New Agents for Alkoxycarbonylation of Amines

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Alkoxycarbonylated pyrazinols and pyrazinethiols were prepared. These compounds were shown to be convenient agents for alkoxycarbonylation of aliphatic amines.

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Protection of functional groups is an indispensable process in organic syntheses [1]. Alkoxycarbonyl groups, such as *t*-butoxycarbonyl and benzyloxycarbonyl groups, are widely used for protection of the amino moiety of amino acids in peptide syntheses [2]. Efforts have been made also for finding various carriers of the alkoxycarbonyl groups [3,4]. We have already reported that acyloxypyrazines and pyrazinethiolcarboxylic esters are employable for acylation of amines [5-7]. In the present paper, emphasis is placed on alkoxycarbonylation of amino groups with 2-alkoxycarbonyloxy-3,6-dialkylpyrazines and alkyl *S*-3,6-dialkylpyrazin-2-ylthiocarbonates which were prepared respectively from the corresponding pyrazinols **1-3** and pyrazinethiols **4-6**.

Scheme I

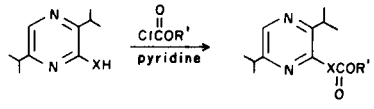
Pyrazinols **1-3** and Pyrazinethiols **4-6** used as Carriers

When 3,6-diisopropyl-2-hydroxypyrazine (**2**) [6] and 3,6-diisopropyl-2-pyrazinethiol (**5**) [5] were treated in pyridine with some alkyl chloroformates obtained commercially, the corresponding oily alkoxycarbonylated pyrazinols **2a-c** and pyrazinethiols **5a-c** were obtained. These substances are not so unstable and can be purified by distillation. In order to prepare the *t*-butoxycarbonyl derivatives, the sodium salts of some pyrazinols **1-3** and pyrazinethiols **4-6** were allowed to react with trichloromethyl chloroformate (diphosgene) and subsequently with *t*-butyl alcohol. Hence, *t*-butoxycarbonylated pyrazinols **1d-3d** and pyrazinethiols **4d-6d** were prepared without difficulty in satisfactory yields.

Alkoxycarbonylated pyrazinols **2a-c** and pyrazinethiols **5a-c** thus obtained were submitted to aminolysis. Namely, these pyrazines were allowed to stand for 10 minutes with various amines in acetonitrile in the presence of triethylamine. After the removal of the solvent by distillation *in vacuo*, the residue was taken up in ether and the ether solution was washed with 10% hydrochloric acid and 10% potassium hydroxide, successively. The results are shown in Table III. Interestingly, arylamines, such as aniline and *N*-methylaniline, were never acylated, even under heating. *t*-Butoxycarbonylation of some amines was also carried out under the same conditions as above and the products were obtained in excellent yields, as shown in Table IV. In this case, the reaction of arylamines was also unsuccessful.

Table I

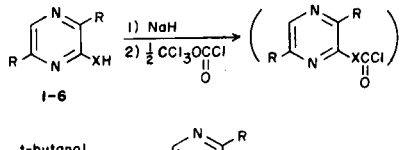
Preparation of Alkoxycarbonylated Pyrazinols **2a-c** and Pyrazinethiols **5a-c**



2 and 5			2a-c and 5a-c
Compounds	X	R'	Yield (%)
2a	O	CH_3	24
2b	O	i-C_3H_7	80
2c	O	i-C_4H_9	99
5a	S	CH_3	35
5b	S	i-C_3H_7	98
5c	S	i-C_4H_9	100

Table II

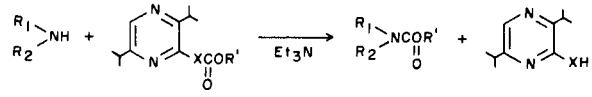
Preparation of *t*-Butoxycarbonylated Pyrazinols **1d-3d** and Pyrazinethiols **4d-6d**



Compounds	X	R	Yield (%)
1d	O	C_2H_5	43
2d	O	i-C_3H_7	53
3d	O	i-C_4H_9	50
4d	S	C_2H_5	75
5d	S	C_3H_7	84
6d	S	C_4H_9	78

Table III

Alkoxycarbonylation of Amines

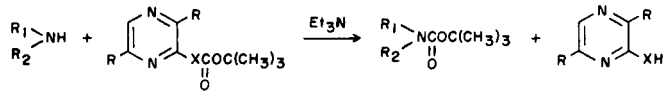


2a-c and 5a-c 7-12 2 and 5

Amines	R_1	R_2	Reagents	R′	X	Products	Yield (%)
Benzylamine	$C_6H_5CH_2$	H	**2a**	CH_3	O	**7** [10]	97
Benzylamine	$C_6H_5CH_2$	H	**2b**	i-C_3H_7	O	**8** [11]	90
Benzylamine	$C_6H_5CH_2$	H	**2c**	i-C_4H_9	O	**9** [12]	93
Benzylamine	$C_6H_5CH_2$	H	**5a**	CH_3	S	**7** [10]	100
Benzylamine	$C_6H_5CH_2$	H	**5b**	i-C_3H_7	S	**8** [11]	92
Benzylamine	$C_6H_5CH_2$	H	**5c**	i-C_4H_9	S	**9** [12]	100
N-Methylbenzylamine	$C_6H_5CH_2$	CH_3	**2a**	CH_3	O	**10** [13]	92
N-Methylbenzylamine	$C_6H_5CH_2$	CH_3	**2b**	i-C_3H_7	O	**11**	93
N-Methylbenzylamine	$C_6H_5CH_2$	CH_3	**2c**	i-C_4H_9	O	**12**	90
N-Methylbenzylamine	$C_6H_5CH_2$	CH_3	**5a**	CH_3	S	**10** [13]	98
N-Methylbenzylamine	$C_6H_5CH_2$	CH_3	**5b**	i-C_3H_7	S	**11**	100
N-Methylbenzylamine	$C_6H_5CH_2$	CH_3	**5c**	i-C_4H_9	S	**12**	100

Table IV

t-Butoxycarbonylation of Amines



1d-6d 13-16 1-6

Amines	R_1	R_2	Reagents	R	X	Products	Yield (%)
Benzylamine	$C_6H_5CH_2$	H	**1d**	C_2H_5	O	**13** [14]	98
Benzylamine	$C_6H_5CH_2$	H	**2d**	i-C_3H_7	O	**13** [14]	97
Benzylamine	$C_6H_5CH_2$	H	**3d**	i-C_4H_9	O	**13** [14]	95
Benzylamine	$C_6H_5CH_2$	H	**4d**	C_2H_5	S	**13** [14]	93
Benzylamine	$C_6H_5CH_2$	H	**5d**	i-C_3H_7	S	**13** [14]	100
Benzylamine	$C_6H_5CH_2$	H	**6d**	i-C_4H_9	S	**13** [14]	92
N-Methylbenzylamine	$C_6H_5CH_2$	CH_3	**1d**	C_2H_5	O	**14** [14]	92
N-Methylbenzylamine	$C_6H_5CH_2$	CH_3	**2d**	i-C_3H_7	O	**14** [14]	100
N-Methylbenzylamine	$C_6H_5CH_2$	CH_3	**3d**	i-C_4H_9	O	**14** [14]	91
N-Methylbenzylamine	$C_6H_5CH_2$	CH_3	**4d**	C_2H_5	S	**14** [14]	90
N-Methylbenzylamine	$C_6H_5CH_2$	CH_3	**5d**	i-C_3H_7	S	**14** [14]	99
N-Methylbenzylamine	$C_6H_5CH_2$	CH_3	**6d**	i-C_4H_9	S	**14** [14]	95
Cyclohexylamine	C_6H_{11}	H	**2d**	i-C_3H_7	O	**15** [15]	91
Cyclohexylamine	C_6H_{11}	H	**5d**	i-C_3H_7	S	**15** [15]	100
n-Octylamine	C_8H_{17}	H	**2d**	i-C_3H_7	O	**16**	100
n-Octylamine	C_8H_{17}	H	**5d**	i-C_3H_7	S	**16**	100

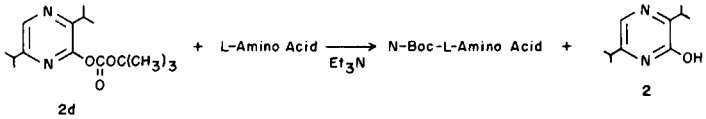
Next, alkoxycarbonylation of L-amino acids will be described. Among the acylating agents prepared, 2-*t*-butoxycarbonyloxy-3,6-diisopropylpyrazine (**2d**) and *t*-butyl *S*-3,6-diisopropylpyrazin-2-ylthiocarbonate (**5d**) were selected for examination of this reaction. The reaction with **2d** was performed in a mixture of acetonitrile and water in the presence of triethylamine. However, in the case of the reaction with **5d**, the addition of 4-*N*,*N*-dimethylaminopyridine was required for obtaining satisfactory results, as shown in Table VI. Namely, as regards yields of the products, *t*-butoxycarbonylated pyrazinols are more convenient than the corresponding pyrazinethiols.

Conclusively, alkoxycarbonylated pyrazinols and pyrazinethiols were found to be good reagents for alkoxycarbon-

ylation of aliphatic amines and amino acids. Since these reagents can be easily prepared from amino acids and are fairly stable, these reagents are of use for orgnaic syntheses.

Table V

N-t-Butoxycarbonylation of L-Amino Acids
using 2-*t*-Butoxycarbonyloxy-3,6-diisopropylpyrazine (**2d**)

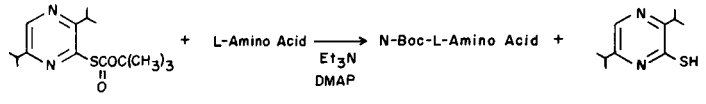


2d 2

L-Amino Acids	Yield (%)	*N-t*-Butoxycarbonylated L-Amino Acids $[\alpha]_D$ (c = 1, acetic acid) Found (22°)	Reported (20°) [4]
Alanine	76	−22.5	−24.0
Valine	98	−5.1	−6.3
Phenylalanine	100	−3.1	−3.9
Proline	79	−57.5	−61.1
Tryptophan	100	−20.0	−22.9
Tyrosine	86	+2.9	+3.8
Threonine	48	−6.0	−7.3

Table VI

N-t-Butoxycarbonylation of L-Amino Acids
using *t*-Butyl S-3,6-Diisopropylpyrazin-2-ylthiolcarbonate (**5d**)



5d 5

L-Amino Acids	Yield (%)	*N-t*-Butoxycarbonylated L-Amino Acids $[\alpha]_D^{22}$ (c = 1, acetic acid)
Alanine	64	−23.8
Valine	63	−5.8
Phenylalanine	55	−3.0
Proline	61	−57.5
Tryptophan	54	−20.0
Tyrosine	48	+3.5
Threonine	51	−5.0

EXPERIMENTAL

Melting points were recorded on a Yanagimoto micro-melting point apparatus and are uncorrected. Boiling points are also uncorrected. All uv spectra were taken in 95% ethanol using Hitachi Model 323 and 557 spectrometers, ir spectra on a Shimadzu IR-400 spectrometer, and pmr spectra in deuteriochloroform using JEOL PS-100 and Varian EM-360 instruments with tetramethylsilane as an internal standard. Mass spectra were obtained with Hitachi RMU-7L and M-80 spectrometers.

General Procedure for Preparation of Alkoxycarbonylated Pyrazinols **2a-c** and Pyrazinethiols **5a-c** using Alkyl Chloroformates.

An alkyl chloroformate (15 mmoles) was dropwise added to a solution of a pyrazinol (10 mmoles) or pyrazinethiol (10 mmoles) in pyridine (20 ml) in 5 minutes under ice-cooling, and the reaction mixture was stirred for one hour at room temperature. After being poured into ice water (40 ml), the reaction mixture was extracted with ether. The ether layer was washed successively with 10% hydrochloric acid, 10% potassium hydroxide and water, and then dried over sodium sulfate, and concentrated. The resulting oil was purified by distillation *in vacuo* to give the product as a colorless oil.

2-Methoxycarbonyloxy-3,6-diisopropylpyrazine (**2a**).

This compound had the following physical properties: bp 87-90°/1 torr; uv: λ max 273.5 (log ε = 3.74), 293 (3.36, shoulder) nm; ir (liquid film): 1780 cm^{-1} (C=O); pmr: δ 1.29 (6H, d, J = 7 Hz, $CH(CH_3)_2$), 1.33 (6H, d, J = 7 Hz, $CH(CH_3)_2$), 2.87-3.50 (2H, m, 2 × $CH(CH_3)_2$), 4.00 (3H, s, OCH_3), 8.53 (1H, s, pyrazine H) ppm; ms: m/e 239 (M^++1), 238 (M^+).

Anal. Calcd. for $C_{12}H_{18}N_2O_3$: C, 60.49; H, 7.61; N, 11.76. Found: C, 60.50; H, 7.71; N, 11.66.

2-Isopropoxycarbonyloxy-3,6-diisopropylpyrazine (**2b**).

This compound had the following physical properties: bp 96-97°/1 torr; uv: λ max 273.5 (log ε = 4.09), 294 (3.68, shoulder) nm; ir (liquid film): 1770 cm^{-1} (C=O); pmr: δ 1.28 (6H, d, J = 7 Hz, $CH(CH_3)_2$), 1.31 (6H, d, J = 7 Hz, $CH(CH_3)_2$), 1.38 (6H, d, J = 6 Hz, $COOCH(CH_3)_2$), 2.87-3.50 (2H, m, 2 × $CH(CH_3)_2$), 4.87-5.30 (1H, m, $COOCH(CH_3)_2$), 8.50 (1H, s, pyrazine H) ppm; ms: m/e 267 (M^++1), 266 (M^+).

Anal. Calcd. for $C_{14}H_{22}N_2O_3$: C, 63.13; H, 8.33; N, 10.52. Found: C, 63.20; H, 8.49; N, 10.45.

2-Isobutoxycarbonyloxy-3,6-diisopropylpyrazine (**2c**).

This compound had the following physical properties: bp 115-117°/1 torr; uv: λ max 273.5 (log ε = 3.94), 295 (3.50, shoulder) nm; ir (liquid film): 1780 cm^{-1} (C=O); pmr: δ 0.99 (6H, d, J = 7 Hz, $CH_2CH(CH_3)_2$), 1.28 (6H, d, J = 7 Hz, $CH(CH_3)_2$), 1.31 (6H, d, J = 7 Hz, $CH(CH_3)_2$), 1.80-2.43 (1H, m, $CH_2CH(CH_3)_2$), 2.87-3.50 (2H, m, 2 × $CH(CH_3)_2$), 4.13 (2H, d, J = 7 Hz, $CH_2CH(CH_3)_2$), 8.50 (1H, s, pyrazine H) ppm; ms: m/e 281 (M^++1), 280 (M^+).

Anal. Calcd. for $C_{15}H_{24}N_2O_3$: C, 64.26; H, 8.63; N, 9.99. Found: C, 64.41; H, 8.63; N, 10.01.

Methyl *S*-3,6-Diisopropylpyrazin-2-ylthiolcarbonate (**5a**).

This compound had the following physical properties: bp 104-106°/1 torr; uv: λ max 284 (log ε = 3.95) nm; ir (liquid film): 1740 cm^{-1} (C=O); pmr: δ 1.28 (6H, d, J = 7 Hz, $CH(CH_3)_2$), 1.34 (6H, d, J = 7 Hz, $CH(CH_3)_2$), 2.90-3.83 (2H, m, 2 × $CH(CH_3)_2$), 3.90 (3H, s, CH_3), 8.60 (1H, s, pyrazine H) ppm; ms: m/e 254 (M^+).

Anal. Calcd. for $C_{12}H_{18}N_2O_2S$: C, 56.67; H, 7.13; N, 11.01. Found: C, 56.75; H, 7.30; N, 11.12.

Isopropyl *S*-3,6-Diisopropylpyrazin-2-ylthiolcarbonate (**5b**).

This compound had the following physical properties: bp 119-120°/1 torr; uv: λ max 284 (log ε = 4.47) nm; ir (liquid film): 1740 cm^{-1} (C=O); pmr: δ 1.24 (6H, d, J = 7 Hz, $CH(CH_3)_2$), 1.27 (6H, d, J = 6 Hz, $COOCH(CH_3)_2$), 1.32 (6H, d, J = 7 Hz, $CH(CH_3)_2$), 2.90-3.83 (2H, m, 2 × $CH(CH_3)_2$), 4.93-5.37 (1H, m, $COOCH(CH_3)_2$), 8.57 (1H, s, pyrazine H) ppm; ms: m/e 282 (M^+).

Anal. Calcd. for $C_{14}H_{22}N_2O_2S$: C, 59.54; H, 7.85; N, 9.92. Found: C, 59.66; H, 7.86; N, 10.01.

Isobutyl *S*-3,6-Diisopropylpyrazin-2-ylthiolcarbonate (**5c**).

This compound had the following physical properties: bp 125-127°/2 torr; uv: λ max 284 (log ε = 4.38) nm; ir (liquid film): 1740 cm^{-1} (C=O); pmr: δ 0.92 (6H, d, J = 6 Hz, $CH_2CH(CH_3)_2$), 1.28 (6H, d, J = 7 Hz, $CH(CH_3)_2$), 1.35 (6H, d, J = 7 Hz, $CH(CH_3)_2$), 1.67-2.33 (1H, m, $CH_2CH(CH_3)_2$), 2.93-3.90 (2H, m, 2 × $CH(CH_3)_2$), 4.08 (2H, d, J = 7 Hz, $CH_2CH(CH_3)_2$), 8.62 (1H, s, pyrazine H) ppm; ms: m/e 296 (M^+).

Anal. Calcd. for $C_{15}H_{24}N_2O_2S$: C, 60.78; H, 8.16; N, 9.45. Found: C, 60.90; H, 8.34; N, 9.44.

General Procedure for Preparation of *t*-Butoxycarbonylated Pyrazinols **1d-3d** and Pyrazinethiols **4d-6d**.

To a solution of a pyrazinol (10 mmoles) or pyrazinethiol (10 mmoles) in dioxane (50 ml), sodium hydride (480 mg, 10 mg-atoms) was added and the reaction mixture was stirred at room temperature, until the generation of hydrogen ceased. Under ice-cooling, trichloromethyl chloroformate (0.9 ml, 7.5 mmoles) was added at once to the reaction mixture, which was stirred overnight at room temperature. After addition of a solution of *t*-butyl alcohol (1.11 g, 15 mmoles) in pyridine (2.5 ml) under ice-cooling, the reaction mixture was stirred for 3 hours under ice-cooling and then allowed to stand overnight at room temperature. In order to decompose trichloromethyl chloroformate, the reaction mixture was stirred with powdered active charcoal (50 mg) for one hour, and filtered. After removing the solvent of the filtrate by distillation *in vacuo*, the resulting oil was dissolved in ether. The ether layer was worked up the same as described in the former paragraph, to afford the product as a colorless oil.

2-*t*-Butoxycarbonyloxy-3,6-diethylpyrazine (**1d**).

This compound had the following physical properties: bp 105-106°/2 torr; uv: λ max 273 (log ε = 4.19), 293 (3.91, shoulder) nm; ir (liquid film): 1760 cm^{-1} (C=O); pmr: δ 1.27 (3H, t, J = 7 Hz, CH_2CH_3), 1.28 (3H, t, J = 7 Hz, CH_2CH_3), 1.53 (9H, s, $C(CH_3)_3$), 2.78 (4H, q, J = 7 Hz, q × CH_2CH_3), 8.27 (1H, s, pyrazine H) ppm; ms: m/e 253 ($M^+ + 1$).

Anal. Calcd. for $C_{13}H_{20}N_2O_3$: C, 61.88; H, 7.99; N, 11.10. Found: C, 61.90; H, 8.09; N, 11.33.

2-*t*-Butoxycarbonyloxy-3,6-diisopropylpyrazine (**2d**).

This compound had the following physical properties: bp 106-107°/2 torr; uv: λ max 274 (log ε = 3.92), 296 (3.50, shoulder) nm; ir (liquid film): 1780 cm^{-1} (C=O); pmr: δ 1.24 (6H, d, J = 7 Hz, $CH(CH_3)_2$), 1.28 (6H, d, J = 7 Hz, $CH(CH_3)_2$), 1.53 (9H, s, $C(CH_3)_3$), 2.80-3.50 (2H, m, 2 × $CH(CH_3)_2$), 8.27 (1H, s, pyrazine H) ppm; ms: m/e 281 ($M^+ + 1$).

Anal. Calcd. for $C_{15}H_{24}N_2O_3$: C, 64.26; H, 8.63; N, 9.99. Found: C, 64.53; H, 8.69; N, 10.01.

2-*t*-Butoxycarbonyloxy-3,6-diisobutylpyrazine (**3d**).

This compound had the following physical properties: bp 104-105°/1 torr; uv: λ max 275 (log ε = 3.72), 297 (3.38, shoulder) nm; ir (liquid film): 1780 cm^{-1} (C=O); pmr: δ 0.93 (12H, d, J = 6 Hz, 2 × $CH_2CH(CH_3)_2$), 1.55 (9H, s, $C(CH_3)_3$), 1.88-2.45 (2H, m, 2 × $CH_2CH(CH_3)_2$), 2.65 (2H, d, J = 6 Hz, $CH_2CH(CH_3)_2$), 2.67 (2H, d, J = 6 Hz, $CH_2CH(CH_3)_2$), 8.40 (1H, s, pyrazine H) ppm; ms: m/e 309 ($M^+ + 1$).

Anal. Calcd. for $C_{17}H_{28}N_2O_3$: C, 66.20; H, 9.15; N, 9.08. Found: C, 66.10; H, 9.14; N, 9.13.

t-Butyl *S*-3,6-Diethylpyrazin-2-ylthiolcarbonate (**4d**).

This compound had the following physical properties: bp 103-105°/2 torr; uv: λ max 284 (log ε = 4.19) nm; ir (liquid film): 1740 cm^{-1} (C=O); pmr: δ 1.25 (3H, t, J = 7.5 Hz, CH_2CH_3), 1.27 (3H, t, J = 7.5 Hz, CH_2CH_3), 1.45 (9H, s, $C(CH_3)_3$), 2.81 (2H, q, J = 7.5 Hz, CH_2CH_3), 2.98 (2H, q, J = 7.5 Hz, CH_2CH_3), 8.43 (1H, s, pyrazine H) ppm; ms: m/e 269 ($M^+ + 1$).

Anal. Calcd. for $C_{13}H_{20}N_2O_2S$: C, 58.18; H, 7.51; N, 10.44. Found: C, 58.23; H, 7.58; N, 10.43.

t-Butyl *S*-3,6-Diisopropylpyrazin-2-ylthiolcarbonate (**5d**).

This compound had the following physical properties: bp 123-125°/1 torr; uv: λ max 284 (log ε = 3.86) nm; ir (liquid film): 1740 cm^{-1} (C=O); pmr: δ 1.23 (6H, d, J = 7 Hz, $CH(CH_3)_2$), 1.29 (6H, d, J = 7 Hz, $CH(CH_3)_2$), 1.43 (9H, s, $C(CH_3)_3$), 2.80-3.80 (2H, m, 2 × $CH(CH_3)_2$), 8.37 (1H, s, pyrazine H) ppm; ms: m/e 297 ($M^+ + 1$).

Anal. Calcd. for $C_{15}H_{24}N_2O_2S$: C, 60.78; H, 8.16; N, 9.45. Found: C, 60.93; H, 8.22; N, 9.33.

t-Butyl *S*-3,6-Diisobutylpyrazin-2-ylthiolcarbonate (**6d**).

This compound had the following physical properties: bp 125-127°/2 torr; uv: λ max 286 (log ε = 3.93) nm; ir (liquid film): 1740 cm^{-1} (C=O); pmr: δ 0.92 (12H, d, J = 6 Hz, 2 × $CH_2CH(CH_3)_2$), 1.47 (9H, s, $C(CH_3)_3$), 1.67-2.50 (2H, m, 2 × $CH_2CH(CH_3)_2$), 2.66 (2H, d, J = 7 Hz, $CH_2CH(CH_3)_2$), 2.84 (2H, d, J = 7 Hz, $CH_2CH(CH_3)_2$), 8.28 (1H, s, pyrazine H) ppm; ms: m/e 325 ($M^+ + 1$).

Anal. Calcd. for $C_{17}H_{28}N_2O_2S$: C, 62.93; H, 8.70; N, 8.63. Found: C, 63.19; H, 8.76; N, 8.88.

Alkoxycarbonylation of Amines.

To a solution of an amine (1 mmole) and triethylamine (121 mg, 1.2 mmoles) in acetonitrile (10 ml), an alkoxycarbonylated pyrazinol or pyrazinethiol (1 mmole) was added and the reaction mixture was stirred for 10 minutes at room temperature. Ths solvent was removed by distillation *in vacuo* and the residue was taken in ether. The ether layer was washed with 10% hydrochloric acid, 10% potassium hydroxide and water, successively. After being dried over sodium sulfate, the ether was removed by distillation and the residual product was purified by distillation or recrystallization. From the 10% potassium hydroxide layer, the starting pyrazinol or pyrazinethiol was recovered in *ca.* 80% yields.

Isopropyl Benzylmethylaminoformate (**11**).

This compound had the following physical properties: colorless oil; bp 102-104°/1 torr; ir (liquid film): 1710 cm^{-1} (C=O); pmr: δ 1.23 (6H, d, J = 6 Hz, $CH(CH_3)_2$), 2.82 (3H, s, NCH_3), 4.43 (2H, s, CH_2), 4.75-5.18 (1H, m, $CH(CH_3)_2$), 7.25 (5H, s, benzene H) ppm; ms: m/e 207 (M^+).

Anal. Calcd. for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.64; H, 8.40; N, 7.04.

Isobutyl Benzylmethylaminoformate (**12**).

This compound had the following physical properties: colorless oil; bp 104-105°/1 torr; ir (liquid film): 1720 cm^{-1} (C=O); pmr: δ 0.92 (6H, d, J = 6 Hz, $CH_2CH(CH_3)_2$), 1.63-2.27 (1H, m, $CH_2CH(CH_3)_2$), 2.85 (3H, s, NCH_3), 3.92 (2H, d, J = 6 Hz, $CH_2CH(CH_3)_2$), 4.47 (2H, s, CH_2N), 7.28 (5H, s, benzene H) ppm; ms: m/e 221 (M^+).

Anal. Calcd. for $C_{13}H_{19}NO_2$: C, 70.56; H, 8.65; N, 6.33. Found: C, 70.42; H, 8.69; N, 6.29.

t-Butyl *n*-Octylaminoformate (**16**).

This compound had the following physical properties: colorless oil; bp 115-116°/2 torr; ir (liquid film): 1700 cm^{-1} (C=O); pmr: δ 0.87 (3H, broad s, $CH_2(CH_2)_6CH_3$), 1.28 (12H, broad s, $CH_2(CH_2)_6CH_3$), 1.43 (9H, s, $C(CH_3)_3$), 2.97-3.27 (2H, m, $CH_2(CH_2)_6CH_3$), 4.53 (1H, broad s, NH) ppm; ms: m/e 229 (M^+).

Anal. Calcd. for $C_{13}H_{27}NO_2$: C, 68.08; H, 11.87; N, 6.11. Found: C, 68.01; H, 11.60; N, 6.34.

t-Butoxycarbonylation of L-Amino Acids.

To a solution of an L-amino acid (2 mmoles) and triethylamine (303 mg, 3 mmoles) in water (10 ml), **2d** (560 mg, 2.4 mmoles) or **5d** (592 mg, 2.4 mmoles), dissolved in acetonitrile (10 ml), was added at once. The reaction mixture was stirred for 24 hours at room temperature, diluted with water (50 ml) and extracted with ethyl acetate. After being acidified to *p*H 4 with 1% hydrochloric acid under ice-cooling, the water layer was extracted with ethyl acetate. The organic layer was dried with sodium sulfate and the solvent was evaporated *in vacuo* to leave the product, which was purified by recrystallization from a mixture of hexane and ether. All the products were confirmed to be identical with the authentic specimens in comparison of the infrared spectra and the optical rotation. In the case of the reaction using **5d**, 4-*N*,*N*-dimethylaminopyridine (0.3 mmoles) was used in addition to triethylamine.

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