resinous matter. Recrystallization from aqueous acetone gave 1.3 g of red crystals, mp 115—130°, which were identified as a mixture of VIb and VIIb by thin-layer chromatography. The solution of the crystals and triethylamine (0.05 ml) in acetone (20 ml) was stirred for 2 hr at room temp. The separated red crystals were collected and washed with acetone to give 0.8 g (42.6%) of VIIb, mp 189—190°. Analytical data are listed in Table II.

Reaction of Ib with Benzylammonium N-Benzylthiolcarbamate. Method D——A mixture of Ib (1.4 g, 4.78 mM) and benzylammonium N-benzylthiolcarbamate (2.0 g, 7.30 mM) in methanol (40 ml) was heated under reflux for 1 min and left standing for 1 hr at room temperature. The separated crystals were collected and washed with methanol to give 0.5 g (32.2%) of Vd, mp 254—270°. On recrystallization from acetic acid it melts at 270°. Analytical data are listed in Table II.

General Procedure for Hydrogenation of V and VII. Method E——To a solution of Vd (0.85 g, 2.0 mM) in acetic acid (30 ml) was added zinc dust (1.0 g) in small portions under reflux. The pale yellow solution was filtered hot in order to remove solid matters. The filtrate was diluted with water. The separated crystals were collected and washed with water to give 0.63 g (75.0%) of IVd, mp 115—120°. Recrystallization from benzene gave 0.45 g of IVd, mp 120—122°. Analytical data are listed in Table II.

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Stereochemical Studies. XXII.[1] Thermal Rearrangement of *S*(−)-1-Phenylethyl Isocyanide[2]

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As a possible reverse reaction of the well-known Hofmann, Curtius, and Schmidt rearrangements,[4,5] the authors paid attention to the thermal rearrangement[6] of isocyanide (I) to cyanide (II) by way of a cyclic transition state such as III. However, since only one report[6a] concerned with the thermal reaction of optically active and simple open chain compound in which *S*(+)-2-butyl isocyanide was converted to *S*(+)-2-butyl cyanide with 87% retention of configuration, we also undertook the thermal rearrangement of *S*(−)-1-phenylethyl isocyanide (*S*(−)-IV) carrying a simple structure similar to *S*(+)-2-butyl isocyanide, to explore the general applicability of this novel rearrangement to synthetic organic chemistry.

Preliminary experiments carried out with racemic compounds were described in detail in experimental part.

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[1] Part XXI: M. Shibasaki, S. Terashima, and S. Yamada, *Chem. Pharm. Bull.* (Tokyo), 21, 552 (1973).

[2] A part of this report has been communicated in the report: S. Yamada, K. Takashima, T. Sato, and S. Terashima, *Chem. Comm.*, **1969**, 811.

[3] Location: *Hongo, Bunkyo-ku, Tokyo.*

[4] K.K. Lee, S. Terashima, K. Achiwa, and S. Yamada, *Chem. Pharm. Bull.* (Tokyo), 17, 2540 (1969).

[5] P.A.S. Smith, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N.Y., 1963, p. 528.

[6] *a*) J. Casanova, Jr., N.D. Werner, and R.E. Schuster, *J. Org. Chem.*, 31, 3473 (1966); *b*) R.W. Horobin, N.R. Khan, and J. Mckenna, *Tetrahedron Letters*, **1966**, 5087; *c*) G.W. van Dine and R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 3227 (1968).

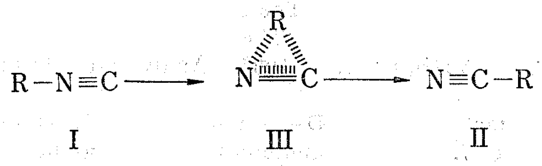
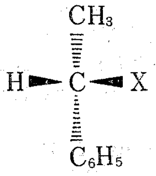


Chart 1



S(−)-IV : X=N≡C
S(−)-V : X=NH_2
S(−)-VI : X=NHCHO
S(−)-VII : X=C≡N
S(+)-VIII : X=COOH

Chart 2

Treatment of 100% optically pure *S*(−)-α-phenethylamine (*S*(−)-V), α_D^{13} −3.995° (*l*=0.1, neat),[7] with acetic and formic mixed anhydride[8] gave *S*(−)-1-formamido-1-phenylethane (*S*(−)-VI), $[\alpha]_D^{8}$ −203° (methanol) in 80% yield, which was dehydrated with phosphorus oxychloride and pyridine,[6a] to afford an oily isocyanide (*S*(−)-IV), α_D^{14} −3.576° (*l*=0.1, neat) in 27% yield. Formed *S*(−)-IV was confirmed by its infrared (IR) and nuclear magnetic resonance (NMR) spectra, and immediately submitted to the thermal reaction under the condition summarized in the Table. That *S*(−)-IV thus obtained was 100% optically pure, was further confirmed by the conversion of *S*(−)-IV to *S*(−)-VI, $[\alpha]_D^{15}$ −204° (methanol), by treatment with dilute aqueous hydrochloric acid and ethanol.

As shown in the Table, reflux of a diphenyl ether solution of (±)- or *S*(−)-IV for 3.0 hr afforded (±)- or *S*(−)-hydratropanitrile[9] ((±)- or *S*(−)-VII) in excellent yields. Structures of formed (±)- and *S*(−)-VII were respectively confirmed by the conversion to (±)- and *S*(+)-hydratropic acid[10] ((±)- and *S*(±)-VIII) using 47% hydrobromic acid and acetic acid. Since *S*(−)-VII showing α_D^{13} −0.616° (*l*=0.1, neat) afforded *S*(+)-VIII, $[\alpha]_D^{12}$ +33.9° (benzene) (37% optically pure)[11] and the treatment of *S*(+)-VIII, $[\alpha]_D^{17}$ +64.3° (benzene), under the same condition as that employed for the hydrolysis of *S*(−)-VII, showed that extent of racemization of *S*(+)-VIII during the hydrolysis was 13.8%, the degree of configuration retention for *S*(−)-VII thus obtained by the thermal reaction was calculated to be 43%. On the other hand, when a diphenyl ether solution of *S*(−)-IV was heated at 200° for 6.0 hr, *S*(−)-VII

TABLE. Thermal Rearrangements of (±)- and *S*(−)-1-Phenylethyl Isocyanide ((±)- and *S*(−)-IV) under Various Conditions[a]

Run	Isocyanides used	Reac. temp. (°C)	Reac. time (hr)	Formed (±)- and *S*(−)-Hydratropanitrile ((±)- and *S*(−)-VII)				
				Crude yield[b] (%)	Isolated yield[c] (%)	Bp (°C) (mmHg)	α_D (*l*=0.1, neat) (t)	Retention[d] of confign. (%)
1	(±)-IV	256[e]	3.0	98	74	106—107 (16)	—	—
2	*S*(−)-IV	256[e]	3.0	89	69	88— 89 (5—6)	−0.616 (13)	43
3	*S*(−)-IV	200	6.0	quantitative	59	93— 98 (11)	−0.812 (8)	56
4	*S*(−)-IV	200	24	81	63	82— 84 (4)	−0.041 (10)	1.4

a) All reactions were carried out using diphenyl ether (bp 256° (760 mmHg)) as a solvent.
b) after purified by silica gel column chromatography
c) after distilled under reduced pressure
d) Determined after *S*(−)-VII was hydrolyzed to *S*(+)-VIII, and extent of racemization of *S*(+)-VIII under the hydrolysis condition (13.8%) was corrected.
e) reflux of a diphenyl ether solution

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7) S. Terashima, M. Wagatsuma, and S. Yamada, *Chem. Pharm. Bull.* (Tokyo), **18**, 1137 (1970).
8) C.W. Hoffmann, *J. Org. Chem.*, **23**, 727 (1968).
9) H. Mizuno, S. Terashima, K. Achiwa, and S. Yamada, *Chem. Pharm. Bull.* (Tokyo), **15**, 1749 (1967).
10) S. Terashima and S. Yamada, *Chem. Pharm. Bull.* (Tokyo), **16**, 1953 (1968).
11) *S*(+)-VIII showing $[\alpha]_D$ +92.5° (*c*=3.4825, benzene), which was the highest optical rotation reported until now, was assumed to be 100% optically pure (C.L. Arcus and J. Kenyon, *J. Chem. Soc.*, **1939**, 916).

showing α_D^{8} −0.812° (l=0.1, neat) was also obtained in quantitative yield. In this case too, the degree of configuration retention was determined to be 56%[12] by the conversion to S(+)-VIII, $[\alpha]_D^{12}$ +44.5° (benzene) (48% optically pure), followed by the calculation based on the experimental results cited above. However, the same reaction mixture was heated for an additional 18 hr at the same temperature (see Table run 4), the S(−)-VII isolated, showed only 1.4% retention of configuration. These results clearly shows that S(−)-VII racemized spontaneously under the reaction conditions. Moreover, since the isocyanide-promoted racemization of S(−)-VII seems to be inevitable in the reaction medium as same as the case of S(+)-2-butyl cyanide,[13] it seems reasonable that the thermal rearrangement of S(−)-IV proceeds through a cyclic transition state (III) as already reported.[6a]

Chemical conversion scheme outlined above using (±)- and S(−)-IV which are easily derived from (±)- and S(−)-V, will surely be one of the most effective methods for preparing carboxylic acid from amine, since the reaction condition employed here is undoubtedly more convenient than heating in a sealed tube without solvent which is the most common condition for the rearrangement. However, that the degree of configuration retention observed in S(−)-VII was at most 56% because of the spontaneous and isocyanide-promoted racemization of S(−)-VII, clearly discloses a definite limitation for the applicability of this thermal rearrangement to a reverse reaction of Hofmann, Schmidt, and Curtius rearrangements.

Experimental[14]

(±)-1-Formamido-1-phenylethane ((±)-VI)——A mixture of acetic anhydride (102.0 ml, 1.00 mole) and 99% formic acid (43.0 ml, 1.00 mole) was stirred at 50—60° for 2.0 hr, giving a solution of acetic formic mixed anhydride,[8] and then cooled to 27°. (±)-V[7] (67.6 g, 0.50 mole) was gradually added to a stirred solution of the mixed anhydride under ice cooling to keep the temperature of the reaction mixture around 30°. After the addition was over, the whole was stirred at 50—60° for 2.0 hr, and then kept at room temperature overnight after diluted with water (200 ml). The aqueous solution was concentrated *in vacuo*, giving an oil (95.6 g), which was dissolved in water (200 ml) and extracted with benzene (200 ml × 2). Combined organic layers were successively washed with 5% Na_2CO_3 (200 ml × 1), 1% Na_2CO_3 (100 ml × 1), satd. NaCl (200 ml × 1), 5% AcOH (200 ml × 1), and satd. NaCl (200 ml × 3), and finally dried over anhyd. Na_2SO_4. Filtration and evaporation *in vacuo* gave a yellow oil (66.7 g), which solidified on standing at room temperature, and showed mp 38—42°. This solid was purified by fractional distillation *in vacuo*, affording pure (±)-VI as a colorless oil (62.7 g, 85%), bp 154—155° (9 mmHg), which immediately solidified, mp 41—43°. A part of this solid was twice recrystallized from isopropyl ether, to give an analytical sample, mp 44—44.5°. *Anal.* Calcd. for $C_9H_{11}ON$: N, 9.39. Found: N, 9.49. IR ν_{max}^{KBr} cm^{-1}: 3300, 3040, 2990, 2900, 1680, 1530, 1500, 770, 700.

***S*(−)-1-Formamido-1-phenylethene (*S*(−)-VI)**——Similar treatment of S(−)-V[7] (bp 89—90° (30—32 mmHg), α_D^{13} −3.995° (l=0.1, neat), 100% optically pure) (lit.[7] $\alpha_D^{27.5}$ −3.747° (l=0.1, neat), $[\alpha]_D^{33.5}$ −31.3° (c=2.82, EtOH)) (38.9 g, 0.28 mole) to the case of (±)-V afforded pure S(−)-VI (37.6 g, 80.0%) as a colorless oil, bp 165—168° (17—14 mmHg), which immediately solidified on standing, mp 33—36°, $[\alpha]_D^{9}$ −194.6° (c=0.871, methanol). Recrystallization from iso-propyl ether gave an analytical sample as colorless prisms, mp 33—35°, $[\alpha]_D^{8}$ −203° (c=0.824, methanol). *Anal.* Calcd. for $C_9H_{11}ON$: N, 9.39. Found: N, 9.69.

(±)-1-Phenylethyl Isocyanide ((±)-IV)——Phosphorus oxychloride (36.3 g, 0.238 mole) was gradually added to a mixture of (±)-VI (61.3 g, 0.375 mole), chloroform (120 g, 1.0 mole), and pyridine (213 g, 2.72 mole) with stirring in an ice-water bath.[6a] A brown solution thus obtained was stirred at room temperature for 5.0 hr, and then diluted with an ice-water (625 ml). Lower chloroform layer was separated and the upper aqueous phase was further extracted with chloroform (200 ml × 2). Combined chloroform layers were washed

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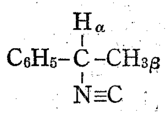
12) This value was erroneously reported as 57% in the communication. See Ref. 2).

13) According to the reference 6*a*), 13% racemization observed in the obtained cyanide was explained as the result of isocyanide-promoted racemization of the rearranged cyanide.

14) All melting and boiling points were uncorrected. IR spectra measurements were performed with spectrometers, Model DS-402 and IR-S, Japan Spectroscopic Co., Ltd. Measurements of NMR spectra were carried out with a spectrometer, Model 3H-60, Japan Electron Optics Lab. Optical Activities were determined with a Yanagimoto Photo Direct Reading Polarimeter Model OR-20. Gas Chromatographic analyses were performed using Yanagimoto Gas Chromatograph Model GCG-3D.

successively with water (300 ml × 1), 5% HCl (300 ml × 1), and water (300 ml × 1), and then dried over anhyd. Na_2SO_4. Filtration and evaporation *in vacuo* gave a dark-colored oil (34.3 g), which was purified by fractional distillation, to give the desired (±)-IV as a colorless oil (21.1 g, 39%), bp 90—91° (12 mmHg). IR $\nu_{\text{max}}^{\text{cap}}$ cm^{-1}: 3000, 2950, 2160, 1600, 1500, 770, 700. NMR (in CCl_4): 1.68 (3H, trebled doublet, $C\underline{H}_3$, $J_{\alpha\beta}=7$ cps, $J_{N\beta}=3$ cps), 4.83 (2H, trebled quartet $C\underline{H}$, $J_{\alpha\beta}=7$ cps, $J_{N\alpha}=2$ cps), 7.35 (s, 5H, $C_6\underline{H}_5$).[15] This oil was directly used for the next thermal reaction.



$$C_6H_5-\overset{\displaystyle H_\alpha}{\underset{\displaystyle N{\equiv}C}{C}}-CH_{3\beta}$$

S(−)-1-Phenylethyl Isocyanide (S(−)-IV)——The same treatment of S(−)-VI (36.5 g, 0.224 mole) as that of (±)-VI gave S(−)-IV as a colorless oil (8.7 g, 27%), bp 93—94° (13 mmHg), α_{D}^{14} −3.576° (l=0.1, neat). IR and NMR spectra of this sample were identical with those of (±)-IV measured in the same states. This oil was immediately used for the next thermal reaction.

In order to examine the optical purity of the formed S(−)-VI, a part of S(−)-VI thus obtained (2.0 g, 0.015 mole) was dissolved in a mixture of 10% HCl and EtOH (1 : 1) (20 ml). The whole was vigorously shaken for 10 min, and then extracted with benzene (10 ml × 3). Combined benzene layers were washed with dil. Na_2CO_3, and satd. NaCl, and dried over anhyd. Na_2SO_4. Filtration and evaporation *in vacuo* gave S(−)-VI as a pale yellow oil (2.0 g), which was purified by fractional distillation, to afford pure S(−)-VI as a colorless oil (1.3 g, 58%), bp 145—147° (3 mmHg), $[\alpha]_{\text{D}}^{15}$ −204° (c=0.804, methanol). This sample was identified with the authentic sample by comparison of their IR spectra. The above-mentioned result clearly shows no racemization occurred during the preparation of S(−)-IV from S(−)-V.

Thermal Rearrangement of (±)- and S(−)-1-Phenylethyl Isocyanide ((±)- and S(−)-IV)——Run 1: A mixture of (±)-IV (1.0 g, 7.6 mmole) in diphenyl ether was gently refluxed for 3.0 hr in metal bath. After the reaction was over,[16] the whole was purified by column chromatography (silica gel: 100 g). First, diphenyl ether was thoroughly washed out from the column by the elution with petr. ether, and then formed (±)-VII was eluted with a mixture of petr. ether and ethyl acetate (95 : 5). Fractions containing (±)-VII was collected and evaporated *in vacuo*, giving crude (±)-VII as a red oil (0.98 g, 98%). IR spectrum of this oil was identical with that of the purified sample in the same state. Purification by fractional distillation afforded pure sample as a pale yellow oil (0.74 g, 74%), bp 106—107° (16 mmHg). IR $\nu_{\text{max}}^{\text{cap}}$ cm^{-1}: 3000, 2220, 1450, 760, 700. This IR spectrum was identical with that of the authentic (±)-VII in the same state.[9] NMR (in $CDCl_3$): 1.55 (3H, doublet, $C\underline{H}_3$, $J=7$ cps), 3.80 (1H, quartet, $C\underline{H}$, $J=7$ cps), 7.24 (s, 5H, $C_6\underline{H}_5$). Gas chromatographic analysis (5% SE-30 on Diasolid L, 3m, 163°) showed a single peak whose retention time was 7.8 min.

Run 2: A mixture of S(−)-IV (3.03 g, 0.023 mole) in diphenyl ether (30 ml) was gently refluxed for 3.0 hr, and then worked up in a manner similar to the case of run 1, giving crude S(−)-VII as a red oil after purification with column chromatography (2.7 g, 89%). Fractional distillation *in vacuo* gave pure S(−)-VII as a colorless oil (2.10 g, 69%), bp 88—89° (5—6 mmHg), α_{D}^{13} −0.616° (l=0.1, neat). IR and NMR spectra of this oil were identical with those of (±)-VII in the same states.

Run 3: A mixture of S(−)-IV (1.94 g, 0.015 mole) in diphenyl ether (19 ml) was heated at 200° for 6.0 hr.[16] After the reaction was over, the whole was worked up the same as the case of run 1, giving crude product as a red oil (2.2 g, quantitative yield). Purification by fractional distillation gave pure S(−)-VII as a colorless oil (1.14 g, 59%), bp 93—98° (11 mmHg), α_{D}^{8} −0.812° (l=0.1, neat). IR spectrum of this oil was identical with that of the authentic (±)-VII in the same state. Gas chromatographic analysis (5% SE-30 on Diasolid L, 3m, 170°) showed a single peak whose retention time was identical with that of the authentic (±)-VII.

Run 4: A mixture of S(−)-IV (3.10 g, 0.024 mole) in diphenyl ether (30 ml) was heat at 200° for 24 hr, and then worked up the same as the case of run 3. Crude cyanide obtained as a red oil (2.4 g, 81%) after chromatographic purification, was purified by fractional distillation *in vacuo*, giving pure S(−)-VII as a colorless oil (1.95 g, 63%), bp 82—84° (4 mmHg), α_{D}^{10} −0.041° (l=0.1, neat). This oil was also identified with the authentic (±)-VII by comparison with their IR spectra measured in a capillary, and by gas chromatographic analysis.

(±)-Hydratropic Acid ((±)-VIII)——A mixture of (±)-VII (3.0 g, 0.023 mole) and 47% hydrobromic acid (20 ml) in acetic acid (20 ml) was refluxed for 3.0 hr, and then evaporated *in vacuo*, to afford a mixture of white minute crystals and brown oil. The mixture was diluted with water (120 ml), and extracted with ether (100 ml × 2). Combined ethereal layers were extracted with satd. $NaHCO_3$ (150 ml). Lower basic aqueous layers was then acidified ($\text{pH} \doteqdot 1.0$) by the addition of 10% HCl, and again extracted with ether (100 ml, 50 ml). Combined ethereal layers were dried over anhyd. Na_2SO_4. Filtration and evaporation *in vacuo* gave a pale yellow oil (3.2 g), which was purified by fractional distillation *in vacuo*, to give pure (±)-VIII as a colorless oil (2.4 g, 71%), bp 132—135° (9—10 mmHg) (Lit.[10]: bp 128.5—131° (5.5 mmHg)).

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15) The same kind of nitrogen-proton coupling was also reported on several kinds of aliphatic isocyanides. See Ref. 6*a*).

16) The reaction can be easily monitored by the periodical measurements of IR spectra on the reaction mixture. (±)-IV: IR $\nu_{\text{max}}^{\text{cap}}$ cm^{-1}: 2160 (N≡C): (±)-VII: IR $^{\text{cap}}_{\text{max}}$ cm^{-1}: 2220 (C≡N).

IR ν_{max}^{cap} cm^{-1}: 2980, 2950, 1710, 1600, 755, 695. This IR spectrum was identical with that of the authentic (±)-VIII[10] in the same state. This acid was further confirmed as its (±)-anilide. (±)-Hydratropanilide mp 132—133°, showed no depression on mixed melting point measurement with the authentic sample,[17] mp 132—133°. IR ν_{max}^{KBr} cm^{-1}: 3300, 1680, 1600, 1540, 760, 700. This IR spectrum was also identical with that of the authentic sample[17] in the same state.

S(+)-Hydratropic Acid (S(+)-VIII)——Treatment of *S*(−)-VII (α_D^{13} −0.616° (l=0.1, neat), bp 88—89° (5—6 mmHg)) (1.00 g, 7.6 mmole) in a manner similar to the case of (±)-VII afforded crude *S*(+)-VII as a pale yellow oil (1.2 g), which was purified by fractional distillation to give pure *S*(+)-VIII as a colorless oil (0.58 g, 51%), bp 121° (5 mmHg), $[\alpha]_D^{12}$ +36.2° (c=11.7, benzene). IR spectrum of this sample was identical with that of the authentic (±)-VIII in the same state. The optical purity of this sample was assumed to be 39%, based on the assumption that *S*(+)-VIII showing $[\alpha]_D$ +92.5° (c=3.4825, benzene)[11] was 100% optically pure.

The same treatment of *S*(−)-VII (α_D^{8} −0.812° (l=0.1, neat) bp 93—98° (11 mmHg) (1.09 g, 8.3 mmole) as that described above, afforded pure *S*(+)-VIII as a colorless oil (0.58 g, 46%), bp 127° (7 mmHg), $[\alpha]_D^{12}$ +44.5° (c=11.6, benzene). IR spectrum of this sample was identical with that of the authentic (±)-VIII in the same state. The optical purity of this acid was calculated to be 48% based on the assumption described above.

When *S*(−)-VII (α_D^{10} −0.041° (l=0.1, neat), bp 82—84° (4 mmHg)) (1.95 g, 0.015 mole) was treated in a manner similar to that described above, *S*(+)-VIII showing bp 132° (9 mmHg), $[\alpha]_D^{11}$ +1.12° (c=28.8, benzene) (optical purity 1.2%) was obtained in 61% yield.

Racemization of S(+)-Hydratropic Acid (S(+)-VIII) under the Hydrolysis Condition of S(−)-Hydratropanitrile (S(−)-VII)——Treatment of *S*(+)-VIII showing $[\alpha]_D^{17}$ +64.3° (c=9.49, benzene) (1.05 g, 7.6 mmole) was treated under the same reaction condition as that employed for the hydrolysis of *S*(−)-VII. Extractive isolation followed by fractional distillation afforded the pure *S*(+)-VIII as a colorless oil (0.42 g, 40%), bp 125° (10 mmHg), $[\alpha]_D^{17}$ +55.4° (c=8.40, benzene). Based on the above experiment, extent of racemization of *S*(+)-VIII under the hydrolysis condition was calculated to be 13.8%.

Acknowledgement The authors are indebted to the members of the Central Analysis Room of this Faculty for elemental analyses and spectra measurements.

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17) S. Terashima, K. Achiwa, and S. Yamada, *Chem. Pharm. Bull.* (Tokyo), **13**, 1001 (1965).

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UDC 547.834.2.057 : 547.821.3.04

Synthesis of 1-Carbethoxyindolizines *via* Intramolecular 1,5-Cyclization of Ylides

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Previously we described that the pyridinium ylide (I) readily undergoes intramolecular 1,5-cyclization followed by dehydrogenation of the intermediate (II) to give the indolizine (III).[2] Later Pohjala[3] showed that the closely related pyridinium ylide (IV) also cyclizes to give a mixture of the dihydroindolizine (V) and the indolizine (VI). In contrast, the ylide (VII) was shown to give a rather unusual product (VIII) presumably by an intermolecular 1,3-dipolar cycloaddition reaction.[4] These results prompted us to examine the scope of the

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1) Location: *Toneyama, Toyonaka, Osaka.*
2) Y. Tamura, N. Tsujimoto, Y. Sumida, and M. Ikeda, *Tetrahedron,* **28**, 21 (1972).
3) E. Pohjala, *Tetrahedron Letters,* **1972**, 2585.
4) Y. Tamura, Y. Sumida, and M. Ikeda, *Chem. Pharm. Bull.* (Tokyo), **20**, 1058 (1972).