Zeugner regarding the boat-half-chair equilibria and side-chain orientation in 1,4-benzodiazepines. Part of this work was supported by KaliChemie, Hannover.

Registry No. 1, 4054-38-0; 2, 21908-58-7; **2H**$^+$, 21995-42-6; 3, 3187-88-0; **3H**$^+$, 21995-41-5; 4, 45673-88-9; **4H**$^+$, 140927-32-8; 5, 5945-91-5; **5H**$^+$, 140927-33-9; 1-Me-**5H**$^+$, 140927-34-0; 1-Me-5, 140927-35-1; 5-Me-**5H**$^+$, 140927-36-2; 5-Me-5, 140927-37-3; 5-Ph-**5H**$^+$, 140927-38-4; 5-Ph-5, 2898-20-6; 6-Me-**5H**$^+$, 140927-39-5; 6-Me-5, 140927-40-8; 9-Me-**5H**$^+$, 140927-41-9; 9-Me-5, 140927-42-0; *S*-6, 141017-65-4; *R*-6, 140927-43-1; *S*-**6H**$^+$, 140927-44-2; *R*-**6H**$^+$, 140927-45-3; *S*-**7H**$^+$, 125228-22-0; *R*-**7H**$^+$, 140927-46-4; *S*-8-F-**7H**$^+$, 140927-47-5; *R*-8-F-**7H**$^+$, 140927-48-6; *S*-8-Me-**7H**$^+$, 140927-49-7; *R*-8-Me-**7H**$^+$, 140927-50-0; *S*-8-MeO-**7H**$^+$, 140927-51-1; *R*-8-MeO-**7H**$^+$, 140927-52-2; *S*-6,8-(Me)$_2$-**7H**$^+$, 140927-53-3; *R*-6,8-(Me)$_2$-**7H**$^+$, 140927-54-4; *S*-7-Br-**7H**$^+$, 140927-55-5; *R*-7-Br-**7H**$^+$, 140927-56-6; *S*-2′-Cl-**7H**$^+$, 140927-57-7; *R*-2′-Cl-**7H**$^+$, 140927-58-8; *S*-2′-F-**7H**$^+$, 140927-59-9; *R*-2′-F-**7H**$^+$, 140927-60-2; *S*-2′-Me-**7H**$^+$, 140927-61-3; *R*-2′-Me-**7H**$^+$, 140927-62-4; *S*-8, 140927-63-5; *R*-8, 140927-64-6; *S*-**8H**$^+$, 140927-65-7; *R*-**8H**$^+$, 140927-66-8; *S*-**9H**$^+$, 140927-67-9; *R*-**9H**$^+$, 140927-68-0; *S*-**10H**$^+$, 140927-69-1; *R*-**10H**$^+$, 140927-70-4; *S*-**11H**$^+$, 140927-71-5; *R*-**11H**$^+$, 140927-72-6.

Synthesis of Pyrrolidines and Pyrrolidinones by the Rhodium Complex Catalyzed Cyclization of Unsaturated Amines

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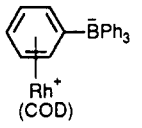
N-Allylic arylamines react with carbon monoxide, sodium borohydride, 2-propanol, and catalytic amounts of the zwitterionic complex η^6-$C_6H_6BPh_3^-Rh(COD)^+$ (1), to form pyrrolidines as the main products in most cases. Pyrrolidinones result from N-allylic alkylamines. An alternate route to the lactams from N-allylic alkylamines involves synthesis gas instead of $CO/NaBH_4$, together with the dual catalytic system $1/[Ru(CO)_3Cl_2]_2$. Complementary to the N-allylic arylamine route to pyrrolidines with $NaBH_4$ and 1 is the use of synthesis gas, 1, and 1,4-bis(diphenylphosphino)butane.

The zwitterionic rhodium complex 1 is a useful catalyst for the hydroformylation (CO/H_2) of a variety of simple and functionalized olefins. The process is highly regios-



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elective, and regiospecific in some instances, with steric effects playing a role in this reaction. For example, branched-chain aldehydes were obtained as the predominant or only products when monosubstituted styrenes were used as reactants, while terminal aldehydes were favored when bulky alkyl substituents were attached to the double bond (e.g., 3,3-dimethyl-1-hexene) or when the olefin was a 1,1-disubstituted one.[1] One can also realize the direct, regioselective preparation of alcohols from olefins by use of carbon monoxide and sodium borohydride (eq 1).[2]

$$RCH{=}CH_2 + CO + NaBH_4 \xrightarrow[500\ psi,\ 100\ °C]{i\text{-}PrOH,\ 1,\ CH_2Cl_2} R(CH_3)CHCH_2OH + R(CH_2)_3OH \quad (1)$$

The metal-catalyzed hydroformylation of allylamine usually results in the formation of 2-pyrrolidinone. Both cobalt carbonyl and chlorocarbonylbis(triphenylphosphine)rhodium catalyze the reaction under rather stringent conditions [e.g. $Co_2(CO)_8$, 125–250 °C and 60–300 atm; $Rh(CO)Cl(PPh_3)_2$, 150 °C and 136 atm].[3-7] It was also observed that use of hydridocarbonyltris(triphenylphosphine)rhodium as the catalyst, with excess triphenylphosphine, gave 1-pyrroline and 2-pyrrolidinone, the product distribution being sensitive to the nature of the solvent.[8] However, it should be noted that treatment of allylamine with rhodium acetate and triphenylphosphine [4:1 ratio of $PPh_3/Rh_2(OAc)_4$] and 1:1 CO/H_2 in benzene (28 atm, 70 °C) gave the lactam in 86% yield.[9] Also, use of rhodium complexes, containing or lacking phosphine ligands, as catalysts for the carbonylation of *N*-allylalkylamines at 65–90 atm, produced *N*-alkyl-2-pyrrolidinones and other products in variable yields.[10] We now report that the carbonylation of allylic amines, catalyzed, under relatively mild conditions, by 1 in the presence of sodium borohydride, selectively affords pyrrolidines or pyrrolidinones in good yields. Both types of products were also obtained in selective hydroformylation reactions catalyzed by 1.

Results and Discussion

Reaction of allyl amine with 1, carbon monoxide, sodium borohydride, and 2-propanol in methylene chloride for 30 h at 100 °C and 34.5 atm gave numerous products, each of which was formed in low yield. However, use of *N*-allylaniline (2, Ar = Ph) as the reactant afforded 1-phenylpyrrolidine (3, Ar = Ph) in 31% isolated yield, to-

(1) Amer, I.; Alper, H. *J. Am. Chem. Soc.* **1990**, *112*, 3674.
(2) Zhou, J. Q.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1991**, 233.
(3) Falbe, J. *Carbon Monoxide in Organic Synthesis*; Springer-Verlag: New York, 1980.
(4) Falbe, J.; Korte, F. *Chem. Ber.* **1965**, *98*, 1928.
(5) Falbe, J.; Weitkamp, H.; Korte, F. *Tetrahedron Lett.* **1965**, 2677.
(6) Falbe, J. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 435.
(7) Knifton, J. F. *J. Organomet. Chem.* **1980**, *188*, 223.
(8) Lin, J. J.; Larkin, J. M.; Knifton, J. F. *Catalysis of Organic Reactions*; Rylander, P. N., Greenfield, H., Augustine, R. L., Eds.; M. Dekker: New York, 1988; p 29.
(9) Anastassiou, D. Ph.D. Thesis, 1990, Monash University. Anastassiou, D.; Jackson, W. R. *J. Oranomet. Chem.* **1991**, *413*, 399.
(10) Jegorov, A.; Truka, T.; Tureček, F.; Hamuš, V. *J. Mol. Catal.* **1990**, *63*, 335.

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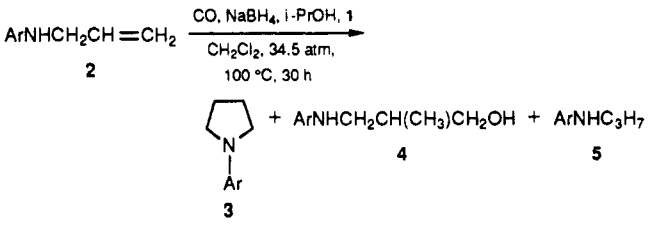
Table I. Reaction of N-Allylic Arylamines with CO/$NaBH_4$/i-PrOH/1[a]

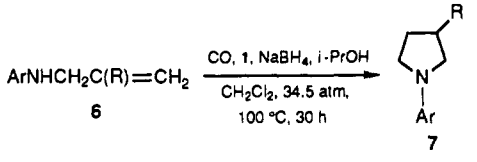
substrate	product[b]	yield, %[c]
2, Ar = Ph	3	31
	4	33
	5	10
2, Ar = *p*-$CH_3OC_6H_4$	3	30
	4	30
2, Ar = 1-$C_{10}H_7$	3	27
	5	14
2, Ar = *o*-$CH_3OC_6H_4$	5	82
2, Ar = *o*-$CH_3C_6H_4$	5	72
6, Ar = Ph, R = CH_3[d]	7	84
6, Ar = *p*-$CH_3OC_6H_4$, R = CH_3	7	68
6, Ar = *o*-$CH_3OC_6H_4$, R = CH_3	7	49
6, Ar = *o*-$CH_3C_6H_4$, R = CH_3	7	45
	N-isobutyl-*o*-toluidine	30
6, Ar = *p*-ClC_6H_4, R = CH_3	7	37[e]
6, Ar = 1-$C_{10}H_7$, R = CH_3	7	57
6, Ar = Ph, R = *n*-C_5H_{11}	7	83
6, Ar = 2-C_5H_4N, R = CH_3	7	26[e]
6, Ar = Ph, R = CH_2SO_2Ph	7, Ar = Ph, R = CH_3	87
$PhNHCH_2CH{=}C(CH_3)_2$	$PhNHCH_2CH_2CH(CH_3)_2$	48

[a] Reaction conditions: substrate (2.0 mmol), 1 (0.02 mmol), $NaBH_4$ (2.25 mmol), i-PrOH (0.5 mL), CH_2Cl_2 (5.0 mL), 34.5 atm CO, 100 °C, 30 h. [b] Products were identified by comparison of spectral data with literature results for known compounds. New compounds were characterized on the basis of analytical and spectral data (see Experimental Section). [c] Isolated yields. [d] Use of 1:1 $NaBH_4$/i-PrOH gave numerous products, none of which was 7. [e] Remainder was unreacted starting material.

gether with 33% of the amino alcohol 4 and 10% of *N*-*n*-propylaniline (5). The heterocycle and amine were formed



in similar yield when the *p*-methoxyphenyl analogue was used as the reactant (see Table I for data). *N*-Allylanilines bearing a substituent at the ortho position (CH_3, OCH_3) experienced reduction on attempted reaction with carbon monoxide and sodium borohydride. Pyrrolidines (7) were isolated in good yields when *N*-methallylanilines (6, R = CH_3) were employed as reactants. Even ortho-substituted



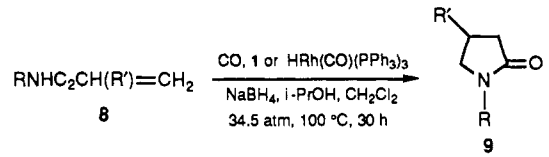
compounds gave the heterocycle as the major or only product, in contrast to the reduction process found for *N*-allyl ortho-substituted anilines. One can replace the methyl of the methallyl unit by *n*-amyl with comparable results, while the use of an unsaturated phenyl sulfone results in loss of the phenyl sulfone unit [i.e., desulfonylation]. A 100:1 ratio of substrate:1 was used for all reactions with the proportion of amine/$NaBH_4$ being 1.00:1.12. 2-Propanol and sodium borohydride are required here since no reaction takes place in the absence of either species. The pyrrolidine does not arise by reduction of a pyrrolidinone since 3-methyl-1-phenyl-2-pyrrolidinone was recovered unchanged on attempted reaction with carbon monoxide, $NaBH_4$, and 1 under identical conditions to those described for 6.

Table II. Reaction of N-Allylic Alkylamines with CO/$NaBH_4$/i-PrOH/$HRh(CO)(PPh_3)_3$[a]

8, R, R′	yield of pyrrolidinone 9, %[b]
C_6H_{11}, H	78[c]
C_6H_{11}, CH_3	46
$PhCH_2$, H	51
n-C_4H_9, H	60
C_8H_{15}, H	79
$PhCH_2$, CH_3	67
$PhCH_2CH_2$, H	92
$CH_2{=}CHCH_2$, H	20
$PhCH_2NHCH_2CH{=}CHCH_3$	40

[a] Reaction conditions: substrate (2.0 mmol), catalyst (0.02 mmol), $NaBH_4$ (2.25 mmol), i-PrOH (0.5 mL), CH_2Cl_2 (5 mL), 34.5 atm, 100 °C, 24 h. [b] Isolated yields. Products were identified by comparison of spectral data [IR, NMR (^1H, ^{13}C,), MS] with literature data. [c] Yield was 48% using 1 as the catalyst.

Pyrrolidinones were isolated as the only products when aliphatic *N*-allyl- or *N*-(methylallyl)amines were used as the reactants. Specifically, *N*-allylcyclohexylamine (8, R = C_6H_{11}, R′ = H) afforded *N*-cyclohexyl-2-pyrrolidinone in 48% yield of analytically pure material. If $HRh(CO)(PPh_3)_3$ replaces 1, then the product yield increases to 78% yield. If, in the latter process, $NaBH_4$ is substituted by other borohydrides (e.g., $NaBH_3CN$), the yield of 9 decreases appreciably. The reaction temperature of 100 °C provides lactams in the highest yields. For example, in the reaction involving *N*-allylcyclohexylamine and $HRh(CO)(PPh_3)_3$, the yield of 9, R = C_6H_{11}, R′ = H, is reduced to 63% if the reaction temperature is increased to 140 °C and to 52% at a temperature of 70 °C. In most cases, pyrrolidinones were isolated in reasonable yields from *N*-allyl- or *N*-methylallyl-substituted aliphatic amines (except *N*-allyl-*tert*-butylamine and diallylamine which gave low product yields) with $HRh(CO)(PPh_3)_3$ as the catalyst (Table II). Note that, in contrast to the aromatic *N*-allylamines, no acyclic products were formed in these reactions. The greater basicity of the reactant is probably responsible for the favored cyclization process.



An alternate synthesis of pyrrolidinones, from allylic amines, and 1 involves the use of synthesis gas instead of carbon monoxide and sodium borohydride. Treatment of *N*-allylcyclohexylamine with 1:1 CO/H_2 and 1 in CH_2Cl_2 at 48 atm and 100 °C for 1 day afforded the lactam 9, R = C_6H_{11}, R′ = H, in 15% yield (no reaction occurs with CO instead of CO/H_2). However, if the dimer of dichlorotricarbonylruthenium is added as a cocatalyst, then the isolated yield of the lactam increases to 59%. Starting material was recovered when $[Ru(CO)_3Cl_2]_2$ was the only catalyst. While ruthenium carbonyl was as effective a cocatalyst as $[Ru(CO)_3Cl_2]_2$, other metal complexes including $RuCl_2(PPh_3)_3$ (24% yield), $PdCl_2(PPh_3)_2$ (11%), $NiCl_2$ (dppp) (8%), and $CuCl_2$ (0%) were not useful in this regard. The $1/[Ru(CO)_3Cl_2]_2$ system was applied to the hydroformylation of a variety of aliphatic allyl amines, and the results are presented in Table III. Comparison of these results with those obtained using $CO/NaBH_4$ (Table II) reveals that superior yields are attained with the borohydride system. However, it must be pointed out that hydrogen is appreciably less expensive than $NaBH_4$ and that the reaction conditions compare favorably with those

Table III. Reaction of N-Allylic Alkylamines with $CO/H_2/1$-$[Ru(CO)_3Cl_2]_2$[a]

8, R, R′	yield of pyrrolidinone 9, %[b]
C_6H_{11}, H	59
C_6H_{11}, CH_3	35
$PhCH_2$, H	17
n-C_4H_9, H	51
C_8H_{15}, H	72
$PhCH_2$, CH_3	54
$PhCH_2CH_2$, H	25
CH_2=$CHCH_2$, H	25

[a] Reaction conditions: substrate (4.0 mmol), 1 (0.02 mmol), $[Ru(CO)_3Cl_2]_2$ (0.04 mmol), CH_2Cl_2 (10 mL), CO/H_2 (1:1), 48 atm, 100 °C, 24 h. [b] Isolated yields. Products were identified by comparison of spectral [IR, NMR (^{1}H, ^{13}C), MS] with literature data.

reported in the literature.[10] Finally, this synthesis gas route is not useful for *N*-allylanilines as many products are formed with such reactants.

One other approach was examined for the hydroformylation of allylic amines. It is known that 1,4-bis(diphenylphosphino)butane (dppb) is an excellent added ligand for several carbonylation reactions. While *N*-allylcyclohexylamine was recovered unchanged on exposure to synthesis gas, 1, and dppb (80 °C, 34.5 atm, 24 h), *N*-allylaniline (2, Ar = Ph) does undergo cyclization under the same conditions to give 1-phenylpyrrolidine (3, Ar = Ph) in 68% yield. Numerous products were formed in the absence of dppb. If 1 and dppb is replaced by a catalytic amount of $[dppb]Rh(COD)^+BF_4^-$ in the *N*-allylaniline reaction, 1-phenylpyrrolidine is obtained in 75% yield. The latter compound was formed in 69% yield by use of $[CODRhCl]_2$/dppb as the catalytic system. Any of these catalytic systems are superior to $CO/NaBH_4$ for the reductive cyclization of *N*-allylaniline. Furthermore, while *N*-allyl-*o*-toluidine and -*o*-anisidine undergo hydrogenation with $CO/NaBH_4$ to give 5, use of CO/H_2/1/dppb affords the pyrrolidines 3 in 67% and 55% yields, respectively, without any of 4 or 5.

In conclusion, these results demonstrate the value of the zwitterionic rhodium complex 1 as a catalyst for the conversion of allylamines to pyrrolidines or pyrrolidinones.

Experimental Section

General Procedure for the Reaction of Allylic Amines with Carbon Monoxide and $NaBH_4$ in the Presence of 1. A mixture of 2.0 mmol of the allylic amine, $NaBH_4$ (2.25 mmol), 1 (0.02 mmol), 2-propanol (0.5 mL), and CH_2Cl_2 (5.0 mL) were placed in a 45-mL autoclave containing a glass linear. The autoclave was pressured to 34.5 atm with carbon monoxide, and the mixture was heated with stirring for 30 h at 100 °C. After cooling to room temperature, the reactor was opened (fume hood) and water was added to remove unreacted $NaBH_4$. The organic phase was concentrated by rotary evaporation, affording an oil. Silica gel column chromatography, using 19:1 hexane/ethyl acetate as the eluant, gave the pyrrolidine (3 or 7) followed by the saturated amine (5, known compounds), if formed. Any amino alcohol (4, known compounds), produced in the reaction, was isolated by elution with ethyl acetate.

The pyrrolidines 3, Ar = Ph,[11] p-$CH_3OC_6H_4$,[11] 1-$C_{10}H_7$;[12] and 7, Ar = Ph, R = CH_3[13] were characterized by comparison with literature results. The following pyrrolidines are new:

7, Ar = p-$CH_3OC_6H_4$, R = CH_3: ^{1}H NMR ($CDCl_3$) δ 1.03 (d, 3 H, J = 7.2 Hz), 1.55 (m, 1 H), 2.07 (m, 1 H), 2.35 (m, 1 H), 2.76 (dd, 1 H, J = 7.5, 8.6 Hz), 3.24 (m, 2 H), 3.35 (dd, 1 H), 3.72 (s, 3 H), 6.45 (dd, 2 H, J = 8.4 Hz), 6.80 (dd, 2 H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 18.45, 33.12, 33.43, 47.94, 55.49, 55.86, 112.22, 115.03, 143.23, 150.71; MS m/z 191 $[M]^+$. Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.95; N, 7.32. Found: 75.55; H, 8.59; N, 7.30.

7, Ar = o-$CH_3OC_6H_4$, R = CH_3: ^{1}H NMR ($CDCl_3$) δ 1.10 (d, 3 H, J = 7.3 Hz), 1.54 (m, 1 H), 2.08 (m, 1 H), 2.32 (m, 1 H), 2.92 (dd, 1 H, J = 7.8, 8.9 Hz), 3.23 (m, 2 H), 3.45 (dd, 1 H), 3.83 (s, 3 H), 6.72 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 18.63, 32.58, 33.16, 50.35, 55.47, 58.08, 111.79, 114.90, 119.12, 121.17, 140.09, 150.19; MS m/z 191 $[M]^+$. Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.95; N, 7.32. Found: C, 75.31; H, 8.83; N, 7.42.

7, Ar = o-$CH_3C_6H_4$, R = CH_3: ^{1}H NMR ($CDCl_3$) δ 1.13 (d, 3 H, J = 7.3 Hz), 1.54 (m, 1 H), 2.10 (m, 1 H), 2.35 (s, 3 H), 2.46 (m, 1 H), 2.90 (dd, 1 H, J = 7.8, 8.9 Hz), 3.24 (m, 2 H), 3.41 (dd, 1 H), 6.85–7.15 (m, 4 H); MS m/z 175 $[M]^+$. Anal. Calcd for $C_{12}H_{17}N$: C, 82.23; H, 9.77; N, 8.00. Found: C, 82.34; H, 9.67; N, 7.61.

7, Ar = p-ClC_6H_4, R = CH_3: ^{1}H NMR ($CDCl_3$) δ 1.11 (d, 3 H, J = 7.4 Hz), 1.64 (m, 1 H), 2.12 (m, 1 H), 2.39 (m, 1 H), 2.83 (dd, 1 H, J = 8.0, 8.8 Hz), 3.32 (m, 3 H), 6.49 (dd, 2 H, J = 8.1 Hz), 7.15 (dd, 1 H, J = 8.1 Hz); MS m/z 195, 197 $[M]^+$.

7, Ar = 1-$C_{10}H_7$, R = CH_3: ^{1}H NMR ($CDCl_3$) δ 1.18 (d, 3 H, J = 7.5 Hz), 1.60 (m, 1 H), 2.17 (m, 1 H), 2.43 (m, 1 H), 3.07 (dd, 1 H, J = 7.7, 8.9 Hz), 3.34 (dd, 1 H), 3.52 (m, 2 H), 6.90–8.20 (m, 7 H) ppm; ^{13}C NMR ($CDCl_3$) δ 18.92, 32.73, 33.28, 52.39, 60.29, 110.71, 120.75, 124.07, 144.91, 125.47, 125.93, 127.81, 128.26, 135.08, 147.87; MS m/z 211 $[M]^+$. Anal. Calcd for $C_{15}H_{17}N$: C, 85.30; H, 8.05; N, 6.63. Found: C, 85.15; H, 8.02; N, 6.65.

7, Ar = Ph, R = n-C_5H_{11}: ^{1}H NMR ($CDCl_3$) δ 0.9–1.4 (m, 12 H), 2.24 (m, 2 H), 2.91 (dd, 1 H), 3.38 (m, 2 H), 3.45 (dd, 1 H), 6.60–7.20 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 18.85, 22.43, 27.87, 31.60, 31.82, 33.70, 38.72, 47.25, 53.34, 111.33, 115.17, 129.13, 147.98; MS m/z 217 $[M]^+$.

7, Ar = 2-C_5H_4N, R = CH_3: ^{1}H NMR ($CDCl_3$) δ 1.12 (d, 3 H), 1.60 (m, 1 H), 2.08 (m, 1 H), 2.36 (m, 1 H), 2.97 (dd, 1 H), 3.50 (m, 3 H), 6.4–8.1 (m, 4 H); MS m/z 162 $[M]^+$.

General Procedure for the Synthesis of Pyrrolidinones 9 from Aliphatic *N*-Allylamines (8). (i) Using $HRh(CO)(PPh_3)_3$, $NaBH_4$, and i-PrOH. The procedure used was identical to that described for 3 or 7, except for the substitution of 1 by $HRh(CO)(PPh_3)_3$.

(ii) Using 1 and $[RuCl_2(CO)_3]_2$ with CO/H_2. A mixture of 4.0 mmol of 8, 0.022 g (0.04 mmol) of 1, 0.008 g of $(RuCl_2(CO)_3)_2$, and CH_2Cl_2 (10 mL) was heated with stirring at 100 °C under 48 atm of 1:1 CO/H_2. After 24 h, the autoclave was cooled to room temperature and the crude product was obtained by rotary evaporation of the mixture. Pure pyrrolidinone 9 was obtained by silica gel column chromatography using 7:3 hexane–ethyl acetate as the eluant.

The 2-pyrrolidinones: 9, R = C_6H_{11}, R′ = H;[10] R = C_6H_{11}, R′ = CH_3;[14] R = $PhCH_2$, R′ = H;[14] R = $PhCH_2$, R′ = CH_3,[14] R = n-C_4H_9, R′ = H;[15] R = $PhCH_2CH_2$, R′ = H;[16] R = CH_2CH=CH_2, R′ = H[17] were characterized by comparison of spectral data with literature results. The following pyrrolidinones have not been reported previously.

9, R = n-C_4H_9, R′ = CH_3: ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3 H, $CH_3(CH_2)_3$, J = 8.1 Hz), 1.11 (d, 3 H, CH_3CH, J = 7.6 Hz), 1.35 (m, 4 H, $CH_3CH_2CH_2$), 2.00 (m, 1 H, $CHCH_3$), 2.42 (m, 2 H, CH_2CO), 3.17 (t, 2 H, NCH_2 ring, J = 7.7 Hz), 3.25 (m, 2 H, NCH_2); ^{13}C NMR ($CDCl_3$) δ 13.51, 19.65, 19.77, 26.14, 29.10, 39.34, 41.93, 54.29, 174.59; MS m/z 155 $[M]^+$. Anal. Calcd for $C_9H_{17}NO$: C, 69.63; H, 11.04; N, 9.02. Found: C, 69.51; H, 10.91; N, 8.88.

9, R = C_8H_{15}, R′ = H: ^{1}H NMR ($CDCl_3$) δ 1.60 (m, 12 H), 1.95 (m, 4 H), 2.45 (t, 2 H, CH_2CO, J = 7.9 Hz), 3.45 (t, 2 H, CH_2N, J = 7.8 Hz), 4.10 (m, 1 H, NCH); ^{13}C NMR ($CDCl_3$) δ 17.99, 24.38, 25.44, 26.41, 30.69, 31.26, 42.86, 50.96, 173.84; MS m/z 195 $[M]^+$. Anal. Calcd for $C_{12}H_{21}NO$: C, 73.84; H, 10.84. Found: C, 73.98; H, 10.74.

(11) Shim, S. C.; Huh, K. T.; Park, W. H. *Tetrahedron* **1986**, *42*, 259.
(12) Alder, R. W.; Bryce, M. R.; Gooda, N. C. *J. Chem. Soc., Perkin Trans. 2* **1982**, 477.
(13) Kanda, N.; Kondo, M. Japan Pat. 61,189,231; *Chem. Abstr.* **1987**, *106*, 32531x.
(14) Lin, T. Y.; Kingsbury, C. A.; Cromwell, N. H. *J. Heterocycl. Chem.* **1984**, *21*, 1871.
(15) Hataka, K.; Ono, Y. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2517.
(16) Mazzocchi, P. H.; Danisi, F.; Thomas, J. J. *J. Polym. Sci., Polym. Lett.* **1975**, *13*, 737.
(17) Inoue, Y.; Taguchi, M.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2721.

Reaction of *N*-Allylaniline with CO/H_2, 1, and dppb. A mixture of 0.532 g (4.0 mmol) of *N*-allylaniline, 0.022 g (0.04 mmol) of 1, 0.042 g (0.10 mmol) of dppb, and 10 mL of CH_2Cl_2 was heated with stirring for 12 h at 80 °C under 48 atm of 1:1 CO/H_2. The solvent was removed by rotary evaporation, and the residue was chromatographed on silica gel using 19:1 hexane–ethyl acetate as the eluant. The yield of pure 1-phenylpyrrolidine was 0.401 g (68%). This method was also applied to *N*-allyl-*o*-anisidine, *N*-allyl-*o*-toluidine, and *N*-allyl-1-naphthylamine affording the pyrrolidines **3**,[18,19] in 55%, 63%, and 59% yields, respectively.

Reaction of *N*-Allylaniline with CO/H_2 and (dppb)Rh(COD)$^+BF_4^-$. The previous procedure was used, except for substitution of both 1 and dppb by 0.030 g of (dppb)Rh(COD)$^+BF_4^-$. In this manner, 1-phenylpyrrolidine was isolated in 75% yield.

Reaction of *N*-Allylaniline with CO/H_2, $[CODRhCl]_2$, and dppb. The reaction and workup procedure using 1 as the catalyst was applied, with substitution of 1 by 0.013 g of $[CODRhCl]_2$. 1-Phenylpyrrolidine was obtained in 69% yield.

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Registry No. 1, 31974-01-3; **2** (Ar = Ph), 589-09-3; **2** (Ar = *p*-$CH_3OC_6H_4$), 71954-46-6; **2** (Ar = 1-$C_{10}H_7$), 22950-23-8; **2** (Ar = *o*-$CH_3OC_6H_4$), 15258-47-6; **2** (Ar = *o*-$CH_3C_6H_4$), 15316-91-3; **3** (Ar = Ph), 4096-21-3; **3** (Ar = *p*-$CH_3OC_6H_4$), 54660-04-7; **3** (Ar = 1-$C_{10}H_7$), 82238-92-4; **4** (Ar = Ph), 139944-54-0; **4** (Ar = *p*-$CH_3OC_6H_4$), 139944-55-1; **5** (Ar = Ph), 622-80-0; **5** (Ar = 1-$C_{10}H_7$), 607-60-3; **5** (Ar = *o*-$CH_3OC_6H_4$), 139944-56-2; **5** (Ar = *o*-$CH_3C_6H_4$), 83627-55-8; **6** (Ar = Ph, R = CH_3), 22774-81-8; **6** (Ar = *p*-$CH_3OC_6H_4$, R = CH_3), 139944-57-3; **6** (Ar = *o*-$CH_3OC_6H_4$, R = CH_3), 139944-58-4; **6** (Ar = *o*-$CH_3C_6H_4$, R = CH_3), 131001-34-8; **6** (Ar = *p*-ClC_6H_4, R = CH_3), 22774-84-1; **6** (Ar = 1-$C_{10}H_7$, R = CH_3), 22774-87-4; **6** (Ar = Ph, R = *n*-C_5H_{11}), 139944-59-5; **6** (Ar = 2-C_5H_4N, R = CH_3), 139944-60-8; **6** (Ar = Ph, R = CH_2SO_2Ph), 139944-61-9; **7** (Ar = Ph, R = CH_3), 106027-38-7; **7** (Ar = *p*-$CH_3OC_6H_4$, R = CH_3), 139944-62-0; **7** (Ar = *o*-$CH_3OC_6H_4$, R = CH_3), 139944-63-1; **7** (Ar = *o*-$CH_3C_6H_4$, R = CH_3), 139944-64-2; **7** (Ar = *p*-ClC_6H_4, R = CH_3), 139944-65-3; **7** (Ar = 1-$C_{10}H_7$, R = CH_3), 139944-66-4; **7** (Ar = Ph, R = *n*-C_5H_{11}), 139944-67-5; **7** (Ar = 2-C_5H_4N, R = CH_3), 139944-68-6; **8** (R = C_6H_{11}, R′ = H), 6628-00-8; **8** (R = C_6H_{11}, R′ = CH_3), 55611-45-5; **8** (R = $PhCH_2$, R′ = H), 4383-22-6; **8** (R = *n*-C_4H_9, R′ = H), 4538-09-4; **8** (R = C_8H_{15}, R′ = H), 17630-23-8; **8** (R = $PhCH_2$, R′ = CH_3), 52853-55-1; **8** (R = $PhCH_2CH_2$, R′ = H), 5263-58-1; **8** (R = CH_2=$CHCH_2$, R′ = H), 124-02-7; **9** (R = C_6H_{11}, R′ = H), 6837-24-7; **9** (R = C_6H_{11}, R′ = CH_3), 96240-05-0; **9** (R = $PhCH_2$, R′ = H), 5291-77-0; **9** (R = *n*-C_4H_9, R′ = H), 3470-98-2; **9** (R = C_8H_{15}, R′ = H), 139944-69-7; **9** (R = $PhCH_2$, R′ = CH_3), 96240-04-9; **9** (R = $PhCH_2CH_2$, R′ = H), 10135-23-6; **9** (R = CH_2=$CHCH_2$, R′ = H), 2687-97-0; $PhNHCH_2CH$=$C(CH_3)_2$, 27125-60-6; $PhNH(CH_2)_2CH(CH_3)_2$, 2051-84-5; $PhCH_2NHCH_2CH$=$CHCH_3$, 4393-07-1; $HRh(CO)(PPh_3)_3$, 17185-29-4; $RuCl_2(PPh_3)_3$, 15529-49-4; $Ru_3(CO)_{12}$, 15243-33-1; $PdCl_2(PPh_3)_2$, 13965-03-2; $NiCl_2$(dppp), 15629-92-2; *N*-isobutyl-*o*-toluidine, 139944-70-0; dichlorotricarbonylruthenium dimer, 22594-69-0; 3-methyl-1-phenylmethylpyrrolidin-2-one, 108303-99-7.

Supplementary Material Available: Spectral data for new allylic amines (2 pages). Ordering information is given on any current masthead page.

(18) Shapiro, S. L.; Freedman, L.; Soloway, H. U.S. Pat. 3,270,024; *Chem. Abstr.* **1966**, *66*, 18675v.
(19) Rozeboom, M. D.; Houk, K. N.; Searles, S.; Seyedrezai, S. E. *J. Am. Chem. Soc.* **1982**, *104*, 3448.

Synthesis of Oxazoles from *O*-Trimethylsilyl Acyltrimethylsilane Cyanohydrins

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Sequential addition of organolithium reagents and acyl chlorides (or anhydrides) to *O*-trimethylsilyl acyltrimethylsilane cyanohydrins affords β-(acyloxy)-*N*,*N*-bis(trimethylsilyl) enamines which cyclize to substituted oxazoles under thermolysis or treatment with trimethylsilyl trifluoromethanesulfonate. Oxazoles were prepared containing alkyl and phenyl substituents at C-5, alkyl, alkenyl, and phenyl substituents at C-4, and alkyl, alkenyl, phenyl, and functionalized substituents at C-2.

The oxazole ring[1] serves as nucleus to a host of compounds which, depending on attendant substitution, are physiologically active,[2] serve as luminescent materials,[3] or may be employed in synthetic methodology.[4] We have reported briefly on a new approach to oxazole assemblage which suggested that substantial control could be exercised over the choice of each ring substituent.[5] Details of this process are presented here, and extension is made to additional examples in order to better define the scope of the method.

Scheme I outlines the synthetic procedure and illustrates the entry methodologies which were explored. The targeted common intermediate was the lithium β-bis(tri-

(1) Reviews: (a) Turchi, I. J., Ed. *Oxazoles*; Wiley: New York, 1986. (b) Boyd, G. V. *Comp. Heterocycl. Chem.*, Vol. 6, Pergamon: Oxford, 1984. (c) Turchi, I. J. *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, *20*, 32. (d) Tarent'ev, P. B.; Lomakina, N. P. *Chem. Heterocycl. Compd.* **1976**, 579. (e) Turchi, I. J.; Dewar, M. J. S. *Chem. Rev.* **1975**, *75*, 389. (f) Lakhan, R.; Ternai, B. *Adv. Heterocycl. Chem.* **1974**, *17*, 99.
(2) Recent examples are given by (a) Fusetani, N.; Sugawara, T.; Matsunaga, S. *J. Am. Chem. Soc.* **1991**, *113*, 7811. (b) Kobayashi, J.; Itagaki, F.; Shigemori, H.; Ishibashi, M.; Takahashi, K.; Ogura, M.; Nagasawa, S.; Nakamura, T.; Hirota, H.; Ohta, T.; Nozoe, S. *J. Am. Chem. Soc.* **1991**, *113*, 7812.
(3) Krasovitskii, B. M.; Bolotin, B. M. *Organic Luminescent Materials*; VCH: Weinheim, 1988.
(4) (a) Boger, D. L. *Chem. Rev.* **1986**, *86*, 781. (b) Lipshutz, B. H. *Ibid.* **1986**, 795. (c) Wasserman, H. H.; McCarthy, K. E.; Prowse, K. S. *Ibid.* **1986**, 845. (d) Dondoni, A.; Fogagnolo, M.; Mastellari, A.; Pedrini, P.; Ugozzoli, F. *Tetrahedron Lett.* **1986**, *27*, 3915. (e) Hassner, A.; Fischer, B. *J. Org. Chem.* **1991**, *56*, 3419.
(5) Cunico, R. F.; Kuan, C. P. *Tetrahedron Lett.* **1990**, *31*, 1945.

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