pentane to give 9.7 g (85%) of 12: colorless prisms; mp 62–64 °C (lit.[10] mp 63–64 °C).

General Procedure for the Ring Closure of 2,2′-Dihydroxybiphenyls (1) in the Presence of Nafion-H. A mixture of 500 mg of 1 and 250 mg (50 wt %) of Nafion-H in 5 mL of *o*-xylene was refluxed until completion of the reaction as monitored by GLC analysis (Silicone OV-1, 2 m). The solid resin sulfonic acid was then filtered off, and the filtrate was analyzed by GLC. The filtrate was evaporated under vacuum to leave a residue, which was recrystallized from MeOH to give corresponding dibenzofurans (2). The reaction conditions and the yields are summarized in Table I.

Dibenzofuran (2a): colorless prisms (MeOH); mp 83–85 °C (lit.[11] mp 83–85 °C).

4,6-Dimethyldibenzofuran (2b): colorless prisms (MeOH); mp 75–81 °C; IR (KBr) 3052, 2923, 2851, 1190, 771, 761, 738 cm^{-1}; NMR ($CDCl_3$) δ 2.59 (6 H, s), 7.15–7.25 (4 H, m), 7.70–7.75 (2 H, m). Anal. Calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.82; H, 6.49.

2,8-Dimethyldibenzofuran (2c): colorless prisms (MeOH); mp 59–62 °C (lit.[12] mp 64 °C); IR (KBr) 3018, 2915, 2856, 1485, 1458, 1213, 1187, 1115, 809, 800 cm^{-1}; NMR ($CDCl_3$) δ 2.49 (6 H, s), 7.31 (2 H, dd, J = 8.3 Hz, J = 1.0 Hz), 7.40 (2 H, d, J = 8.3 Hz), 7.68 (2 H, s). Anal. Calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.61; H, 6.39.

Regeneration of Nafion-H Catalyst. The used catalyst was washed five times with acetone and deionized water, followed by drying at 105 °C for 10 h. The catalytic activity of regenerated catalyst was as good as that of fresh catalyst.

(10) Koenig, K. E.; Lein, G. M.; Stuckler, P.; Kaneda, T.; Cram, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 3553.
(11) *Dictionary of Organic Compounds*, 4th ed.; Oxford University: New York, 1978.
(12) Sugi, Y.; Shindo, H. *J. Pharm. Soc. Jpn.* **1933**, *53*, 97.

Prototropic Tautomerism of 2-(Phenylimino)tetrahydro-1,3-thiazine and 2-Anilino-4*H*-5,6-dihydro-1,3-thiazine

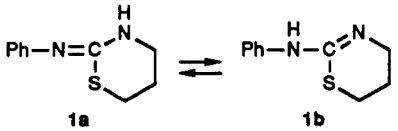
Aiko Nabeya* and Tadatoshi Endo

Tsurumi University, School of Dental Medicine, 2-1-3 Tsurumi, Tsurumi-ku, Yokohama, Japan

Received August 27, 1990

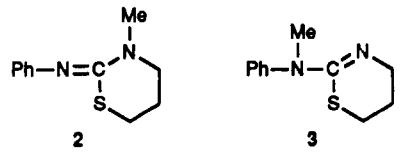
Introduction

In the tautomeric equilibrium **1a** ⇄ **1b**, the identity of the predominant tautomer has been a subject of controversy ever since Tišler obtained 1 by the isomerization of *N*-(thiocarbamoyl)azetidine and assigned it the structure **1a**.[1] This assignment of structure was based on a comparison of the IR spectrum of 1 with those of what were presumed to be the 3-methyl and 3-phenyl derivatives of 1. However, what Tišler believed to be the 3-methyl derivative of 1 was later shown to be **3**, not **2**, by Najer et al.[2]



1a **1b**

(1) Tišler, M. *Tetrahedron Lett.* **1959**, *12*, 12.



2 **3**

They prepared both **2** and **3** in an unequivocal way and concluded that **1b** was the predominant structure after comparing the UV spectrum and the pK_a value[3] of 1 with those of the model compounds **2** and **3** and the 3-phenyl derivative of 1. Since then, a number of workers have become interested in this subject. ^1H NMR[4,5] mass,[6] and UV[7] spectroscopy were used to determine the structure of 1. It was claimed that **1a** was the predominant structure because the spectra of 1 were similar to those of **2**. However, none of the arguments presented seemed sufficiently convincing. Years later, an extensive study of tautomerism in this sort of system was published by Jackman and Jen.[8] They concluded that **1a** predominated because the respective ^{13}C NMR spectra indicated that the ortho and para carbon atoms of the phenyl group of both 1 and **2** were abnormally magnetically shielded compared to those of **3**. They also showed that the ^1H NMR spectrum of 1 and those of a variety of model compounds possessing an exocyclic carbon–nitrogen double bond were similar. At this point, what was the predominant structure of 1 seemed to have been established. More recently, however, Tôth and Almásy,[9] in a study of the **1a** ⇄ **1b** equilibrium by ^1H, ^{13}C, and ^{15}N NMR spectroscopy, concluded that **1a** and **1b** were rapidly interconverted and calculated the tautomeric ratio, n_a/n_b, from the ^{15}N chemical shifts of **1**, **2**, and **3**. It was assumed that the chemical shifts of the endo and exo nitrogens of **1a** would be very close to those of **2**, and that the corresponding chemical shifts of **1b** would be very close to those of **3**. The n_a/n_b ratio was reported to be 75:25 (calculated from the chemical shifts of the endo nitrogens) or 73:27 (calculated from the chemical shifts of the exo nitrogens). Furthermore, they suggested a nearly planar geometry for N(3) based on the relatively high values of $J_{C(2)-N(3)}$ and $J_{N(3)-C(4)}$, despite the predominance of **1a**.

It had been shown earlier[10] that the reaction of isocyanates with 1 occurred exclusively at N(3) and that the carbamoyl group then migrated to the exo nitrogen intramolecularly. It was not clear if reaction at N(3) exclusively was due to a higher reactivity of an endo-NH compared to that of an exo-NH, or because 1 existed in solution only in the **1a** form. The large difference in the ^{15}N chemical shifts of N(3) in 1 and **2** (44.7 ppm), reported by Tôth and Almásy,[9] cannot be explained without assuming the existence of an equilibrium between **1a** and **1b**. In $CDCl_3$ solution, the ^{15}N chemical shift differences between *N*H and *N*Me of pyrrole-type nitrogen atoms were reported to be within 1.8 ppm,[11] and within 5 ppm for the nitrogen atoms of other heterocycles.[9] The difference in the values of the ^{15}N chemical shift of the amide nitrogen

(2) Najer, H.; Giudicelli, R.; Menin, J. *Bull Soc. Chim. Fr.* **1965**, 2120.
(3) Najer, H.; Armand, J.; Menin, J.; Voronine, N. *C. R. Acad. Sci.* **1965**, 4343.
(4) Rabinowitz, J. *Helv. Chim. Acta* **1969**, *52*, 255.
(5) Toldy, L.; Sohár, P.; Faragó, K.; Tôth, I.; Bartalits, L. *Tetrahedron Lett.* **1970**, *25*, 2167.
(6) Tamás, J.; Toldy, L. *Tetrahedron Lett.* **1970**, *25*, 2173.
(7) Toldy, L.; Liptâk, J. *Tetrahedron Lett.* **1970**, *49*, 4319.
(8) Jackman, L. M.; Jen, T. *J. Am. Chem. Soc.* **1975**, *97*, 2811.
(9) Tôth, G.; Almásy, A. *Org. Magn. Reson.* **1982**, *19*, 219.
(10) Nabeya, A.; Endo, T.; Saito, J.; Mitsuishi, T.; Inahara, M. *J. Heterocycl. Chem.* **1990**, *27*, 903.
(11) Wofford, D. S.; Forkey, D. M.; Russell, J. G. *J. Org. Chem.* **1982**, *47*, 5132.

0022-3263/91/1956-3194$02.50/0

Table I. ^{13}C and ^{15}N Spectroscopic Data for 1, 2, and 3[a]

compd	^{13}C chemical shifts (ppm)						^{15}N chemical shifts (ppm):
	C(2)	C(4)	C(5)	C(6)	CH_3	Ph-C(1)	N(3)[b]
1	152.39	42.45	22.48	26.78		146.74	129.8[c]
	$\|J\|$ = 17.1	$\|J\|$ = 7.7		$\|J\|$ = 0.9		$\|J\|$ = 2.6	
2	151.52	49.89	23.95	27.07	39.38	149.58	84.6[c]
	$\|J\|$ = 20.1	$\|J\|$ = 10.1		$\|J\|$ = 0.9	$\|J\|$ = 0.7	$\|J\|$ = 3.0	
3	150.87	45.89	20.26	27.18	39.15	144.72	223.1[c]
	$\|J\|$ = 9.0	$\|J\|$ = 0.0			$\|J\|$ = 3.0	$\|J\|$ = 1.3	

[a] $CDCl_3$ solution. [b] 50:50 (by volume) $MeNO_2/CDCl_3$ was the external standard (δ = 379.6 ppm relative to liquid ammonia).[12] [c] The reported value[9] is −253.9 ppm for 1, −298.6 ppm for 2, and −161.5 ppm for 3, relative to $MeNO_2$ ($CDCl_3$ solution).

Table II. ^{13}C Chemical Shifts and C–N Coupling Constants of 1 at Various Temperatures

solvent	T (°C)	chemical shifts (δ)				$\|J\|$ (Hz)	
		C(2)	C(4)	C(5)	C(6)	C(2)–N(3)	N(3)–C(4)
C_6D_6	100	150.38	43.74	22.68	26.99	14.96	5.56
	90	150.63	43.61	22.70	26.98	14.96	5.98
	80	150.93	43.47	22.73	26.95	14.96	5.98
	70	151.24	43.31	22.75	26.92	16.24	6.41
	60	151.57	43.16	22.76	26.90	15.82	6.84
	40	152.26	42.84	22.82	26.84	17.10	7.27
	25	152.75	42.67	22.84	26.80	17.52	8.12
CD_2Cl_2	25	152.30	43.51	23.23	27.65	16.24	7.26
	0	153.01	42.98	23.12	27.51	17.10	7.70
	−20	153.56	42.57	23.01	27.37	18.38	8.55
	−40	154.00	42.19	22.84	27.24	19.23	8.97
	−60	154.27	41.85	22.62	27.10	19.66	9.40

Table III. ^{13}C Chemical Shifts and C–N Coupling Constants of 2 at Various Temperatures

solvent	T (°C)	chemical shifts (δ)				$\|J\|$ (Hz)	
		C(2)	C(4)	C(5)	C(6)	C(2)–N(3)	N(3)–C(4)
C_6D_6	100	151.59	50.33	24.88	27.36	19.66	10.26
	80	151.51	50.21	24.78	27.35	19.24	10.26
	60	151.43	50.17	24.68	27.25	19.64	10.26
	40	151.34	50.08	24.57	27.27	19.24	10.68
	25	151.27	49.51	24.48	27.24	20.09	10.26
CD_2Cl_2	25	152.11	50.91	25.06	28.16	19.66	10.68
	0	151.87	50.72	24.79	28.03	19.66	10.26
	−20	151.69	50.54	24.55	27.91	20.08	10.26
	−40	151.50	50.40	24.31	27.78	20.09	10.69
	−60	151.27	50.22	24.05	27.65	20.09	10.68

atom of δ-valerolactam (4, 117.6 ppm) and that of the amide nitrogen atom of *N*-methyl δ-valerolactam (5, 111.5 ppm), determined during the study reported here, was 6.1 ppm in $CDCl_3$ solution. This relatively large difference can be attributed to the contribution of mesomeric structures[12] to the structure of 4.

Results and Discussion

This study was undertaken to obtain more information about the structure of 1 and to determine if it really exists in solution as a tautomeric mixture of **1a** and **1b**. For this purpose, ^{15}N-ring-labeled 1 and its *N*-methyl derivatives 2 and 3 were prepared, and their ^{13}C and ^{15}N NMR spectra were recorded (Table I). The values of the coupling constants $|J_{C(2)-N(3)}|$ and $|J_{N(3)-C(4)}|$ suggested that a structural similarity existed between 1 and 2, but not between 1 and 3. The value of $|J_{C(2)-N(3)}|$ was 17.1 Hz for 1, 20.1 Hz for 2, and 9.0 Hz for 3. The value of $|J_{N(3)-C(4)}|$ was 7.7 Hz for 1, 10.3 Hz for 2, and 0.0 Hz for 3. These results contradict the arguments of Tôth and Almásy,[9] who predicted a large negative value of J_{N-C} for a planar nitrogen and a small positive value for a pyramidal nitrogen.

Table IV. ^{15}N Chemical Shifts[a] of 1 and 2 at Various Temperatures in 50:50 (by Volume) $EtNO_2/CD_2Cl_2$

T (°C)	chemical shifts (ppm)	
	1	2
25	143	86.8
0	134	86.9
−30	122	87.0
−60	104	87.1

[a] Relative to that of $EtNO_2$ (δ = 392.0 ppm), which was determined with a 50% solution of $MeNO_2$ in CD_2Cl_2 as the external standard.

The temperature dependence of the ^{13}C NMR spectra of 1 (Table II) and 2 (Table III) was determined. The change in the chemical shift of C(2) of 1 with temperature was rather dramatic compared with that of C(2) of 2, for 1, the chemical shift change was 2.4 ppm between room temperature and 100 °C, and 2 ppm between room temperature and −60 °C. For 2, the change was less than 1 ppm over both temperature ranges. A more striking temperature dependence was observed for the C(2)–N(3) coupling constant of 1. $|J_{C(2)-N(3)}|$ varied from 17.5 Hz at room temperature to 15.0 Hz at 80 °C. In the case of 2, the change in $|J_{C(2)-N(3)}|$ was less than 1 Hz over the same temperature range. These results clearly showed the ex-

(12) Levy, G. C.; Lichter, R. L. *Nitrgen-15 Nuclear Magnetic Resonance Spectroscopy*; Arata, Y., Kainosho, M., Eds. (Japanese Translation); Baifu-kan, 1981; p-56.

Table V. ^{15}N Chemical Shifts[a] of 1 at Various Temperatures

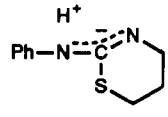
solvent	T (°C)	δ N(3) (ppm)
C_6D_6	120	161.4
	100	157.3
	80	150.9
	60	142.4
	40	132.9
	25	125.5[b]
CD_2Cl_2	25	135[c]
	-10	119
	-40	107
	-70	98

[a] A 50% (by volume) solution of $MeNO_2$ in each solvent was the external standard. [b] The chemical shift of N(3) of 2 was 83.3, and that of N(3) of 3 was 229.4 under the same conditions. [c] The chemical shift of N(3) of 2 was 85.2, and that of N(3) of 3 was 225.2.

istence of an equilibrium between 1a and 1b, as Tôth and Almâsy predicted.[9] The change in the value of the coupling constant in 1 with temperature suggested that structure 1a was favored at low temperatures, and that at -60 °C the structure of 1 very closely resembled 1a.

To obtain additional evidence for the existence of an equilibrium between 1a and 1b, the ^{15}N NMR spectra of CD_2Cl_2 solutions of 1 and 2 were recorded at various temperatures. $EtNO_2$ was the internal standard (Table IV). The chemical shift of N(3) of 1 changed from 143 ppm at room temperature to 104 ppm at -60 °C. In contrast, the chemical shift of N(3) of 2 did not change appreciably. It changed from 86.8 ppm at room temperature to 87.1 ppm at -60 °C. Thus, the existence of an equilibrium between 1a and 1b was confirmed. The ^{15}N NMR spectra of C_6D_6 solutions of 1 were recorded at temperatures between room temperature and 120 °C, and those of CD_2Cl_2 solutions were recorded at temperatures between room temperature and -70 °C (Table V). These spectra also suggested that the 1a form was favored at low temperatures.

If it is assumed that the chemical shift of N(3) of 1a (δa) is very close to that of N(3) of 2, and that the chemical shift of N(3) of 1b (δb) is very close to that of N(3) of 3,[9] then the ratio n_b/n_a is equal to $(\delta - \delta a)/(\delta b - \delta)$, where δ is the observed chemical shift of N(3) of 1. A plot of log $(\delta - \delta a)/(\delta b - \delta)$ against $1/T$ for the high temperature region is linear to 80 °C (Figure 1). From the slope of the linear portion of the plot, ΔG, for the isomerization, 1a → 1b was calculated to be 2.9 kcal/mol. The reasons for the deviation of the plot from linearity at temperatures greater than 80 °C are not known. It should be noted that $J_{C(2)-N(3)}$ and $J_{N(3)-C(4)}$ of 1 did not change further when the temperature was raised above 80 °C (Table II). It is thus conceivable that at high temperatures the structure of 1 in solution may be best described by a structure like that shown below:



In the low temperature region (Figure 2), the plot was not linear, presumably because the error in assuming that $\delta a = \delta$ for 2, and $\delta b = \delta$ for 3 becomes pronounced as the ratio $(\delta - \delta a)/(\delta b - \delta)$ becomes small. The n_a/n_b ratio at room temperature was calculated to be 67:33 in $CDCl_3$,[13] 64:36 in CD_2Cl_2, and 71:29 in C_6D_6.

(13) Using the δ values reported by Tôth and Almâsy[9] (footnote, Table I), the ratio was calculated to be 67:33.

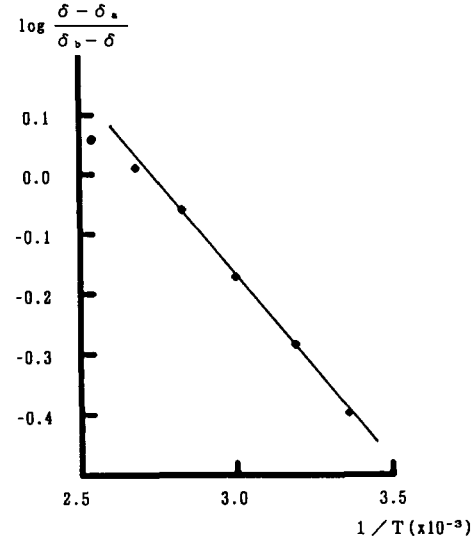


Figure 1. Plot of log $(\delta - \delta_a)/(\delta_b - \delta)$ against $1/T$.

In summary, it has been shown that 1 does exist as a tautomeric mixture of 1a and 1b at ambient temperature, and that the equilibrium strongly favors 1a at low temperatures. However, on raising the temperature, the equilibrium shifts to favor 1b, until the values of n_a and n_b remain constant at temperatures above 80 °C. At still higher temperatures, 1 may not exist as a mixture of tautomers, but as a single species.

Experimental Section

Melting points (determined with a MEL-TEMP apparatus) and boiling points are uncorrected. ^1H, ^{13}C, and ^{15}N NMR spectra were recorded with a JEOL GSX-270 spectrometer. Mass spectra were recorded with a Hitachi M-80 spectrometer.

***N*-Methyl δ-Valerolactam (5).** To an ice-cooled mixture of 1.5 g of NaH (50% suspension in oil), 100 mg of 18-crown-6 (Aldrich), and 20 mL of THF was added a solution of 2.5 g (25 mmol) δ-valerolactam in 10 mL of THF. MeI (2.5 mL) was then added, and the reaction mixture was stirred overnight at room temperature. The mixture was treated with water and was concentrated. After concentrated aqueous NaOH was added to the concentrate, the mixture was extracted with ether. Distillation of the extract gave 1.0 g (36%) of pure 5: bp 76 °C (4 mmHg); ^1H NMR ($CDCl_3$) δ 1.81 (m, β- and γ-CH_2), 2.37 (t, δ-CH_2), 2.94 (s, CH_3), 3.29 (t, α-CH_2).

^{15}N-Ring-Labeled 1. 3-Aminopropanol-^{15}N was prepared from potassium phthalimide-^{15}N (98% atom % ^{15}N, Aldrich) and 3-bromopropanol by the Gabriel synthesis. After removal of phthalhydrazide, the amino alcohol was obtained as an ethanolic solution. This solution was then allowed to react with phenyl thioisocyanate. The reaction mixture was concentrated, and the residue was purified by column chromatography on silica gel (benzene/ethyl acetate) to give almost pure (3-hydroxypropyl)-*N'*-phenylthiourea-^{15}N as a syrup. A benzene solution of the thiourea and TsOH was heated. The cooled solution was extracted with 2 N aqueous H_2SO_4. Addition of NaOH to the acidic extract gave white crystals. These were recrystallized from benzene/petroleum ether (bp 35–70 °C) to give pure 1-^{15}N: mp 122–125 °C; ^1H NMR ($CDCl_3$) δ 2.01 (q, 5-CH_2), 2.98 (t, 6-CH_2), 3.45 (broad s, 4-CH_2). The coupling of the C4 and C5 protons was not observed in the ^1H NMR spectra of dilute (10 mg/1 mL) solutions in $CDCl_3$, CD_2Cl_2, or C_6D_6. However, upon raising the temperature of a dilute solution of 1 in C_6D_6 to 90 °C, or on lowering the temperature of a dilute solution of 1 in CD_2Cl_2 to -20 °C, the signal due to the C4 protons began to resolve into a triplet. At 100 °C, the spectra of dilute C_6D_6 solutions showed a well-defined triplet, as did the spectra of dilute CD_2Cl_2 solutions at -50 °C. The spectra of more concentrated (100 mg/1 mL) solutions showed a well-defined triplet at room temperature. However, the addition of a trace amount of NaOH to a concentrated solution of 1 in $CDCl_3$ caused coalescence of the signal.

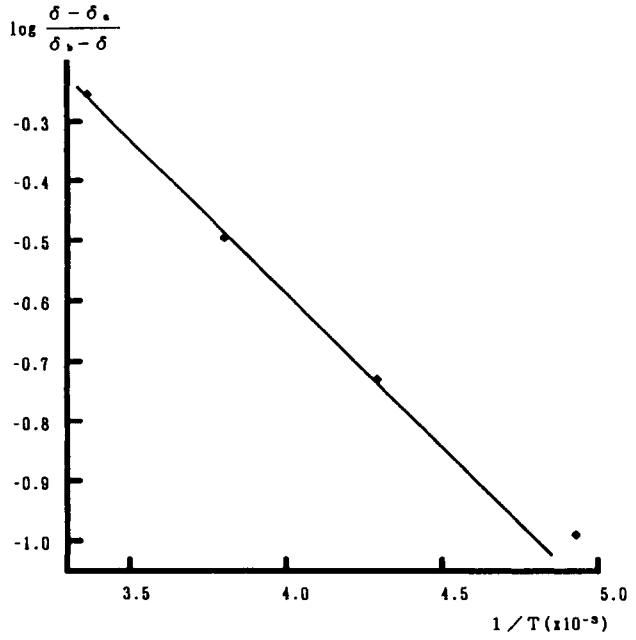


Figure 2. Plot of log $(\delta - \delta_a)/(\delta_b - \delta)$ against $1/T$.

Addition of a trace amount of NaOH to a dilute solution of 1 in $CDCl_3$, on the other hand, resolved the broad singlet into a well-defined triplet. The ^1H NMR spectrum of N-deuterated 1 showed a well-defined triplet for the signal of the C4 protons. Thus, the absence of a splitting pattern caused by C4–C5 proton coupling was due to the adjacent NH. In dilute solutions at ambient temperatures, the proton exchange between the two nitrogen atoms took place at an intermediate rate, so that the splitting pattern that arose from the coupling of the C4 and C5 protons was obscured. On raising the temperature, the exchange rate increased and the proton on nitrogen did not disturb the splitting pattern caused by the C4–C5 proton coupling. At low temperatures, or in concentrated solutions at ambient temperatures, the exchange rate slowed sufficiently to show the splitting pattern caused by the coupling of the C4 and C5 protons, but not to the point that the splitting pattern caused by the coupling of the C4 and N3 protons was revealed.

Anal. Calcd for $C_{10}H_{12}{}^{14}N^{15}NS$ (193.28): C, 62.14; H, 6.26; N, 15.01. Found: C, 62.25, 62.18; H, 6.26, 6.26; N, 14.67, 14.55.

^{15}N-Ring-Labeled 2 (2-^{15}N) and 3 (3-^{15}N). Sodium hydride suspension (220 mg) was washed with benzene, and then 3 mL of THF and 0.2 mL of HMPA were added. The mixture was cooled in ice, and a solution of 290 mg (1.5 mmol) 1-^{15}N in THF (3 mL) was added. The mixture was stirred for 30 min at 0–5 °C, and then MeI (0.3 mL) was added. The mixture was stirred for 5 h at 0–5 °C. Analysis of the mixture by TLC then showed no residual 1. Benzene and a small amount of water were added to the mixture. The mixture was then concentrated by rotary evaporator. The residue was dissolved in benzene, the solution was washed with water, dried (Na_2SO_4), and concentrated to give 330 mg of a syrup. ^1H NMR analysis showed that the syrup was a 60:40 mixture of 2 and 3 containing some HMPA. Column chromatography of the syrup ($CHCl_3$/MeOH, 98:2) gave 200 mg of crystals of 2 and an oil (3 containing some HMPA).

Crude 2-^{15}N was recrystallized from petroleum ether to give an analytical sample: mp 87–88 °C (lit.[2] mp 91 °C); ^1H NMR ($CDCl_3$) δ 2.16 (q, 5-CH_2), 2.89 (t, 6-CH_2), 3.16 (s, CH_3), 3.39 (t, 4-CH_2).

Anal. Calcd for $C_{11}H_{14}{}^{14}N^{15}NS$ (207.32): C, 63.72; H, 6.82; N, 13.99. Found: C, 63.83, 63.69; H, 6.82, 6.83; N, 13.73, 13.60.

No attempt to isolate 3-^{15}N from the syrup was made. 3-^{15}N: MS *m/e* 207 (M^+, 28), 206 ($(M-1)^+$, 100), 192 ($(M-CH_3)^+$, 6), 178 ($(M-(CH_2)_2-1)^+$, 18), 150 ($(M-(CH_2)_3{}^{15}N)^+$, 11), 149 ($(M-(CH_2)_3{}^{15}N-1)^+$, 27), 106 ($(PhNMe)^+$, 60); ^1H NMR ($CDCl_3$) δ 1.80 (q, 5-CH_2), 2.92 (t, 6-CH_2), 3.24 (s, CH_3), 3.70 (t, 4-CH_2).

Acknowledgment. The authors thank Dr. Jacques Reuben (Hercules Incorporated, USA) for helpful suggestions.

An Improved Synthesis of Ethyl *N*-(Methoxycarbonyl)-2,5-dihydro-1*H*-pyrrole-3-carboxylate[1]

Brian Dupré*,[2] and A. I. Meyers

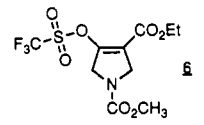
Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Received October 12, 1990

The title compound (4, Scheme I) has been used as a key intermediate in the synthesis of racemic supinidine (5)[3] and due to the functionality embodied within is envisioned as a useful precursor for many target compounds that incorporate a pyrroline or pyrrolidine ring.[4] The published route to 4 involves reduction of the pyrrolidone 1[5] to give a mixture of alcohols, which were converted to the benzoate esters 3. Base-induced elimination resulted in dihydropyrrole 4 in 34% overall yield from 1.

Because of the potential for 4 to serve as a pivotal intermediate in the construction of cyclic alkaloids and other important compounds,[6] attempts were made to improve on the synthesis of this important heterocycle. Thus, although 1 could readily be converted to the tosylhydrazone,[7a] attempts to decompose the crystalline derivative with methyllithium in ether or sodium methoxide in ethylene glycol[7b] to produce 4 were unsuccessful. Likewise, attempts to reduce the crude bis(dimethylamino) phosphonamide derivative of 1 with lithium[8] failed also. In addition, treatment of 1 with chlorotrimethylsilane and zinc metal in tetrahydrofuran[9] resulted in destruction of the starting material and none of the desired product could be isolated.

In an earlier report on palladium-catalyzed coupling of vinyl triflates with organotin compounds,[10] Stille and coworkers observed that vinyl triflates B could be reduced to olefins C with tributyltin hydride (Scheme II). We felt that this methodology might be suitable for the conversion of 1 to 4. Thus, the keto ester 1 was treated with trifluoromethanesulfonic anhydride in the presence of 1,8-bis(*N*,*N*-dimethylamino)naphthalene or 2,6-lutidine[11] to give the vinyl triflate 6. The crude triflate was reduced



6

with tributyltin hydride in the presence of catalytic tet-

(1) In memory of Professor John K. Stille, May 8, 1930–July 19, 1989.
(2) Present address: Alcon Laboratories, Inc., 6201 South Freeway, Fort Worth, TX 76134.
(3) Macdonald, T. L.; Narayanan, B. A. *J. Org. Chem.* **1983**, *48*, 1129.
(4) For a review of pyrrolizidine alkaloids, see: Robins, D. J. *Adv. Heterocycl. Chem.* **1979**, *24*, 247.
(5) Kuhn, R. *Chem. Ber.* **1956**, *89*, 1423.
(6) Pinder, A. R. *Nat. Prod. Rep.* **1985**, *2*, 181.
(7) (a) Recrystallized from methanol, mp 199–200 °C dec; ^1H NMR (DMSO-d_6, 270 MHz) δ 9.60 (br s, 1 H), 7.72 (d, J = 7.5 Hz, 2 H), 7.40 (d, J = 7.5 Hz, 2 H), 4.42 (s, 2 H), 4.20 (s, 2 H), 4.08 (q, J = 7.5 Hz, 2 H), 3.70 (s, 3 H), 2.58 (br s, 1 H), 2.49 (s, 3 H), 1.20 (t, J = 7.5 Hz, 3 H); IR (KBr) 3350, 1685, 1640, 1595, 1335, 1100 cm^{-1}. (b) Shapiro, R. H. *Org. React.* **1976**, *23*, 405.
(8) Ireland, R. E.; Muchmore, D. C.; Hengartner, U. *J. Am. Chem. Soc.* **1972**, *94*, 5098.
(9) (a) Motherwell, W. B. *J. Chem. Soc., Chem. Commun.* **1973**, 935. (b) Hodge, P.; Khan, M. N. *J. Chem. Soc., Perkin Trans. I* **1975**, 809.
(10) Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033.
(11) For leading references on triflate chemistry see: (a) Stang, P. J.; White, M. R. *Aldrichemica Acta*, **1983**, *16*, 14 and (b) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, *2*, 85.

0022-3263/91/1956-3197$02.50/0