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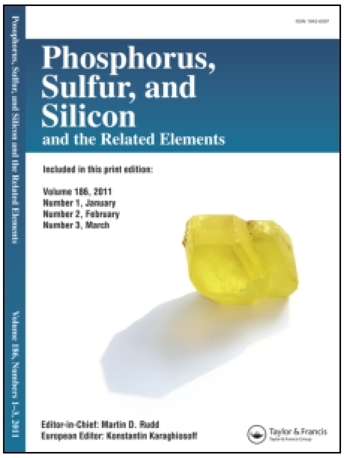

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The Preparation of Per-Deuterated Aromatic Hydrocarbons Using Organosulfur Compounds

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THE PREPARATION OF PER-DEUTERATED AROMATIC HYDROCARBONS USING ORGANOSULFUR COMPOUNDS

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Abstract Per-deuteration of benzothiophene (1), benzenethiol (2) and p-methylbenzenethiol (3) has been accomplished by reaction with D_2O containing dissolved metal salts at 250° - 315°C. Desulfurization of the products gave per-deutero ethylbenzene, benzene and toluene in high overall yield (> 95%).

INTRODUCTION

Per-deuteration of aromatic hydrocarbons has been achieved by heating the compounds at high temperatures (200° - 350°C) at low pH[1,2]. Usually, a strong mineral acid is employed and heating periods of many days are required. The mechanism of deuteration in acid is believed to follow standard electrophilic substitution pathways[1]. Consequently, deuteration of toluene and ethylbenzene occurs most readily at the ring positions and only in the alkyl side-chain under very forcing conditions. As a result, per-deuterated toluene and ethylbenzene are very expensive and their use as NMR solvents is limited. This communication describes the deuteration of organosulfur compounds (1 - 3) using metal salts as the means of providing the necessary acidity. The sulfur functional groups activate the molecules towards deuteration and the metal salts furnish D^+ by solvolysis of coordinated D_2O:

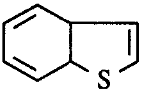
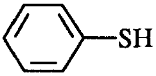
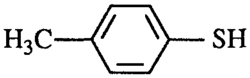
$$[M(D_2O)_6]^{n+} \rightleftharpoons [M(D_2O)_5OD]^{(n-1)+} + D^+ \qquad (M = Fe, Ru)$$

Desulfurization of the organosulfur products by standard methods[3] allows preparation of per-deuterated aromatic hydrocarbons in good yields.

RESULTS AND DISCUSSION

In a typical experiment an organosulfur compound (15 mmol) was heated in a sealed quartz tube with a metal salt (0.05 mmol) dissolved in D_2O (500 mmol) at 200° - 315°C (see Table I). Comparison of data obtained for deuteration of (1 - 3) with either ruthenium or iron catalysis with control experiments indicates that these metal species are as or more effective than DCl solutions of equivalent acidity. (1) was readily per-deuterated at 250°C over 24 h and desulfurization of the product using D_2 and an alumina supported Co/Mo at 350°C gave per-deutero ethylbenzene in quantitative yield. Per-deuteration of (2) and (3) required more forcing conditions (315°C) and, in the case of (3), iron or ruthenium catalysis facilitated deuteration of the alkyl side-chain. Although the prime mechanism of metal catalysis may be the production of an acidic medium by solvolysis of coordinated water molecules and exchange via D+, these observations suggest that interaction between the metal species and the sulfur functional groups may enhance deuterium exchange. This conclusion is tentative at this time since it requires that the pH values of the DCl/D_2O solutions measured at 20°C remains unchanged at the reaction conditions. Since this may not be true, comparison of these control experiments with those employing metal salts may not be valid. Per-deuterated (2) and (3) are readily converted to D_6-benzene and D_8-toluene by hydrodesulfurization techniques.

Table I Deuteration of Organosulfur Compounds under Selected Conditions [a]

	(1) 		(2) 		(3) 	
T (°C), t (h)	250, 0.5	250, 24	250, 24	315, 48	250, 48	315, 48
D_2O	-	6	58	-	28	-
DCl/D_2O [b]	57	92	79	95	43	94
$RuCl_3/D_2O$	57	93	79	95	51	94
DCl/D_2O [b]	36	92	59	90	58	93
$FeCl_3/D_2O$	53	94	59	93	67	93

[a] Maximum deuteration possible was 95%.

[b] These solutions had pH's of 1.5 and 2.2 which mimic those of the $RuCl_3$ and $FeCl_3$ solutions at 20°C.

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