

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

enone	RX	isolated yield, % ^a
2-cyclopenten-1-one	PhCH ₂ OCOCI	46
	EtOCOCI	52
	PhCOF	52
2-cyclohexen-1-one	PhCH ₂ OCOCI	73
	EtOCOCI	61
	PhCOF	65
carvone	PhCH ₂ OCOCI	51(64) ^b
	PhCOF	25(47) ^b
		52(60) ^b
4-hexen-3-one	PhCH ₂ OCOCI	56
	EtOCOCI	53
	PhCOF	58

^aBased on enones. ^bBased on recovered starting material. ^cTributylphosphine was used.

ed to room temperature, TBAF (1.3 ml, 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 Techno-

logy.

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. König, *Chem. Ber.*, **107**, 1493 (1974); (b) H. Lerche, D. König 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. Blaszcak, *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

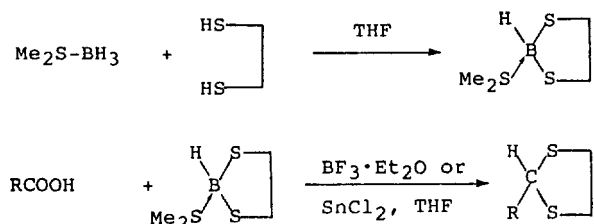
Sunggak Kim*, Sungtaek Lim, and Sung Soo Kim

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 complex³ or ethyl ether complex⁴



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 ¹¹BNMR [a doublet (J_{BH} = 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-

Table 1. Direct Conversion of Carboxylic Acids into 1,3-Dithiolanes^a

R	Method ^b	time, h	isolated yield of 1,3-dithiolanes	R	Method ^b	time, h	isolated yield of 1,3-dithiolanes
CH ₃ (CH ₂) ₆	A	3	83	p-CH ₃ C ₆ H ₄	A	12	63(27) ^c
	B	3	88		B	18	73
C ₆ H ₅ CH ₂	A	4	83	p-CH ₃ OC ₆ H ₄	B	20	71
	B	3	92	BrCH ₂ (CH ₂) ₉	A	6	98
(CH ₃) ₂ CH	A	3	85		B	4	92
	B	4	86	MeOOCCH ₂ (CH ₂) ₃	A	6	87
cyclohexyl	A	5	87		B	3.5	87
	B	4	85	Et ₂ NCOCH ₂ (CH ₂) ₃	A	6	75
(CH ₃) ₃ C	A	6	81		B	4	75
	B	4.5	84	CH ₂ = CH(CH ₂) ₈	A	17	25
1-adamantanyl	A	7	90		B	7	78
	B	3	91	CH ₂ = CHCH ₂ CH ₂	B	20	71
C ₆ H ₅	B	5	79	CH ₂ = CHCH ₂	B	24	82
m-BrC ₆ H ₄	B	18	78	C ₆ H ₅ CH = CH	B	24	75

^aThe reaction was carried out in THF at room temperature. ^bMethod A: Reacted with 1.5 equiv of the reagent in the presence of 1.0 equiv of boron trifluoride etherate. Method B: Reacted with 1.7 equiv of the reagent for aliphatic acids and 2.0 equiv for aromatic acids in the presence of 1.0 equiv of stannous chloride. ^cThe yield of *p*-methylbenzyl alcohol.

responding thioacetals, as shown in Table 1. However, selective reduction of acids in the presence of olefins failed under the present conditions. Thus, reaction of 11-undecylenic acid with 1.5 equiv of the reagent in the presence of 1.0 equiv of boron trifluoride etherate gave the desired thioacetal in 25% yield along with 30% of the starting material, 35% of the hydroxy-acid, and 10% of the hydroxy thioacetal. Apparently, the hydroxy compounds are resulted from hydroboration reaction. Also, the present method does not work well with aromatic acids. Under the present condition, *p*-toluic acid gave a 70:30 mixture of the desired thioacetal and *p*-methylbenzyl alcohol.³⁰ These problems were solved by the use of stannous chloride.

Clean reaction of aromatic acids and selective reaction with acids in the presence of olefins become possible in the presence of stannous chloride. The yields, the reaction conditions, and the scope of the present method were very similar with those of the previously reported one using 1,3,2-dithiaborinane.¹ Thus, 1.5 equiv of the reagent and 1.0 equiv of stannous chloride for aliphatic carboxylic acids and 2 equiv of the reagent and stannous chloride for aromatic acids (Method B) are recommended to obtain maximum yields. As shown in Table 1, Method B works well with both aliphatic and aromatic acids. Of synthetic significance of Method B is selective reduction of acids without attacking isolated ole-

finic double bonds. The result are summarized in Table 1.

Acknowledgement. This research was financially supported by Korea Science and Engineering Foundation.

References

1. S. Kim, S. S. Kim, S. T. Lim and S. C. Shim, *J. Org. Chem.*, **52**, 2114 (1987).
2. S. Kim and S. S. Kim, *Tetrahedron Lett.*, 1913 (1987).
3. S. Thaisrivongs and J. D. Wuest, *J. Org. Chem.*, **42**, 3243 (1977).
4. B. Z. Egan, S. G. Sore and J. E. Bonnel, *Inorg. Chem.*, **3**, 1024 (1964).
5. To a stirred solution of borane-dimethyl sulfide in tetrahydrofuran (5.0 ml, 10 M, 50 mmol) at 0°C under nitrogen was added freshly distilled 1,2-ethanedithiol (4.71 g, 50 mmol) dropwise over a period of 30 min. The reaction mixture, from which gas evolved slowly, was stirred at room temperature for 24 h. The concentration of 1,3,2-dithiaborolane-dimethyl sulfide in tetrahydrofuran was adjusted to 1.0 M solution by adding tetrahydrofuran.
6. The preparation of 1,3,2-dithiaborinane required much longer reaction times (7 days).
7. The use of boron trifluoride etherate as a catalyst (0.1 equiv) did not improve the reaction.

Syntheses and Spectral Properties of Pd(II)- and Pt(II)-bis(diphenylphosphino)methane Complexes

Yu Chul Park* and Young Je Cho

Department of Chemistry, Kyungpook National University, Taegu 702-701. Received December 7, 1988

The binuclear complexes of palladium and platinum bridged by bis(diphenylphosphino)methane(dppm) ligand are ex-

tensively investigated, especially relevance to the catalytic effects^{1,2} and the structural properties.^{3,4} It is known that the