Tetrahedron Letters,Vol.30,No.17,pp 2265-2266,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

GENERATION AND REACTION OF 2,2,2-TRIFLUORO-1-PHENYLSULFENYLETHYL CARBOCATION

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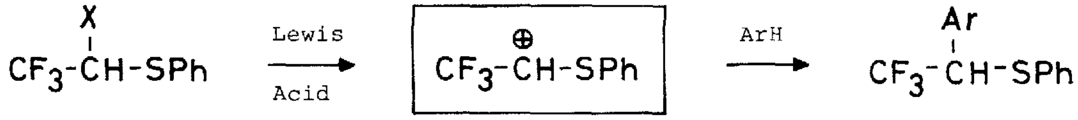
Summary: Lewis acid-catalyzed dechlorination of 1-chloro-2,2,2-trifluoroethyl phenyl sulfide generates 2,2,2-trifluoro-1-phenylsulfenylethyl carbocation which undergoes electrophilic reaction with aromatic compounds.

Development of reactions at the carbon atom bearing trifluoromethyl group is a subject of interest from the point of preparing biologically active trifluoromethylated organic compounds.1) Carbanions bearing α-trifluoromethyl group are too reactive to be alkylated and mostly undergo defluorination.2,3) On the other hand, reactions of the corresponding carbocation are scarcely investigated presumably because of the difficulty for generation due to the strong electron-withdrawing nature of trifluoromethyl group.4),5) Here, we describe a first generation and electrophilic reaction of 2,2,2-trifluoro-1-phenylsulfenylethyl carbocation 16) in which divalent sulfur atom plays essential roles not only in stabilization of the cation **1**, but also easy preparation of the chloride 3 from 27) and displacement with hydrogen on the methine carbon of **4**, affording trifluoroethyl aromatic compounds.



$$CF_3\text{-}\overset{X}{CH}\text{-}SPh \xrightarrow[\text{Acid}]{\text{Lewis}} \boxed{CF_3\text{-}\overset{\oplus}{C}H\text{-}SPh} \xrightarrow{ArH} CF_3\text{-}\overset{Ar}{CH}\text{-}SPh$$

2 X = H
3 X = Cl

1

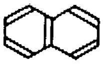
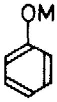
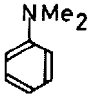
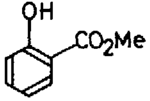
4

A suspension of 3 (0.5 mmol), $ZnCl_2$ (0.55 mmol) and benzene (0.15 ml) in CH_3NO_2 (1 ml) was refluxed for 30 min. The usual work-up and chromatography (SiO_2, hexane-benzene) provided **4** in a 66% yield. In contrast to the failure of carbon-oxygen bond cleavage of 2,2,2-trifluoro-1-methoxyethyl phenyl sulfide,5) Lewis acids cleave carbon-chlorine bond selectively to generate 1.

It is notable that the weaker acid such as $ZnCl_2$ is useful for heteroaromatics since the stronger one such as $SnCl_4$ partially induces a decomposion of **4** in the reaction conditions. Nitromethane is a more effective solvent for enhancing the reaction rate than CH_2Cl_2, $ClCH_2CH_2Cl$, C_6H_6, and MeCN.

The cation **1** can be trapped with most of aromatic compounds with electron-donating groups. Reaction of 3 with methyl salicylate provides the carbon-attacked products on the para-position to the hydroxyl group although the phenolic products are rather unstable under the reaction conditions. Hetero-aromatics such as furan and thiophene are also reactive. Desulfurization of **4B** with Bu_3SnH undergoes smoothly, affording 1-(2,2,2-trifluoroethyl)naphthalene (90%). Therefore, the present sequence (**2** → **3** → **4**) provides a new entry to 2,2,2-trifluoroethylaromatics which are prepared with difficulty.[8]

Table 1. Electrophilic Reaction of **1** with Aromatic Compounds.

ArH	a) 	b,c) 	b,d) 	a,e) 	a,g) 	a,e) 	a,f) 
4	A	B	C	D	E	F	G
Yield(%)	66	80	70	41	41	51	73

a) CH_3NO_2-$ZnCl_2$; b) $ClCH_2CH_2Cl$-$SnCl_4$; c) 1-substituted compound ; d) ortho: para=30 : 70 ; e) 2-substitution ; f) ratio of 2 and 3-substitution = 80/20; g) 5-substitution.

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9) The authors are greatful to The Asahi Glass Foundation and the 500 MHz NMR Laboratory of Okayama University.

(Received in Japan 6 March 1989)