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Conversion of Hydroxyl Groups in Alcohols to Other Functional Groups with *N*-Hydroxy-2-thiopyridone, and Its Application to Dialkylamines and Thiols

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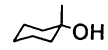
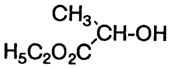
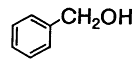
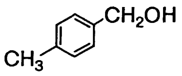
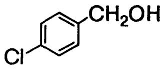
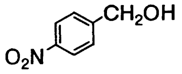
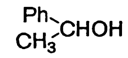
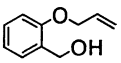
The radical decarboxylation reaction of *N*-alkoxyoxalyloxy-2-thiopyridone which was prepared by the reaction of alcohol, oxalyl chloride, and *N*-hydroxy-2-thiopyridone was studied both in the absence and presence of olefinic compounds. The same reactions with olefinic and acetylenic alcohols gave the corresponding lactone derivatives. On the other hand the unsymmetrical alkyl 2-pyridyl disulfides were obtained by the same reaction with aliphatic thiols.

Recently, free radical reactions have been used in organic synthesis extensively and their high functional abilities have been recognized.[1] In those reactions, Barton's method which is the radical decarboxylation reaction of thiohydroxamic esters (*O*-acyl derivatives of *N*-hydroxy-2-thiopyridone) prepared from carboxylic acid chlorides and *N*-hydroxy-2-thiopyridone, is very attractive because both the reaction procedure and the purification of the reaction products are simple.[2] We studied this reaction for intermolecular carbon–carbon bond formation with olefinic compounds previously.[3] On the other hand a few reports on the same radical decarboxylative reaction with alcohols instead of carboxylic acids have been known.[4] But in those reports, the reactions only with tertiary alcohols were studied and detailed study was not carried out.

As the applications of this decarboxylation reaction to other functional groups instead of carboxylic acids, herein we report the reactions with alcohols, amines, and thiols.

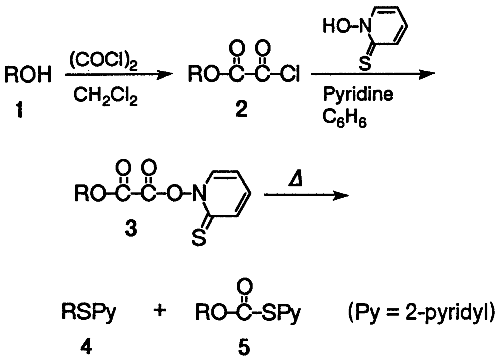
Table 1. Decarboxylative Reaction of Alcohols **1** to Sulfide **4** and S-2-Pyridyl Thiocarbonate **5**[a)]

	ROH	Solvent	Reaction time/min	Yield **4**/%	Yield **5**/%
1a	$CH_3(CH_2)_7$–OH	Benzene	60	<3	60
		Toluene	30	8	65
		Chlorobenzene	10	12	34
1b	*c*-C_6H_{11}–OH	Benzene	60	11	48
1c		Benzene	60	41	4
1d	 $CH_3CH(OH)CO_2C_2H_5$	Benzene	60	47	—
1e		Toluene	30	50	0
1f		Benzene	60	54	0
1g		Benzene	60	53	0
1h		Benzene	60	68	0
1i	 $PhCH(CH_3)OH$	Toluene	30	47	0
1j		Benzene	90	58	0
1k	CH_3CH_2OH	Benzene	60	0	59[b)]
		Dichloromethane[c)]	40	0	75

a) The reaction was carried out in refluxing conditions. b) Diethyl oxalate and 2,2′-dipyridyl disulfide were obtained in 26 and 34% yields, respectively. c) The reaction was carried out under irradiation conditions (500 W tungsten lamp) at −16—−18 °C.

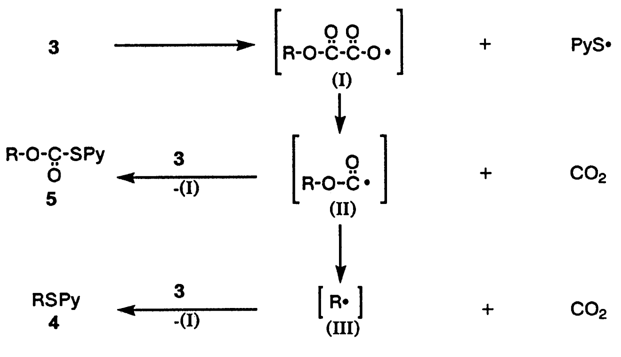
Results and Discussion

I). The Reaction with Saturated Alcohols. At first, when the reaction was carried out with 1-octanol we obtained both compounds; **4a** as a minor product and **5a** as a major product. The mixed diester **3**, which is prepared in situ from the corresponding alcohol, oxalyl chloride, and *N*-hydroxy-2-thiopyridone, is so unstable that it is hydrolyzed on silica gel TLC plate easily and completely. But **3** can be observed both by NMR and IR measurements as a crude state. Thus **3k** which was prepared from ethyl chloroglyoxylate with *N*-hydroxy-2-thiopyridone at 0 °C was obtained as a yellow oil, which was unstable on TLC, sunlight, and heat. The compound (**3k**) had two characteristic carbonyl absorptions in its IR spectrum and gave ethyl *S*-2-pyridyl thiocarbonate (**5k**) by heating in benzene. The same reaction was carried out with some primary, secondary, tertiary, and benzylic alcohols as shown in Table 1.



(1)

The reaction probably proceeds as follows: Cleavage of N–O bond[2] of ester (**3**) followed by decarboxylation gives alkoxycarbonyl radical (**II**). In the case of primary and secondary alcohols, the dissociation energies of C–O bond are large as compared with those of tertiary and benzylic alcohols.[5] Thus the major product of the former two compounds is a *S*-2-pyridyl thiocarbonate, while that of the latter two compounds is a 2-pyridylthio compound. Especially in both benzylic alcohols and α-hydroxyester, the corresponding 2-pyridylthio compounds **4** were formed dominantly. The result in the reaction with **3j** suggests that the formed benzylic radical does not cyclize to give chroman derivative because of the high stability of benzylic radical.

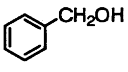
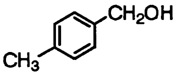
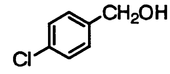
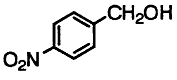
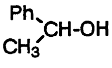


Scheme 1.

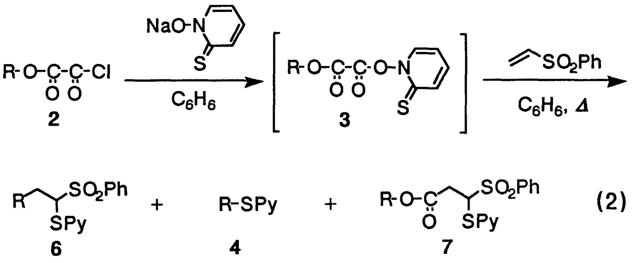
II). Inter- and Intramolecular Carbon-Carbon Bond Formations. Then, we attempted carbon–carbon bond formation starting from alcohol via alkoxycarbonyl radical (**II**) or alkyl radical (**III**) in the presence of phenyl vinyl sulfone. The reaction was carried out by dropping of the prepared chloroglyoxylic ester (**2**) to the mixture of sodium salt of *N*-hydroxy-2-thiopyridone and phenyl vinyl sulfone in refluxing benzene. The results were shown in Table 2.

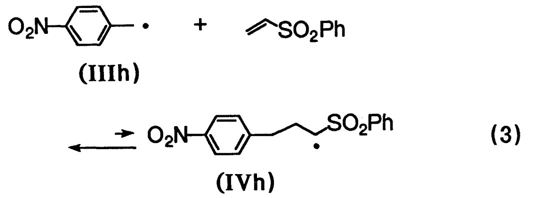
In the case of cyclohexanol, the major product was **7**, which was formed by the reaction of decarboxylated radical (**II**) with phenyl vinyl sulfone. While the activated alcohol like benzyl alcohol gave **6** as a major product by the reaction of double decarboxylated radical (**III**) with phenyl vinyl sulfone. But, in *p*-nitrobenzyl alcohol (**1h**), *p*-nitrobenzyl 2-pyridyl sulfide was obtained as a sole product. The reason is that the addition reaction of (**IIIh**) onto phenyl vinyl sulfone is reversible as shown in Eq. 3 and its equilibrium declines to left-hand side probably because the high stability of (**IIIh**) as compared with the adduct radical (**IVh**). Next we tried to trap the formed benzyloxycarbonyl radical with 5-*exo* cyclization method starting from **1l**. But the 5-*exo*-trig cyclized lactone derivative (**9l**) was not obtained (Eq. 4). This result suggests that the rate of decarboxylation reaction of (**II**) to (**III**) in benzylic alcohols is perhaps over $>10^5\ \mathrm{s}^{-1}$.[6]

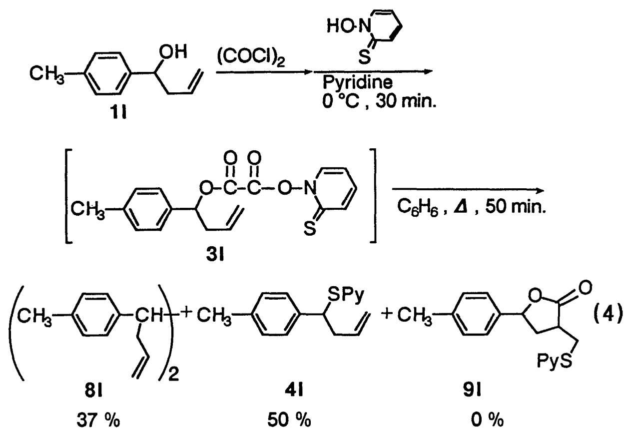
Table 2. Intermolecular Carbon–Carbon Bond Formation[a]

	R–OH	Yield **6**/%	Yield **4**/%	Yield **7**/%
1b		18	0	>80[b]
1e		45	9	0
1f		58	—	0
1g		60	13	0
1h		0	>95	0
1i		44	12	0

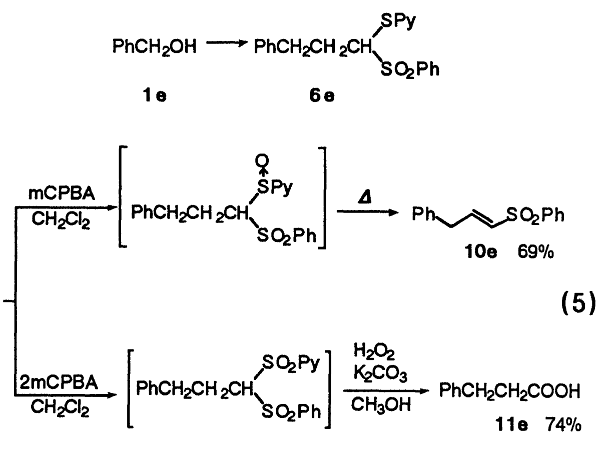
a) The yields were determined by NMR. b) Without H_2NNH_2 treatment.







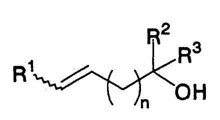
Adduct (**6e**) in Table 2 was converted to the other useful compounds as shown in Eq. 5. Particularly the conversion to carboxylic acid (**11e**) is equivalent to the preparation of C_2-gained carboxylic acid from alcohol.



As mentioned above, the alkoxycarbonyl radical (**II**) formed from non-activated alcohol like primary and secondary alcohols does not decarboxylate to give (**III**). This result suggests that the formed alkoxycarbonyl radical (**II**) can be captured by olefinic groups via intra- and intermolecular carbon-carbon bond formation. Thus, when we carried out this reaction with 3-buten-1-ol (**1m**),[7] the γ-butyrolactone derivative (**12m**), which was a very important component for the synthesis of natural products,[8] was obtained in a moderate yield via intramolecular radical cyclization (5-*exo*-trig) as shown in Table 3 and Scheme 2.

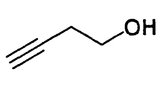
A similar kind of reaction, which was the formation of α-methylene-γ-butyrolactone derivatives by the

Table 3. Reactions of Mediated Alkenyloxycarbonyl Radicals[a)]

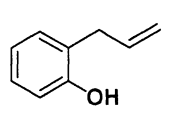


1

m: n=1, $R^1=R^2=R^3=H$
n : n=1, $R^1=C_2H_5$, $R^2=R^3=H$
o: n=1, $R^1=R^2=H$, $R^3=CH_3$
p: n=1, $R^1=H$, $R^2=R^3=C_2H_5$
q: n=2, $R^1=R^2=R^3=H$
t : n=1, $R^1=R^2=H$, $R^3=CH_2$=$CH(CH_2)_8$



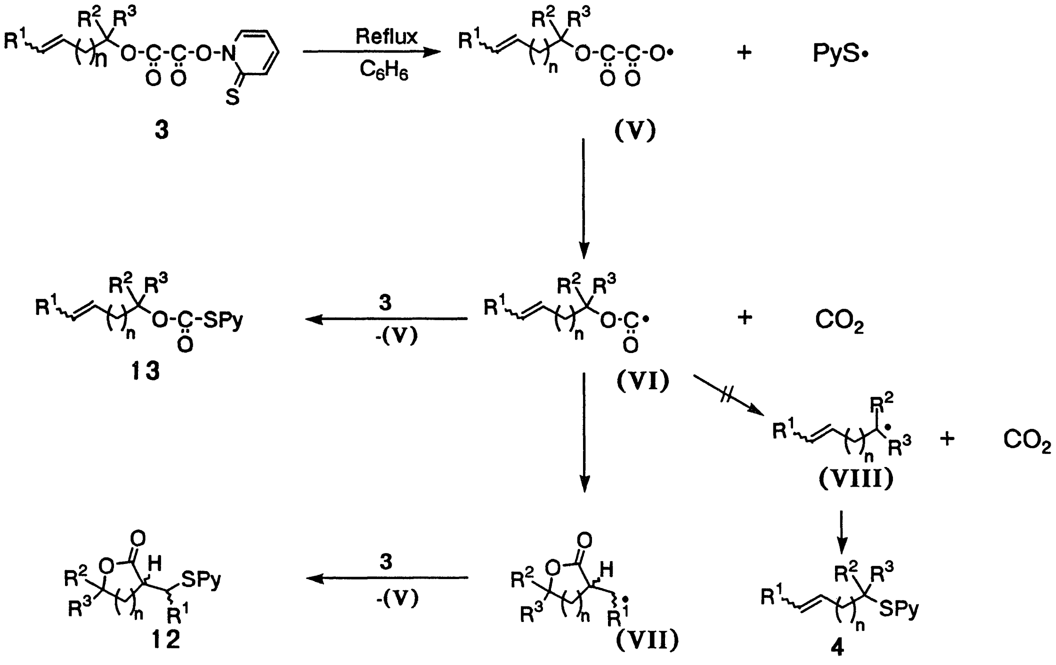
1r



1s

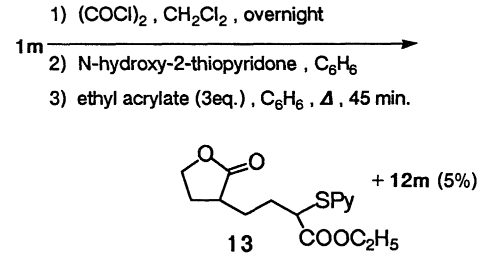
Substrate (2 mmol)	$(COCl)_2$/ml	Lactone **12**/%	S-2-Pyridyl thiocarbonate **5**/%
1m	0.8	42	1
1m	1.0	51	5
1m	1.5	46	4
1n-*trans*	1.0	71 (*RS*,*SR*):(*RR*,*SS*)=29:71	7
1n-*cis*	1.0	74 (*RS*,*SR*):(*RR*,*SS*)=29:71	6
1o	1.0	51 (ratio=34:66)	4
1p	1.0	43	—
1q	1.0	0	48
1q	1.0[b)]	18	23
1r	1.0	40 (cis)	8
1s	1.0	41	—
1t	1.0	69 (ratio=34:66)	4

a) The reactions were carried out in benzene for 1 h. b) Dropping procedure of chloroglyoxylic ester of **1** into the sodium salt of *N*-hydroxy-2-thiopyridone over 4 h was used.



Scheme 2. Reaction Pathway (n=1, 2)

reaction of chloroformates, *Se*-phenyl selenocarbonates, and *S*-methyl dithiocarbonates of homopropargylic alcohol derivatives with Bu_3SnH[9] and Bu_3SnH/Et_3B[10], was reported recently. But in our system, γ-butyrolactone derivatives can be obtained in one pot reaction from olefinic and acetylenic alcohols, and further this reaction does not require the toxic organotin compounds. γ-Butyrolactone derivatives (**12o** and **12p**) could be also obtained in moderate yields from sec- and tert-alcohols (**1o** and **1p**), respectively. Then, the obtained lactone (**12m**) was oxidized with mCPBA (1.1 equiv) and the sulfoxide thus formed was heated at about 100 °C under reduced pressure to give α-methylene-γ-butyrolactone in 49% yield, which was tulipalin A isolated from tulip bulbs.[11] Both *trans* and *cis* isomers of 3-hexen-1-ol (**1n**) gave **12n** in good yields and the ratios of the formed diastereomers of **12n** in both reactions were same. This result suggests that both reactions proceed via the same intermediate (**VIIn**) to give **12n**. While, the use of 4-penten-1-ol (**1q**) yielded *S*-2-pyridyl thiocarbonate (**5q**) as a sole product. This result can be explained by the big difference in the cyclization rates between 3-butenoxycarbonyl radical (**VIm**) and 4-pentenoxycarbonyl radical (**VIq**). Thus, the difference is deduced from the cyclization rates of 5-hexenyl radical (k=2.3×10^5 s^{-1} at 25 °C) and 6-heptenyl radical (k=5.4×10^3 s^{-1} at 25 °C), respectively.[12] However, the formation of δ-valerolactone could be accelerated by adding dropwise a chloroglyoxylic ester (**2q**) (chloroglyoxylic ester of **1q**) to the sodium salt of *N*-hydroxy-2-thiopyridone in benzene. By this procedure, δ-valerolactone was obtained in 18% yield. While 3-propanolide could not be obtained from allyl alcohol.



(6)

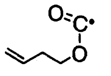
Further, the present reaction was carried out in the presence of ethyl acrylate to give an ester (**13**) in 40% yield, which was formed via both intra- and intermolecular radical reactions, along with **12m**. Finally α-pyridylthiomethylene-γ-butyrolactone was obtained in 40% yield from 3-butyn-1-ol (**1r**) by this system.

The formations of **12o** and **12p** mean that the formed carbonyl radicals (**VIo**) and (**VIp**) cyclize before the decarboxylation to alkenyl radicals (**VIIIo**) and (**VIIIP**), and therefore the sulfides (**4**) were not formed. While, in these reactions the small amount (≤10%) of dialkenyl oxalates were observed after the reaction. Most of these products were formed by radical coupling reaction[13] of alkenoxycarbonyl radicals (**VI**) because they were not formed during the preparation of **3**. The same reaction was carried out with diethylamine and *N*-(3-butenyl)aniline. In the former reaction, **15**, an *N*-analogue compound of **5**, was obtained in good yield in the presence of triethylamine. While the latter amine gave the cyclized

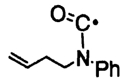
Table 4. Reactions of Mediated Carbamoyl Radicals[a]

	RR′NH **14**	Base	RR′N-C(=O)-SPy **15**/%	γ-Lactam **16**/%
a	Et_2NH (2 mmol)	—	20	—
	Et_2NH (4 mmol)	C_5H_5N (2 mmol)	39	—
	Et_2NH (6 mmol)	C_5H_5N (2 mmol)	53	—
	Et_2NH (3 mmol)	Et_3N (5 mmol)	80	—
b	PhMeNH (6 mmol)	—	71	—
c	 NHPh (6 mmol)	—	39	12
	 NHPh (6 mmol)	Dropping procedure[b]	35	20

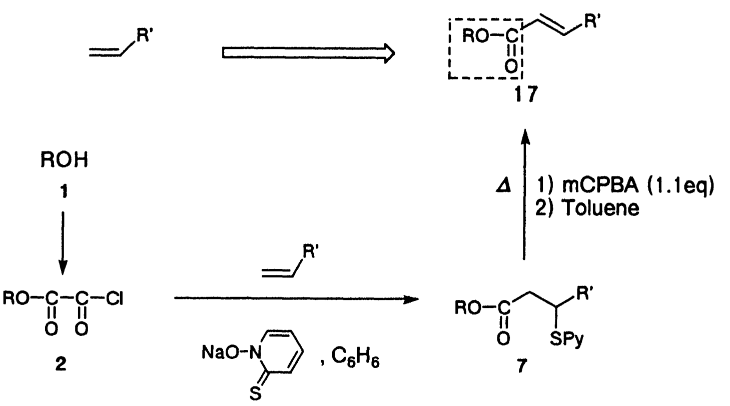
a) The reactions were carried out in benzene for 1 h and the yields were calculated based on 2 mmol of *N*-hydroxy-2-thiopyridone. b) Dropping procedure of diethylamidooxalyl chloride into the sodium salt of *N*-hydroxy-2-thiopyridone over 4.5 h was used.



(IX)

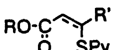
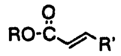
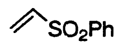
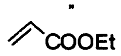
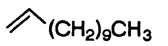


(X)



Scheme 3. Intermolecular Radical Reaction with Olefins

Table 5. Reactions of Mediated Alkoxycarbonyl Radical with Olefin[a]

	ROH 1		 (or ≡—R′)		 7 (%)	 5 (%)	 17 (%)
a	*n*-$C_8H_{17}OH$			(3 equiv)	70	0	92
b	*c*-$C_6H_{11}OH$		▪	(5 equiv)	80	—	66
k	C_2H_5OH	i)	▪	(3 equiv)	70	0	84
			▪	(3 equiv)	42[b]	42	—
		ii)		(3 equiv)	40	—	70
			▪	(3 equiv)	35[b]	41	—
		iii)		(3 equiv)	34	27	49
		iv)		(3 equiv)	31	36	68
		v)	$HC\equiv C\text{-}(CH_2)_4CH_3$	(3 equiv)	3	51	—
		vi)	$HC\equiv C\text{-}Ph$	(3 equiv)	11	34	—

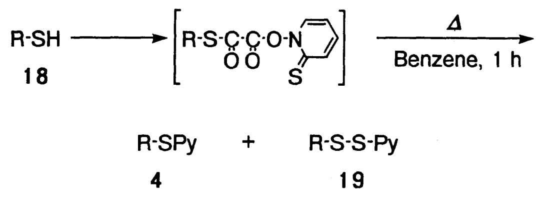
a) Dropping procedure of chloroglyoxylic ester of **1** into the sodium salt of *N*-hydroxy-2-thiopyridone over 1 h was used. b) *hν*/0 °C.

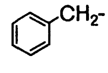
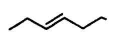
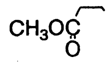
product (**16**), a γ-lactam derivative, but the yield was low. Even when the dropping procedure of dialkylamidooxalyl chloride to *N*-hydroxy-2-thiopyridone in benzene was employed, the major product was **15**. So, we believe that the cyclization rate of (**IX**) is larger than that of (**X**).

Then we carried out this reaction in the presence of olefinic compound. If the adduct compound (**7**) could be obtained, it would be easily converted to α,β-unsaturated ester (**17**) as shown in Scheme 3. Practically, the alkoxycarbonyl radical (**II**) formed from alcohol (Scheme 1), reacted with some olefinic compounds to give the corresponding adducts (**7**) in good to moderate yields depending upon the olefinic compounds via intermolecular radical addition reaction.

The results in Table 5 suggests that the alkoxycarbonyl radical is nucleophilic. Therefore the yield of addition product with phenyl vinyl sulfone was high, while that with 1-dodecene was lower. These obtained compounds (**7**) were oxidized by mCPBA to give the corresponding sulfoxides which were then heated in benzene to give α,β-unsaturated esters (**17**) in good yields.

Table 6. Decarboxylative Reactions of Thiols

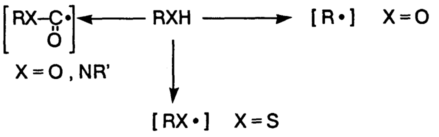


	18 R-	4	19
b		—	40[a)]
e		25	5
n		—	50[a)]
t		—	38[a)]

a) RSSR was obtained ca. 10%.

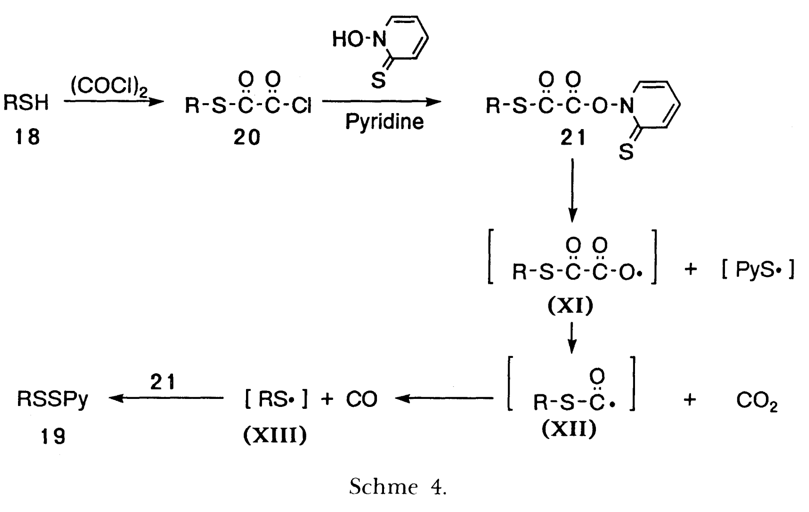
III). The Reaction with Thiols. We also studied the radical decarboxylative reaction with thiols. Phenylmethanethiol (**18e**) gave benzyl 2-pyridyl sulfide (**4e**) as a main product like benzyl alcohol. While, cyclohexanethiol (**18b**) and methyl 3-mercaptopropionate (**18t**) gave the corresponding unsymmetrical disulfides (**19b** and **19t**) which disproportionated slowly to two symmetrical disulfides respectively.

This result suggests that the formed alkylthiocarbonyl radical easily decomposes to give alkylthio radical (**XIII**) and carbon monooxide. Even when the reaction was carried out with 3-hexene-1-thiol, the major product was the corresponding unsymmetrical disulfide (**19n**). Therefore, the fragmentation reaction of (**XII**) to (**XIII**) should be extremely fast.



(7)

In conclusion, the radical decarboxylative reactions of *N*-alkoxyoxalyloxy-2-thiopyridones which were prepared from activated alcohols, oxalyl chloride, and *N*-hydroxy-2-thiopyridone gave the corresponding sulfides or C–C bonded compounds in the presence of olefinic compounds. On the other hand those reactions with general prim-, sec-, tert-alcohols, and dialkylamines gave the corresponding *S*-2-pyridyl thiocarbonates and thiocarbamates respectively, and the cyclized products, γ-lactones and γ-lactams were obtained starting from 3-olefinic alcohols or amines in one-pot reaction via intramolecular radical cycliza-



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tion. And further the intermolecular radical addition reactions with alcohols onto olefins gave the adducts which were easily converted to the α,β-unsaturated esters. On the other hand, the reactions with thiols gave the unsymmetrical disulfides via alkylthio radical.

Experimental

Microanalyses were performed with a Perkin–Elmer 240 elemental analyser at the Chemical Analysis Center of Chiba University. IR and ^{1}H NMR spectra were measured with Hitachi 215, JEOL-MH-100, JEOL-JNM-FX270, and JEOL-GSX-500 spectrometers, respectively. Wakogel C-200 was used for column chromatography, Kieselgel 60 F_{254} (Merck) was used for TLC, and Wakogel B-5F was used for preparative TLC (pTLC).

N-hydroxy-2-thiopyridone is commercially available as aqueous solution of sodium salt (sodium omadine). This solution (100 ml) was treated with concd HCl at pH 2, and the formed precipitates were separated by filtration and recrystallized from methanol. Sodium salt of *N*-hydroxy-2-thiopyridone was prepared as follows. To the ice-cold solution of *N*-hydroxy-2-thiopyridone (50 mmol) in methanol (100 ml) was added the ice-cold solution of sodium hydroxide (50 mmol) in methanol (100 ml). Then solvent was removed and the residue was washed with benzene and dried with vacuum pump.

1) The Preparation of *N*-Ethoxyoxalyloxy-2-thiopyridone 3k. To ethyl chloroglyoxylate (3.2 mmol) in benzene (7 ml) were added *N*-hydroxy-2-thiopyridone (3 mmol) and pyridine (4 mmol) dissolved in benzene (3 ml) under cooling by ice bath. Then the reaction mixture was stirred at 0 °C for 30 min. During this reaction, the reaction vessel was wrapped with aluminium foil tightly. Then, the reaction mixture was filtered quickly and the filtrate was evaporated to give **3k** as a yellow oil in quantitative yield.

3k: Oil; ^{1}H NMR ($CDCl_3$) δ=1.40 (t, 3H, J=6.7 Hz, $-CH_3$), 4.40 (q, 2H, J=6.7 Hz, $-CH_2-$), 7.00—7.30 (m, 2H, aromatic-4, 5H), 7.72 (dd, 1H, J=7.6, 2.7 Hz, aromatic-3H), 8.10 (dd, 1H, J=6.1, 2.7 Hz, aromatic-6H); IR (NaCl) 1810, 1730—1760 cm^{-1}.

2) General Procedure for the Conversion of Alcohol to 2-Pyridyl Sulfide. A solution of alcohol (2 mmol) in dichloromethane (2 ml) was added to a mixture of oxalyl chloride (1 ml, 11 mmol) and dichloromethane (3 ml). After keeping at room temperature overnight, the excess chloride and solvent were removed by evaporation. Then, the reaction vessel was wrapped with aluminium foil tightly, and benzene (3 ml), *N*-hydroxy-2-thiopyridone (2.1 mmol), and pyridine (3 mmol) in benzene (2 ml) were added successively at 0 °C. After stirring at 0 °C for 30 min, the obtained yellow solution was refluxed for one hour. Then the solvent was removed and the residue was washed with water and purified by pTLC. (eluent; $CHCl_3$). The reaction with thiols was carried out by using the same procedure.

4a: Oil; ^{1}H NMR (CCl_4) δ=0.85 (t, 3H, J=6.1 Hz, $-CH_3$), 1.20—1.80 (m, 12H, $-(CH_2)_2-$), 3.10 (t, 2H, J=7.6 Hz, $-CH_2S$), 6.70—7.40 (m, 3H, Py-3, 4, 5H), 8.30 (d, 1H, J=6.1 Hz, Py-6H); IR (NaCl) 2900, 2840, 1575, 1553 cm^{-1}.

Found: C, 69.40; H, 9.41; N, 5.76%. Calcd for $C_{13}H_{21}NS$: C, 69.90; H, 9.48; N, 6.27%.

4d: Oil; ^{1}H NMR (CCl_4) δ=1.19 (t, 3H, J=6.6 Hz, $-CH_3$), 1.58 (d, 3H, J=7.5 Hz, $-CH_3$), 4.06 (q, 2H, J=6.6 Hz, $-CH_2$), 4.55 (q, 1H, J=7.5 Hz, $-CH$), 6.76—7.14 (m, 2H, Py-4, 5H), 7.25—7.46 (m, 1H, Py-3H), 8.22 (b, 1H, Py-6H); IR (NaCl) 1725, 1580, 1417, 1260, 1165, 1130 cm^{-1}.

Found: C, 56.73; H, 6.17; N, 6.58%. Calcd for $C_{10}H_{13}NO_2S$: C, 56.84; H, 6.20; N, 6.63%.

4g: Oil; ^{1}H NMR (CCl_4) δ=4.56 (s, 2H, $-CH_2$), 6.70—7.36 (m, 8H, aromatic), 8.24 (d, 1H, J=4.5 Hz, Py-6H); IR (NaCl) 1570, 1488, 1410, 1120 cm^{-1}.

Found: C, 61.06; H, 4.30; N, 5.87%. Calcd for $C_{12}H_{10}ClNS$: C, 61.14; H, 4.28; N, 5.94%.

4h: Mp 61—63 °C; ^{1}H NMR (CCl_4) δ=4.37 (s, 2H, $-CH_2$), 6.74—7.04 (m, 2H, Py-4, 5H), 7.20—7.50 (m, 3H, aromatic), 7.90 (d, 2H, J=9.0 Hz, aromatic), 8.24 (d, 1H, J=5.4 Hz, Py-6H); IR (KBr) 1575, 1515, 1415, 1350, 1130 cm^{-1}.

Found: C, 58.66; H, 4.15; N, 11.18%. Calcd for $C_{12}H_{10}N_2O_2S$: C, 58.52; H, 4.09; N, 11.38%.

4i: Oil; ^{1}H NMR (CCl_4) δ=1.68 (d, 3H, J=7.5 Hz, $-CH_3$), 5.06 (q, 1H, J=7.5 Hz, $-CH$), 6.68—7.52 (m, 8H, aromatic), 8.26 (d, 1H, J=4.1 Hz, Py-6H); IR (NaCl) 1575, 1552, 1412, 1123 cm^{-1}.

Found: C, 72.49; H, 6.11; N, 6.26%. Calcd for $C_{13}H_{13}NS$: C, 72.52; H, 6.09; N, 6.51%.

4j: Oil; ^{1}H NMR (CCl_4) δ=4.38 (s, 2H, $-CH_2$), 4.48 (d, 2H, J=3.6 Hz, OCH_2), 5.24 (m, 2H, $=CH_2$), 5.74—6.08 (m, 1H, $-CH=$), 6.58—7.38 (m, 7H, aromatic), 8.28 (d, 1H, J=4.6 Hz, Py-6H); IR (NaCl) 1595, 1575, 1552, 1490, 1412, 1250, 1125 cm^{-1}.

Found: C, 69.52; H, 6.00; N, 4.18%. Calcd for $C_{15}H_{15}NOS$: C, 70.01; H, 5.88; N, 5.44%.

5a: Oil; ^{1}H NMR (CCl_4) δ=0.90 (t, 3H, J=6.1 Hz, $-CH_3$), 1.16—1.45 (m, 10H, $-(CH_2)_5-$), 1.45—1.80 (m, 2H, $-CH_2-$), 4.20 (t, 2H, J=6.1 Hz, $-OCH_2-$), 7.10 (t, 1H, J=6.2 Hz, Py-5H), 7.40—7.75 (m, 2H, Py-3, 4H), 8.40 (d, 1H, J=5.5 Hz, Py-6H); IR (NaCl) 2900, 2840, 1720, 1160, 1115 cm^{-1}.

Found: C, 62.68; H, 7.84; N, 5.16%. Calcd for $C_{14}H_{21}NO_2S$: C, 62.89; H, 7.92; N, 5.24%.

5b: Oil; ^{1}H NMR (CCl_4) δ=1.04—2.04 (m, 10H, $-(CH_2)_5-$), 4.72 (b, 1H, $-CH$), 6.90—7.18 (m, 1H, Py-5H), 7.38—7.77 (m, 2H, Py-3, 4H), 8.38 (d, 1H, J=4.5 Hz, Py-6H); IR (NaCl) 1570, 1560, 1420, 1170, 1112 cm^{-1}.

Found: C, 61.02; H, 6.44; N, 5.84%. Calcd for $C_{12}H_{15}NO_2S$: C, 60.73; H, 6.37; N, 5.90%.

5c: Oil; ^{1}H NMR (CCl_4) δ=1.04—1.74 (m, 11H, $-CH_3$ and cyclohexyl), 1.99—2.30 (m, 2H, cyclohexyl), 6.92—7.10 (m, 1H, Py-5H), 7.34—7.70 (m, 2H, Py-3, 4H), 8.26 (d, 1H, J=4.5 Hz, Py-6H); IR (NaCl) 1720, 1572, 1560, 1422, 1182, 1115 cm^{-1}.

5k: Oil; ^{1}H NMR ($CDCl_3$) δ=1.25 (t, 3H, J=7.6 Hz, $-CH_3$), 4.28 (q, 2H, J=7.6 Hz, $-CH_2-$), 7.10—7.30 (m, 1H, Py-5H), 7.72—7.60 (m, 2H, Py-3, 4H), 7.50 (d, 1H, J=6.1 Hz, Py-6H); IR (NaCl) 1720, 1150, 1115 cm^{-1}.

Found: C, 52.08; H, 5.00; N, 7.52%. Calcd for $C_8H_9NSO_2$: C, 52.44; H, 4.95; N, 7.64%.

19b: Oil; ^{1}H NMR (CCl_4) δ=1.08—2.12 (m, 10H, $-(CH_2)_5-$), 2.60—2.98 (br, 1H, CH), 6.77—7.02 (m, 1H, Py-5H), 7.30—7.70 (m, 2H, Py-3, 4H), 8.22 (d, 1H, J=4.5 Hz, Py-6H); IR (NaCl) 1570, 1560, 1418, 1122 cm^{-1}.

Found: C, 58.57; H, 6.74; N, 6.20%. Calcd for $C_{11}H_{15}NS_2$: C, 58.62; H, 6.71; N, 6.22%.

19e: Oil; ^{1}H NMR (CCl_4) δ=3.92 (s, 2H, $-CH_2$), 6.72—7.34 (m, 8H, Ph, Py-3, 4, 5H), 8.20 (d, 1H, J=4.5 Hz, Py-6H);

IR (NaCl) 1560, 1392, 1412, 1115 cm^{-1}.

19t: Oil; ^{1}H NMR (CCl_4) δ=2.55—3.06 (m, 4H, $-CH_2CH_2-$), 3.60 (s, 3H, $-CH_3$), 6.76—6.96 (m, 1H, Py-5H), 7.34—7.60 (m, 2H, Py-3, 4H), 8.26 (d, 1H, J=4.5 Hz, Py-6H); IR (NaCl) 1732, 1570, 1560, 1418, 1360, 1250, 1150, 1120 cm^{-1}.

Found: C, 47.00; H, 4.88; N, 6.04%. Calcd for $C_9H_{11}NO_2S_2$: C, 47.13; H, 4.83; N, 6.11%.

19n: Oil; ^{1}H NMR ($CDCl_3$) δ=0.95 (t, 3H, J=7.6 Hz, $-CH_3$), 1.80—2.10 (m, 2H, $-CH_2-$), 2.20—2.50 (m, 2H, $-CH_2-$), 2.85 (t, 2H, J=7.6 Hz, $-SCH_2-$), 5.35—5.60 (m, 2H, $-CH=CH-$), 6.90—7.20 (m, 1H, Py-5H), 7.40—7.80 (m, 2H, Py-3, 4H), 8.50 (d, 1H, J=4.5 Hz, Py-6H); IR (NaCl) 1560, 1442, 1416, 1120 cm^{-1}.

Found: C, 59.24; H, 7.09; N, 5.51%. Calcd for $C_{11}H_{15}NS_2$: C, 58.62; H, 6.71; N, 6.22%.

3) Typical Procedure for the C–C Bond Formation. A solution of a chloroglyoxylic ester (**2**) (2 mmol) prepared as described above in benzene (8 ml) was added dropwise to the refluxing solution of sodium salt of *N*-hydroxyl-2-thiopyridone (2.1 mmol) and phenyl vinyl sulfone (10 mmol) in benzene (4 ml) over one hour. After the addition, refluxing was continued for one hour. Then the solvent was removed and the residue was diluted with THF (16 ml) and hydrazine (1.6 g) was added at 0 °C. After the addition, the ice bath was removed and the solution was stirred at room temperature for 10 min. Then the solvent was removed by evaporation and the residue was chromatographed on silica gel (eluent; CH_2Cl_2:Et_2O=9:1).

6b: Mp 78.2—79.5 °C; ^{1}H NMR (CCl_4) δ=0.64—2.34 (m, 13H, cyclohexyl), 5.53 (dd, 1H, J=12.0, 3.6 Hz, CH), 6.62—6.91 (m, 3H, aromatic), 7.03—7.34 (m, 5H, aromatic), 7.60—7.84 (m, 2H, aromatic), 8.06 (d, 1H, J=4.5 Hz, Py-6H); IR (Nujol) 1575, 1555, 1420, 1380, 1310, 1300, 1155 cm^{-1}.

6e: Mp 85.0—86.0 °C; ^{1}H NMR (CCl_4) δ=1.78—3.06 (m, 4H, $-CH_2CH_2-$), 5.50 (dd, 1H, J=10.5, 3.6 Hz, CH), 6.58—7.32 (m, 11H, aromatic), 7.58—7.80 (m, 2H, aromatic), 7.84—8.06 (m, 1H, Py-6H); IR (KBr) 1570, 1415, 1305, 1290, 1145, 1125 cm^{-1}.

Found: C, 64.97; H, 5.20; N, 3.80%. Calcd for $C_{20}H_{19}NO_2S_2$: C, 65.01; H, 5.18; N, 3.79%.

6f: Mp 88.2—89.5 °C; ^{1}H NMR (CCl_4) δ=2.22 (s, 3H, $-CH_3$), 2.34—3.02 (m, 4H, $-CH_2CH_2-$), 5.50 (dd, 1H, J=10.5, 3.0 Hz, CH), 6.58—7.43 (m, 10H, aromatic), 7.36—7.77 (m, 2H, $PhSO_2$-2, 6H), 7.95 (d, 1H, J=4.5 Hz, Py-6H); IR (KBr) 1570, 1560, 1515, 1415, 1305, 1290, 1150, 1120 cm^{-1}.

Found: C, 65.64; H, 5.51; N, 3.60%. Calcd for $C_{21}H_{21}NO_2S_2$: C, 65.75; H, 5.52; N, 3.65%.

6g: Mp 90.7—91.5 °C; ^{1}H NMR (CCl_4) δ=1.88—3.08 (m, 4H, $-CH_2CH_2-$), 5.42 (dd, 1H, J=10.5, 3.6 Hz, CH), 6.62—7.38 (m, 11H, aromatic), 7.60—7.82 (m, 2H, $PhSO_2$-2, 6H), 7.96 (d, 1H, J=4.5 Hz, Py-6H); IR (NaCl) 1575, 1560, 1495, 1417, 1310, 1155, 1128 cm^{-1}.

Found: C, 59.39; H, 4.55; N, 3.47%. Calcd for $C_{19}H_{18}NO_2S_2Cl$: C, 59.39; H, 4.63; N, 3.57%.

6i: Oil (diastereomeric mixture); ^{1}H NMR (CCl_4) δ=1.27 (d, 3H, J=6.0 Hz, CH_3), 1.80—2.20 (m, 1H, CH), 2.36—2.77 (m, 1H, CH), 3.03 (bs, 1H, CH), 5.14 (dd, 1/2H, J=12.0, 3.3 Hz, $CHSO_2$), 6.64 (dd, 1/2H, J=10.5, 3.3 Hz, $CHSO_2$), 6.54—7.40 (m, 11H, aromatic), 7.31—7.84 (m, 2H, $PhSO_2$-2, 6H), 7.97 (d, 1H, J=3.6 Hz, Py-6H); IR (NaCl) 1578, 1560, 1500, 1420, 1320, 1310, 1150, 1122 cm^{-1}.

Found: C, 65.66; H, 5.51; N, 3.59%. Calcd for $C_{21}H_{21}NO_2S_2$: C, 65.76; H, 5.52; N, 3.65%.

4) Conversion of Compound 6e to Vinyl Sulfone 10e. To **6e** (0.28 g, 0.77 mmol) in dichloromethane (8 ml) at 0 °C was added *m*-chloroperbenzoic acid (0.21 g, 1.1equiv). Then, ice bath was removed and the reaction mixture was stirred at room temperature for one hour. The reaction mixture was washed with sat. aq $NaHCO_3$ and water. The organic layer was dried over Na_2SO_4, filtered, and the solvent was removed. 1 M-HCl (10 ml 1 M=1 mol dm^{-3}) was added to the residue and the mixture was heated at 100 °C for 2 h. The organic components were extracted with ethyl acetate, and dried over Na_2SO_4. After the purification by pTLC. (eluent; $CHCl_3$:AcOEt=40:1), 0.14 g of **10e** was obtained (69% yield).

10e: Mp 107—109 °C (Et_2O/hexane); ^{1}H NMR (CCl_4, $CDCl_3$) δ=7.84—6.82 (m, 11H, aromatic and $-CH=$), 6.11 (d, 1H, J=13.5 Hz, $-CH=$), 3.40 (d, 2H, J=6.0 Hz, $-CH_2-$); IR (KBr) 1310, 1150 cm^{-1}.

Found: C, 69.55; H, 5.51%. Calcd for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46%.

5) Conversion of 6e to Dihydrocinnamic Acid 11e. To **6e** (0.28 g, 0.76 mmol) in dichloromethane (6 ml) was added mCPBA (0.56 g, 3 equiv) under cooling by ice bath. Then, the reaction mixture was stirred at room temperature for 5 h. The reaction mixture was poured into ether, wased with sat. aq $NaHCO_3$, and dried over Na_2SO_4 to give disulfone as a crude state. The formed disulfone was dissolved in methanol containing K_2CO_3 (8 mmol). Hydrogen peroxide (30%) was added dropwise to the solution under refluxing conditions for 3 h. After the reaction was completed, the solvent was removed and the residue was acidified with concd. HCl and then extracted with ether to give dihydrocinnamic acid in 74% yield which was identified with authentic commercial compound.

6) General Procedure for the Preparation of γ-Lactones 12. Dichloromethane solution containing olefinic alcohol (2 mmol) were added to a stirred oxalyl chloride (0.8—1.5 ml) at room temperature and the mixture was stirred overnight. After the evaporation of solvent and excess oxalyl chloride, *N*-hydroxy-2-thiopyridone (2.1 mmol) and 4 ml of dry benzene solution of pyridine (3 mmol) were added to the mixture and the resulting solution was stirred at 0 °C for 30 min under nitrogen atmosphere. Then the reaction mixture was refluxed for 60 min. After the removal of solvent, compounds (**5** and **12**) were separated by column chromatography on silica gel.

12m: Oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ=2.10—2.18 (m, 1H, $-CH_2-$), 2.38—2.45 (m, 1H, $-CH_2-$), 3.05 (dtd, 1H, J=10.5, 8.4, 4.5 Hz, $-CHCO-$), 3.25 (dd, 1H, J=14.0, 8.4 Hz, $-SCH_2-$), 3.84 (dd, 1H, J=14.0, 4.5 Hz, $-SCH_2-$), 4.16 (td, 1H, J=8.8, 6.6 Hz, $-OCH_2-$), 4.34 (td, 1H, J=8.8, 2.5 Hz, $-OCH_2-$), 6.98 (ddd, 1H, J=7.9, 5.0, 1.0 Hz, Py-5H), 7.17 (dt, 1H, J=7.9, 10 Hz, Py-3H), 7.47 (td, 1H, J=7.9, 2.0 Hz, Py-4H), 8.40 (m, 1H, Py-6H); IR (NaCl) 1765, 1150, 1025 cm^{-1}.

Found: C, 57.22; H, 5.34; N, 6.64%. Calcd for $C_{10}H_{11}NSO_2$: C, 57.39; H, 5.30; N, 6.69%.

5m: Oil; ^{1}H NMR ($CDCl_3$) δ=2.40 (t, 2H, J=7.6 Hz, $-CH_2-$), 4.23 (t, 2H, J=7.6 Hz, $-OCH_2-$), 4.90—5.20 (m, 2H, $=CH_2$), 5.45—6.00 (m, 1H, $=CH-$), 7.10—7.20 (m, 1H, Py-5H), 7.55—7.70 (m, 2H, Py-3, 4H), 8.50 (d, 1H, J=6.1 Hz, Py-6H); IR (NaCl) 1720, 1150, 1110 cm^{-1}.

Found: C, 57.72; H, 5.43; N, 6.55%. Calcd for $C_{10}H_{11}NSO_2$:

C, 57.39; H, 5.30; N, 6.69%.

Next, the obtained lactone (**12m**) was oxidized with mCPBA (1.1 equiv) and the sulfoxide thus formed was heated at about 100 °C under reduced pressure to give in 49% yield α-methylene-γ-butyrolactone, which was identified with commercial compound.

13: Oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ=8.37—8.40 (m, 1H, Py-6H), 7.48—7.51 (m, 1H, Py-3, 4H), 7.19—7.21 (m, 1H, Py-3, 4H), 6.99—7.02 (m, 1H, Py-5H), 4.32—4.38 (m, 1H, $-OCH_2$), 4.14—4.24 (m, 3H, $-OCH_2$), 2.55—2.63 (m, 1H, CHCO), 2.41—2.45 (m, 1H, CHCO), 1.93—2.18 (m, 4H, $-CH_2-$), 1.58—1.69 (m, 2H, $-CH_2-$), 1.22—1.29 (m, 3H, $-CH_3$); IR (NaCl) 1760, 1725, 1245, 1180, 1150, 1025 cm^{-1}.

Found: C, 58.25; H, 6.31; N, 4.26%. Calcd for $C_{15}H_{19}NSO_4$: C, 58.23; H, 6.19; N, 4.53%.

12r: Mp 111—112 °C (AcOEt/Hexane); cis; ^{1}H NMR ($CDCl_3$) δ=2.88 (td, 2H, *J*=7.5, 3.0 Hz, $-CH_2C=$), 4.40 (t, 2H, *J*=7.5 Hz, $-OCH_2-$), 7.00—7.30 (m, 2H, Py), 7.40—7.60 (m, 1H, Py), 8.40—8.55 (m, 2H, Py-6H); IR (NaCl) 1725, 1185 cm^{-1}.

Found: C, 57.98; H, 4.39; N, 6.73%. Calcd for $C_{10}H_9NSO_2$: C, 57.95; H, 4.38; N, 6.76%.

5q: Oil; ^{1}H NMR ($CDCl_3$) δ=1.75 (q, 2H, *J*=6.4 Hz, $-CH_2-$), 2.00—2.25 (m, 2H, $-CH_2-$), 4.20 (t, 2H, *J*=6.8 Hz, $-OCH_2-$), 4.85—5.10 (m, 2H, $CH_2=$), 5.50—6.00 (m, 1H, $=CH-$), 7.10—7.30 (m, 1H, Py-5H), 7.60—7.70 (m, 2H, Py-3, 4H), 8.50 (d, 1H, *J*=6.1 Hz, Py-6H); IR (NaCl) 1710, 1150, 1110 cm^{-1}.

Found: C, 60.67; H, 6.35; N, 5.87%. Calcd for $C_{11}H_{13}NSO_2$: C, 60.73; H, 6.37; N, 5.90%.

12q: Oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ=1.64—1.72 (m, 1H, $-CH_2-$), 1.86—1.98 (m, 2H, $-CH_2-$), 2.28—2.35 (m, 1H, $-CH_2-$), 2.91—2.97 (m, 1H, $-CH-$), 3.33 (dd, 1H, *J*=14.0, 7.40 Hz, $-CH_2-S-$), 3.81 (dd, 1H, *J*=14.0, 5.0 Hz, $-CH_2-S-$), 4.30 (t, 2H, *J*=5.9 Hz, $-OCH_2-$), 6.98 (ddd, 1H, *J*=7.1, 5.0, 1.0 Hz, Py-5H), 7.19 (dt, 1H, *J*=8.3, 1.1 Hz, Py-3H), 7.47 (ddd, 1H, *J*=8.3, 7.1, 1.9 Hz, Py-4H), 8.41 (ddd, 1H, *J*=5.0, 1.9, 1.1 Hz,, Py-6H); IR (NaCl) 1730, 1150, 1130 cm^{-1}.

Found: C, 59.23; H, 5.96; N, 6.13%. Calcd for $C_{11}H_{13}NSO_2$: C, 59.17; H, 5.87; N, 6.27%.

12n: Oil; (mixture of two diastereomers); ^{1}H NMR ($CDCl_3$, 500 MHz) Less polar (minor amount) δ=1.10 (t, 3H, *J*=7.4 Hz, $-CH_3$), 1.74—1.84 (m, 2H, $-CH_2-$), 2.22—2.30 (m, 1H, $-CH_2-$), 2.33—2.39 (m, 1H, $-CH_2-$), 3.30 (ddd, 1H, *J*=10.7, 9.3, 3.3 Hz, $-CHCO-$), 4.17 (td, 1H, *J*=9.3, 7.1 Hz, CH-S-), 4.36—4.31 (m, 2H, $-O-CH_2-$), 6.99 (ddd, 1H, *J*=7.7, 5.0, 0.8 Hz, Py-5H), 7.19 (dt, 1H, *J*=7.7, 0.8 Hz, Py-3H), 7.48 (td, 1H, *J*=7.7, 1.9 Hz, Py-4H), 8.41 (ddd, 1H, *J*=5.0, 1.9, 0.8 Hz, Py-6H); Polar (major amount) δ=1.08 (t, 3H, *J*=7.1 Hz, $-CH_3$), 1.82—1.97 (m, 2H, $-CH_2-$), 2.25—2.33 (m, 1H, $-CH_2-$), 2.45—2.38 (m, 1H, $-CH_2-$), 3.03 (td, 1H, *J*=9.0, 5.2 Hz, $-CHCO-$), 4.21 (td, .1H, *J*=9.0, 7.4 Hz, -CH-S-), 4.38—4.44 (m, 2H, $-O-CH_2-$), 6.98 (ddd, 1H, *J*=7.7, 5.0, 0.8 Hz, Py-5H), 7.20 (dt, 1H, *J*=7.7, 0.8 Hz, Py-3H), 7.46 (td, 1H, *J*=7.7, 1.9 Hz, Py-4H), 8.42 (ddd, 1H, *J*=5.0, 1.9, 0.8 Hz, Py-6H); IR (NaCl) 1760, 1160, 1122, 1022 cm^{-1}.

Found: C, 59.15; H, 5.92; N, 6.21%. Calcd for $C_{12}H_{15}NSO_2$: C, 59.17; H, 5.87; N, 6.27%.

The assignment of two diastereomers (29:71) was carried out by the NMR measurement of α-propylidene-γ-lactones [32(cis):68(trans)] which were obtained by the treatment of **12n** with mCPBA (1.1 equiv) followed by heating at 70 °C for 50 min.

12o: Oil; [mixture of two diastereomers: A and B (34:66)] ^{1}H NMR ($CDCl_3$, 500 MHz)
A 1.36 (d, 3H, *J*=6.68 Hz, $-CH_3$),
B 1.41 (d, 3H, *J*=6.1 Hz, $-CH_3$),
B 1.70 (td, 1H, *J*=12.1, 10.4 Hz, $-CH_2-$),
A 2.06 (ddd, 1H, *J*=13.2, 9.1, 4.1 Hz, $-CH_2-$),
A 2.32 (dt, 1H, *J*=13.2, 8.0 Hz, $-CH_2-$),
B 2.54 (ddd, 1H, *J*=12.1, 8.2, 5.5 Hz, $-CH_2-$),
A,B 3.12—3.20 (m, 1H, $-CHCO-$),
B 3.23 (dd, 1H, *J*=13.7, 8.5 Hz, $-CH_2S-$),
A 3.31 (dd, 1H, *J*=13.7, 8.7 Hz, $-CH_2S-$),
A 3.80 (dd, 1H, *J*=13.7, 4.7 Hz, $-CH_2S-$),
B 3.87 (dd, 1H, *J*=13.7, 4.4 Hz, $-CH_2S-$),
B 4.45—4.51 (m, 1H, -O-CH-),
A 4.70—4.74 (m, 1H, O-CH-),
A,B 6.98—7.01 (m, 1H, Py-5H),
A,B 7.18—7.20 (m, 1H, Py-3H),
A,B 7.47—7.50 (m, 1H, Py-4H),
A,B 8.41—8.43 (m, 1H, Py-6H),
IR (NaCl) 1760, 1185, 1125 cm^{-1}.

Found: C, 58.88; H, 5.89; N, 6.18%. Calcd for $C_{11}H_{13}NSO_2$: C, 59.17; H, 5.87; N, 6.27%.

12t: Oil; [mixture of two diastereomers: A and B (34:66)] ^{1}H NMR ($CDCl_3$, 270 MHz)
A,B 1.40—1.80 [m, 14H, $-(CH_2)_7-$],
A,B 1.95—2.55 (m, 4H, 2-CH_2-),
A,B 3.05—3.35 (m, 2H, -SCH-CHCO-),
A 3.80 (dd, 1H, *J*=13.8, 4.9 Hz, -SCH-),
A 3.85 (dd, 1H, *J*=13.0, 4.1 Hz, -SCH-),
B 4.34 (dtd, 1H, *J*=10.8, 7.3, 5.4 Hz, -OCH-),
A 4.54 (tt, 1H, *J*=7.8, 5.4 Hz, -OCH-),
A,B 4.90—5.04 (m, 2H, $CH_2=$),
A,B 5.72—5.90 (m, 1H, $-CH=$),
A,B 6.98—7.04 (m, 1H, Py-5H),
A,B 7.20 (d, 1H, *J*=8.1 Hz, Py-3H),
A,B 7.44—7.55 (m, 1H, Py-4H),
A,B 8.41 (d, 1H, *J*=4.6 Hz, Py-6H);
IR (NaCl) 1760, 1175 cm^{-1}.

Found: C, 68.89; H, 8.69; N, 4.13%.Calcd for $C_{20}H_{29}NSO_2$: C, 69.12; H, 8.41; N, 4.03%.

5n: Oil; ^{1}H NMR ($CDCl_3$, 500 MHz)

Trans isomer δ=0.97 (t, 3H, *J*=7.4 Hz, $-CH_3$), 1.99—2.04 (m, 2H, $-CH_2-$), 2.35—2.40 (m, 2H, $-CH_2-$), 4.27 (t, 2H, *J*=6.8 Hz, $-OCH_2-$), 5.38—5.32 (m, 1H, $-CH=$), 5.55—5.60 (m, 1H, $-CH=$), 7.29—7.26 (m, 1H, Py-5H), 7.75—7.70 (m, 2H, Py-3, 4H), 8.60—8.59 (m, 1H, Py-6H);

Cis isomer δ=0.98 (t, 3H, *J*=7.5 Hz, $-CH_3$), 2.01—2.09 (m, 2H, $-CH_2-$), 2.42—2.47 (m, 2H, $-CH_2-$), 4.26 (t, 2H, *J*=7.0 Hz, $-OCH_2-$), 5.32—5.29 (m, 1H, $-CH=$), 5.51—5.55 (m, 1H, $-CH=$), 7.26—7.29 (m, 1H, Py-5H), 7.70—7.75 (m, 2H, Py-3, 4H), 8.60—8.59 (m, 1H, Py-6H); IR (NaCl) 1720, 1150, 1115 cm^{-1}.

Found: C, 60.26; H, 6.35; N, 5.77%. Calcd for $C_{12}H_{15}NSO_2$: C, 60.73; H, 6.37; N, 5.90%.

12p: Oil; ^{1}H NMR ($CDCl_3$) δ=0.90 (t, 6H, *J*=7.6 Hz, $-CH_3\times2$), 1.65 (q, 4H, *J*=7.6 Hz, $-CH_2-\times2$), 1.80—2.40 (m, 2H, $-CH_2-$), 3.00—3.40 (m, 2H, $-CH_2S-$, $-CHCO-$), 3.70—4.00 (m, 1H, $-CH_2S-$), 6.80—7.00 (m, 1H, Py-5H), 7.00—7.20 (m, 1H, Py-3H), 7.30—7.50 (m, 1H, Py-4H), 8.35 (d, 1H, *J*=6.1 Hz, Py-6H); IR (NaCl) 1760, 1125, 1220 cm^{-1}.

Found: C, 63.18; H, 7.21; N, 5.17%. Calcd for $C_{14}H_{19}NSO_2$:

C, 63.36; H, 7.22; N, 5.28%.

12s: Oil; ^{1}H NMR (CDCl$_3$) δ=2.80—3.40 (m, 4H, -CH$_2$-×2), 3.60—4.05 (m, 1H, -CH-), 6.70—7.45 (m, 7H, Py-3, 4, 5H, aromatic), 8.30 (d, 1H, J=6.1 Hz, Py-6H); IR (NaCl) 1760, 1575, 1125 cm^{-1}.

Found: C, 66.93; H, 4.98; N, 4.82%. Calcd for $C_{15}H_{13}NSO_2$: C, 66.40; H, 4.83; N, 5.16%.

4l: Oil; ^{1}H NMR (CDCl$_3$) δ=2.25 (s, 3H, -CH$_3$), 2.85—2.65 (m, 3H, -CH$_2$-), 4.90—5.05 (m, 2H, CH$_2$=), 5.50—5.90 (m, 1H, -CH=), 6.80—7.40 (m, 3H, Py-3, 4, 5H), 7.00 (d, 2H, J=7.6 Hz, aromatic), 7.22 (d, 2H, J=7.6 Hz, aromatic), 8.35 (d, 1H, J=6.1 Hz, Py-6H); IR (NaCl) 1570, 1410, 1125 cm^{-1}.

Found: C, 75.22; H, 6.78; N, 5.39%. Calcd for $C_{16}H_{17}NS$: C, 75.25; H, 6.71; N, 5.49%.

7ki: Mp 90—91 °C; ^{1}H NMR (CDCl$_3$) δ=1.17 (t, 3H, J=7.1 Hz, -CH$_3$), 2.85 (dd, 1H, J=16.7, 10.6 Hz, -CH$_2$-), 3.45 (dd, 1H, J=16.7, 4.5 Hz, -CH$_2$-), 4.12 (q, 2H, J=7.1 Hz, -O-CH$_2$-), 6.24 (dd, 1H, J=10.6, 4.5 Hz, -CH-SO$_2$-), 6.80—7.00 (m, 2H, Py), 7.25—7.50 (m, 4H, PhSO$_2$-3, 4, 5H and Py), 7.94 (dd, 2H, J=9.1, 3.0 Hz, PhSO$_2$-2, 6H), 8.22 (d, 1H, J=5.1 Hz, Py-6H); IR (Nujol) 1740, 1455, 1314, 1222, 1150 cm^{-1}.

Found: C, 54.73; H, 4.89; N, 3.94%. Calcd for $C_{16}H_{17}NS_2O_4$: C, 54.68; H, 4.88; N, 3.99%.

17ki: Oil; ^{1}H NMR (CDCl$_3$) δ=1.30 (t, 3H, J=7.6 Hz, -CH$_3$), 4.26 (q, 2H, J=7.6 Hz, -CH$_2$-), 6.82 (d, 1H, J=13.9 Hz, -CH=), 7.36 (d, 1H, J=13.9 Hz, -CH=), 7.50—7.70 (m, 3H, PhSO$_2$-3, 4, 5H), 7.90—8.00 (dd, 2H, J=9.1, 3.0 Hz, PhSO$_2$-2, 6H); IR (NaCl) 1712, 1295, 1145 cm^{-1}.

Found: C, 55.15; H, 5.01%. Calcd for $C_{11}H_{12}SO_4$: C, 54.99; H, 5.03%.

15a: Oil; ^{1}H NMR (CDCl$_3$) δ=1.20 (t, 6H, J=7.6 Hz, -CH$_3$×2), 3.35 (q, 4H, J=7.6 Hz, -CH$_2$-×2), 6.90—7.10 (m, 1H, Py-5H), 7.35—7.65 (m, 2H, Py-3, 4H), 8.35 (d, 1H, J=5.1 Hz, Py-6H); IR (NaCl) 1650, 1400, 1250, 1112 cm^{-1}.

Found: C, 56.90; H, 6.71; N, 13.19%. Calcd for $C_{10}H_{14}N_2SO$: C, 57.12; H, 6.91; N, 13.32%.

15b: Mp 80—82 °C; ^{1}H NMR (CDCl$_3$) δ=3.50 (s, 3H, -CH$_3$), 7.10—7.20 (m, 1H, Py-5H), 7.30 (s, 5H, Ph), 7.50—7.70 (m, 2H, Py-3, 4H), 8.45 (d, 1H, J=5.1 Hz, Py-6H); IR (KBr) 1660, 1340, 1268, 1108 cm^{-1}.

Found: C, 63.74; H, 4.94; N, 11.45%. Calcd for $C_{13}H_{12}N_2SO$: C, 63.91; H, 4.95; N, 11.47%.

15c: Mp 54—56 °C; ^{1}H NMR (CDCl$_3$) δ=2.30 (q, 2H, J=7.9 Hz, -CH$_2$-), 3.85 (t, 2H, J=7.9 Hz, -NCH$_2$-), 4.90—5.10 (m, 2H, CH$_2$=), 5.40—5.90 (m, 1H, -CH=), 7.00—7.20 (m, 1H, Py-5H), 7.30 (s, 5H, Ph), 7.50—7.60 (m, 2H, Py-3, 4H), 8.40 (d, 1H, J=5.1 Hz, Py-6H); IR (KBr) 1660, 1360, 1250, 1115 cm^{-1}.

Found: C, 67.57; H, 5.72; N, 9.89%. Calcd for $C_{16}H_{16}N_2S_2O$: C, 67.58; H, 5.69; N, 9.85%.

16c: Mp 63—65 °C; ^{1}H NMR (CDCl$_3$, 500 MHz) δ=2.01 (m, 1H, β-H), 2.35 (m, 1H, β-H), 3.07 (ddd, 1H, J=17.5, 9.4, 3.8 Hz, α-H), 3.34 (dd, 1H, J=13.1, 9.4 Hz, -CH$_2$S-), 3.76 (dd, 1H, J=9.4, 2.2 Hz, γ-H), 3.77 (d, 1H, J=9.4 Hz, γ-H), 3.88 (dd, 1H, J=13.1, 3.8 Hz, -CH$_2$S-), 6.96 (dd, 1H, J=7.8, 5.0 Hz, Py-4H), 7.12 (t, 1H, J=7.8 Hz, Ph-4H), 7.19 (dd, 1H, J=7.8, 0.8 Hz, Py-3H), 7.34 (t, 2H, J=7.8 Hz, Ph-3, 5H), 7.46 (td, 1H, J=7.8, 2.5 Hz, Py-4H), 7.62 (d, 2H, J=7.8 Hz, Ph-2, 6H), 8.40 (ddd, 1H, J=5.0, 2.5, 0.8 Hz, Py-6H); IR (KBr) 1678, 1400 cm^{-1}.

Found: C, 67.35; H, 5.67; N, 9.79%. Calcd for $C_{16}H_{16}N_2S_2O$: C, 67.58; H, 5.67; N, 9.85%.

8l: Oil; ^{1}H NMR (CDCl$_3$, mixture of two diastereomers) δ=2.25 (s, 6H, -CH$_3$×2), 2.30 (s, 6H, -CH$_3$×2), 2.00—3.00 (m, 12H, -CH$_2$CH-×4), 4.50—5.00 (m, 8H, CH$_2$=×4), 4.10—4.70 (m, 4H, -CH=×4), 6.65 (d, 4H, J=9.1 Hz, aromatic), 6.90 (4H, J=9.1 Hz, aromatic), 6.90—7.30 (m, 8H, aromatic); IR (NaCl) 1635, 1510, 920, 825 cm^{-1}.

Found: C, 90.90; H, 9.08%. Calcd for $C_{22}H_{26}$: C, 90.98; H, 9.02%.

7a: Melt at room temperature (25 °C); ^{1}H NMR (CDCl$_3$) δ=0.60 (m, 3H, -CH$_3$), 1.20—1.90 (bs, 12H, -(CH$_2$)$_6$-), 2.90 (dd, 1H, J=16.4, 10.6 Hz, -CH$_2$CO-), 3.42 (dd, 1H, J=16.4, 5.2 Hz, -CH$_2$CO-), 4.04 (t, 2H, J=12.1, -OCH$_2$-), 6.15 (dd, 1H, J=10.6, 5.2 Hz, -CH-), 6.80—7.10 (m, 1H, Py-5H), 7.20—7.60 (m, 5H, Ph-3, 4, 5H, Py-3, 4H), 7.90 (d, 2H, J=6.1 Hz, Ph-2, 6H), 8.20 (d, 1H, J=5.1 Hz, Py-6H); IR (NaCl) 1740, 1320, 1153, 1087 cm^{-1}.

Found: C, 60.91; H, 6.77; N, 3.17%. Calcd for $C_{22}H_{29}NS_2O_4$: C, 60.66; H, 6.71; N, 3.22%.

7b: Mp 102.5—103.5 °C; ^{1}H NMR (CCl$_4$) δ=1.03—2.02 (m, 10H, -(CH$_2$)$_5$-), 2.73 (dd, 1H, J=19.4, 10.5 Hz, CH$_2$CO), 3.31 (dd, 1H, J=19.4, 4.5 Hz, CH$_2$CO), 2.62 (br, 1H, CH-O-), 5.93 (dd, 1H, J=10.5, 4.5 Hz, -SO$_2$CH-), 6.66—7.43 (m, 6H, aromatic), 7.62—7.90 (m, 2H, aromatic), 8.04 (d, 1H, J=4.5 Hz, Py-6H); IR (KBr), 1740, 1710, 1570, 1412, 1375, 1310, 1150, 1120 cm^{-1}.

Found: C, 59.38; H, 5.71; N, 3.39%. Calcd for $C_{20}H_{23}NO_2S_2$: C, 59.23; H, 5.72; N, 3.45%.

17a: Mp 38—39 °C; ^{1}H NMR (CDCl$_3$) δ=0.90 (m, 3H, -CH$_3$), 1.30 (br s, 10H, -(CH$_2$)$_5$-), 1.50—1.80 (m, 2H, -CH$_2$-), 4.16 (t, 2H, J=6.4 Hz, -OCH$_2$-), 6.80 (d, 1H, J=15.2 Hz, -CH=), 7.30 (d, 1H, J=15.2 Hz, -CH=), 7.45—7.65 (m, 3H, Ph-3, 4, 5H), 7.87 (d, 2H, J=7.6 Hz, Ph-2, 6H); IR (NaCl) 1714, 1460, 1300, 1150 cm^{-1}.

Found: C, 63.41; H, 7.51%. Calcd for $C_{17}H_{24}SO_4$: C, 62.93; H, 7.46%.

17b: Oil; ^{1}H NMR (CDCl$_3$) δ=1.08—2.18 (m, 10H, -(CH$_2$)$_5$-), 4.80 (br s, 1H, CHO), 6.70 (d, 1H, J=15.0 Hz, CH=), 7.22 (d, 1H, J=15 Hz, CH=), 7.36—7.72 (m, 3H, Ph-3, 4, 5H), 7.86 (d, 2H, J=7.8 Hz, Ph-2, 6H); IR (NaCl) 1715, 1320, 1290, 1225, 1145, 965 cm^{-1}.

Found: C, 61.39; H, 6.16%. Calcd for $C_{15}H_{18}O_4S$: C, 61.20; H, 6.16%.

7kii: Oil; ^{1}H NMR (CDCl$_3$) δ=1.20 (t, 3H, J=7.6 Hz, -CH$_3$), 1.22 (t, 3H, J=7.6 Hz, -CH$_3$), 2.90—3.10 (m, 2H, -CH$_2$-), 4.10 (q, 2H, J=7.6 Hz, -OCH$_2$-), 4.13 (q, 2H, J=7.6 Hz, OCH$_2$-), 4.86 (dd, 1H, J=7.9, 6.1 Hz, -CH-), 6.90—7.00 (m, 1H, Py-5H), 7.00—7.20 (m, 1H, Py-3H), 7.30—7.50 (m, 1H, Py-4H), 8.28 (d, 1H, J=5.1 Hz, Py-6H); IR (NaCl) 1730, 1575, 1150—1260 (broad), 1030 cm^{-1}.

Found: C, 55.26; H, 6.16; N, 4.79%. Calcd for $C_{13}H_{17}NSO_4$: C, 55.11; H, 6.05; N, 4.94%.

7kiv: Oil; ^{1}H NMR (CDCl$_3$) δ=0.85 (m, 3H, -CH$_3$), 2.24 (m, 21H, -(CH$_2$)$_9$-, -CH$_3$), 1.50—2.00 (m, 2H, -CH$_2$CO-), 2.70 (m, 1H, PySCH-), 4.06 (q, 2H, J=6.7 Hz, -OCH$_2$-), 6.80—7.40 (m, 3H, Py-3, 4, 5H), 8.30 (d, 1H, J=5.1 Hz, Py-6H); IR (NaCl) 2910, 1740, 1580, 1170 cm^{-1}.

Found: C, 68.33; H, 9.45; N, 3.89%. Calcd for $C_{20}H_{33}NSO_2$: C, 68.33; H, 9.46; N, 3.98%.

7kvi: Oil; ^{1}H NMR (CDCl$_3$) δ= 1.02 (t, 3H, J=6.4 Hz, -CH$_3$), 3.90 (q, 2H, J=6.4 Hz, -OCH$_2$-), 6.00 (s, 1H, -CH=), 6.90—7.56 (m, 8H, Ph, Py-3, 4, 5H), 8.40 (d, 1H, J=5.1 Hz, Py-6H); IR (NaCl) 1692, 1266, 1194, 1152, 1030 cm^{-1}.

Found: C, 67.33; H, 5.38; N, 4.82%. Calcd for $C_{16}H_{15}NSO_2$: C, 67.34; H, 5.30; N, 4.91%.

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