Reduction *vs.* Acetalisation of some Carbonyl Compounds by means of Methylselenol and Lewis Acids

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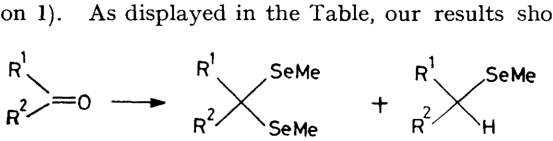
Summary Aliphatic ketones and aromatic carbonyl compounds on reaction with methylselenol and a Lewis acid, are shown to undergo acetalisation and/or reduction to methyl selenide, the unexpected reduction reaction being predominant in most cases.

IN synthesising selenoacetals derived from aromatic carbonyl compounds (*i.e.*, benzaldehyde and substituted acetophenones) as well as from hindered aliphatic ketones, such as di-isopropyl ketone using our recently described method[1] [a carbonyl compound (1 equiv.), a selenol (2 equiv.), and $ZnCl_2$ (0·5 equiv.) in CH_2Cl_2 at room temperature] we were surprised to find that as well as the desired selenoacetal, a small but significant quantity of the corresponding selenide was obtained.

TABLE. Reaction of carbonyl compounds with methylselenol (2·2 equiv.) in the presence of $ZnCl_2$ (5 equiv.)

Compound	Reaction time/h	Overall yield/%	Products Acetal (**2**)	 Selenide (**3**)
(**1a**)	16	91	0	100
(**1b**)	16	98	100	0
(**1c**)	9	82	0	100
(**1d**)	17	47	17	83
(**1e**)	20	49	0	100
(**1f**)	26	89	85	15
(**1g**)	26	90	0	100
(**1h**)	26	98	0	100
(**1i**)	17	95	0	100
(**1j**)	0·3	98	70	30
	16	93	22	78
	26	78	0	100

Therefore, we investigated this reaction in more detail and found that, with the exception of undecanal (**1b**), all the carbonyl compounds studied yielded exclusive or substantial amounts of the selenide (**3**), when they were allowed to react with the selenol (2·2 equiv.) and $ZnCl_2$ (5 equiv.) in dichloromethane at room temperature (equation 1). As displayed in the Table, our results show that overall yields are good to excellent and the outcome of the reaction greatly depends on the structure of the starting carbonyl compound and on reaction conditions. Thus, as exemplified by undecanal (**1b**), aliphatic aldehydes are not reduced and the selenoacetal (**2b**) is formed in high yield. Similarly, *p*-nitroacetophenone gives only a small amount of the selenide (**3f**). These observations seem to indicate that the reduction is somehow linked to the ability of the starting structure to stabilise electron-deficient (cationic or free radical) centres.



(1) (2) (3) (1)

Reagents: $ZnCl_2$ (5 equiv.), MeSeH (2·2 equiv.) in CH_2Cl_2 at 20°C.

a; $R^1 = C_9H_{19}$, $R^2 = Me$
b; $R^1 = C_{10}H_{21}$, $R^2 = H$
c; $R^1, R^2 = -CH_2CH_2CHBu^tCH_2CH_2-$
d; $R^1 = R^2 = Pr^i$
e; $R^1 = Ph$, $R^2 = H$
f; $R^1 = p\text{-}NO_2C_6H_4$, $R^2 = Me$
g; $R^1 = p\text{-}ClC_6H_4$, $R^2 = Me$
h; $R^1 = Ph$, $R^2 = Me$
i; $R^1 = p\text{-}MeC_6H_4$, $R^2 = Me$
j; $R^1 = p\text{-}MeOC_6H_4$, $R^2 = Me$

It is also important to note the effect of reaction time as shown by the behaviour of *p*-methoxyacetophenone (**1j**). This suggests that the selenoacetal (**2**) should be an intermediate in the formation of the corresponding selenide. This hypothesis is strengthened by the observation that the reaction of the selenoacetal (**2i**) (prepared by another route) with methylselenol (2·2 equiv.) in the presence of $ZnCl_2$ (5 equiv., CH_2Cl_2, room temperature, 15 h) gives exclusively the selenide (**3i**) in 95% yield, together with some dimethyl diselenide.

Undoubtedly, we have here an unprecedented reaction of carbonyl compounds activated by selenium groups in which $ZnCl_2$ appears to play a major role. As expected, other Lewis acids are able to perform the same reaction. For example, di-isopropyl ketone (**1d**) reacts (−40 °C, 16 h, CH_2Cl_2) with methylselenol (2·2 equiv.) in the presence of $TiCl_4$ (0·3 mol. equiv.) to produce trace amounts of the acetal (**2d**) and the selenide (**3d**) (61% yield). The same ketone gives, in the presence of $SnCl_4$ [1 mol. equiv., MeSeH (2·2 equiv.), CH_2Cl_2 −21 °C, 4·5 h] the selenide (**3d**) (50% yield) free of any selenoacetal (**2d**). The acetophenones (**1h**—**j**) behave in much the same way under similar conditions.

Interestingly, we also found that secondary and tertiary amines greatly diminish or eventually suppress the ability of titanium tetrachloride to promote the reduction reaction. Thus, *p*-methoxyacetophenone produces, on reaction with MeSeH (2·2 equiv.) in the presence of $TiCl_4$ (1 mol. equiv.) and *N*-methylaniline[2] (1 equiv., CH_2Cl_2, room temperature, 14 h), a mixture of the acetal (**2j**) (67%) and the selenide (**3j**) (33%). When conducted in the presence of triethylamine (1 equiv.) instead of *N*-methylaniline, the same reaction gives a 63% yield of (**2j**) free of any selenide (**3j**). We have not yet investigated the effect of amines on the reaction with $ZnCl_2$.

Although the above observations do not explain the reduction, they provide a simple method for the one step transformation of ketones into the corresponding alkyl selenides.

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