Tetrahedron Letters No. 44, pp 4141 - 4142, 1971. Pergamon Press. Printed in Great Britain.

ALDEHYDES AND KETONES FROM MERCAPTALS VIA OXIDATION

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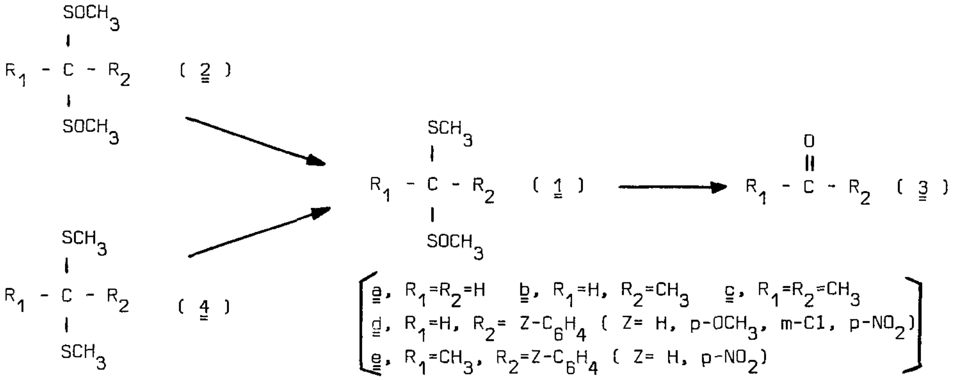
(Received in UK 17 September 1971; accepted for publication 1 October 1971)

A recent report[1] on the preparation of aldehydes **3** from mercaptal S-oxides **1** --- via alkylation of the carbanion of **1a**[2] --- prompts us to communicate some pertinent data and views gained from our studies on disulfoxides and related compounds[3].

We have observed that disulfoxides **2** --- in $CHCl_3$ upon treatment with HCl gas at 0 - 20°C --- are rapidly converted into their carbonyl analogues **3** plus CH_3SSCH_3 and $CH_3SO_2SCH_3$. As chlorine is formed as an intermediate, the first step --- involving oxidation of HCl --- is the conversion of **2** into **1**[4]. In fact, runs involving some selected monosulfoxides (**1b**; **1c**; **1d**, Z=p-NO_2) showed very rapid production of **3** and CH_3SSCH_3 in good yields. The latter findings are in perfect agreement with those of Ogura and Tsuchihashi[1]. The successful alkylation of carbanions from mercaptal S-oxides (e.g., 1,3-dithiane-1-oxide[5], **1a**[1,3b] and **1b**[3b]) indeed makes process **1** → **3** a versatile method for the synthesis of aldehydes and ketones, superior to the rather cumbersome "direct" conversion **4** → **3**[6].



(**2**) (**1**) (**3**) (**4**)

a, R_1=R_2=H **b**, R_1=H, R_2=CH_3 **c**, R_1=R_2=CH_3

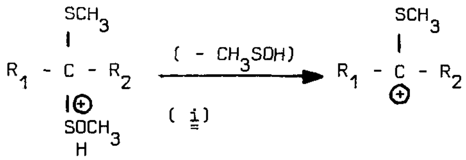
d, R_1=H, R_2= Z-C_6H_4 (Z= H, p-OCH_3, m-Cl, p-NO_2)

e, R_1=CH_3, R_2=Z-C_6H_4 (Z= H, p-NO_2)

Alternatively the carbanion of **4a** --- and its mono-alkyl or -aryl derivatives like **4b,d** --- may be alkylated first, followed by oxidation and decomposition **4** → **1** → **3**[7]. Depending on R_1,R_2 and further conditions step **1** → **3** may or may not occur during reaction **4** → **1**.

We have studied the oxidation of **4b**-**e** with H_2O_2 in aqueous acetone or with $NaIO_4$ in water at room temperature. Whereas **4b**, **4c** and **4d**, Z=p-NO_2 led to isolable **1** in 85 - 90 % yields, the other substrates "directly" produced **3** (50 - 70 %). These facts are in accord with the mechanism outlined by Kuhn et al.[9], involving (i) which --- depending on its structure --- may or may not solvolyze via cation (ii) to give 3.

In our opinion the rapid acid-catalyzed conversion 1 ⟶ 3 also occurs in other cases. Thus, the


(i) (ii)

low yields in attempted oxidations of sugar mercaptals[10] suggest that here too, conversions 4 ⟶ 1 are followed by 1 ⟶ 3 rather than by further oxidation 1 ⟶ 2.

Finally we believe that highly comparable mechanisms obtain in (some of) the"direct" conversions 4 ⟶ 3 *documented earlier; e.g., reactions of type 4 compounds with N-Br-succinimide*[6] *may also* involve sulfonium derivatives capable of giving cations (ii).

NOTES AND REFERENCES.

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4. From 2a we have indeed observed -intermediate- 1a through NMR spectroscopy
5. R.M. Carlson and P.M. Helquist, J. Org. Chem. 33, 2596 (1968)
6. D. Seebach, Synthesis, 19 (1969)
7. The alkylation of the anion of 2a or 2b was found to be a sluggish reaction[3b] (cf. also ref.8), making this a much less attractive route to 3.
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