Alkylation of 1,3-Oxathian

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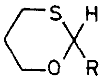
Summary Reaction of 1,3-oxathienyl-lithium (**1a**) with halides gives 2-alkyl-1,3-oxathians.

Recently a number of alkylated 1,3-oxathians have been synthesised[1,2] and their conformational behaviour has been extensively studied.[1,3] However, their chemical properties have received little attention from synthetic organic chemists. Here we describe C–C bond formation using the anionic species (**1a**) derived from 1,3-oxathian (**1b**).



(1)

a; R = Li
b; R = H

1,3-Oxathien-2-yl-lithium (**1a**) in tetrahydrofuran prepared from 1,3-oxathian (**1b**) and s-butyl-lithium at −78 °C was quenched with D_2O. The ^1H n.m.r. spectrum of the product purified by g.l.c., indicated > 95% deuterium incorporation at C-2 in (**1b**). Addition of halides to (**1b**) yielded a variety of 2-alkylated oxathians (**1c**—**h**) in fair to excellent yields depending on halides.

Table

Product[a]	Halide	% Yield[b]
(**1c**), R=Me	MeI	99
(**1d**), R=Et	EtI	90
(**1e**), R=Pr^n	Pr^{n}I	83
(**1f**), R=Bu^n	Bu^{n}Br	25
(**1g**), R=Pr^i	Pr^{i}I	35[c]
(**1h**), R=CH_2Ph	$PhCH_2Br$	26[d]

[a] All compounds gave C and H analyses and ^1H n.m.r. spectra consistent with the assigned structure. [b] By g.l.c. based on 1,3-oxathian after stirring at −78 °C for 1—2 h unless otherwise indicated. [c] At −20 °C for 6 days. [d] 1,2-Diphenylethane was also obtained (20%).

Since 1,3-oxathians are cleaved under mild conditions to give the parent carbonyl compounds,[4] 1,3-oxathians would be expected to have a wide range of synthetic utility as acyl anion equivalents.

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