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A NEW METHOD FOR CONVERTING ALKYL HALIDES TO HOMOLOGOUS ALDEHYDES

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Summary Phenylthiotrimethylsilylmethyl lithium can be alkylated and the product hydrolysed to the aldehydes by oxidation and rearrangement.

1,3-Dithians[1,2] have found wide use in organic synthesis. They do, however, suffer from the problem of being difficult to hydrolyse[2]. In the continuing search for alternatives, we have investigated the use of phenylthiotrimethylsilylmethane (1). The lithium derivative of (1) is known[3] and has been used to prepare vinyl sulphides[3,4,5].

Carey[4] noted that alkylation of the lithium derivative was not very good except with methyl iodide. We have found that the alkylation can be carried out in good yield if hexane is used as the solvent, instead of THF, in the presence of N,N,N',N'-tetramethylethylenediamine (TMEDA).

$$\mathrm{PhSMe}\ \xrightarrow[\text{2) }\mathrm{Me_3SiCl}]{\text{1) }{}^{n}\mathrm{BuLi/Et_2O}}\ \underset{(1)}{\mathrm{PhSCH_2SiMe_3}}\ \xrightarrow[\text{2) }\mathrm{RX}^{\text{hexane}}]{\text{1) }{}^{n}\mathrm{BuLi/TMEDA}}\ \underset{(2)}{\mathrm{PhSCHRSiMe_3}}$$

Phenylthiotrimethylsilylmethane (1) is easily prepared in high yield (95%) by treating thioanisole with n-butyllithium in hexane-ether, heating under reflux for 18h. and quenching the resulting suspension of the lithium derivative with chlorotrimethylsilane[6].

The results of the alkylation experiments are given in table 1.

Note that alkylation occurred with sec-butyl bromide but not with cyclohexyl bromide.

Table 1.

$$\underset{(1)}{\mathrm{PhSCH_2SiMe_3}} \xrightarrow[\mathrm{2)\ RX}]{\mathrm{1)\ ^nBuLi/TMEDA/hexane/0^0C}} \underset{(2)}{\mathrm{PhSCHRSiMe_3}}$$

RX	Yield of alkylated product (2)[a]
MeI	99
EtI	90
^{n}PrBr	82
$CH_2{=}CHCH_2Br$	85
^{n}BuBr	84
^{s}BuBr	45
$^nC_5H_{11}Br$	82
$^nC_5H_{11}I$	86
$^nC_6H_{13}Br$	81
$^nC_{12}H_{25}Br$	78
$PhCH_2Br$	83
$^cC_6H_{11}Br$	0

[a] All new compounds have been fully characterised.

The alkylated compounds were oxidised with m-chloroperoxybenzoic acid (MCPBA) in dichloromethane at -23^{0}C. The sulphoxides were then heated under reflux in benzene for 4h to give the O-trimethylsilyl-S-phenylthioacetals[7,8] which have already been proposed as a method of protecting carbonyl compounds[9], and could in turn be converted to the aldehyde by treatment with dilute hydrochloric acid.

The results of the oxidation and rearrangement experiments are given in table 2.

Table 2.

$$\mathrm{PhSCHRSiMe_3} \xrightarrow[\mathrm{CH_2Cl_2/-23^{0}C}]{\mathrm{MCPBA}} \mathrm{PhS(O)CHRSiMe_3} \xrightarrow{\Delta} \mathrm{PhSCHROSiMe_3} \xrightarrow{\mathrm{H_3O^+}} \mathrm{RCHO}$$

	Yields (%)		
(2), R=	Sulphoxide[a]	Acetal[a]	Aldehyde[b]
H	91	89[c]	-[d]
Me	83	97	-
Et	89	88	-
^{n}Pr	92	85	-
$CH_2=CHCH_2-$	90	81	-
^{n}Bu	92	83	72[a,e]
^{s}Bu	92	83	74[a,e]
$^{n}C_5H_{11}$	88	82	68[a,e]
$^{n}C_6H_{13}$	91	85	77[a,e]
$^{n}C_{12}H_{25}$	96	88	80[a] (71[f])
$PhCH_2$	96	92	85[a] (77[f])

a. Yield by n.m.r.

b. Overall yield.

c. The rearrangement was carried out by heating under reflux in carbon tetrachloride for 3h.

d. Denotes the acetal was not hydrolysed.

e. Isolated as 2,4-dinitrophenylhydrazone.

f. Isolated yield.

In a typical experiment phenylthiotrimethylsilylmethane (1.96g, 10mmol) was added to a stirred suspension of the n-butyllithium (10mmol in hexane) - TMEDA (15.1ml, 10mmol) at 0°C, under nitrogen[3]. After 1h, the alkyl halide (10mmol) was added dropwise. The reaction was worked up with saturated aqueous ammonium chloride to give after distilliation or chromatography the alkylated compound (2).

m-Chloroperoxybenzoic acid (1.05mmol) in dry dichloromethane (30ml) was slowly added to a cooled (dry ice-carbon tetrachloride) solution of (2) (1.0mmol) in dichloromethane (20ml) under nitrogen. After being stirred for 2h, the mixture was washed with saturated aqueous sodium hydrogen carbonate and water, dried, evaporated in vacuo to give an oil which was dissolved in dry benzene (10ml) and boiled under nitrogen for 4h to give the O-trimethylsilylphenylthioacetal identical to that prepared by the method of Chan[9].

The reactions of the lithium derivative of phenylthiotrimethylsilylmethane (1) with other electrophiles (such as epoxides and unsaturated ketones) and the preparation of ketones will be the subject of future papers.

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