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# Regioselective Perfluoroalkylation of Heteroaromatic Compounds by Perfluoroalkanesulfonyl Chloride in the Presence of a Ruthenium(II) Complex

Nobumasa Kamigata<sup>a</sup>; Takeshi Ohtsuka<sup>a</sup>; Toshio Shimizu<sup>a</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Tokyo, Japan

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### REGIOSELECTIVE PERFLUOROALKYLATION OF HETERO-AROMATIC COMPOUNDS BY PERFLUOROALKANESULFONYL CHLORIDE IN THE PRESENCE OF A RUTHENIUM(II) COMPLEX

NOBUMASA KAMIGATA, TAKESHI OHTSUKA and TOSHIO SHIMIZU Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Minami-ohsawa, Hachioji, Tokyo 192-03, Japan

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.<sup>1</sup> The reaction was found to be applicable to the direct perfluoroalkylation of aromatic nucleus.<sup>2</sup> 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.

+ 
$$C_6F_{13}SO_2CI$$
 Ru $Cl_2(PPh_3)_3$  Ru $Cl_2(PPh_3)_3$  Ru $C_6F_{13}$ 

2-perfluoroalkylation: R = CH<sub>2</sub>Ph, SO<sub>2</sub>Ph, COCH<sub>3</sub>, COPh, CO<sub>2</sub>Me, Me<sub>3</sub>Si

3-perfluoroalkylation:  $R = (i-Pr)_3Si$ 

The trialkylsilyl group on the nitrogen atom of 1-trimethylsilyl-2-perfluorohexyl-pyrrole 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-trimethylsilyl-pyrrole 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 (%)	
	<b>€</b> C <sub>6</sub> F <sub>13</sub> 30	(N)	<b>⟨</b> N C <sub>6</sub> F <sub>13</sub> ⟨	N C <sub>6</sub> F <sub>13</sub>
X = H	X C <sub>6</sub> F <sub>13</sub>	$\dot{X}$ $X = H$ $CH_2Ph$ $SO_2Ph$	Х 0 53 65	X 0 0 7
Me SiMe <sub>3</sub> Br	73 56 50	Ac COPh	80 92	, 6 F <sub>13</sub>
CHO	38 26 C <sub>6</sub> F <sub>13</sub>	Me N Me	/	52 le
X X = Me SiMe <sub>3</sub> CI	x√ <sub>S</sub> √ <sub>X</sub> 41 23		$\lambda_{C_6F_{13}}$	F <sub>13</sub> (N) C <sub>6</sub> F <sub>13</sub>
Oi	30	X = SiMe <sub>3</sub> 5 Si <sup>'</sup> Pr <sub>3</sub> 2		8 59

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