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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 $(\underline{4})$. The reagent $\underline{4}$ so generated has been shown to serve effectively as an equivalent of the formyl anion by alkylation of $\underline{4}$ 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 $(\underline{1})^{2}$ and methyl methylthiomethyl sulfoxide $(2)^{3}$ has been vigorously established.

 $CH_{2}(SR')_{2} + RX \longrightarrow RCH(SR')_{2} \longrightarrow RCHO$ (1) $H_{2}C \xrightarrow{S}{} (\underline{1}) \qquad H_{2}C \xrightarrow{SOMe}{} (\underline{2}) \qquad H_{2}C \xrightarrow{SCSNMe_{2}}{} (\underline{3})$

We wish to report here that methylenebis(N,N-dimethyldithiocarbamate) $(\underline{3})$ 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.

 $\underline{3} \xrightarrow{\text{n-BuLi}} [\stackrel{\Theta}{\longrightarrow} \text{CH}(\text{SCSNMe}_2)_2] \xrightarrow{\text{RX}} \text{RCH}(\text{SCSNMe}_2)_2 \xrightarrow{\text{Hg}(\text{II})/\text{H}_2\text{O}} \text{RCHO} + \text{Hg}(\text{SCSNMe}_2)_2 \quad (2)$ $\underline{4} \qquad \underline{5}$

Bis(dithiocarbamate) $\underline{3}^{4}$) was obtained quantitatively from dichloromethane and sodium N,N-dimethyldithiocarbamate. Treatment of $\underline{3}$ in THF at -78°C with n-butyllithium (l equiv) in n-hexane gave a yellow solution containing the anion $\underline{4}$, which was stable at this temperature for at least 2 hr. At -78°C, the anion $\underline{4}$ reacted smoothly with alkyl halides giving alkylated bis(dithiocarbamate) ($\underline{5}$) 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 <u>3</u> is readily accessible. (2) The anion <u>4</u> is easily generated and highly reactive. (3) Alkylated bis(dithiocarbamate) (<u>5</u>) is very stable and easily purified; the major impurity is unreacted <u>3</u> which can be easily separated from <u>5</u> with the aid of the poor solubility of <u>3</u> in carbon tetrachloride. (4) Bis(dithiocarbamate) <u>5</u> 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 <u>5</u> (R=PhCH₂) 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)

RX	Bis(dithiocarbamate) 5				RCHO"
	Yield, ^{a,b)} %	Mp, °C	δ (HC≡)	in NMR ^{C)}	Yield, Yi
CH3I	98	106-108	6.07	(q)	97
CH3CH2I	74	93-96	6.06	(t)	95
n-BuI	65	liquid	6.07	(t)	90
PhCH2I	83	173-175	6.30	(t)	97
PhCH (SCSNMe ₂) 2 ^{f)}					75 ^{g)}

Table 1 Alkylation of The Anion 4 and Hydrolysis of 5

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 CDCl₃(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.

REFERENCES AND NOTES

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4) <u>3</u>: mp 153-154°C(EtOH); NMR(CDCl₃):δ 5.40 (s, CH₂) and 3.30, 3.40 (2s, NCH₃).
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