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NEW METHODS AND REAGENTS IN ORGANIC SYNTHESIS. 62[1] TRIMETHYLSILYLDIAZOMETHANE: A CONVENIENT REAGENT FOR THE PREPARATION OF ACYLSILANES

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The lithium salt of trimethylsilyldiazomethane smoothly reacts with alkyl halides to give α-trimethylsilyldiazoalkanes which are easily oxidized with m-chloroperbenzoic acid (m-CPBA), giving the corresponding acylsilanes (α-ketosilanes) in good yields.

Acylsilanes (α-ketosilanes) are an interesting class of compounds as intermediates in organic synthesis.[2] Although a number of methods for the preparation of acylsilanes have been reported,[2] only a few show useful flexibility. Recent report[3] involving the use of methoxy(phenylthio)trialkylsilylmethane has prompted us to record our results.

Our continued interest on the use of trimethylsilyldiazomethane ($TMSCHN_2$, $(CH_3)_3SiCHN_2$) as a reagent for introducing a C_1-unit[4] has revealed that acylsilanes can be very easily prepared in 2 steps from alkyl halides by alkylation of the lithium salt of $TMSCHN_2$, followed by oxidation with m-chloroperbenzoic acid (m-CPBA).

$$RX + (CH_3)_3SiC(Li)N_2 \longrightarrow \underset{\underset{2}{\sim}}{R\text{-}\overset{N_2}{\overset{\|}{C}}\text{-}Si(CH_3)_3} \xrightarrow{\text{m-CPBA}} \underset{\underset{3}{\sim}}{R\text{-}\overset{O}{\overset{\|}{C}}\text{-}Si(CH_3)_3}$$

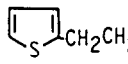
$\underset{\sim}{1}$

We have found that lithium trimethylsilyldiazomethane ($\underset{\sim}{1}$), prepared from $TMSCHN_2$ and n-butyllithium, smoothly reacts with alkyl halides in tetrahydrofuran to give α-trimethylsilyldiazoalkanes ($\underset{\sim}{2}$). Conversion of the resulting $\underset{\sim}{2}$ to acylsilanes ($\underset{\sim}{3}$) is easily achieved by the oxidation with m-CPBA in a two-phase solvent system of benzene and phosphate buffer (pH 7.6).

The results are summarized in Table. Alkylation of $\underset{\sim}{1}$ with various alkyl halides as well as the oxidation of $\underset{\sim}{2}$ with m-CPBA smoothly proceeds under mild reaction conditions. The double bond of $\underset{\sim}{2}$e is intact under the oxidation conditions. Phosphate buffer is essential to conduct the reaction cleanly since a complicated mixture is formed without the buffer. Although 31% aqueous hydrogen peroxide in dioxane can also be used for the oxidation, a longer reaction time (for $\underset{\sim}{2}$b; room temperature, 23 h) is required for the completion of the reaction.

The present method using commercially available trimethylsilyldiazomethane is simple and easy to conduct, and will provide an added flexibility in the acylsilane synthesis.

Table Conversion of Alkyl Halides to Acylsilanes (3) using $TMSCHN_2$

Product No.	RX	Yield(%)[a,b] of 2	bp(°C)/mmHg	Yield(%)[c,d] of 3	bp(°C)/mmHg
a	$PhCH_2Cl$	77	50-60/0.25	56	45-50/0.05
b	$PhCH_2CH_2Br$	87	50-55/0.15	65	50-55/0.01
c	$CH_3(CH_2)_9Br$	65	70-75/0.15	62	70-75/0.15
d	$CH_3(CH_2)_3CH(CH_3CH_2)CH_2I$	79	50-55/0.1	71	40-45/0.04
e	$CH_2=CH(CH_2)_9I$	72	80-85/0.08	63[e]	70-75/0.01
f	$PhO(CH_2)_3Br$	62	80-85/0.03	66[f]	75-80/0.02
g		65	65-70/0.15	61[g]	60-65/0.01
h	$CH_3(CH_2)_5CH(CH_3)I$	—	—	31[h,i]	50-55/0.05

a) A solution of RX (5 mmol) in THF (5 ml) was added dropwise to a solution of 1 (prepared from $TMSCHN_2$[5] (6 mmol) and n-BuLi (6 mmol) in THF (25 ml)) at -70°C under argon and the mixture was stirred at -50~-20°C for 4.5~7 h. b) Isolated yield after a Kugelrohr distillation. c) Unless otherwise stated, a solution of 2 (2 mmol) in benzene (6 ml) was added dropwise to a mixture of m-CPBA (2.1 mmol), benzene (14 ml), and 0.1M phosphate buffer (pH 7.6, 30 ml) at 5~10°C, and the mixture was stirred at 5~10°C for 5 min, then at room temperature for 1 h. d) Isolated yield after silica gel column chromatography followed by distillation. e) The reaction was carried out at 0°C for 10 min. f) The reaction was carried out at 6~10°C for 5 min, then at room temperature for 30 min. g) The reaction was carried out at 6~10°C for 30 min. h) The reaction was carried out at 6~10°C for 20 min. i) Yield based upon the starting halide.

References and Notes

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