hedron Lett., **1986,** 3461 and 5042.
7. J. E. Baldwin, M. F. Chan, G. Gallacher, M. Otsuka, P. Monk and K. Prout, *Tetrahedron,* **40,** 4513 (1984).
8. *idem., J. Chem. Soc. Chem. Comm.,* **1983,** 250.
9. E. Lee, *Proc. 7th Symp. Org. Chem.,* April 1988, KRICT, Kor. Chem. Soc. Compound **7** was recently bound to have no bioactivity-personal communication with professor E. Lee.
10. J. G. Gleason, T. F. Buckley, K. G. Holden, D. B. Bryan and P. Siler, *J. Am. Chem. Soc.,* **101,** 4730 (1979).
11. C. L. Branch and M. J. Pearson, *Tetrahedron Lett.,* **1982,** 3003.
12. J. M. Indelicato and C. E. Pasini, *J. Med. Chem.,* **31,** 1227 (1988).
13. D. Agathocleus, S. Buckwell, P. Proctor and M. I. Page, "Recent Advances in the Chemistry of β-Lactam Antibiotics", S. M. Roberts and A. G. Brown, Eds., The Royal Society of Chemistry, Burlington House, London, 1985, p. 209.
14. G. Lowe and S. Swain, in *ibid.,* p. 209.
15. W. H. Koster, C. M. Cimarusti and R. B. Sykes, "Chemistry and Biology of β-Lactam Antibiotics", R. B. Morin and M. Gorman, Eds., vol. 3, Academic Press, New York, NY, 1982.
16. R. B. Sykes, C. M. Cimarusti, D. P. Bonner, D. M. Floyd, N. H. Georgopapadakou, W. H. Koster, W. C. Liu, W. L. Parker, P. A. Principe, M. L. Rathnum, W. A. Slusarchyk, W. H. Trejo and J. S. Wells, *Nature,* **291,** 489 (1981).
17. K. Kamiya, M. Takamoto, Y. Wada and M. Asai, *Acata Crystal., Sect. B.,* **B37,** 1626 (1981).

A New Procedure for β-Alkoxycarbonylation and β-Acylation of Enones

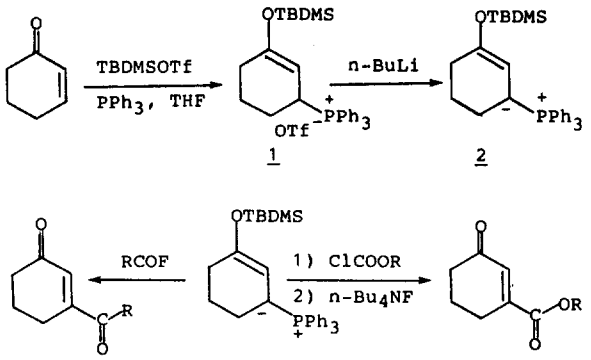
Sunggak Kim*, Phil Ho Lee, and Sung Soo Kim

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 130-012.

Received January 19, 1989

The generation of specific enolates via Michael addition of nucleophiles to α,β-unsaturated ketones has proven to be an extremely useful process for functionalization of enones.[1-5] In this regard, we have recently reported that ylides derived from enones via phosphoniosilylation serve effectively as enone β-anion equivalents to give 2,3-unsaturated-1,6-dicarbonyl and β-hydroxyalkylated compounds in high yields.[6] On the basis of these results, it has been studied the possibility of β-alkoxycarbonylation and β-acylation of enones. Moreover, there are no general methods for the synthesis of 2,3-unsaturated-1,4-dicarbonyl compounds[7] which is important in organic synthesis.[8] Therefore, we have examined the reaction of ylides (2) derived from phosphonium salt silyl enol ether (1) with alkyl chloroformates and acid halides, as shown in Scheme I.

Alkoxycarbonylation of enones at β-position was achieved by the reaction of ylide (2) with benzyl chloroformate or ethyl chloroformate followed by the elimination of triphenylphosphine with tetrabutylammonium fluoride to obtain 2,3-unsaturated-1,4-dicarbonyl compounds in good yields by one-pot procedure. In order to obtain β-acylated, β-enones, acid chlorides such as benzoyl chloride and acetyl chloride were used as an electrophile but gave poor results under the present conditions. Thus, the reaction of ylide (2) with benzoyl chloride and acetyl chloride gave β-benzoyl-and β-acetyl-2-cyclohexen-1-one in 13% and 10% yield, respectively along with predominantly several unidentified byproducts. However, the reaction of this Wittig reagent with benzoyl fluoride instead of benzoyl chloride proceeded rapidly and much more cleanly, yielding β-benzoylated 2-cyclohexene-1-one in 65% yield. In the case of the β-benzoylation of carvone, the yield was improved by the use of tributylphosphine instead of triphenylphosphine. This result is probably due to more reactive ylide of tributylphosphine than that of triphenylphosphine. Some experimental results are given in Table 1 and illustrate the efficiency and applicability of the present method. Especially, it is noteworthy that this overall conversions can be accomplished by one-pot procedure from $\alpha\beta$-unsaturated ketonones without any isolation of the intermediates.



Scheme 1

The typical procedure for β-benzyloxycarbonylation of enones is as follows. To a solution of triphenylphosphine (231 mg, 0.9 mmol) in tetrahydrofuran (4 m*l*) were added 2-cyclohexen-1-one (85 mg, 0.9 mmol) and TBDMSOTf (244 mg, 0.9 mmol) at -30 °C. After being stirred at room temperature for 30 min, the reaction mixture was cooled to -78 °C and n-butyllithium (0.6 m*l*, 1.0 mmol) was added dropwise to give a black-colored ylide solution. The reaction mixture was stirred for 30 min at -78 °C and benzyl chloroformate (165 mg, 1.0 mmol) was added to the ylide solution. After being warm-

Table 1. β-Alkoxycarbonylation and β-Acylation of Enones

enone	RX	isolated yield, %[a]
2-cyclopenten-1-one	$PhCH_2OCOCl$	46
	EtOCOCl	52
	PhCOF	52
2-cyclohexen-1-one	$PhCH_2OCOCl$	73
	EtOCOCl	61
	PhCOF	65
carvone	$PhCH_2OCOCl$	51(64)[b]
	PhCOF	25(47)[b]
		52[c](60)[b]
4-hexen-3-one	$PhCH_2OCOCl$	56
	EtOCOCl	53
	PhCOF	58

[a] Based on enones. [b] Based on recovered starting material. [c] Tributylphosphine was used.

ed to room temperature, TBAF (1.3 m*l*, 1.3 mmol) was added and stirred at room temperature for 2 h. The extractive work-up and chromatographic separation gave 3-(benzyloxycarbonyl)-2-cyclohexen-1-one (143 mg, 73%).

Acknowledgement. This research was financially supported by Korea Advanced Institute of Science and Technology.

References

1. T. Mukaiyama, K. Inomata and M. Muraki, *J. Am. Chem. Soc.*, **95,** 967 (1973).
2. W. R. Leonard and T. Livinghouse, *J. Org. Chem.*, **50,** 730 (1985).
3. A. Itoh, S. Ozawa, K. Oshma and H. Nozaki, *Tetrahedron Lett.*, 361 (1980).
4. M. Suzuki, T. Kawagishi and R. Noyori., *Tetrahedron Lett.*, 1809 (1981).
5. (a) A. P. Kozikowski and S. H. Jung, *J. Org. Chem.*, **51,** 3402 (1986); (b) A. P. Kozikowski and S. H. Jung, *Tetrahedron Lett.*, 3227 (1986); (c) H. Cristau, E. Torreilles and C. Barois-Gacherieu, *Synth. Commun.*, **18,** 185 (1988).
6. S. Kim and P. H. Lee, *Tetrahedron Lett.*, 5413 (1988).
7. (a) T. Severin and D. Konig, *Chem. Ber.*, **107,** 1493 (1974); (b) H. Lerche, D. Konig and T. Severin. *Ibid.*, **107,** 1509 (1974).
8. (a) R. K. Boeckmann, J. Fayos and J. Clardy, *J. Am. Chem. Soc.*, **96,** 5954 (1974); (b) J. E. McMurry and L. C. Blaszczak, *J. Org. Chem.*, **39,** 2217 (1974); (c) T. A. Hase, A. Ourila and C. Holmberg, *J. Org. Chem.*, **46,** 3137 (1981).

One-Pot Procedure for the Preparation of Cyclic Ethylene Thioacetals from Carboxylic Acids with 1,3,2-Dithiaborolane-Dimethyl Sulfide

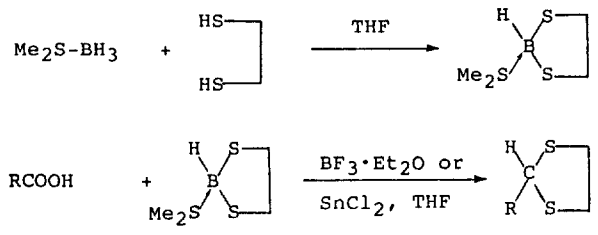
Sunggak Kim*, Sungtaek Lim, and Sung Soo Kim

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 130-012

Received January 18, 1988

Recently, we have reported a novel method for direct conversion of carboxylic acids to 1,3-dithianes by 1,3,2-dithiaborinane-dimethyl sulfide and stannous chloride.[1] Since this initial discovery we have examined several additional substrates and the similar reagents to ascertain the generality of the method.[2] We wish to report that direct conversion of carboxylic acids into synthetically important cyclic ethylene thioacetals (1,3-dithiolanes) can be easily carried out with 1,3,2-dithiaborolane.

Although the preparation of 1,3,2-dithiaborolane as a form of trimethylamine complex[3] or ethyl ether complex[4] was reported, a new procedure using borane-dimethyl sulfide was adopted. 1,3,2-Dithiaborolane-dimethyl sulfide was prepared by treatment of borane-dimethyl sulfide in tetrahydrofuran with 1,2-ethanedithiol at room temperature for 24 h.[5,6] Its structure was determined by ^{11}BNMR [a doublet ($J_{B\text{-}H}$ = 160 Hz) at +78 ppm relative to boron trifluoride etherate].



As we reported previously,[1] without the addition of an appropriate Lewis acid the reaction of an acid with the reagent gave a significant amount of the corresponding alcohol. It has been found that boron trifluoride etherate is very effective for clean conversion of aliphatic acids into cyclic ethylene thioacetals. After much experimentation to find out an optimum condition, the use of 1.5 equiv of the reagent and 1.0 equiv of boron trifluoride etherate (Method A) has been found to be the best condition for maximum yields without overreduction products.[7]

Method A works well with a variety of structurally different aliphatic acids. Carboxylic acids containing other reducible functional groups are cleanly converted into the cor-