectivity 3·00 : 1. Thus, the selectivity to the desired benzotrihalide is very temperature dependent. Pyrolysis of the 2,4-dichloro-derivative also gave considerable amounts (10–20%) of trichloroacetyl chloride.

Thermolysis of aryl acetates is well documented and several mechanisms have been proposed to account for the products, phenol and keten. The pyrolysis of the trichloroacetates requires cleavage of an aromatic carbon–oxygen bond. The pyrolysis of phenylfluoroformates to fluorobenzene appears to be the only example of this type of bond cleavage reported to date.[4] Preliminary experiments on the pyrolysis of 4-chlorophenyl trifluoroacetate at 650 °C over graphite pellets gave a 12% conversion and 60% yield of 4-chlorobenzotrifluoride. We consider it likely that cleavage of the trihalogenomethylcarbonyl carbon bond is the rate determining step in the pyrolysis.

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† Catalyst activity varied with different lots of $CaCl_2$ and with different sources.

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