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A Convenient Synthesis of Thioacetates and Thiobenzoates Using Silica-Gel Supported Potassium Thioacetate and Thiobenzoate

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Recently, many reactions using supported reagents have been reported. We have found that potassium thioacetate can be remarkably activated by support on silica gel, and silica gel-supported potassium thioacetate (CH_3COSK/SiO_2) reacts with alkyl halides in nonpolar solvents such as benzene to give alkyl thioacetates in good yields.

$$\underset{1}{X-R}\xrightarrow[X=Cl,Br,I]{R'COSK/SiO_2}\underset{\substack{2\text{ or }3\\2:R'=Me,3:R'=Ph}}{R'COS-R}$$

Benzyl bromide did not react with finely ground potassium thioacetate suspended in benzene at room temperature. In contrast, similar reactions with CH_3COSK/SiO_2 proceeded easily under similar conditions to afford benzyl thioacetate in 83% yield after 1 h. Silica gel was the most effective among the inorganic supports tested. Aluminas (neutral, acidic, and basic) were also effective but less than silica gel (33–58%). Molecular sieves 4A was much less effective. Kieselgur, Montmorillonite K10, and charcoals were ineffective for activating potassium thioacetate. The reaction of a series of organic halides with CH_3COSK/SiO_2 in benzene gave the corresponding thioacetates in high yields. The reaction of benzyl chloride with CH_3COSK/SiO_2 required more strong conditions than that of benzyl bromide. Substituted benzyl bromides were converted into the corresponding thioacetates in excellent yields

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at room temperature independent of the substituent. For instance, 4-methyl and 4-nitrobenzyl bromide were converted into the corresponding thioacetates in 98% and 97% yields. Xylylene dibromides produced only disubstituted compound. Mono-substituted compounds were not detected.

The reactivity of *n*-alkyl halides decreased as follows: I > Br > Cl. Octyl thioacetate was obtained quantitatively from octyl iodide at 80°C after 3 h, whereas octyl chloride gave only 32% yield of octyl thioacetate after 24 h. In the case of 1,4-dibromopentane, 4-bromopentyl thioacetate was formed along with a small amount of disubstituted compound, but 4-bromo-1-methylbutyl thioacetate was not detected. Using silica gel-supported potassium thiobenzoate ($PhCOSK/SiO_2$), the reaction rapidly occurred at room temperature to give the corresponding thiobenzoates in high yields. The reactivity of $PhCOSK/SiO_2$ was higher than CH_3COSK/SiO_2. Octyl bromide reacted with CH_3COSK/SiO_2 to afford the octyl thioacetate in 89% yield at 80°C after 8 h, whereas the reaction with $PhCOSK/SiO_2$ gave octyl thiobenzoate (**3a**) in 94% yield after 4 h. Moreover, octyl chloride gave **3a** in 52% yield after 24 h.

The present procedure using silica gel-supported potassium thioacetate and thiobenzoate allows for an efficient transformation of organic halides into thioesters. The notable advantages of this procedure are operational simplicity, good yield, and mild reaction conditions. Moreover, the products are easily isolated by filtering the used supported reagent and removing the solvent under vacuum, and are generally spectroscopically pure.