Y. Lee and Y. M. Goo, *J. Korean Chem. Soc.*, **30**, 138 (1986)

2. (a) J. C. Sheehan, "Molecular Modification in Drug Design", R. F. Gould, ed., American Chemical Society, 1964, p. 15 (b) D. H. R. Barton, F. Comer and P. G. Sammes, *J. Am. Chem. Soc.*, **91**, 1529 (1969)
3. W. J. Leanza, F. Dininno, D. A. Muthard, R. R. Wikening, K. J. Wildonger, R. W. Ratcliffe and B. G. Christensen, *Tetrahedron*, **39**, 2505 (1983)
4. D. I. John, N. D. Tyrrel and E. J. Thomas, *Tetrahedron*, **39**, 2477 (1983).
5. (a) K. Prasad, K. Adlgasser, R. Sharma and P. Stütz, *Heterocycles*, **19**, 2099 (1982); (b) H. Fliri and C.-P. Mak, *J. Org. Chem.*, **50**, 3438 (1985).
6. (a) A.G.M. Barrett and P. Quayle, *Chem. Commun.*, 1076 (1981); (b) P. J. Reider, R. Rayford, and E. J. J. Grabowski, *Tetrahedron Lett.*, **23**, 379 (1982); (c) P. J. Reider, and E. J. J. Grabowski, *ibid*, **23**, 2293 (1982); (d) R. P. Attrill, A. G. M. Barrett, P. Quayle and J. van derWesthuizen, *J. Org. Chem.*, **49**, 1679 (1984); (e) A. I. Meyers, T. J. Sowin, S. Scholz and Y. Ueda, *Tetrahedron Lett.*, **28**, 5103 (1987).

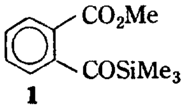
Acylsilanes in Aromatic Annulation for Hydroquinones

Jahyo Kang*, Jae Hyoung Lee, Jong Gil Rim, and Chongsuh Pyun

Department of Chemistry, Sogang University Mapoku, Seoul 121-742. *Received July 8, 1988*

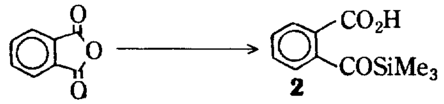
Michael addition followed by base-induced cyclization is a versatile method for the construction of carbocyclic 6-membered rings. Generally, the Michael acceptors supply 4 carbons out of 6 carbons (e.g. Robinson annulation[1]). Another useful variant is one in which 4 carbons are supplied by Michael donors. And this has been a major impetus for the ready construction of hydroquinon-quinone subunits which are present in anthracycline antibiotics[2] and potentially other naphthazarin natural products such as chrysophanol and fredericamycins. The Michael donors which act as 1,4-dipoles are typified by the presence of the o-carboalkoxybenzylic anion. These include anions of dimethyl homophthalate[3] 3-phenylsulfonyl- and 3-cyano-phthalide[4], o-toluoyl esters[5] and homophthalic anhydrides[6].

In this paper, we wish to introduce another 1,4-dipole, o-carbomethoxybenzoyltrimethylsilane (**1**), which is conceptually related but functionally different, and its behavior toward Michael acceptors.

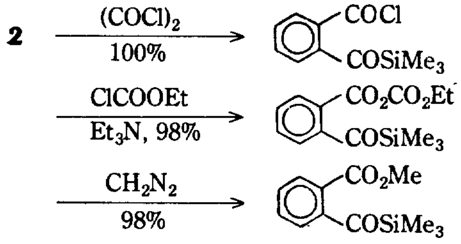


1

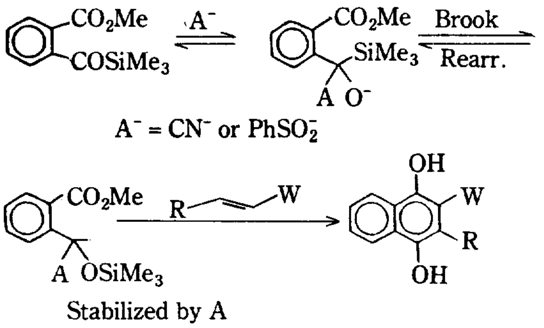
Acylsilanes are a versatile class of compounds which undergo a variety of interesting reactions[7,8]. A facile method for the preparation of multi-functional acylsilanes is lacking even though there are available in literature a number of preparatively useful methods, most of which utilize acyl anion equivalents[9], due to the difficulties associated with generation of silyl anions under mild conditions[10,11]. Consequently, a new methodology was developed[12] using the readily available $LiAl(SiMe_3)_4$ and $Al(SiMe_3)_3$[13]. Thus, phthalic anhydride could be converted, in the presence of CuCN, to the corresponding acylsilane **2** using either $LiAl(SiMe_3)_4$ or $LiMeAl(SiMe_3)_3$ in 80-90% yield[12].



Having accomplished the preparation of o-carboxybenzoyltrimethylsilane **2**, it was further converted to the corresponding acid derivatives.

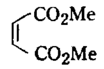
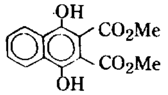
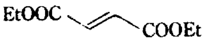
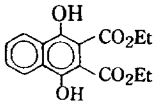
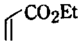
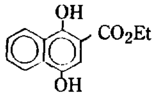
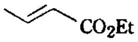
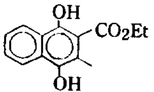
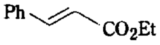
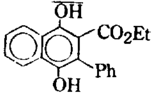
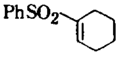
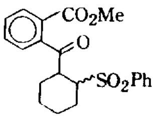


Subsequently, among the 3 derivatives, only o-carbomethoxybenzoyltrimethylsilane **1** was found to behave properly as a 1,4-dipole. Thus, ester **1** was treated with a variety of anions in the presence of dimethyl maleate as a representative Michael acceptor. Cyanide and benzenesulfinate were added in anticipation of the reaction path shown below.



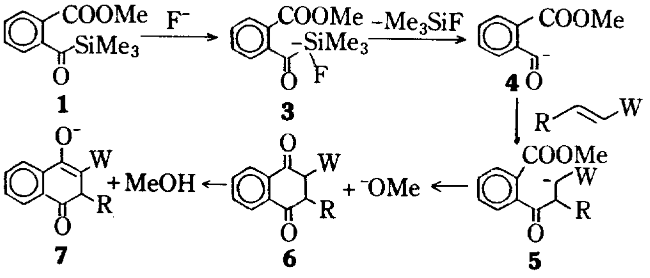
However, under no circumstance did the reaction proceed. The starting material either remained intact below 23 °C or decomposed to an array of products at higher temperature. But soluble fluoride sources, especially cesium fluoride and tetrabutylammonium fluoride, gave acceptable results; here the fluoride had to be vigorously dried, otherwise the corresponding aldehyde was obtained[7] (Table 1).

Table 1. Reaction of Acylsilane 1 with Michael Acceptors in the Presence of Fluoride

Entry	**1** equiv	Michael Acceptors	Fluoride (equiv)	Condition	Product (Yield)	
1	1.0		CsF[a] (1.5)	DMSO, 23 °C		(22%)
2	1.0		" (")	HMPA, 0 °C		(54%)
3	1.0		TBAF[b] (1.2)	THF, -78 °C		(51%)
4	2.0		" (2.2)	"		(62%)
5	3.0		" (3.2)	"		(80%)
6	1.0		" (1.2)	"		(53%)
7	3.0		" (3.2)	"		(73%)
8	"		" (")	"		(33%)
9	"		" (")	"		(43%)
10	"		" (")	"		(32%)
11	1.0		" (1.2)	"		(55%)
12	1.0		CsF[a] (1.2)	HMPA, 0 °C		(59%)

[a] Dried in vacuo at 150 °C for 3 h. [b] Dried over activated molecular sieve 3A for 3 h.

One problem that had to be resolved before proceeding to other cases was that a 1:1 ratio of acylsilane and Michael acceptor did not give a good result. This was understandable, considering the reaction path leading to the product (Scheme): By the fact that only fluoride, but neither cyanide nor sulfinate, was essential for the successful outcome, fluoride attacks directly the silicon atom to form a transient pentavalent species **3**[14], which decomposes to an acyl anion **4**. The resulting adduct **5** with a Michael acceptor would cyclize to form dihydronaphthoquinone and methoxide, which would undergo acid-base reaction to provide **7** and methanol.



Scheme

Unfortunately, the overall species, **7** and MeOH, were thought to destroy acyl anion **4**. Various attempts to scavenge these proton sources by employing additional NaH, LDA etc. were fruitless. Thus, it was imperative to utilize 3 equiv. of acylsilane to get a good yield of the product. Under this condition, various Michael acceptors underwent the projected reaction although the yields were moderate. But 1-cyclohexenyl phenyl sulfone provided only uncyclized Michael adduct in 59% yield (Table 1).[15,16]

References

1. M. E. Jung, *Tetrahedron,* **32,** 3 (1977).
2. (a) K. Krohn, *Angew. Chem. Int. Ed.,* **25,** 790 (1986); (b) T. R. Kelly, Ed., *Tetrahedron,* **40,** 4537-4793 (1984); (c) R. H. Thomson, "Naturally Occuring Quinones, III", Chapman and Hall, 1987; pp. 527-563.
3. W. Eisenmuth, H. B. Renfroe and H. Schmid, *Helv. Chim. Acta,* **48,** 375 (1965).
4. (a) G. A. Kraus, H. Cho, S. Crowley, B. Roth, H. Sugimoto and S. Prugh, *J. Org. Chem.,* **48,** 3439 (1983); (b) B. L. Chenard, M. G. Dolson, A. D. Sercel and J. S. Swenton, *ibid,* **49,** 318 (1983); (c) N. J. Broom and P. G. Sammes, *J. Chem. Soc. Chem. Commun.,* 162 (1978).
5. J. H. Dodd and S. M. Weinreb, *Tetrahedron Lett.,* 3593 (1979).
6. (a) Y. Tamura, M. Sasho, K. Nakagawa, T. Tsugoshi, and Y. Kita, *J. Org. Chem.,* **49,** 473 (1984); (b) Y. Tamura, M. Sasho, H. Ohe, S. Hkai and Y. Kita, *Tetrahedron Lett.,* **26,** 1549 (1985).
7. (a) A. G. Brook, *Adv. Organomet. Chem.,* **7,** 96 (1968); *Acc. Chem. Res.,* **7,** 77 (1974); (b) D. Schinzer and C. H. Heathcock, *Tetrahedron Lett.,* **22,** 1881 (1981); (c) H. J. Reich, M. J. Kelly, R. E. Olson and R. C. Holtan, *Tetrahedron,* **39,** 949 (1983); (d) J. Enda and I. Kuwajima, *J. Am. Chem. Soc.,* **107,** 5495 (1985); (e) H. J. Reich and E. K. Eisenhart, *J. Org. Chem.,* **49,** 5282 (1984).
8. (a) M. E. Scheller and B. Frei, *Helv. Chim. Acta,* **67,** 1734 (1984); (b) C. Shih and J. S. Swenton, *J. Org.*

Chem., **47**, 2668 (1982).
9. For most recent ones; T. Mandai, M. Yamaguchi, Y. Nakayama, J. Otera and M. Kawada, *Tetrahedron Lett.*, **26**, 2675 (1985); T. Aoyama and *T.* Shioiri, *ibid*, **27**, 2005 (1986).
10. (a) D. C. Davis, *Organomet. Chem. Rev.* **A, 6**, 283 (1970); (b) W. C. Still, *J. Org. Chem.*, **41**, 3063 (1976); (c) T. Hiyama, M. Obayashi, I. Mori and H. Nozaki, *J. Org. Chem.*, **48**, 912 (1983).
11. Acysilanes from silyl anions, (a) with Ph_3SiLi, see N, Duffaut, J. Dunogues, C. Biran and R. Calas, *J. Organomet. Chem.*, **161**, C23 (1978); (b) with $(Me_3Si)_2$, see A. Ricci, A. Degl'Innocenti, S. Chimichi, M. Fiorenza and G. Rossini, *J. Org. Chem.*, **50**, 130 (1985).
12. J. Kang, J. H. Lee, K. S. Kim, J. U. Jeong and C. Pyun, *Tetrahedron Lett.*, 3261 (1987).
13. L. Roesch and G. Altnau, *J. Organomet. Chem.*, **195**, 47 (1980); *Chem. Ber.*, **112**, 3934 (1979).
14. P. C. B. Page, S. Rosenthal and R. V. Williams, *Tetrahedron Lett.*, **28**, 4455 (1987).
15. α,β-Acetylenic esters and α,β-unsaturated ketones gave complex mixtures.
16. This was supported by the Korea Research Foundation.

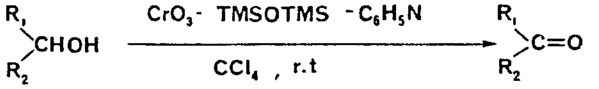
Oxidation of Alcohols by Chromic Anhydride-Hexamethyldisiloxane-Pridine

Jong Gun Lee*, Dong Soo Ha, and Hee Jong Lim

Department of Chemistry, Pusan National University, Pusan 609-735. Received July 22, 1988

One of the most important application of chromium (VI) compounds is the oxidation of alcohols to the carbonyl compounds[1,2]. Chromium salts and complexes of heteroaromatic bases seem to be preferable to the conventional reagents in aqueous acids[3-5]. Excellent procedures utilizing neutral chromium(VI) compounds such as chromyl chloride[6] and di-t-butyl chromate(DTBC)[7] are also available.

The insertion of chromic anhydride into silicon-oxygen bonds of siloxanes to form silyl chromates has been known for a long time[8]. However, the useful application of these silyl chromates in organic reactions are scarce. Bis(triphenylsilyl) chromate was reported as an initiator for the polymerization of olefins[9] and as an oxidizing agent for hydroxyalkyl ferrocenes[10]. Chromic anhydride is known to be easily inserted to produce bis(trimethylsilyl) chromate[11]. We now report that this reagent in the presence of pyridine is mild and efficient for the oxidation of alcohols to carbonyl compounds. The procedure is very simple and convenient.



Chromic anhydride was stirred with hexamethyldisiloxane in carbon tetrachloride. It was readily dissolved to form a red nearly homogeneous solution. Pyridine (0.1 mol) was added followed by an alcohol to be oxidized in a minimum amount of carbon tetrachloride. After 4 hour of stirring, the reaction mixture was filtered through a short column of silica gel. Carbonyl compounds of high purity can usually be obtained by simply evaporating off the low boiling solvents and by-products.

All primary alcohol tested were oxidized to aldehydes and secondary alcohols to ketones. Allylic alcohols were oxidized without carbon-carbon double bond cleavage. The role of pyridine remains unclear. In the absence of it, however, the oxidation is very sluggish yielding aldehyde in less than 30% yield. The reaction conditions and the yield of the carbonyl compounds are listed in Table 1.

Table 1. Oxidation of Alcohols with BTSC-Pridine[a]

Substrate	Time (hr)	Product	% Yield[b]
1-hexanol	4	1-hexanal	80.0
1-Octanol	4	1-octanal	84.6
2-hexanol	4	2-hexanone	87.5
cyclohexanol	4	cyclohexanone	81.6
menthol	4	menthone	81.6
borneol	4	camphor	77.9
cinnamyl alcohol	2	cinnamaldehyde	91.0
benzyl alcohol	2.5	benzaldehyde	85.0
p-methoxybenzyl alcohol	2	p-anisaldehyde	88.5
geraniol	3	geranial	67.3[c]
2-methyl-3-buten-2-ol	2[d]	3-methyl-2-butenal	72.5
2-phenyl-3-buten-2-ol	1.5[d]	3-phenyl-2-butenal	18.0[e]
1-vinylcyclopentanol	1.5[d]	α,β-unsaturated aldehyde	43.0
1-methyl-2-cyclohexen-1-ol	1.5[d]	3-methyl-2-cyclohexenone	84.0

[a] 2 equivalents of BTSC and pyridine were used. [b] isolated yield. [c] starting alcohol was not recovered. [d] Reaction at -10 °C. [e] Acetophenone was the major product (72%).

The oxidizing properties of BTSC closely resemble those of di-t-butyl chromate(DTBC). When prepared in an anhydrous form from the reaction of chromyl chloride and t-butyl alcohol in the presence of pyridine, DTBC can oxidize alcohols to carbonyl compounds in very high yields[7].

Chromic anhydride-hexamethyldisiloxane-pyridine system has definite advantages over anhydrous DTBC. The reagent system can be easily prepared from the cheap off the shelf chemicals. The reaction conditions are very mild. The workup procedure is simple. The yield is higher or comparable to those using the other popular chromium(VI) oxidizing agents.

Some tertiary allylic alcohols were oxidized to produce α,β-unsaturated carbonyl compounds. 2-Methyl-3-buten-2-ol,