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SULFUR HETEROCYCLES. I. USE OF 4,4-DIMETHYL-1,3-OXATHIOLANE-3,3-DIOXIDE AS A CARBONYL ANION EQUIVALENT

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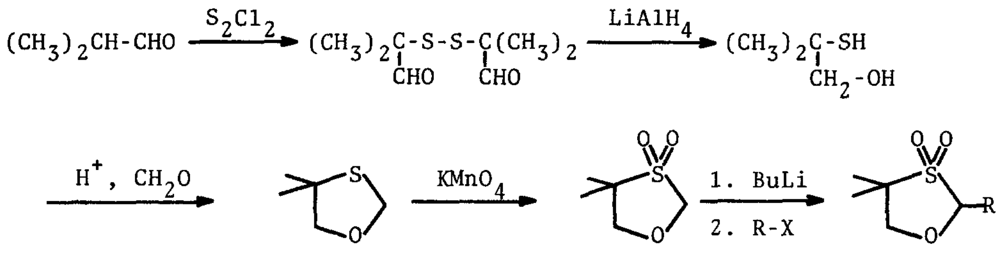
Summary: The title heterocycle is used as a carbonyl anion equivalent in the preparation of aldehydes and α-silyl ketones; the key step is the thermal demasking of the heterocycle by loss of isobutylene and sulfur dioxide.

The principle of reversible carbonyl umpolung[1] is now well-established, but not all of the problems associated with the use of dithiane[2] and its numerous variants,[3] have been resolved. We record here, in preliminary form, the development of a formyl anion equivalent which readily demasks under thermal rather than hydrolytic conditions.

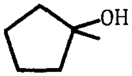
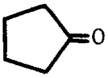
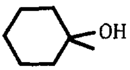
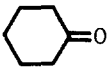
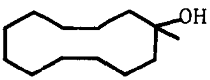
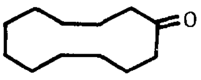
4,4-Dimethyl-1,3-oxathiolane-3,3-dioxide (**1**) is available (see equation 1) from 2,2-dimethylmercaptoethanol (bp 78-80°C/40 torr)[4] which, in turn, can be prepared by treating isobutyraldehyde successively with S_2Cl_2[5] and lithium aluminum hydride. The mercaptoalcohol reacts readily with paraformaldehyde[6] in the presence of catalytic toluenesulfonic acid and the oxathiolane is distilled and then oxidized directly[7] to **1** (yield from isobutyraldehyde, 22%), mp 46-50°C; calc'd for $C_5H_{10}O_3S$: C, 40.00%; H, 6.67%; found: C, 39.63%; H, 6.68%



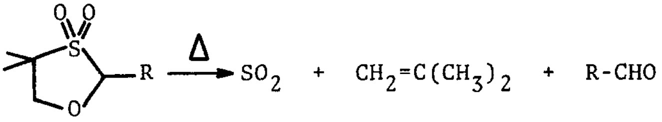
1 2

Compound **1**, when treated with n-butyllithium (1 eq.) in tetrahydrofuran solution (-80°C) metallates in the 2-position (the 4-position is blocked[6] by methyl groups which also hinder a possible β-elimination initiated by deprotonation at position 5). Alkylation of the anion derived from **1** by the electro philes shown in table I gave products of the general structure **2** in the indicated yields.

TABLE I. ALKYLATION OF COMPOUND **1**

Cpd. No.	R in Compound **2**	Alkylating Agent	Melt. Pt.	% Yield[8]
3	D-	D_2O	oil	84
4	CH_3-	CH_3I	53.5-54.5°	85
5	C_6H_5-CH_2-	C_6H_5-CH_2Br	69-70°	96 (84)
6	CH_2=CH-CH_2-	CH_2=CH-CH_2Br	oil	93
7	$CH_3(CH_2)_5$-	$CH_3(CH_2)_5I$	oil	57
8			79-80°	94 (74)
9			87.5-89°	94 (79)
10			108-110°	100 (70)
11	C_6H_5-CHOH-	C_6H_5-CHO	100-125[9]	100 (73)
12	C_6H_5-C(CH_3)OH-	C_6H_5-CO-CH_3	85-125[9]	92 (73)
13	$(CH_3)_3Si$-	$(CH_3)_3Si$-Cl	80-82°	100

Both 2-phenyl-1,3-oxathiolane-3,3-dioxide (**14**) and the corresponding 4,4-dimethyl compound (**15**) (both prepared from benzaldehyde and the appropriate mercaptoalcohol by the scheme described for **1**) undergo ring-opening in boiling benzene solution in the presence of a trace of boron trifluoride etherate. In these experiments, benzaldehyde could be isolated quantitatively as its DNP-derivative after heating at reflux for five hours. The demasking could be achieved more rapidly (often 10-15 min) by subliming the material through a 20-cm Vigreux column packed loosely with 4 x 15 mm Pyrex tubes and maintained at 400°C with an internal pressure of ca. 0.1 torr. In these experiments, sulfur dioxide could be detected (ms, 70 ev, m/e = 64) in the effluent gas and isobutylene could be identified by ms, ^{1}H- and ^{13}C-nmr. Pyrolysis of compounds **5**, **6**, **7**, and **15** where R = benzyl, allyl, n-hexyl and phenyl, afforded the corresponding aldehydes in 100%, 90%, 97%, and 94% yields, respectively. In the R = allyl (**6**) case, a mixture of 3-butenal and crotonaldehyde (1:3) was isolated.



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(2)

When hydroxyoxathiolanes **8**, **9**, and **10** were pyrolyzed, either the corresponding α-hydroxyaldehyde or the acyloin was isolated depending on a variety of factors.[10]

2-Trimethylsilyl-4,4-dimethyl-1,3-oxathiolane-3,3-dioxide (**13**), yields the anion of **1** on treatment with benzyltrimethylammonium fluoride[11] in tetrahydrofuran solution at 25°C. In the presence of 2 eq. of benzaldehyde, **11** is formed in 83% yield (after aqueous work-up). In addition, if **13** is metallated and alkylated with iodomethane, the 2-trimethylsilyl-2-methyl derivative of **1** (**16**) is obtained. Pyrolysis of **16** yields (30%) a compound identical in every respect to that reported by Brook[12] and Corey[13] to be acetyltrimethylsilane.

Notwithstanding the success achieved in alkylating compound **16**, 2-alkylated derivatives of **1** are generally poorer nucleophiles than the corresponding dithianes. Details of this survey and studies of other methods for demasking the carbonyl group will be reported in the full paper.

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NOTES AND REFERENCES

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7. The reaction was performed in dichloromethane solution (0.6-0.9 M) using $KMnO_4$ (200 mole-% excess) as oxidant.
8. The yields recorded are for material with the appropriate ir, proton and carbon nmr spectral properties and which are suitable for further use without additional purification. Yields in parenthesis are for analytically pure material. All new compounds gave satisfactory combustion analyses.
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