FORMATION OF 2,6-DIALKOXY-3,5-DIALKYL-1,4-OXASELENANE 1,1-DICHLORIDES BY REACTION OF ALIPHATIC ALDEHYDES WITH SeO_2 IN ALCOHOLS CONTAINING AQUEOUS HCl

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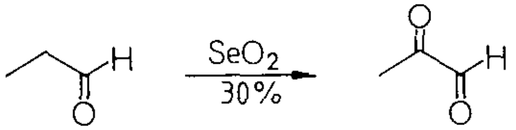
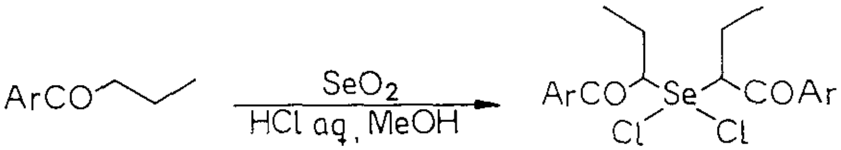
Abstract — A variety of aliphatic aldehydes reacts with SeO_2 in alcohols containing aqueous HCl, yielding 2,6-dialkoxy-3,5-dialkyl-1,4-oxaselenane 1,1-dichlorides, albeit unstable, as nicely crystalline compounds. The corresponding Cl-stripped compounds are much more stable (distillable) and can be deselenated with degassed Raney nickel to the corresponding 3,4-dialkylfurans.

The oxidation of a CH_2 group α to a carbonyl in ketones and, to a lesser extent, aldehydes with SeO_2 is a well-established[1-3] procedure for the synthesis of 1,2-dicarbonyl compounds (eq. 1). It is likely that this type of oxidation is initiated by an electrophilic attack by a Se^{IV} species, thus creating a C-Se bond α to the carbonyl group. In the presence of aqueous HCl in e.g. methanol such Se^{IV} compounds (eq. 2) can often be isolated.[4-6]

(1)



(2)



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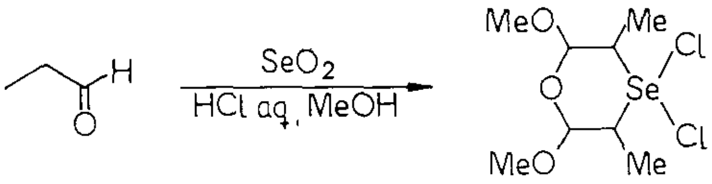

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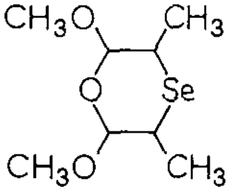
Interaction of aldehydes with SeO_2 in aqueous HCl has been studied extensively by Futekov[7] in the area of analytical chemistry particularly for specific separation of selenium by solvent extraction. The results of the Bulgarian workers clearly indicate the formation of defined (albeit unstable) extractable species.

We have now developed conditions (reaction of SeO_2 dissolved in conc. aqueous HCl/methanol (1:1) with the aldehyde) for the preparation and isolation of these, often relatively unstable, species, in crystalline form (yields 50-90%). The compounds give highly characteristic ^{13}C and ^1H NMR spectra and these data in combination with IR, MS and elemental analysis leave no doubt that e.g. the product[8] obtained from CH_3CH_2CHO has structure 1 (eq. 3).



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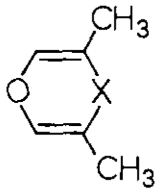
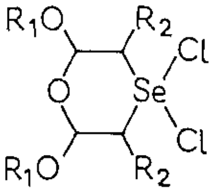
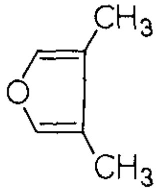


3 a X=S
b X=Se



4 a $R_1=CH_3, R_2=C_2H_5$
b $R_1=R_2=C_2H_5$
c $R_1=CH_3, R_2=C_4H_9$
d $R_1=C_2H_5, R_2=C_4H_9$
e $R_1=CH_3, R_2=C_6H_5$
f $R_1=C_2H_5, R_2=CH_2C_6H_5$



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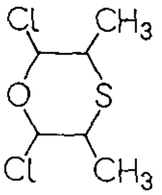

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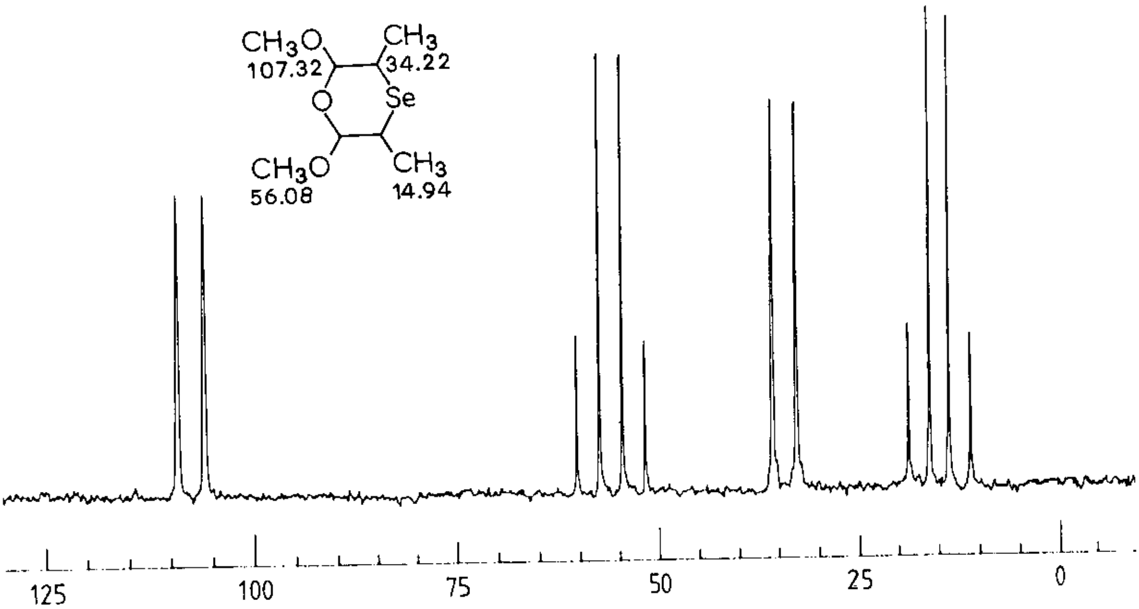
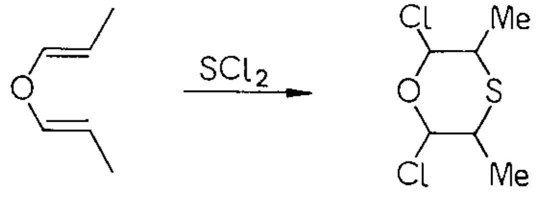
Several other aldehydes (e.g. $CH_3(CH_2)_4CHO$, $C_6H_5CH_2CH_2CHO$) and alcohols (e.g. C_2H_5OH) and acetals (e.g. $C_6H_5CH(OCH_3)_2$) gave similar adducts[9] (4c, 4f and 4e respectively). The adducts from CH_3CHO could not be isolated due to rapid decomposition with formation of Se. Compound 1 can be readily reduced by sulphite or by zinc in alcohol to the corresponding selenide (2), a low-melting (47-48°C), distillable (86-88 °C, 10 mm) solid,[10] that easily sublimes already at room temperature. The ^{13}C NMR spectrum of 2 is shown in the figure. For PMR data see ref. 10. The shift (1.13 Hz) to higher field observed for the hydrogen atoms in 2-position when removing the 1,1-Cl atoms in 1, is similar to that (1.40 Hz) observed[11] for simple derivatives, such as the pair, $(CH_3)_2SeCl_2$ and $(CH_3)_2Se$.
Attempts to convert 2 into 3b (a known[12] compound, earlier prepared by dehydrochlorination of an adduct of diallyl ether and $SeOCl_2$) have so far failed. Treatment of 2 with degassed Raney nickel produced 3,4-dimethylfuran (5) in high yield.



^{13}C NMR spectrum of 2,6-dimethoxy-3,5-dimethyl-1,4-oxaselenane (2)

The detailed stereochemistry of 1 or 2 is not known and therefore X-ray investigations are intended. In this connection the conformational analyses[13] of 2,6-dichloro-1,4-oxathianes (e.g. 6) are of interest. (C.f. also ref 15) The adduct 6 was prepared according to equation (4) by Brandsma *et al*.[14] Elimination of 6 induced by K-*t*Bu gave 3a.

(4)



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8. Compound 1, mp 130-132°C, PMR (CDCl$_3$): δ 5.10 (d, 2H, 3-CH J=8.4 Hz, 4.25 (m, 2H, 2-CH, 3.60 (s, 6H, OCH$_3$), 1.73 (d, 6H, CH$_3$, J=6.8 Hz).

9. Compound 4a, mp 148-150°C dec, PMR (CDCl$_3$): δ 5.05 (d, 2H, 3-CH, J=8.4), 4.23 (m, 2H, 2-CH), 3.52 (s, 6H, OCH$_3$), 2.22 (m, 4H, CH$_2$, J=6.8), 1.25 (t, 6H, CH$_3$). 13C (CDCl$_3$): 11.98 (q), 21.00 (t), 56.85 (q), 75.83 (d), 102.21 (d).

Compound 4d, mp 78-80°C, ^{13}C (CDCl$_3$): 13.75 (q), 15.06 (q), 22.53 (t), 27.17 (t), 29.40 (t), 65.46 (t), 73.94 (d), 100.84 (d).

Compound 4e, mp 230°C dec, ^{13}C (DMSO-d$_6$): 44.74 (d), 55.45 (q), 104.64 (d), 127.38 (d), 128.17 (d), 128.49 (d), 136.69 (s).

Compound 4f, mp 128-130°C, ^{13}C (CDCl$_3$): 15.10 (q), 33.55 (t), 65.58 (t), 75.57 (d), 100.86 (d), 127.65 (d), 128.75 (d), 129.43 (d), 134.69 (s).

All these, nicely crystalline, compounds are stable for at least 4 months at -20°C. At +20°C rapid decomposition (within hours) will occur. The corresponding Cl-stripped compounds are much more stable.

10. Compound 2, mp 47-48°C, PMR (CDCl$_3$): δ 4.33 (d, 2H, 3-CH, J=8.2 Hz), 3.44 (s, 6H, OCH$_3$), 3.12 (m, 2H, 2-CH), 1.15 (d, 6H, CH$_3$, J=6.4 Hz).

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