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Reactions of Perfluoroalkanesulfonyl Chlorides with Aromatic Compounds Catalyzed by a Ruthenium(II) Complex

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The reactions of perfluoroalkanesulfonyl chlorides with aromatic compounds in the presence of a catalytic amount of dichlorotris(triphenylphosphine)ruthenium(II) were found to give perfluoroalkylated compounds in good yield.

Recently, much attention has been paid in the perfluoroalkylated compounds since they have characteristic features such as water- or oil-repellency and low friction.[1)] However, the introduction of a perfluoroalkyl group into alkenes or aromatic compounds is not easy because the usual methods for alkylation cannot be applied to perfluoroalkylation. Thus, the new methods for introduction of perfluoroalkyl group have been the subject of much research in organofluorine chemistry. During our systematic investigations of a ruthenium(II) catalyzed reactions of sulfonyl chlorides with alkenes,[2)] we found that the reactions of trifluoromethanesulfonyl chloride with alkenes in the presence of a ruthenium(II) complex gave the corresponding 1:1 adducts with extrusion of sulfur dioxide in good yield.[3)] Now, we found that perfluoroalkanesulfonyl chlorides reacted with aromatic compounds in the presence of a ruthenium(II) complex to give perfluoroalkylated arenes in good yield, and the results will be described herein.

Typically, a solution containing perfluorohexanesulfonyl chloride (2.0 mmol), and dichlorotris(triphenylphosphine)ruthenium(II) (0.02 mmol) in benzene (5.0 ml) was degassed and heated at 120 °C in a sealed tube for 19 h. Flash column chromatography on Florisil using benzene and then gel permeation chromatography using chloroform gave perfluorohexylbenzene in 44% yield. Similarly, several aromatic compounds were treated with trifluoromethane- or perfluorohexanesulfonyl chloride in the presence of the ruthenium(II) catalyst under similar conditions. The results are summarized in Table 1.

$$\mathrm{ArH} + \mathrm{R_FSO_2Cl} \xrightarrow{\mathrm{RuCl_2(PPh_3)_3}} \mathrm{Ar\text{-}R_F} + \mathrm{SO_2}$$

$$\mathrm{R_F} = \text{perfluoroalkyl}$$

Table 1. Reactions of Perfluoroalkanesulfonyl Chlorides with Aromatic Compounds

R_F	ArH	Conditions	Products	Yield / %
CF_3	C_6H_6	120 °C, 18 h	$C_6H_5CF_3$	41
C_6F_{13}	C_6H_6	120 °C, 19 h	$C_6H_5C_6F_{13}$	44
CF_3	$C_6H_5CH_3$	120 °C, 18 h	$CF_3C_6H_4CH_3$[a)]	36
C_6F_{13}	$C_6H_5CH_3$	120 °C, 18 h	$C_6F_{13}C_6H_4CH_3$[b)]	54
CF_3	$C_6H_5OCH_3$	120 °C, 18 h	$CF_3C_6H_4OCH_3$[c)]	58
C_6F_{13}	$C_6H_5OCH_3$	120 °C, 18 h	$C_6F_{13}C_6H_4OCH_3$[d)]	59
CF_3	p-$CH_3C_6H_4CH_3$	120 °C, 18 h	$CF_3C_6H_3(CH_3)_2$	63
C_6F_{13}	p-$CH_3C_6H_4CH_3$	120 °C, 24 h	$C_6F_{13}C_6H_3(CH_3)_2$	41
CF_3	p-$CH_3OC_6H_4OCH_3$	120 °C, 18 h	$CF_3C_6H_3(OCH_3)_2$	71
C_6F_{13}	p-$CH_3OC_6H_4OCH_3$	120 °C, 24 h	$C_6F_{13}C_6H_3(OCH_3)_2$	63

a) A mixture of *o*-, *m*-, and *p*-isomers. b) The isomer distribution: *o*-,32%; *m*-, 36%; *p*-, 32%. c) The isomer distribution: *o*-, 53%; *m*-, 25%; *p*-, 22%. d) The isomer distribution: *o*-, 49%; *m*-, 20%; *p*-, 31%.

The perfluoroalkylation proceeded smoothly for such aromatic compounds possessing electron donating group as toluene, anisole, p-xylene, 1,4-dimethoxybenzene, whereas, chlorobenzene, bromobenzene, and ethyl terephthalate were not perfluoroalkylated under similar conditions. The ruthenium(II) catalyzed reactions of perfluoroalkanesulfonyl chlorides will be an useful method for the introduction of perfluoroalkyl group into activated aromatic nucleus. So far, trifluoromethyl iodide has been used for trifluoromethylation, however, it is a gas at atmospheric pressure and difficult to handle in laboratories. On the other hand trifluoromethanesulfonyl chloride is a liquid and can be treated easily. Studies on the scope and limitations of this novel perfluoroalkylation of aromatic compounds are now in progress.

References

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