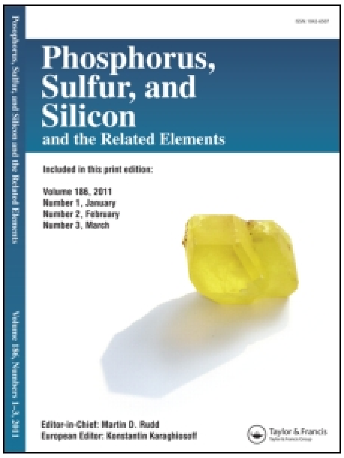

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REGIOSELECTIVE PERFLUOROALKYLATION OF HETEROAROMATIC COMPOUNDS BY PERFLUOROALKANESULFONYL CHLORIDE IN THE PRESENCE OF A RUTHENIUM(II) COMPLEX

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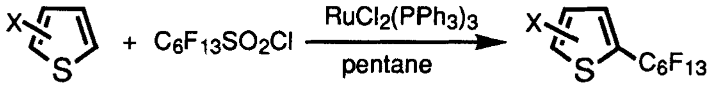
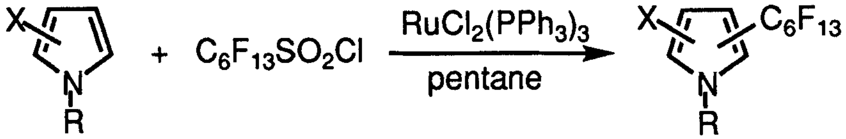
Abstract Regioselective perfluoroalkylation of heteroaromatic compounds by perfluoroalkanesulfonyl chloride in the presence of a catalytic amount of ruthenium(II) phosphine complex is described.

Recently, we reported a novel chloroperfluoroalkylation of alkenes with perfluoroalkanesulfonyl chloride catalyzed by a ruthenium(II) complex.[1] The reaction was found to be applicable to the direct perfluoroalkylation of aromatic nucleus.[2] Now, we extended the technique to the perfluoroalkylation of heteroaromatic compounds such as furan, thiophenes, and pyrroles, and the results are described herein. When the reaction of perfluorohexanesulfonyl chloride (**1**) with furan was carried out in the presence of a catalytic amount of dichlorotris(triphenylphosphine)ruthenium(II) (**2**) in pentane in a degassed sealed tube at 120 °C, 2-perfluorohexylfuran was formed in 30% yield together with a lot of black tar. The reactions of **1** with substituted thiophenes catalyzed by **2** proceeded smoothly with extrusion of sulfur dioxide to give regioselectively perfluoroalkylated thiophenes at the 2-position in good yield. The perfluoroalkylations of 2,5-dimethylthiophene, 2,5-bis(trimethylsilyl)thiophene, and 2,5-dichlorothiophene with **1** under similar conditions occurred at the 3-position in moderate yields.



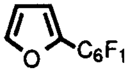
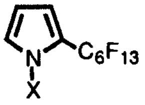
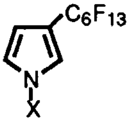
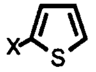
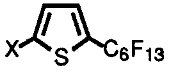
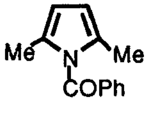
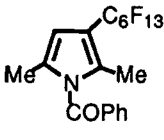
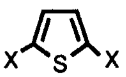
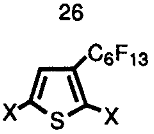
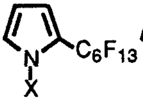
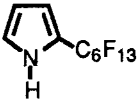
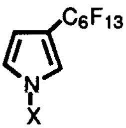
On the other hand, no expected perfluoroalkylated compound was obtained in the reaction of **1** with pyrrole, 2-methylpyrrole or 2,5-dimethylpyrrole catalyzed by **2**. However, 1-substituted pyrroles such as 1-benzylpyrrole, 1-phenylsulfonylpyrrole, 1-acetylpyrrole, 1-benzoylpyrrole, and 1-methoxycarbonylpyrrole were regioselectively perfluoroalkylated at the 2-position in good to high yield. The reverse of the regioselectivity was found in the perfluoroalkylation of 1-trimethylsilylpyrrole and 1-triisopropylsilylpyrrole; namely, 1-trimethylsilylpyrrole was selectively perfluoroalkylated at the 2-position, whereas, 1-triisopropylsilylpyrrole was selectively perfluoroalkylated at the 3-position. The results are summarized in Table I.



2-perfluoroalkylation: R = CH_2Ph, SO_2Ph, $COCH_3$, COPh, CO_2Me, Me_3Si
3-perfluoroalkylation: R = $(i\text{-}Pr)_3Si$

The trialkylsilyl group on the nitrogen atom of 1-trimethylsilyl-2-perfluorohexylpyrrole or 1-triisopropylsilyl-3-perfluorohexylpyrrole was easily removed by treatment with tetrabutylammonium fluoride. Thus, protection of the hydrogen on the nitrogen atom of pyrrole by a trialkylsilyl group, the reaction of 1-trimethylsilylpyrrole or 1-triisopropylsilylpyrrole with perfluoroalkanesulfonyl chloride catalyzed by the ruthenium(II) complex, and deprotection of the trialkylsilyl group by fluoride ion is a very useful method for the regioselective introduction of a perfluoroalkyl group at the 2- or 3-position of pyrrole, respectively.

TABLE I Perfluoroalkylation of furan, thiophenes, and pyrroles.

Substrate	Product (%)	Substrate	Product (%)		
	 30				
		X = H	0	0	
X = H	77	CH_2Ph	53	0	
Me	73	SO_2Ph	65	7	
$SiMe_3$	56	Ac	80	4	
Br	50	COPh	92	6	
Cl	38		 52		
CHO	26				
					
X = Me	41	X = $SiMe_3$	53	25	8
$SiMe_3$	23	Si^iPr_3	25	0	59
Cl	30				

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2. N. Kamigata, T. Fukushima, and M. Yoshida, *Chem. Lett.*, **1990**, 549.