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PRELIMINARY NOTE

Flash Thermolysis of Aryl Trifluoroacetates: A New Approach to Trifluoromethylated Aromatic Compounds

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SUMMARY

Flash thermolysis of aryl trifluoroacetates yield trifluoromethyl aromatic compounds along with trifluoromethoxy compounds.

There are several methods for the synthesis of aromatic trifluoromethyl compounds, such as the reaction of benzotrichlorides with HF or SbF_3[1], reaction of carboxylic acids with sulfur tetrafluoride [2] or trifluoromethylation of aryl halides using the trifluoromethyl copper complex [3].

However, these methods require several steps or highly expensive and/or toxic reagents. Therefore, the development of new methods for the synthesis of trifluoromethyl aromatics, which are more economical and easily carried out, is desirable.

The work of Christe et al. on the preparation of aromatic fluorine compounds by the thermolysis of aryl fluoroformate [4] attracted our attention.

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Since the trifluoromethyl group often acts as a pseudo halogen, we anticipated that aryl trifluoroacetates might behave similarly. A preliminary experiment on pyrolysis of 4-chlorophenyl trifluoroacetate had been reported previously [5]. Thus, we have investigated the preparation of aromatic trifluoromethyl compounds by the decarboxylative thermolysis of aryl trifluoroacetates and observed that in some cases fairly good yields of trifluoromethyl compounds were obtained, while a considerable amount of trifluoromethoxy compounds were formed as by-product

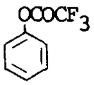
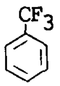
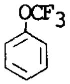
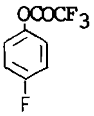
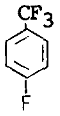
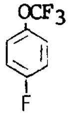
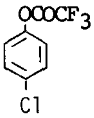
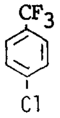
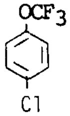
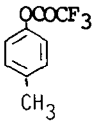
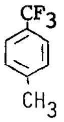
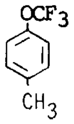
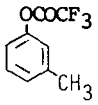
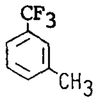
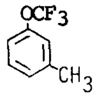
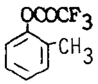
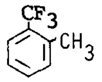
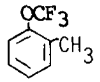
$$ArOH \longrightarrow ArOCOCF_3 \xrightarrow[heat]{-CO_2} ArCF_3 + ArOCF_3$$

The thermolysis of phenyl trifluoroacetate through a quartz tube under reduced pressure below 500°C resulted in the recovery of the starting material. Thus, we attempted the thermolysis through a quartz tube packed with platinum wire. The starting material was passed through the tube in a stream of argon at 6 - 10mm Hg pressure. At 600°C, benzotrifluoride was obtained in 7.1% conversion with recovery of a large amount of the starting material. At 650°C, the conversion increased to 15.5% with recovery of about one-half of the starting material (yield: ca. 60%). At 700°C, the conversion to benzotrifluoride was 11%, while the starting material was no longer detectable. In these experiments, a trace of trifluoromethoxybenzene was observed. The formation of this by-product is probably due to the primary bond-fission of the C-O bond. The yield of benzotrifluoride has not been fully optimized. Improvements in the experimental conditions, including flow rate, are being investigated

We then examined the thermolysis at 650°C of a series of aryl trifluoroacetates under the same conditions. The results are summarized in Table I.

TABLE I.

Flash Thermolysis of Aryl Trifluoroacetates

Run	Starting material	CF_3-compound [a]		CF_3O-compound [a]	
1 [b]			(15.5%)		(trace)
2 [b]			(2.0%)		(19.2%)
3 [b]			(10.0%)		(6.6%)
4 [c]			(12.9%)		(22.0%)
5 [c]			(19.5%)		(6.0%)
6 [c]			(25.3%)		(10.3%)

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[a] The fractions of the trifluoromethyl and trifluoromethoxy compounds were isolated by preparative g.l.c. and the amounts of the components were estimated from the peak-ratio in g.l.c.

[b] In runs 1 to 3, about half of the starting material was recovered. However, those reactants bearing a methyl group (runs 4 to 6) suffered some demethylation.

[c] In runs (4 to 6), considerable amount of benzotrifluoride was observed in g.l.c.

The data reveal that the formation of trifluoromethoxy compound is remarkable when the aryl group bears a fluoro substituent at the para position. This result suggests that the substituent stabilizes the phenoxy radical and that the CO-O bond becomes especially labile toward fission. This trend is also observed in the case of the p-chloro compound and o- or p-methyl compounds, while the effect is much weaker for the m-methyl compound. The thermolysis of the p-nitro compound resulted in the formation of tarry substances and no products were isolated.

The formation of the trifluoromethyl compounds occurred regioselectively. If a radical mechanism were operative, other isomers, which were not observed, might have been detected. While it is possible that the reaction involves an ionic process, similar to that proposed by Christe [6], further studies are necessary to elucidate the mechanism of this complex thermolytic reaction.

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