room temperature) followed by gas chromatographic analysis (160 °C, 6 ft, 2% Carbowax).

B. From Ether (*S*)-(+)-9. When the procedure described above was followed 0.256 g (1.0 mmol) of allylic ether (*S*)-**9** [$[\alpha]^{30}_D$ +35.8 (*c* 4.78, $CHCl_3$)], 1.9 mL (3.0 mmol) of 1.6 M *n*-butyllithium in hexane, and 0.95 mL (5.7 mmol) of hexamethylphosphoramide in 4 mL of tetrahydrofuran afforded 0.028 g (11%) of recovered ether, 0.036 g (14%) of mixed byproducts, and 0.131 g (51%) of alcohol (*R*)-(+)-**10**, a clear liquid: $[\alpha]^{30}_D$ +11.1 (*c* 3.34, $CHCl_3$); IR (film) ν 3300, 2900, 1640, 1470, 1440, 920 cm^{-1}; ^1H NMR ($CDCl_3$) 1.1-1.7 (ring H), 1.7 (s, vinyl CH_3), 1.85 (s, OH), 2.0-2.6 (m, allylic H), 4.2 (m, carbinyl H), 5.2 (m, C=CH_2), and 5.8 ppm (m, RCH=C). Anal. Calcd for $C_{17}H_{30}O$: C, 81.54; H, 12.08. Found: C, 81.51; H, 11.94.

The Mosher ester derivative showed signals at 4.64 and 4.46 ppm (relative to external trifluoroacetic acid) with integrated areas of 79:21 in the ^{19}F NMR spectrum.

Sharpless Resolution of Alcohol (*R*,*S*)-10. Following the procedure described for the preparation of epoxide **6**, 0.387 g (1.5 mmol) of the racemic alcohol (±)-**10**, 0.49 mL (1.6 mmol) of titanium isopropoxide, 0.49 mL (2.3 mmol) of (+)-diethyl tartrate, and 0.30 mL (1.0 mmol) of 3.29 M *tert*-butyl hydroperoxide in dichloroethane afforded 0.34 g (87%) of a yellow liquid. Column chromatography (silica gel, 10% ethyl acetate-hexane) afforded 0.10 g (26%) of the resolved alcohol (*R*)-(+)-**10**: $[\alpha]^{30}_D$ +2.9 (*c* 3.4, $CHCl_3$); IR (film) ν 3300, 2875, 1640, 920 cm^{-1}; ^1H NMR ($CDCl_3$) 1.2-1.7 (ring H), 1.5 (s, vinyl CH_3), 1.6 (s, -OH), 1.9-2.5 (m, allylic H), 4.2 (m, carbinyl H), 5.1 (m, C=CH_2), and 5.9 ppm (m, RC*H*=C). Continued elution afforded 0.14 g (35%) of the epoxide **12**: $[\alpha]^{30}_D$ -1.3 (*c* 5.93, $CHCl_3$); IR (film) ν 3450, 2900, 2840, 1640, 1000, and 930 cm^{-1}; ^1H NMR ($CDCl_3$) 1.2-1.8 (ring H), 1.35 (s, CH_3), 3.5 (s, OH), 4.55 (m, carbinyl H), 5.2 (m, C=CH_2), and 5.8 ppm (m, RCH=C). Anal. Calcd for $C_{17}H_{30}O_2$: C, 76.64; H, 11.35. Found: C, 76.59; H, 11.10.

Acknowledgment. Support from the National Science Foundation and the National Institutes of Health (National Cancer Institute) through research grants CHE-8026013 and CA-34247 is gratefully acknowledged. We are indebted to Prof. Koji Nakanishi and Greg Verdine for determining the CD spectra of *p*-bromobenzoate (*R*)-**11** and its enantiomer at Columbia University.

Note Added in Proof. A report describing chirality transfer in the [2,3] Wittig rearrangement of (*S*),(*Z*)-1-methyl-2-butenyl 3-(trimethylsilyl)propargyl ether appeared after submission of this manuscript (Sayo, N.; Azuma, K.; Mikami, K.; Nakai, T. *Tetrahedron Lett.* **1984**, *25*, 565-568). The proposed transition-state model and the absolute sense of the transfer are concordant with the present findings.

Registry No. **2**, 4017-60-1; **3**, 89462-79-3; **4**, 89462-80-6; **5**, 89462-81-7; (1*S*,2*S*)-**6**, 89462-82-8; (1*S*,2*S*)-**7**, 89462-83-9; (*S*)-**8**, 89462-84-0; (*S*)-**9**, 89462-85-1; (±)-**9**, 89462-96-4; (*R*)-**10**, 89462-86-2; (*R*,*S*)-**10**, 89497-14-3; (*R*)-**11**, 89462-87-3; **12**, 89462-97-5; **14**, 89462-88-4; **15**, 89462-89-5; **16**, 89462-90-8; **17**, 89462-91-9; **18**, 89462-92-0; **19**, 87336-89-8; **20**, 89462-93-1; **21**, 89462-94-2; **22**, 89462-95-3; diethyl phosphorochloridate, 814-49-3.

Copper Ion Promoted Esterification of *S*-2-Pyridyl Thioates and 2-Pyridyl Esters. Efficient Methods for the Preparation of Hindered Esters

Sunggak Kim* and Jae In Lee

Department of Chemistry, Korea Advanced Institute of Science & Technology, Seoul 131, Korea

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The esterification of *S*-2-pyridyl thioates and 2-pyridyl esters with alcohols in acetonitrile is greatly facilitated by the addition of cupric bromide and copper ion is observed to catalyze the reaction. The ester formation is found to be sensitive to solvents, metal salts, and reaction temperatures. The esterification of *S*-2-pyridyl thioates is much more rapid than the esterification of 2-pyridyl esters under the reaction conditions employed. This method is exceedingly effective in the preparation of sterically hindered esters and has advantages over known methods in many respects such as high yields, the mildness of the reaction, and the rapidity of the reaction.

Esterification is an important and well-established reaction which is widely used in organic synthesis for various purposes. Although a number of useful and reliable methods for the preparation of esters have been known,[1] there are only several methods available in the literature for the preparation of hindered esters.

The preparation of hindered esters by the reaction of the mixed anhydrides of carboxylic acids using trifluoroacetic anhydride with alcohols is well-known and useful.[2] However, its synthetic application is limited due largely to the strongly acidic condition. The method using the reaction of acid chlorides with lithium alkoxides has not been a generally applicable method due to the strongly alkaline condition and limitations to acid chlorides without labile α hydrogens.[3] Recently, it has been reported that hindered esters can be prepared from acid chlorides and alcohols in the presence of an excess amount of silver cyanide in benzene or hexamethylphosphoramide.[4] This method, which proceeds under mild conditions, is useful and complementary to the methods developed previously. A great need still exists for an efficient method to prepare hindered esters in high yields under mild conditions.

There has been a continuing search for various methods to activate the carboxyl group toward facile esterification. Among many available methods, the combination of the metal ion and the thiol ester has gained a recent attention for macrolactonization.[5] The efficient synthesis of macrocyclic lactones and esters by activation of thiol esters with metal salts has been reported by Masamune.[6] However, the reaction depends critically on the structure

(1) For an excellent review, see: Haslam, E. *Tetrahedron* **1980**, *36*, 2409 and references cited theirin.
(2) Parish, R. C.; Stock, L. M. *J. Org. Chem.* **1965**, *30*, 927.
(3) Kaiser, E. M.; Woodruff, R. *J. Org. Chem.* **1970**, *35*, 1198.
(4) Takimoto, S.; Inanaga, J.; Katsuki, T.; Yamaguchi, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2335.
(5) For reviews, see: (a) Masamune, S.; Bates, G. S.; Corcoran, J. W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 585. (b) Nicolaou, K. C. *Tetrahedron* **1977**, *33*, 683. (c) Back, T. G. *Ibid.* **1977**, *33*, 3041.
(6) Masamune, S.; Hayase, Y.; Schilling, W.; Chan, W. K.; Bates, G. S. *J. Am. Chem. Soc.* **1977**, *99*, 6756.

0022-3263/84/1949-1712$01.50/0

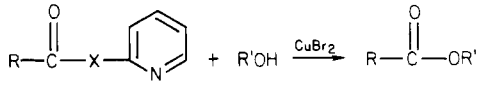
Table I. Effects of Solvent on the Rate of Ester Formation[a]

solvent	ester formation (isolated yield),[b] % 10 min	30 min	2 h	6 h
acetonitrile	96			
dichloromethane	74 (21)	96		
tetrahydrofuran	17 (71)		93	
diethyl ether	0	0	0	0 (91)
toluene	0	0	0	0 (89)

[a] All reactions were carried out at room temperature, using 1 equiv of *S*-2-pyridyl mesitothioate, 1.2 equiv of *tert*-butyl alcohol, and 1 equiv of cupric bromide. [b] The numbers in parentheses indicate the isolated yield of the recovered *S*-2-pyridyl mesitothioate.

of thiol esters and metal salts employed. Activation of *S*-2-pyridyl thioates with silver ion in the synthesis of macrocyclic lactones and esters was briefly studied by Gerlach but the scope and limitations of the reaction have not been determined.[7]

The present paper describes a rapid and convenient preparation of sterically hindered esters by the reaction of *S*-2-pyridyl thioates[8] and 2-pyridyl esters[9] with alcohols in the presence of cupric bromide.



X = S, O

Results and Discussion

During the course of studying the synthetic utility of *S*-2-pyridyl thioates and 2-pyridyl esters, we have observed that *S*-2-pyridyl mesitothioate was smoothly and rapidly esterified with equimolar amounts of *tert*-butyl alcohol in the presence of cupric bromide in tetrahydrofuran at room temperature. Since this initial discovery we have examined a number of reactions to optimize the reaction condition by using an equimolar mixture of *S*-2-pyridyl mesitothioate and *tert*-butyl alcohol as a model study. *S*-2-Pyridyl thioates used in this study were prepared in essentially quantitative yields by using the following procedures: (a) reaction of carboxylic acid chlorides with 2-mercaptopyridine in the presence of triethylamine, (b) reaction of carboxylic acids with 2-thiopyridyl chloroformate in the presence of triethylamine.[10]

Table I shows the relative rates of the formation of *tert*-butyl mesitoate by use of 1 equiv of cupric bromide in various solvents. Among the solvents employed, acetonitrile was found to be the most effective and the reaction was complete within 10 min at room temperature without any changes of original dark blue color. Methylene chloride and tetrahydrofuran were also effective, while diethyl ether and toluene were totally ineffective.

Table II. Effects of Metal Salt on the Rate of Ester Formation in CH_3CN[a]

metal salt[b]	ester formation (isolated yield),[c] % 10 min	1 h	2 h	6 h
$CuBr_2$	96			
$CuCl_2$	95			
$Cu(OAc)_2$	0			6 (86)
CuI	0	0	0	0 (98)
$SnCl_2$	12 (85)	84 (9)	91	
$NiBr_2$	0		5 (91)	14 (80)
$MgBr_2$	0	0		<2 (95)
$ZnCl_2$	0	0		<2 (96)

[a] All reactions were carried out at room temperature, using 1 equiv of *S*-2-pyridyl mesitothioate and 1.2 equiv of *tert*-butyl alcohol. [b] 1 equiv of each metal salt was utilized. [c] The numbers in parentheses indicate the isolated yield of the recovered *S*-2-pyridyl mesitothioate.

The relative effectiveness of various metal salts was examined in acetonitrile and is indicated in Table II. Among various metal salts employed, cupric bromide and cupric chloride were the most effective. However, cupric acetate was not effective, indicating that the counter anion plays an important role in the esterification. Stannous chloride was less effective than cupric bromide but much more effective than nickel bromide. Other metal salts such as cuprous iodide, magnesium bromide, and zinc chloride were totally ineffective and the starting material was recovered unchanged.[11]

The effect of the amount of cupric bromide was briefly studied in acetonitrile. In the absence of cupric bromide, *S*-2-pyridyl mesitothioate was not esterified to an observable extent, even after 24 h at room temperature. In the presence of 0.1 and 0.2 equiv of cupric bromide, the reaction proceeded slowly at room temperature, yielding *tert*-butyl mesitoate in the yields of 21% and 72% together with the recovery of the starting material after 24 h. However, the reaction was complete within 1 h at 80 °C in the presence of 0.2 equiv of cupric bromide, indicating that cupric ion effectively catalyzes the esterification of *S*-2-pyridyl thioates. Employment of 0.5 equiv of cupric bromide shortened the reaction time and the reaction proceeded smoothly to afford *tert*-butyl mesitoate in 95% yield at room temperature in 1.5 h.

Table III summarizes the results obtained with a number of additional *S*-2-pyridyl thioates chosen to demonstrate the effectiveness of this method. In general, the reaction was carried out with an equimolar mixture of *S*-2-pyridyl thioates and alcohols in the presence of 0.2, 0.5, and/or 1 equiv of cupric bromide in acetonitrile at room temperature and/or 80 °C. In the presence of 1 equiv of cupric bromide, the reaction proceeded rapidly and smoothly at room temperature to afford the corresponding esters in high yields. *S*-2-Pyridyl mesitothioate, upon treatment with methanol, was instantly converted into methyl mesitoate. Similar results were obtained with hindered alcohols such as mesitol and triethyl carbinol. However, it is interesting to note that the reaction of *S*-2-pyridyl benzothioate with *tert*-butyl alcohol proceeded slowly and required 7 h for completion of the reaction. *S*-2-Pyridyl thioates of tertiary aliphatic carboxylic acids such as pivalic acid and 1-adamantanecarboxylic acid were converted to the corresponding esters in high yields at

(7) (a) Gerlach, H.; Thalmann, A. *Helv. Chim. Acta* **1974**, *57*, 293. (b) Gerlach, H.; Obertle, K.; Thalmann, A.; Servi, S. *Ibid.* **1975**, *58*, 2036.

(8) For the synthetic utility of *S*-2-pyridyl thioates, see: (a) Mukaiyama, T.; Matsueda, R.; Suzuki, M. *Tetrahedron Lett.* **1970**, 1901. (b) Mukaiyama, T.; Araki, M.; Takei, H. *J. Am. Chem. Soc.* **1973**, *95*, 4763. (c) Corey, E. J.; Nicolaou, K. C. *Ibid.* **1974**, *96*, 5614. (d) Kobayashi, S.; Limori, T.; Izawa, T.; Ohno, M. *Ibid.* **1981**, *103*, 2406. (e) Kim, S.; Lee, J. I.; Chung, B. Y. *J. Chem. Soc., Chem. Commun.* **1981**, 1231. (f) Goto, T.; Onaka, M.; Mukaiyama, T. *Chem. Lett.* **1980**, 51. (g) Onaka, M.; Matsuoka, Y.; Mukaiyama, T. *Ibid.* **1980**, 905.

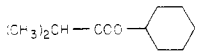
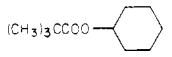
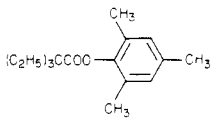
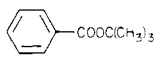
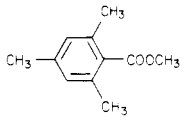
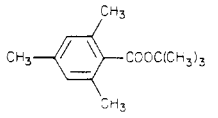
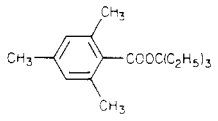
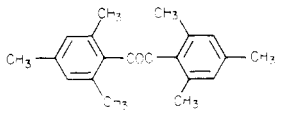
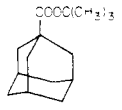
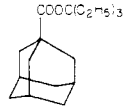
(9) For the synthetic utility of 2-pyridyl esters, see: (a) Broadbent, W.; Morley, J. S.; Stone, B. E. *J. Chem. Soc. C* **1967**, 2632. (b) Araki, M.; Sakata, S.; Takei, H.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1777. (c) Onaka, M.; Goto, T.; Mukaiyama, T. *Chem. Lett.* **1979**, 1483. (d) Kim, S.; Lee, J. I. *J. Org. Chem.* **1983**, *48*, 2608.

(10) Corey, E. J.; Clark, D. A. *Tetrahedron Lett.* **1979**, 2875.

(11) Metal salts employed in this study are readily soluble in acetonitrile except $Cu(OAc)_2$ and $NiBr_2$. Thus, it seems that the differences in effectiveness of the various metal salts do not reflect differences in their solubility in acetonitrile.

Table III. Ester Formation from *S*-2-Pyridyl Thioates and Alcohols in the Presence of $CuBr_2$ in CH_3CN[a]

$$RCO\text{-}S\text{-}2\text{-}Py + R'OH \xrightarrow[CH_3CN]{CuBr_2} RCOOR'$$

no.	ester RCOOR'	molar equiv of $CuBr_2$	temp, °C[b]	time, h	isolated yield, %
1	$CH_3(CH_2)_6COOC(CH_3)_3$	0.2	80	0.75	93
		1	rt	0.25	94
2		1	rt	0.3	92
3		0.5	rt	1.5	88
		1	rt	0.3	90
4	$(CH_3)_3CCOOC(C_2H_5)_3$	0.2	80	4	75
		0.5	rt	4	78
		1	rt	0.75	76
5	$(CH_3)_3CCOOC(C_2H_5)(CH_3)_2$	1	rt	0.5	76
6	$(C_2H_5)_3CCOOC(C_2H_5)_3$	0.2	80	4	70
		1	rt	4	72
7		0.2	80	5	72
		1	rt	5	75
8		1	rt	7	91
9		1	rt	0.1	98
10		0.2	80	1	92
		0.5	rt	1.5	95
		1	rt	0.2	96
11		0.2	80	2	82
		0.5	rt	1.5	84
		1	rt	0.25	86
12		0.2	80	2.5	91
		0.5	rt	2	89
		1	rt	0.5	96
13		0.5	rt	2	85
		1	rt	0.3	89
14		1	rt	0.75	80

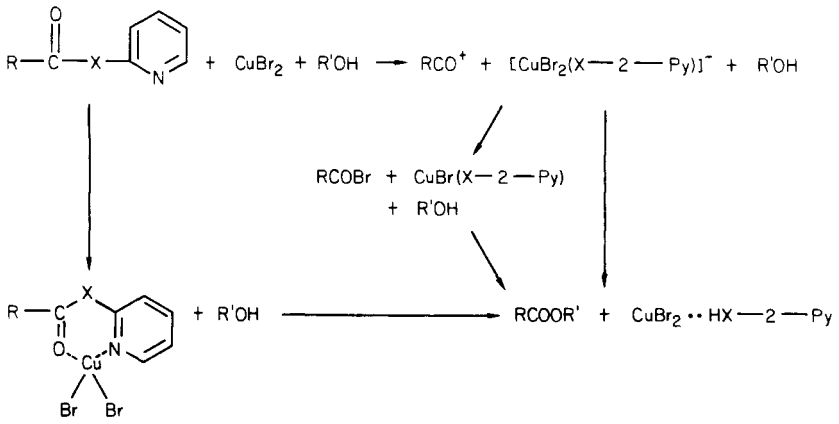
[a] All reactions were carried out with 1 equiv of (*S*)-2-pyridyl thioates and 1.2 equiv of alcohols. [b] rt = room temperature.

room temperature within 1 h. However, reaction of *S*-2-pyridyl 2,2-diethylbutanethioate with triethylcarbinol and mesitol was somewhat slower and required 4 h and 5 h, respectively. Employment of 0.5 equiv of cupric bromide resulted in the high yield formation of hindered esters at room temperature but required only longer reaction times than that of 1 equiv of cupric bromide. In the presence of 0.2 equiv of cupric bromide, the reaction required a gentle heating for completion of the reaction for a short period of time and hindered esters were obtained in high yields as shown in Table III.

In view of encourging results obtained with *S*-2-pyridyl thioates, we have studied the reaction using 2-pyridyl esters. 2-Pyridyl esters used in this study were prepared in high yields by the reaction of carboxylic acid chlorides with 2-hydroxypyridine in the presence of triethylamine or the reaction of carboxylic acids with 2-pyridyl chloroformate in the presence of triethylamine and a catalytic amount of 4-(dimethylamino)pyridine.[9d]

It was found that the reaction using 2-pyridyl esters proceeded more rapidly in acetonitrile than in methylene chloride as being observed with *S*-2-pyridyl thioates. For example, reaction of 2-pyridyl mesitoate with *tert*-butyl alcohol in the presence of 1 equiv of cupric bromide in methylene chloride at room temperature required 24 h for completion of the reaction, whereas the reaction in acetonitrile required 8 h. Thus, the remaining reactions using 2-pyridyl esters were carried out in acetonitrile. Reaction

Scheme I



X = S or O

of 2-pyridyl esters proceeded very slowly at room temperature, when compared with that of *S*-2-pyridyl thioates, and generally required a gentle heating for completion of the reaction. For example, reaction of 2-pyridyl pivalate with triethylcarbinol in the presence of 1 equiv of cupric bromide at room temperature in 24 h afforded the desired ester in only 15% yield along with the recovery of the unreacted 2-pyridyl ester in 73% yield, whereas the reaction proceeded to completion at 80 °C in 3 h. Furthermore, employment of 0.2 equiv of cupric bromide did not give good results at 80 °C in 24 h, yielding the ester in 36% yield along with the unreacted 2-pyridyl ester in 44% yield. Thus, it seems that 1 equiv of cupric bromide is required for the synthetically useful method for the preparation of hindered esters.

Table IV summarizes the results obtained with several 2-pyridyl esters in the presence of 1 equiv of cupric bromide in acetonitrile. 2-Pyridyl esters of sterically hindered aliphatic acids such as pivalic acid and triethylacetic acid, upon treatment with sterically hindered alcohols, such as *tert*-butyl alcohol, *tert*-amyl alcohol, and mesitol at 80 °C, were converted to the corresponding esters in high yields within 5 h. Reaction of 2-pyridyl mesitoate proceeded more rapidly than that of 2-pyridyl esters of sterically hindered aliphatic acids. Thus, reaction of 2-pyridyl mesitoate with sterically hindered alcohols such as *tert*-butyl alcohol and *tert*-amyl alcohol afforded the corresponding esters in high yields within 24 h at room temperature.

Although clear conclusions regarding the reaction mechanism await further study, possible mechanisms are shown in Scheme I. The reaction may proceed via the intermediacy of the six-membered chelated complex. It is expected that the formation of the chelated complex should allow very facile nucleophilic carbonyl addition by alcohols due to the polarization of the carbon–oxygen bond induced by chelation. Similar phenomena have been previously noted in the metal ion promoted hydrolysis of esters[12] and amides.[13] However, we were unable to confirm the formation of the chelated complex by spectroscopic methods. When *S*-2-pyridyl mesitothioate was treated with 1 equiv of cupric bromide in methylene chloride at room temperature for 1 h, mesitoyl bromide was isolated in 73% yield. However, in the infrared spectrum of an equimolar mixture of 2-pyridyl mesitoate and cupric bromide in methylene chloride at room temperature for 0.5 h, the intensity of the carbonyl stretching band of the original 2-pyridyl ester at 1745 cm^{-1} was decreased to some extent, while the intensity of the band at 1610 cm^{-1} was considerably increased, when compared with the infrared spectrum of 2-pyridyl mesitoate (1745 (strong), 1610 cm^{-1} (weak)). It is unclear whether the increase of the absorption at 1610 cm^{-1} results from the formation of the chelated complex or not.[14]

It seems that the greater reactivity of *S*-2-pyridyl and 2-pyridyl esters of mesitoic acid over those of benzoic acid and other aliphatic carboxylic acids suggests the importance of the acylium ion intermediate,[2,15] although clear evidence has not been obtained. Also, it was found that the reaction depended critically on the electronic effects of the substituents on *S*-2-pyridyl esters of benzoic acid. Thus, reaction of *S*-2-pyridyl *p*-methoxybenzothioate with *tert*-butyl alcohol in the presence of 1 equiv of cupric bromide in acetonitrile at room temperature required 3 h

Table IV. Ester Formation from 2-Pyridyl Esters and Alcohols in the Presence of 1 Equiv of $CuBr_2$ in CH_3CN[a]

$$\text{RCO-O-2-Py} + \text{R'OH} \xrightarrow[CH_3CN]{CuBr_2} \text{RCOOR'}$$

ester no. RCOOR'	temp, °C	time, h	isolated yield,[b] % RCOOR'
1	rt	24	65 (30)
	80	0.5	88
2	80	1.5	87
3	80	2.5	91
4	rt	24	15 (73)
	80	3	68
5	80	3	75
6	80	4	76
7	80	5	87
8	80	12	24 (55)
10	rt	8	94
	80	0.25	90
11	rt	24	84 (8)
	80	0.5	85
12	80	0.5	98

[a] All reactions were carried out with 1 equiv of 2-pyridyl esters and 1.2 equiv of alcohols. [b] The numbers in parentheses indicate the isolated yields of the recovered 2-pyridyl esters.

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for completion of the reaction, while *S*-2-pyridyl *p*-chlorobenzothioate gave only 17% of *tert*-butyl *p*-chlorobenzoate with recovery of the starting material, even after 24 h under the same reaction condition, indicating the importance of the acylium ion intermediate.[2] If the acylium ion has been produced, it must react rapidly with alcohols to afford esters or may be in part converted into acid bromides, which may be further converted into esters with the help of electrophilic catalysis of copper ion. A small involvement of the acid bromide intermediate in the reaction of *S*-2-pyridyl mesitothioate with mesitol in the presence of 1 equiv of cupric bromide was indicated by thin-layer chromatography and the infrared spectrum.

In conclusion, although the reaction mechanism has not been elucidated, the results obtained here clearly indicate that cupric bromide greatly promotes and catalyzes the reaction of *S*-2-pyridyl thioates and 2-pyridyl esters with alcohols.[16] This method appears to offer several advantages over previous methods for the preparation of hindered esters with respects to (i) an efficient high yield synthesis, (ii) the rapidity of the reaction, (iii) the mildness of the reaction, (iv) the simple workup, and (v) the use of a catalytic amount of cupric bromide with *S*-2-pyridyl thioates and should, therefore, find many useful applications in organic synthesis.

Experimental Section

NMR spectra were recorded with a Varian T-60A spectrometer, and chemical shifts are expressed as δ units relative to tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer 267 and the frequences are given in reciprocal centimeters. Melting points were determined on an Electrothermal melting point apparatus and are uncorrected. Reported boiling points are those observed during distillation with a Kugelrohr apparatus and are uncorrected. Elemental analysis were performed by Korea Research Institute of Chemical Technology. Analytical thin-layer chromatography was performed on precoated silica gel plates (0.25 nm, 60F-254, E. Merck) and silica gel (activity III, 04526, ICN) was used for column chromatography.

Since the reactions performed are all similar in many respects, typical reactions will be described as specific examples.

Preparation of Mesityl Mesitoate (12) Using *S*-2-Pyridyl Mesitothioate. To a suspended solution of *S*-2-pyridyl mesitothioate (515 mg, 2.0 mmol) and $CuBr_2$ (445 mg, 2.0 mmol) in anhydrous acetonitrile (6 mL) at room temperature was added mesitol (320 mg, 2.4 mmol). The reaction mixture was stirred at room temperature for 30 min, poured into a mixture of saturated NH_4Cl solution (20 mL) and saturated $NaHCO_3$ solution (10 mL), and extracted three times with methylene chloride (20 mL × 3). The combined extracts were dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The residue was subjected to silica gel column chromatography with methylene chloride as an eluant to yield mesityl mesitoate (542 mg, 96%).

Preparation of 3-Ethyl-3-pentyl Pivalate Using 2-Pyridyl Pivalate. To a suspended solution of 2-pyridyl pivalate (358 mg, 2.0 mmol) and $CuBr_2$ (442 mg, 2.0 mmol) in anhydrous acetonitrile (6 mL) at room temperature was added 3-ethyl-3-pentanol (280 mg, 2.4 mmol). The reaction mixture was stirred at 80 °C for 3 h, poured into a mixture of saturated NH_4Cl solution (20 mL) and saturated $NaHCO_3$ solution (10 mL), and extracted three times with methylene chloride (20 mL × 3). The combined extracts were dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The residue was purified by distillation with a Kugelrohr apparatus to yield 3-ethyl-3-pentyl pivalate (273 mg, 68%) as a colorless oil.

Preparation of Mesitoyl Bromide from *S*-2-Pyridyl Mesitothioate and $CuBr_2$. A suspension of *S*-2-pyridyl mesitothioate (513 mg, 2.0 mmol) and $CuBr_2$ (445 mg, 2.0 mmol) in anhydrous methylene chloride (8 mL) was stirred at room temperature for 1 h. Methylene chloride was evaporated under reduced pressure, and the residue was distilled with a Kugelrohr apparatus to afford mesitoyl bromide (330 mg, 73%) as a colorless oil: bp 105–112 °C (8.5 mm) [lit.[17] 150–153 °C (43 mm)]; ^1H NMR ($CDCl_3$) δ 2.35 (s, 3 H), 2.46 (s, 6 H), 6.84 (s, 2 H); IR (CH_2Cl_2) 1790 cm^{-1}.

Spectral Data of Esters. *tert*-Butyl caprylate (1): bp 55–58 °C (2 mm) [lit.[18] bp 91.5 °C (13 mm)]; ^1H NMR (CCl_4) δ 0.94–1.94 (m, 13 H), 1.57 (s, 9 H), 2.24 (t, 2 H, J = 6); IR (film) 1735 cm^{-1}.

Cyclohexyl isobutyrate (2): bp 52–54 °C (2 mm) [lit.[19] bp 204 °C (760 mm)]; ^1H NMR (CCl_4) δ 1.24 (d, 6 H, J = 7), 1.10–2.22 (m, 10 H), 2.50 (m, 1 H), 4.50–4.98 (m, 1 H); IR (film) 1730 cm^{-1}.

Cyclohexyl pivalate (3):[20] bp 45–48 °C (1.3 mm); ^1H NMR (CCl_4) δ 1.25–2.22 (m, 10 H), 1.38 (s, 9 H), 4.60–5.05 (m, 1 H); IR (film) 1730 cm^{-1}.

3-Ethyl-3-pentyl pivalate (4): bp 44–49 °C (2 mm) [lit.[3] bp 32 °C (0.5 mm)]; ^1H NMR (CCl_4) δ 0.90 (t, 9 H, J = 7), 1.21 (s, 9 H), 1.85 (q, 6 H, J = 7); IR (film) 1730 cm^{-1}.

***tert*-Amyl pivalate (5)**: bp 47–51 °C (30 mm); ^1H NMR (CCl_4) δ 0.96 (t, 3 H, J = 6), 1.20 (s, 9 H), 1.47 (s, 6 H), 1.80 (q, 2 H, J = 6); IR (film) 1725 cm^{-1}.

3-Ethyl-3-pentyl 2,2-diethylbutyrate (6): bp 73–78 °C (8 mm); ^1H NMR ($CDCl_3$)[4] δ 0.84 (t, 9 H, J = 7), 0.87 (t, 9 H, J = 7), 1.20–2.22 (m, 12 H); IR (film) 1725 cm^{-1}.

Mesityl 2,2-diethylbutyrate (7): bp 87–96 °C (0.7 mm); ^1H NMR ($CDCl_3$) δ 0.92 (t, 9 H, J = 7), 1.80 (q, 6 H, J = 7), 2.14 (s, 6 H), 2.24 (s, 3 H), 6.82 (s, 2 H); IR (film) 1745 cm^{-1}. Anal. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99. Found: C, 77.38; H, 9.59.

***tert*-Butyl benzoate (8)**: bp 69–72 °C (1.5 mm) [lit.[3] bp 88–90 °C (3 mm)]; ^1H NMR ($CDCl_3$) δ 1.60 (s, 9 H), 7.26–7.55 (m, 3 H), 7.82–8.08 (m, 2 H); IR (film) 1725 cm^{-1}.

Methyl mesitoate (9): bp 79–84 °C (2 mm) [Lit.[2] bp 116 °C (10 mm)]; ^1H NMR (CCl_4) δ 2.33 (s, 9 H), 3.82 (s, 3 H), 6.78 (s, 2 H); IR (film) 1725 cm^{-1}.

***tert*-Butyl mesitoate (10)**: bp 93–97 °C (1.6 mm) [lit.[2] bp 114 °C (2 mm)]; ^1H NMR (CCl_4) δ 1.65 (s, 9 H), 2.40 (s, 9 H), 6.80 (s, 2 H); IR (film) 1725 cm^{-1}.

3-Ethyl-3-pentyl mesitoate (11): bp 110–117 °C (1.6 mm); ^1H NMR (CCl_4)[4] δ 0.94 (t, 9 H, J = 7), 1.95 (q, 6 H, J = 7), 2.24 (s, 3 H), 2.33 (s, 6 H), 6.80 (s, 2 H); IR (film) 1720 cm^{-1}.

Mesityl mesitoate (12): mp 70–71.5 °C [lit.[2] mp 71–71.5 °C]; ^1H NMR ($CDCl_3$) δ 2.30 (s, 12 H), 2.62 (s, 6 H), 6.85 (s, 4 H); IR (KBr) 1735 cm^{-1}.

***tert*-Butyl 1-adamantanecarboxylate (13)**:[21] bp 80–84 °C (1.2 mm); ^1H NMR (CCl_4) δ 1.53 (s, 9 H), 1.70–2.26 (m, 15 H); IR (film) 1725 cm^{-1}.

3-Ethyl-3-pentyl 1-adamantanecarboxylate (14): bp 104–110 °C (1.6 mm); ^1H NMR (CCl_4) δ 1.00 (t, 9 H, J = 7), 1.70–2.40 (m, 21 H); IR (film) 1725 cm^{-1}. Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86. Found: C, 77.90; H, 11.19.

Registry No. 1, 5457-66-9; 2, 1129-47-1; 3, 29878-49-7; 4, 23293-82-5; 5, 89397-96-6; 6, 61666-32-8; 7, 89397-97-7; 8, 774-65-2; 9, 2282-84-0; 10, 1795-80-8; 11, 61666-34-0; 12, 1504-38-7; 13, 24556-20-5; 14, 89397-98-8; *S*-2-pyridyl mesitothioate, 81787-27-1; 2-pyridyl pivalate, 59658-05-8; mesitoyl bromide, 67958-02-5; *tert*-butyl alcohol, 75-65-0; cupric bromide, 7789-45-9; *S*-2-pyridyl thiocaprylate, 89397-99-9; *S*-2-pyridyl isothiobutyrate, 81357-56-4; *S*-2-pyridyl thiopivalate, 81357-57-5; *S*'-2-pyridyl 2,2-diethylthiobutyrate, 89398-00-5; *S*-2-pyridyl benzoate, 10002-30-9; *S*-2-pyridyl 1-adamantanecarboxylate, 89398-01-6; 1,1-diethylpropanol, 597-49-9; 2-methyl-2-butanol, 75-85-4; mesityl alcohol, 527-60-6; 2-pyridyl octanoate, 89398-02-7; 2-pyridyl isobutyrate, 86014-54-2; 2-pyridyl 2,2-diethylbutyrate, 89398-03-8; 2-pyridyl benzoate, 5005-35-6; $CuCl_2$, 7447-39-4.

(16) Although the fate of Cu(II) has not been fully determined, it is evident that Cu(II) is not reduced to Cu(I) due to the facts of the catalysis of Cu(II), the ineffectiveness of Cu(I), and no color change in the esterification. It is believed that Cu(II) forms the complex with 2-mercaptopyridine or 2-hydroxypyridine as shown in Scheme I, which is readily soluble in acetonitrile and aqueous solution.

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