# Selective Reaction of Silyl Enol Ethers with α-Chloro-sulphides containing a Ketone Group

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*Summary* Reaction of silyl enol ethers (**1**) with α-acyl-α-chloro-sulphides (**2**; $n = 0$) gives furans (**4**), whereas with β- or γ-acyl-α-chloro-sulphides (**2**; $n = 1$ or 2) diketones (**3**) are obtained.

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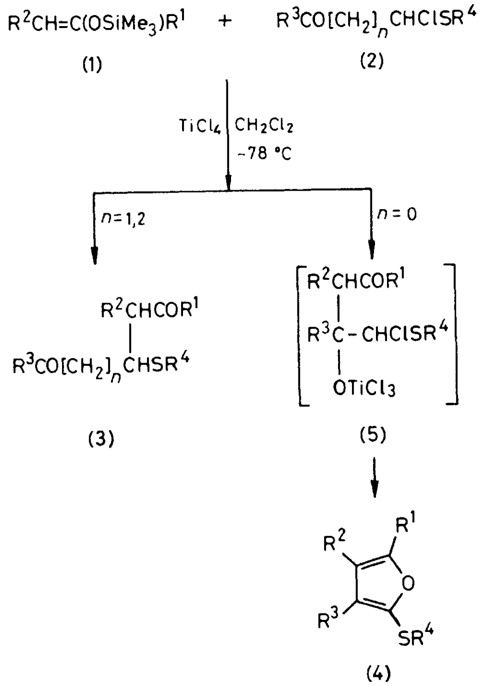
IN the presence of a Lewis acid α-chloro- or α-trifluoroacetoxy sulphides are known to react with aromatic compounds,[1,2] sulphides,[3] and thiols.[3] The reaction of α-chloro-sulphides and silyl enol ethers provides an efficient method for the regioselective monoalkylation of ketones and esters.[4] Here we report that the reaction of silyl enol ethers (**1**) and α-chloro-sulphides (**2**) containing a ketone group takes place selectively at the α-methylene carbon atom or the carbonyl carbon atom depending upon the structure of (**2**).

Compounds (**2**) were prepared from the corresponding sulphides by treatment with *N*-chlorosuccinimide. A solution of 3-trimethylsilyloxypent-2-ene (**1a**; $R^1$ = Et, $R^2$ = Me; 1 mol. equiv.), 1-chloro-1-phenylthiobutan-3-one (**2a**; $R^3$ = Me, $R^4$ = Ph; 1·2 mol. equiv.), and $TiCl_4$ (1·1 mol. equiv.) was stirred at −78 °C for 8 h. After the usual work-up chromatography on silica gel afforded the diketone (**3a**) in 58% yield. Similarly, (**3b**) was prepared from (**1a**) and (**2b**; $R^3$ = Me, $R^4$ = Ph) in 65% yield.

On the other hand, similar treatment of (**1a**) with 1-chloro-1-phenylthiopropan-2-one (**2c**; $R^3$ = Me, $R^4$ = Ph) and $TiCl_4$ led to the formation of the furan (**4a**) in 88% yield. The structure of (**4a**) was confirmed by its spectral data, and by direct comparison of authentic 2-ethyl-3,4-dimethylfuran with the compound obtained by reductive desulphurization of (**4a**) using deactivated (acetone-treated) W-2 Raney Ni (Scheme).[5] The results of other experiments are summarized in the Table.

TABLE. Preparation of the furans (**4**).

| Product | $R^1$ | $R^2$ | $R^3$ | $R^4$ | Isolated yield/% |
|---|---|---|---|---|---|
| (**4a**) | Et | Me | Me | Ph | 88 |
| (**4b**) | Et | Me | Me | Me | 61 |
| (**4c**) | Et | Me | n-Hexyl | Me | 54 |
| (**4d**) | Ph | H | Me | Ph | 70 |
| (**4e**) | Ph | H | Me | Me | 61 |
| (**4f**) | $-[CH_2]_4-$ | | Me | Me | 60 |



SCHEME. **a**; $n = 1$
**b**; $n = 2$
**c**; $n = 0$

The formation of the furans is presumably due to the reactivity of the α-methylene carbon atom in the α-acyl-α-chloro-sulphides (**2**; $n = 0$) which is deactivated by the adjacent electronegative carbonyl group, and compounds (**1**) selectively react with the ketone function activated by $TiCl_4$.[6] Interestingly there are some differences between these findings and those for electrophilic reactions of α-acyl-α-chloro-sulphides with aromatic compounds, in which the reaction occurs at the α-methylene carbon atom,[7] presumably because in the former case the irreversible nucleophilic attack of the carbonyl oxygen in the intermediate (**5**) takes place rapidly.

We thank the Ministry of Education of Japan for a Grant-in-Aid.

(*Received*, 20*th July* 1981; *Com.* 867.)

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