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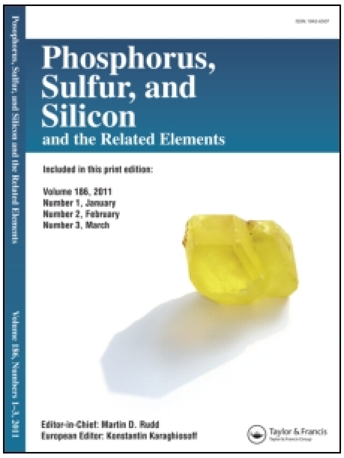

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An Alternatively Facile Preparation of Acylsulfenyl Bromides and Iodides

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Lead thiocarboxylates [$RCOSPbPh_3$, $(RCOS)_2PbPh_2$, $(RCOS)_2Pb$] were found to readily react with halogen, and *N*-bromo- and *N*-iodo-succinimides to give the corresponding acylsulfenyl bromides and iodides.

Keywords: Acylsulfenyl bromide; Acylsulfenyl iodide; Triphenyllead thiocarboxyalte; Sulfenyl bromide; Sulfenyl iodide

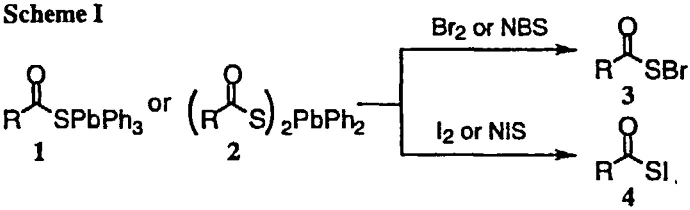
INTRODUCTION

In 1952 Böhme and Clement reported the first synthesis of acylsulfenyl halides, acetylsulfenyl chloride, by the reaction of diacetyl sulfide with thionyl chloride [1]. Unfortunately this method cannot be applied to the preparation of acylsulfenyl bromides and iodides due to the difficulty to obtain thionyl bromide and iodide. In 1982 we reported the first isolation of acylsulfenyl iodides from the reaction of phenylmercury thiocarboxylates with iodine [3]. Later we have found that the reaction of organotin [3a,3b] and silver thiocarboxylates [3c] and *O*-trimethylsilyl thiocarboxylates [63d with *N*-bromo- (NBS) and *N*-iodosuccinnimide (NIS) provide an alternative preparation of acylsulfenyl bromides **3** and iodides **4**. We report here an alternatively facile preparation of **3** and **4** by the reaction of lead thiocarboxylates with NBS and NIS.

RESULTS AND DISCUSSION

The starting triphenyllead thiocarboxylates **1** and diphenyllead bis(thiocarboxylates) **2** were readily prepared by the reaction of corresponding organolead chlorides with piperidinium or potassium thiocarboxylates in dichloro/methane at 20 °C for 2 h. **1** were found to readily react with these halogenating agents in dichloromethane/hexane at 0 °C to give the expected acylsulfenyl bromides **3** and iodides **4** in 20-90% yields (Scheme I). The reaction of **2** with iodine led to 45-60% of **4**, while the isolation of **4** from the reaction **2** with NIS appeared to be difficult. It is noted that the reaction of lead-bis(thiocarboxlates) **5** $(RCOS)_2Pb$ with Br_2 and I_2 give **3** and **4** in moderate yields. Their structures were determined by comparison of the IR and ^{13}C NMR spectra with those of the authentic samples and finally by X-ray structural analysis.

Scheme I



The X-ray analysis have revealed that these acylsulfenyl halides are monomer in which the carbonyl oxygen intramolecularly interact with halogen.

ACKNOWLEDGMENT

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