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.

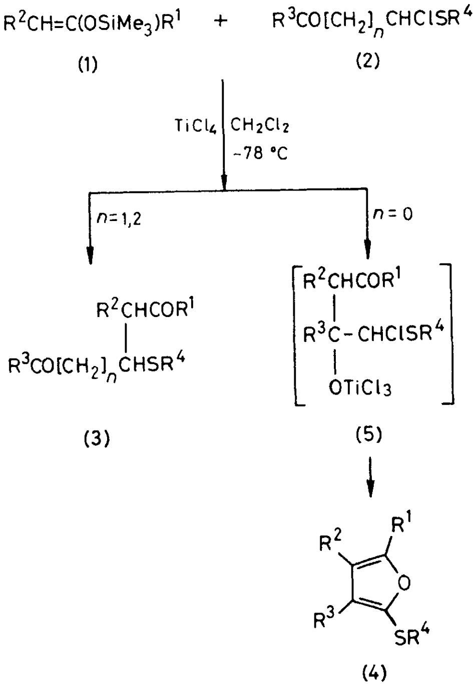
IN the presence of a Lewis acid α-chloro- or α-trifluoroacetoxy sulphides are known to react with aromatic compounds,[1,2] sulphides,[3] and thiols.[3] The reaction of α-chloro-sulphides and silyl enol ethers provides an efficient method for the regioselective monoalkylation of ketones and esters.[4] 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.

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