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A NEW REAGENT FOR ALDEHYDE SYNTHESIS:
METHYLENEBIS(N,N-DIMETHYLDITHIOCARBAMATE)[1]

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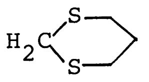
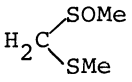
Treatment of the title compound with n-butyllithium produces the lithiomethylene derivative (4). The reagent 4 so generated has been shown to serve effectively as an equivalent of the formyl anion by alkylation of 4 with alkyl halides followed by hydrolysis with mercuric ion to the corresponding aldehyde.

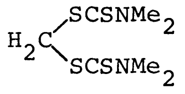
A reasonable number of methods are available for aldehyde synthesis from formaldehyde dithioacetal (eq 1). The synthetic potential of 1,3-dithiane (1)[2] and methyl methylthiomethyl sulfoxide (2)[3] has been vigorously established.

$$CH_2(SR')_2 + RX \longrightarrow RCH(SR')_2 \longrightarrow RCHO \qquad (1)$$


(1)


(2)

$H_2C(SOMe)(SMe)$


(3)

$H_2C(SCSNMe_2)_2$

We wish to report here that methylenebis(N,N-dimethyldithiocarbamate) (3) is very useful for aldehyde synthesis in a similar way. The overall transformation is depicted by eq 2. The method is certainly an addition to the host of recently developed aldehyde syntheses.

$$3 \xrightarrow{\text{n-BuLi}} \underset{4}{[^{\ominus}CH(SCSNMe_2)_2]} \xrightarrow{RX} \underset{5}{RCH(SCSNMe_2)_2} \xrightarrow{Hg(II)/H_2O} RCHO + Hg(SCSNMe_2)_2 \qquad (2)$$

Bis(dithiocarbamate) 3[4] was obtained quantitatively from dichloromethane and sodium N,N-dimethyldithiocarbamate. Treatment of 3 in THF at -78°C with n-butyllithium (1 equiv) in n-hexane gave a yellow solution containing the anion 4, which was stable at this temperature for at least 2 hr. At -78°C, the anion 4 reacted smoothly with alkyl halides giving alkylated bis(dithiocarbamate) (5) in good yields (Table 1). Hydrolysis of 5 in 80% aqueous acetonitrile in the presence of mercuric chloride (2.2 equiv) and mercuric oxide (2.2 equiv) at 50°C for 1 hr gave the corresponding aldehyde in excellent yields (Table 1).

The present aldehyde synthesis appears to be advantageous in the following points. (1) The starting material 3 is readily accessible. (2) The anion 4 is easily generated and highly reactive. (3) Alkylated bis(dithiocarbamate) (5) is very stable and easily purified; the major impurity is unreacted 3 which can be easily separated from 5 with the aid of the poor solubility of 3 in carbon tetrachloride. (4) Bis(dithiocarbamate) 5 is much more easily hydrolyzed to aldehyde than the corresponding 1,3-dithiane due to the stronger affinity of the dithiocarbamate moiety for mercuric ion. For example, complete hydrolysis of 5 ($R=PhCH_2$) required only 1 hr at 50°C whereas that of the 1,3-dithiane counterpart required more than 4 hr at 60°C under the similar conditions.5)

Table 1 Alkylation of The Anion 4 and Hydrolysis of 5

RX	Bis(dithiocarbamate) 5			RCHO d)
	Yield a,b) %	Mp, °C	δ(HC≡) in NMR c)	Yield b,e) %
CH_3I	98	106-108	6.07 (q)	97
CH_3CH_2I	74	93-96	6.06 (t)	95
n-BuI	65	liquid	6.07 (t)	90
$PhCH_2I$	83	173-175	6.30 (t)	97
	$PhCH(SCSNMe_2)_2$ f)			75 g)

a) Based on 3. Yields based on reacted 3 were ca.100% except for n-BuI.
b) The yields are not neccessarily optimum. c) In $CDCl_3$(TMS). d) Isolated as the 2,4-dinitrophenylhydrazone. e) Based on 5. f) Prepared from benzylidene chloride and sodium N,N-dimethyldithiocarbamate: Y. Ueno and M. Okawara, Chem. Lett., 863 (1973). g) In the absence of mercuric oxide.

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4) 3: mp 153-154°C(EtOH); NMR($CDCl_3$):δ 5.40 (s, CH_2) and 3.30, 3.40 (2s, NCH_3).

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