

The reaction of ketene silyl acetals and silyl enol ethers with CCl₄ without a promoter

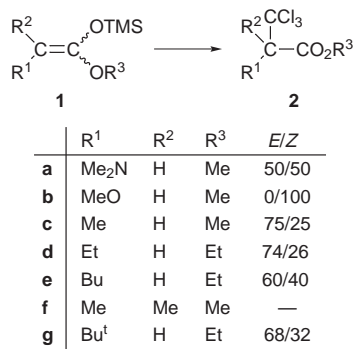
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The reaction of CCl₄ with ketene silyl acetals and silyl enol ethers in the absence of a promoter at ambient temperature or at reflux, or under photo-irradiation, was performed to form products *via* addition of the trichloromethyl group to those silyl substrates.

The reaction¹ of ketene silyl acetals or silyl enol ethers with a variety of carbon nucleophiles, including carbonyl compounds, conjugated enones or organic halides, with promotion by a Lewis acid or in the presence of a desilylative reagent, such as a fluoride compound, is well known to give α -functionalized carbonyl compounds. As with organic halides, while monohalogen compounds such as tertiary, benzyl and allyl halides afford alkylated products in the presence of a Lewis acid, *e.g.* titanium(IV) chloride,² zinc(II) chloride³ or silver(I) perchlorate,⁴ polyhalides such as carbon tetrachloride give β -halo- α,β -unsaturated carbonyl derivatives in the reaction catalyzed with copper(I) chloride,⁵ triethylborane⁶ or a Ru^{II} complex.⁷ We have found that ketene silyl acetals and silyl enol ethers react with CCl₄ at ambient temperature or under reflux, or under photo-irradiation conditions, in the absence of a promoter to form products derived from addition of the trichloromethyl group to the ene moieties of those silyl substrates.

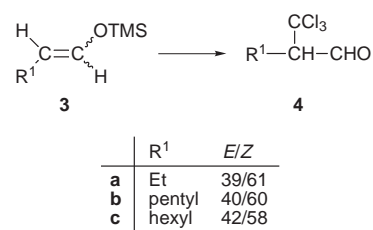
A CCl₄ solution of the ketene silyl acetal **1a**⁸ from *N,N*-dimethylglycine methyl ester was stirred at ambient temperature for 3 h; VPC analysis of the resulting mixture revealed consumption of **1a** and the appearance of one product (Scheme 1). The product was assigned as *N,N*-dimethyl(trichloromethyl)glycine methyl ester **2a** *via* its spectral data after isolation (57% yield). Raising or lowering the reaction temperature resulted in the reduction of the yield of **2a** (18 and 27% at 76 and 0 °C, respectively). The ketene silyl acetal **1b**⁹ from methyl methoxyacetate in a CCl₄ solution furnished the α -trichloromethyl ester **2b** in 81% yield under reflux conditions; no reaction occurred at ambient temperature. The ketene silyl acetal **1c** from methyl propionate, which lacks a strongly electron-donating substituent like the amino or alkoxy moieties in **1a** or **1b**, afforded the α -trichloromethyl ester **2c** in a good yield (81%) upon photo-irradiation,[‡] while **2c** was formed in only low yield (29%) under reflux conditions. The ketene silyl



Scheme 1

acetals **1d–g** from linear or branched aliphatic esters also gave α -trichloromethylation products **2d–g** upon photo-irradiation. In the case of **1b**, however, photoreaction diminished the yield of **2b** compared with that obtained *via* thermal reaction.

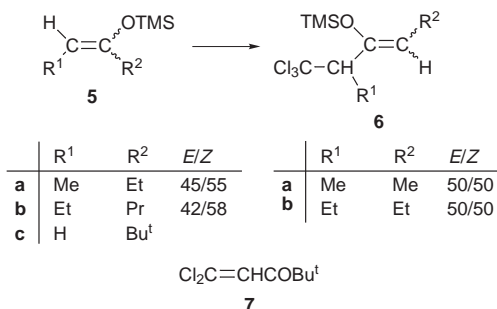
Next, the silyl enol ethers were subjected to photoreaction in CCl₄ solution. The silyl enol ethers **3a–c** derived from aliphatic aldehydes formed the aldehydes **4a–c** bearing α -trichloromethyl substituents in good yields (85, 79 and 68%, respectively) (Scheme 2). Photoreaction of the silyl enol ethers



Scheme 2

derived from aliphatic ketones afforded products other than the above-mentioned ones, *i.e.* while 3-trimethylsiloxy-pent-2-ene **5a** and 4-trimethylsiloxyhept-3-ene **5b**, derived from unbranched ketones, gave the products **6a,b** *via* addition of the trichloromethyl group followed by migration of the C=C double bond while retaining the silyl group, 3,3-dimethyl-2-trimethylsiloxybut-1-ene **5c** effected the β,β -dichloro- α,β -unsaturated ketone **7** based on dehydrochlorination after addition of the trichloromethyl group (Scheme 3). These results are collected in Table 1.

Concerning the reaction mechanism, it is postulated that the trichloromethyl radical fragment from CCl₄ attacks the C=C double bond moiety of the silyl substrate to form the product. The spontaneous bond scission of CCl₄ at ambient temperature or under reflux conditions is difficult and thus the formation of **2a,b** may be derived from the reaction of the trichloromethyl radical generated *via* single electron transfer (SET) between CCl₄ and the ketene silyl acetals **1a,b** bearing strongly electron-donating substituents. Actually, in reactions using either polar (THF) or non-polar (hexane) solvents, the yields of **2a** were better in the former compared with the latter (34 and 2%,



Scheme 3

Table 1 Reaction of silyl substrates **1,3** and **5** with CCl₄

Substrate	Conditions	Product	Yield ^a (%)
1a	3 h/room temp.	2a	57
1a	3 h/76 °C	2a	18
1a	20 h/0 °C	2a	27
1b	3 h/76 °C	2b	81
1b	4 h/room temp.	2b	0
1b	3 h/hv	2b	65
1c	3 h/76 °C	2c	29
1c	1 h/hv	2c	81
1d	1 h/hv	2d	73
1e	4 h/hv	2e	62
1f	1 h/hv	2f	50
1g	1 h/hv	2g	18
3a	1 h/hv	4a	85
3b	1 h/hv	4b	79 (65) ^b
3c	1 h/hv	4c	68
5a	1 h/hv	6a	67
5b	2 h/hv	6b	61
5c	1 h/hv	7	69

^a Determined by VPC analysis. ^b Based on TLC isolation

respectively). The reaction of the ketene silyl acetals upon photo-irradiation should also proceed *via* a SET process, as is suggested by the fact that the formation of **2c** from **1c** was enhanced by addition of LiClO₄¹⁰ (Table 2). However, the homolytic scission of the C–Cl bond may preferentially operate

Table 2 Effect of LiClO₄ on reaction of **1c** with CCl₄ in THF^a

Conditions	Yield of 2c (%)
hν/LiClO ₄	32
hν	14
76 °C/LiClO ₄	3
76 °C	0

^a Conditions: **1c** (2 mmol), CCl₄ (4 mmol), LiClO₄ (2 mmol) and THF (5 ml), 3.5 h.

in the case of the silyl enol ethers, judging from the fact that the formation of the trichloromethylated product **4b** from **3b** was enhanced in a non-polar solvent compared with a polar solvent (77% in hexane; 68% in THF; 51% in MeCN) and suppressed by addition of LiClO₄. The reaction of polyhalides other than CCl₄ with ketene silyl acetals and silyl enol ethers is under way.

Notes and References

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‡ *Experimental procedure*: A solution consisting of **1c** (0.3200 g, 2 mmol) and CCl₄ (10 ml) was irradiated using a high pressure Hg lamp (500 W) in a quartz tube for 1 h under N₂ atmosphere and then concentrated under reduced pressure. The residue was submitted to preparative VPC.

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