2-Lithio-2-trimethylsilyl-1,3-oxathian: A Possible Acyl Dianion Equivalent

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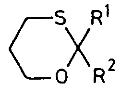
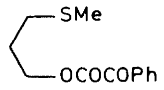
2-Lithio-2-trimethylsilyl-1,3-oxathian was treated successively with the two electrophiles cyanobenzene and methyl iodide, to give 2-benzoyl-2-methyl-1,3-oxathian in a 'one pot' reaction.

Although the conformational aspects of the derivatives of 1,3-oxathian have been studied extensively,[1,2] details of the chemical properties of this interesting ring system are rather limited.[3,4] Recently, we reported[5] the reaction of 2-hetero-substituted 1,3-oxathians with s-butyl-lithium and suggested their utility in synthetic organic chemistry. Here we report that the anion (2) derived from 2-trimethylsilyl-1,3-oxathian (1)† can be attacked by two different electrophiles to give a product formally derived from the acyl dianion.

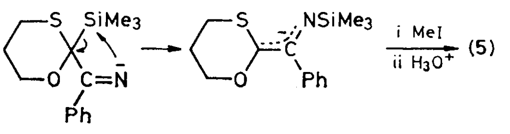
The anion (2) was allowed to react with cyanobenzene at −78 °C and this was followed by addition of methyl iodide to afford (3),† (4),† and (5)† in 13, 10, and 45% yield, respectively. The mechanism for the formation of (5) may be rationalised as electrophilic attack of cyanobenzene on the anion (2) to give (6) followed by a C → N shift[6] of the trimethylsilyl group to give another anion (7) which then reacts with methyl iodide to give (5) [equation (1)].



(1) $R^1 = H, R^2 = SiMe_3$
(2) $R^1 = Li, R^2 = SiMe_3$
(3) $R^1 = H, R^2 = COPh$
(5) $R^1 = Me, R^2 = COPh$



(4)



(6) (7) (1)

The generation of (5) is most interesting because the 2-trimethylsilyl-1,3-oxathianyl anion (2) can be regarded as an equivalent of the acyl dianion (A), if the successive conversion of (5) into the parent carbonyl compound can be successfully achieved. We have found that 2-benzoyl-2-

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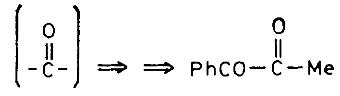
† Selected spectroscopic data, i.r. spectra measured in $CHCl_3$, ^1H n.m.r. in $CDCl_3$ at 100 MHz. Compound (**1**): ν_{max} at 1250 and 1070 cm^{-1}; δ 0.10 (s, 9 H, $SiMe_3$), 1.56—2.35 (m, 2 H, 5-H_2), 2.73 (br.d, 1 H, 4-eq-H), 3.01 (dt, 1 H, 4-ax-H), 3.53 (dt, 1 H, 6-ax-H), 4.12 (br.d, 1 H, 6-eq-H), 4.65 (s, 1 H, 2-H). Compound (**3**): ν_{max} at 1682 cm^{-1}; δ 1.60—2.36 (m, 2 H, 5-H_2), 2.92 (br.d, 1 H, 4-eq-H), 3.20 (dt, 1 H, 4-ax-H), 3.80 (dt, 1 H, 6-ax-H), 4.36 (br.d, 1 H, 6-eq-H), 6.09 (s, 1 H, 2-H), 7.28—8.12 (m, 5 H, arom. H). Compound (**4**): ν_{max} at 1730 and 1682 cm^{-1}; δ 1.80—2.24 (m, 2 H, $-CH_2-$), 2.12 (s, 3 H, SMe), 2.64 (t, 2 H, $-SCH_2-$), 4.51 (t, 2 H, $-OCH_2-$), 7.34—8.16 (m, 5 H, arom. H). Compound (**5**): ν_{max} at 1678 cm^{-1}; δ 1.70—2.30 (m, 2 H, 5-H_2), 1.85 (s, 3 H, CH_3), 2.76 (br.d, 1 H, 4-eq-H), 3.02 (dt, 1 H, 4-ax-H), 3.72 (dt, 1 H, 6-ax-H), 3.97 (br.d, 1 H, 6-eq-H), 7.20—7.68 (m, 3 H, arom. H), 8.00—8.32 (m, 2 H, arom. H).



$$\left[-\overset{\displaystyle O}{\overset{\|}{C}}-\right] \Rightarrow \Rightarrow \mathrm{PhCO}-\overset{\displaystyle O}{\overset{\|}{C}}-\mathrm{Me}$$

(A) (8)

methyl-1,3-oxathian (**5**) was easily deblocked with nitryl iodide[7] to give 1-phenylpropane-1,2-dione (**8**) in 83% yield. To our knowledge, this is the first example of the formation of an acyl dianion equivalent by 1 mol. equiv. of base. Although an increase in yield, especially in the alkylation step, is required for the 2-trimethylsilyl-1,3-oxathianyl anion (**2**) to be an acyl dianion equivalent of synthetic utility, this sequence of reactions suggests the possibility of extending the method to the synthesis of other 1,2-diketones.

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