Regiospecific Synthesis of Aza-β-lactams from Diaziridines

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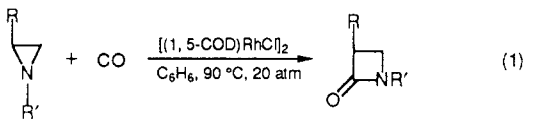
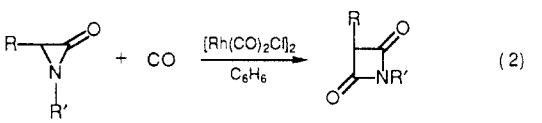
1,3-Diazetidinones are obtained by bis(dibenzylideneacetone)palladium(0)-catalyzed carbonylation of diaziridines having one substituent attached to the ring carbon atom. This regiospecific insertion into the nitrogen–nitrogen bond also occurs for 3,3-disubstituted diaziridines, provided one uses stoichiometric quantities of cobalt carbonyl.

There has been considerable interest in recent years in the use of metal complexes for the synthesis of β-lactams.[1] A novel approach involves metal-catalyzed carbonylation and ring expansion of appropriate three-membered-ring heterocycles. Rhodium(I) compounds catalyze the enantiospecific and stereospecific carbonylation of 2-arylaziridines to β-lactams (eq 1). This process is also re-



(1)

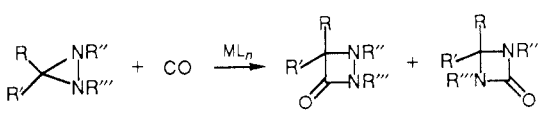
giospecific, with carbon monoxide insertion occurring into the aryl ring carbon–nitrogen bond.[2] Azetidine-2,4-diones are obtained from α-lactams by rhodium(I)-catalyzed carbonyl insertion into the saturated ring carbon–nitrogen bond (eq 2).[3] Finally, either tetrakis(triphenyl-



(2)

phosphine)palladium(0) or 4:1 triphenylphosphine–palladium acetate is capable of converting methyleneaziridines to α-methylene-β-lactams with insertion of carbon monoxide here proceeding into the unsaturated ring carbon–nitrogen bond.[4]

It seemed conceivable to us that diaziridines (**1**),[5] three-membered-ring heterocycles containing two nitrogen atoms, would be good candidates for the carbonylation–ring-expansion reaction. Two classes of aza-β-lactams may



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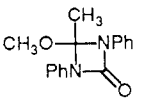
form, with 1,2-diazetidinones (**2**) resulting from carbon monoxide insertion into one of the two ring carbon–nitrogen bonds while 1,3-diazetidinones (**3**) would arise by "stitching" carbon monoxide into the nitrogen–nitrogen bond. Previously, it was found that 1,2-diaroyldiaziridines, which have weakly basic nitrogen atoms, undergo intramolecular displacement–rearrangement with dicobalt octacarbonyl to give oxazolines.[6] We now wish to report that regiospecific carbonyl insertion occurs into the nitrogen–nitrogen bond of diaziridines to give 1,3-diazetidinones, the reaction proceeding in a catalytic or stoichiometric manner, subject to the nature of the diaziridine.

Results and Discussion

1,2-Dimethyl-3-*n*-heptyldiaziridine (1(R = *n*-C_7H_{15}, R′ = H, R″ = R‴ = CH_3)), prepared in 81% yield from *n*-octanal, methylamine, and *N*-methylhydroxylamine-*O*-sulfonic acid,[7] was chosen as a representative substrate to determine conditions for attaining the desired carbonylation reaction. While rhodium(I) complexes (e.g. $(Rh(CO)_2Cl)_2$, $((1,5\text{-COD})RhCl)_2$, $Rh_4(CO)_{12}$) and palladium acetate or trifluoroacetate were inert, the electrophilic palladium(II) complex tetrakis(acetonitrile)palladium bis(tetrafluoroborate) (20:1 ratio of $1\text{–}(CH_3CN)_4Pd^{2+}\text{-}(BF_4^-)_2$) did catalyze the carbonylation of **1** in acetonitrile at reflux to give 1,3-diazetidinone (**3**), albeit in a 37% yield of pure material. Superior to this palladium(II) catalyst is the use of bis(dibenzylideneacetone)palladium(0) ($Pd(dba)_2$), which, in *N*,*N*-dimethylformamide at 120 °C (1 atm of CO), afforded **3** in quantitative yield. Following purification, the yield of analytically pure material was 66%. Other polar solvents, including acetonitrile, 4-methyl-2-pentanone, and sulfolane (no reaction), are less effective than DMF for the reaction (see Table I for results). Added triphenylphosphine completely inhibits the $Pd(dba)_2$-catalyzed process in DMF, and triphenyl phosphite is also detrimental for the carbonylation process. Attempts to use cobalt carbonyl on a stoichiometric basis (2:1 ratio of $1\text{–}Co_2(CO)_8$) resulted in either the apparent polymerization of **1** (black unidentified material formed) or no reaction (also, no reaction occurs with catalytic quantities of $Co_2(CO)_8$).

The structure of the aza-β-lactam **3**(R = *n*-C_7H_{15}, R′ = H, R″ = R‴ = CH_3) was established on the basis of analytical and spectral data (Table II). The mass spectrum gave a parent ion at *m*/*e* 198 and a major fragment at *m*/*e* 141 due to loss of methyl isocyanate. The proton magnetic resonance spectrum showed, in addition to the signals for the *n*-heptyl substituent, a singlet for the two *N*-methyl groups at δ 2.75 (the two N–CH_3 groups of the 1,2-diazetidinone **2** would appear at different chemical shifts) and a triplet at δ 4.20 for the proton attached to the saturated ring carbon. Noteworthy features of the ^{13}C NMR spectrum include a signal at δ 29.0 for the two N–CH_3 carbons at δ 76.4 for the saturated ring carbon, and at δ 160.6 for the carbonyl carbon. While the last signal is at somewhat lower field than the carbonyl carbon (δ 148.5) signal for 4,[8] it is mainly a consequence of the fact that **4** has aryl



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† Partial contribution to this work.

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Table I. Conversion of Diaziridines 1 to 1,3-Diazetidinones[a] 3

R, R′, R″, R‴ for 1	ML_n	time, h	temp, °C	solvent	amt of 3,[b] %
n-C_7H_{15}, H, CH_3, CH_3	$Pd(dba)_2$	24	120	DMF	66
	$Pd(dba)_2$	24	90	4-methyl-2-pentanone	24
	$Pd(dba)_2$	20	80	CH_3CN	13
	$Pd(dba)_2$–$P(OPh)_3$	24	120	DMF	42
	$Pd(CH_3CN)_4^{2+}(BF_4^-)_2$	24	80	CH_3CN	37
	$Co_2(CO)_8$	22	78	C_6H_6	polymer
	$Co_2(CO)_8$	48	25	C_6H_6	no reacn
	$Co_2(CO)_8$	4	90	DMF	no reacn
CH_3, H, CH_3, Ph	$Pd(dba)_2$	24	120	DMF	39
$(CH_3)_2CHCH_2$, H, CH_3, $CH_2CH{=}CH_2$	$Pd(dba)_2$	24	120	DMF	47
$(CH_2)_5$,[c] CH_3, C_6H_{11}	$Co_2(CO)_8$	3.3	78	C_6H_6	55
$(CH_2)_5$, CH_3, $CH_2C_{10}H_7$-1	$Co_2(CO)_8$	4.5	78	C_6H_6	50
$(CH_2)_5$, CH_3, CH_3	$Co_2(CO)_8$	1.3	78	C_6H_6	42
$(CH_2)_5$, CH_3, n-$C_{12}H_{25}$	$Co_2(CO)_8$	6.0	78	C_6H_6	65
$(CH_2)_4$, CH_3, n-C_4H_9	$Co_2(CO)_8$	5.0	78	C_6H_6	11

[a] Reactions with $Pd(dba)_2$ were carried out with a 20:1 ratio of 1–$Pd(dba)_2$. A 2:1 ratio of 1–$Co_2(CO)_8$ was used in the case of $Co_2(CO)_8$. [b] Yields are of analytically pure materials. See Experimental Section for analytical data. [c] This and subsequent compounds refer to R = R′ = $(CH_2)_n$ (i.e., spirodiaziridines).

Table II. Spectral Data for 3

R, R′, R″, R‴ for 3	ν(CO), cm^{-1}	^1H NMR, δ,[a] ppm	^{13}C NMR, δ,[a,b] ppm	MS, m/e
n-C_7H_{15}, H, CH_3, CH_3	1770 (neat)	0.90 (t, 3 H, CH_3), 1.10–1.80 (m, 12 H, $(CH_2)_6$), 2.75 (s, 6 H, $NCH_3)_4$, 4.20 (t, 1 H, CH)	14.1 (CH_3), 22.7, 24.7, 29.2, 29.6, 31.8 (methylene carbons), 29.0 (NCH_3), 76.4 (CH), 160.6 (CO)	198 $[M]^+$, 141 $[M - CH_3NCO]^+$
CH_3, H, CH_3, Ph	1775 (neat)	1.60 (d, 3 H, CH_3CH), 2.85 (s, 3 H, NCH_3), 4.82 (q, 1 H, $CHCH_3$), 7.20 (m, 5 H, Ph)	17.3 (CH_3), 27.3 (NCH_3), 70.5 (CH), 114.8, 121.9, 129.1, 138.5 (aromatic carbons), 154.8 (CO)	176 $[M]^+$
$(CH_3)_2CHCH_2$, H, CH_3, $CH_2CH{=}CH_2$	1770 (neat)	0.93 (d, 6 H, $(CH_3)_2$CH), 1.43 (m, 2 H, $CH_2CH(CH_3)_2$), 1.80 (m, 1 H, $CH(CH_3)_2$), 2.67 (s, 3 H, CH_3), 3.65 (m, 2 H, $CH_2CH{=}CH_2$), 4.18 (t, 1 H, CH_2), 4.80–5.30 (m, 2 H, $CH{=}CH_2$), 5.60 (m, 1 H, CH=)	22.8 (CH_3), 24.7 (CH_2CH_3), 28.7 (NCH_3), 40.9 ($CH_2CH(CH_3)_2$), 45.4 (NCH_2), 73.4 (ring CH), 117.3 (CH_2=), 133.6 (CH=), 159.9 (CO)	182 $[M]^+$
$(CH_2)_5$, CH_3, C_6H_{11}[d]	1770 (neat)	1.05–1.90 (m, 20 H, methylene protons), 2.72 (s, 3 H, NCH_3), 3.00 (m, 1 H, CHN)	24.0, 24.8, 25.4, 25.5, 32.8 34.4 (CH_2's), 28.7 (NCH_3), 52.5 (CHN), 79.1 (saturated ring carbon), 158.4 (CO)	236 $[M]^+$, 179 $[M] - CH_3NCO]^+$, 111 $[M - C_6H_{11}NCO]^+$
$(CH_2)_5$, CH_3, $CH_2C_{10}H_7$-1	1775 (C_6H_6)	1.20–1.70 (m, 10 H, ring methylene protons), 2.78 (s, 3 H, NCH_3), 4.72, (s, 2 H, CH_2N), 7.20–8.20 (m, 7 H, $C_{10}H_7$)	23.6, 24.6, 33.5 (methylene ring carbons), 28.2 (NCH_3), 42.6 (CH_2N), 80.2 (saturated ring carbon), 123.8, 125.0, 126.3, 128.3, 128.5, 131.4, 133.3, (aromatic carbons), 159.2 (CO)	295 $[M + 1]^+$ (CI)
$(CH_2)_5$, CH_3, CH_3	1760 ($CHCl_3$)	1.15–1.70 (m, 10 H, methylene protons), 2.66 (s, 6 H, NCH_3)	23.8, 24.8, 33.0 (CH_2), 27.2 (NCH_3), 78.6 (saturated ring carbon), 159.4 (CO)	168 $[M]^+$, 111 $[M - CH_3NCO]^+$
$(CH_2)_5$, CH_3, n-$C_{12}H_{15}$	1765 ($CDCl_3$)	0.89 (t, 3 H, CH_3CH_2), 1.20–1.80 (m, 30 H, methylene protons), 2.78 (s, 3 H, NCH_3), 3.06 (t, 2 H, CH_2N)	14.2 (CH_3CH_2), 22.8, 23.8, 24.8, 27.0, 29.3, 29.4, 29.6, 29.7, 30.1, 32.0, 33.7 (methylene carbons), 28.1 (NCH_3), 40.7 (CH_2N), 79.0 (saturated ring carbon), 159.7 (CO)	323 $[M + 1]^+$ (CI)[c]
$(CH_2)_4$, CH_3, n-C_4H_9	1775 (C_6H_6)	0.90 (t, 3 H, CH_3CH_2), 1.23–1.89 (m, 12 H, 6 CH_2), 2.66 (s, 3 H, NCH_3), 3.02 (t, 2 H, NCH_2)	196 $[M]^+$, 139 $[M - CH_3NCO]^+$, 97 $[M - C_4H_9NCO]^+$	

[a] $CDCl_3$ with tetramethylsilane as internal standard. [b] NMR assignments corroborated by use of COSY and HETCOR techniques. [c] CI = chemical ionization. EI: m/e 265 $[M - CH_3NCO]^+$, 111 $[M - C_{12}H_{25}NCO]^+$. [d] This and subsequent compounds refer to R = R′ = $(CH_2)_n$.

groups attached to the nitrogen atoms while **3** has methyl substituents. Similarly, the carbonyl carbon of 1,3-diphenylurea occurs at δ 152.6 while that of 1,3-diethylurea is at δ 158.2.[9]

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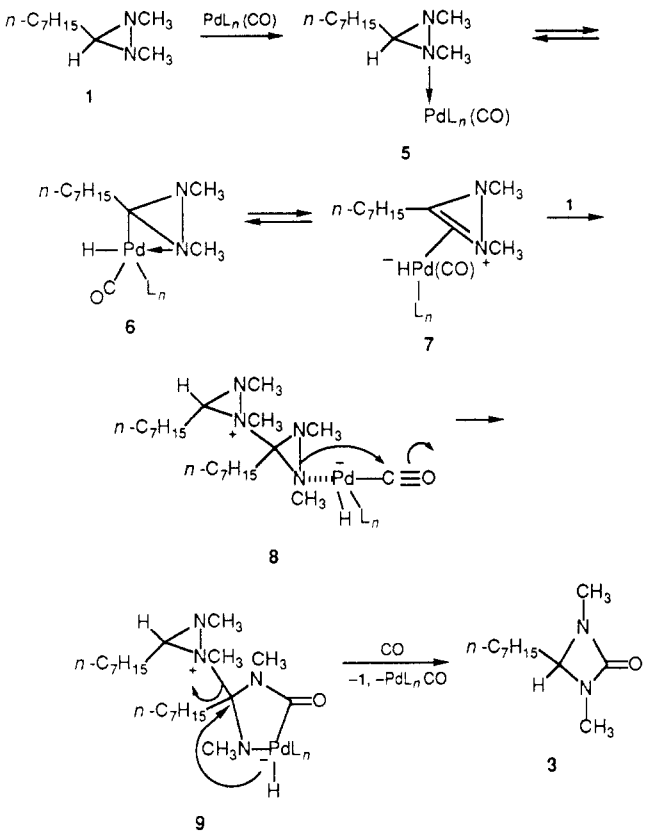
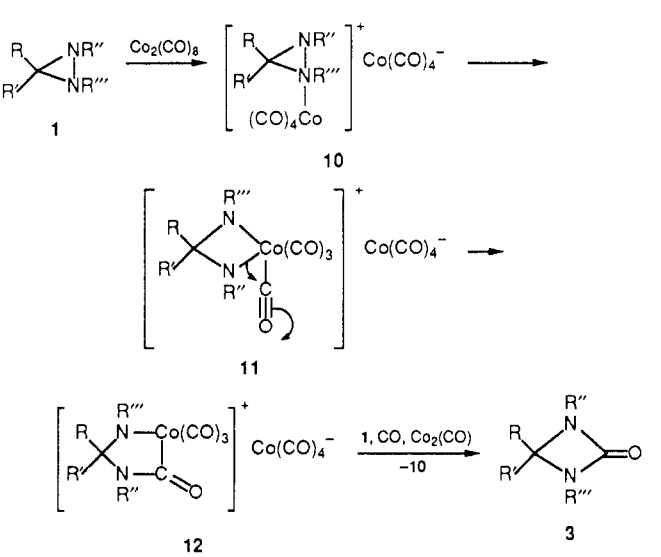
Scheme I



Scheme II



The palladium-catalyzed reaction was also applied to the synthesis of several other aza-β-lactams from diaziridines having one substituent attached to the ring carbon. However, repeated attempts to effect palladium-catalyzed carbonylation of 3,3-disubstituted diaziridines resulted in recovery of the reactant heterocycle. In contrast, cobalt carbonyl, which is incapable of forming 1,3-diazetidinones from diaziridines monosubstituted at C-3, cleanly carbonylates 3,3-disubstituted diaziridines to give aza-β-lactams in reasonable yields. The reaction, while stoichiometric in cobalt carbonyl, is regiospecific with carbonyl insertion again occurring into the nitrogen–nitrogen bond of **1** to give **3** (see Table I for yields and Table II for spectral data). A possible mechanism for the palladium-catalyzed reaction is outlined in Scheme I (illustrated for **1**(R = *n*-C_7H_{15}, R′ = H, R″ = R‴ = CH_3). Complexation of the diaziridine to in situ generated $Pd(CO)L_n$ (from $Pd(dba)_2$ and CO) may give **5**. Palladium can insert into the α-C–H bond of **5** to form **6** and then **7**. Precedence for such a reaction sequence comes from work by Murahashi and co-workers[10] on palladium-catalyzed tertiary amine exchange reactions. Attack by another molecule of **1** on **7** would produce **8**, which on ligand migration affords the metallacycle **9**. 1,3-Hydrogen transfer accompanied by regeneration of the palladium(0) catalyst and diaziridine would give the aza-β-lactam **3**. This scheme accounts for the requirement of a ring C–H bond in the reactant.

In the case of cobalt carbonyl–diaziridine reactions, the initial step probably involves formation of the ionic complex **10** (Scheme II). Insertion of cobalt into the N–N bond would afford **11**, which on ligand migration gives **12**. Reaction of the latter complex with carbon monoxide, cobalt carbonyl, and diaziridine would result in the formation of the 1,3-diazetidinone and regenerate **10**. It is not clear why diaziridines with one ring carbon substituent give polymeric material rather than aza-β-lactams, unless cobalt undergoes facile C–H bond insertion followed by ring cleavage and polymerization rather than generation of analogues of **7**.

A major effort has been made in medicinal chemistry to develop modified β-lactam antibiotics.[11] One approach involves the replacement of one of the carbon atoms of the β-lactam unit by a nitrogen atom, affording either 1,2-diazetidinones[12] or 1,3-diazetidinones.[8,15] The latter class of compounds can now be synthesized by a simple, regiospecific carbonylation process with catalytic quantities of palladium compounds or stoichiometric amounts of cobalt carbonyl.

Experimental Section

General Considerations. NMR spectra were recorded on Varian XL 300-MHz and Gemini 200-MHz spectrometers. A VG 7070E spectrometer was used for mass spectral determinations, while infrared spectra were recorded on a Perkin-Elmer 783 spectrometer. Elemental analyses were carried out by Guelph Chemical Laboratories, Guelph, Ontario, Canada, and by MHW Laboratories, Phoenix, AZ.

The palladium and cobalt complexes were purchased from commercial sources and were used as received. Organic solvents were dried and distilled prior to use.

Diaziridines. The diaziridines were prepared according to literature methods.

(a) 1(R = *n*-C_7H_{15}, R′ = H, R″ = R‴ = CH_3). Application of the procedure of Schmitz and co-workers[7] gave the diaziridine in 81% yield: bp 36–37 °C (1.2 mm); MS (*m/e*) 170 $[M]^+$. Anal. Calcd for $C_{10}H_{22}N_2$: C, 70.53; H, 13.02; N, 16.45. Found: C, 70.33; H, 13.11; N, 16.48.

(b) 1(R = CH_3, R′ = H, R″ = CH_3, R‴ = Ph). This diaziridine was synthesized in 88% yield according to the method of Akiyama and co-workers;[16] bp 36–37 °C (0.9 mm) (lit.[16] bp 68–71 °C (2.0

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mm)). Spectral data are in accord with literature results.

(c) 1(R = $(CH_3)_2CHCH_2$, H, CH_3, $CH_2CH{=}CH_2$). Use of the same procedure as in (a) gave the diaziridine: bp 56–60 °C (7.0 mmHg); MS (*m/e*) 154 $[M]^+$. Anal. Calcd for $C_9H_{18}N_2$: C, 70.08; H, 11.76; N, 18.16. Found: C, 70.25; H, 11.41; N, 18.01.

(d) 1(R = R′ = $(CH_2)_5$, R″ = CH_3, R‴ = C_6H_{11}). Treatment of the imine obtained in 85% yield from cyclohexanone and cyclohexylamine with hydroxylamine-*O*-sulfonic acid and cyclohexylamine in methanol[7,17] afforded 1-cyclohexyl-3,3-pentamethylenediaziridine in 79% yield; bp 90–92 °C (5 mm). N-Methylation of the diaziridine was best achieved as follows (N_2 atmosphere). To 7.6 mL of 2.5 M *n*-C_4H_9Li in dry ether (20 mL) at 0 °C was added 2.50 g (12.9 mmol) of the diaziridine. The reaction mixture was then stirred at room temperature for 3 h and cooled again to 0 °C, methyl iodide (25 mmol) in ether (5.0 mL) was added, and the reaction mixture was stirred overnight at room temperature. Following filtration and concentration of the filtrate, the resulting oil was treated with ether (50 mL), washed with water, dried, and concentrated. Pure diaziridine (1.54 g, 58%) was obtained by silica gel chromatography with 4:1 ether–hexane as the eluant: MS (*m/e*) 208 $[M]^+$. Anal. Calcd for $C_{13}H_{24}N_2$: C, 74.94; H, 11.61; N, 13.45. Found: C, 75.02, H, 11.71, N, 13.20.

(e) 1(R = R′ = $(CH_2)_5$, R″ = CH_3, R‴ = $CH_2C_{10}H_7$-1). Treatment of the imine obtained in 93% yield from cyclohexanone and 1-naphthylmethylamine with *N*-methylhydroxylamine-*O*-sulfonic acid and 1-naphthylmethylamine in methanol[17] afforded 1-methyl-2-(1-naphthylmethyl)-3,3-pentamethylenediaziridine in 80% yield: MS (*m/e*) 266 $[M]^+$; ^1H NMR ($CDCl_3$) δ 1.20–1.80 (m, 10 H, cyclohexyl protons), 2.43 (s, 3 H, NCH_3), 4.14 (q, 2 H, CH_2N), 7.30–8.20 (m, 7 H, $C_{10}H_7$); ^{13}C NMR ($CDCl_3$) δ 25.2, 26.0, 30.8 (methylene carbons of cyclohexane ring), 39.9 (NCH_3), 54.6 (NCH_2), 65.7 (diaziridine carbon), 124.2, 125.4, 125.8, 127.4, 128.4, 131.8, 133.7, 135.5 (aromatic carbons). Anal. Calcd for $C_{18}H_{22}N_2$: C, 81.16; H, 8.32; N, 10.52. Found: C, 80.93; H, 8.19; N, 10.79.

(f) 1(R = R′ = $(CH_2)_5$, R″ = CH_3, R‴ = CH_3). The procedure described by Schmitz et al.[7] (cyclohexanone, methylamine (40% in water), *N*-methylhydroxylamine-*O*-sulfonic acid) was used to synthesize 1,2-dimethyl-3,3-pentamethylenediaziridine in 98% yield: MS (*m/e*) 140 $[M]^+$; ^{13}C NMR ($CDCl_3$) δ 25.2, 25.9, 29.9 (methylene carbons), 39.5 (NCH_3), 64.9 (diaziridine carbon). Anal. Calcd for $C_8H_{16}N_2$: C, 68.52; H, 11.50; N, 19.98. Found: C, 68.24; H, 11.48; N, 20.11.

(g) 1(R = R′ = $(CH_2)_5$, R″ = CH_3, R‴ = *n*-$C_{12}H_{25}$). The procedure used in (e) was applied here with *n*-dodecylamine used instead of 1-naphthylmethylamine. The yield of diaziridine was 84%: MS (*m/e*) 294 $[M]^+$; ^1H NMR ($CDCl_3$) δ 0.86 (t, 3 H, CH_3), 1.20–1.70 (m, 30 H, 15 methylene groups), 2.50 (s, 3 H, CH_3), 2.63 (m, 2 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 14.2 (CH_3), 22.8, 25.2, 25.4, 26.0, 27.6, 29.4, 29.6, 29.7, 30.1, 30.4, 32.0 (methylene carbons), 40.0 (NCH_3), 52.7 (NCH_2), 65.1 (diaziridine carbon). Anal. Calcd for $C_{19}H_{38}N_2$: C, 77.48; H, 13.01; N, 9.51. Found: C, 77.56; H, 12.81; N, 9.46.

(h) 1(R = R′ = $(CH_2)_4$, R″ = CH_3, R‴ = *n*-C_4H_9). Treatment of the imine prepared from cyclopentanone and *n*-butylamine with *N*-methylhydroxylamine-*O*-sulfonic acid according to known methodology[17] gave 1-methyl-2-*n*-butyl-3,3-tetramethylenediaziridine in 75% yield (workup by alumina TLC with pentane): MS (*m/e*) 168 $[M]^+$; ^1H NMR ($CDCl_3$) δ 0.91 (t, 3 H, CH_3), 1.32–1.83 (m, 12 H, 6 CH_2), 2.23 (m, 1 H, proton of NCH_2), 2.40 (s, 3 H, NCH_3), 2.49 (m, 1 H, proton of NCH_2); ^{13}C NMR ($CDCl_3$) δ 14.2 (CH_3), 20.8, 24.9, 28.6, 31.4 (methylene carbons), 42.0 (CH_3N), 54.8 (CH_2N), 72.9 (diaziridine carbon). Anal. Calcd for $C_{10}H_{20}N_2$: C, 71.37; H, 11.98; N, 16.65. Found: C, 71.12; H, 11.83; N, 16.90.

General Procedure for the Palladium-Catalyzed Carbonylation of Diaziridines. A mixture of 1.0 mmol of diaziridine and 0.05 mmol of $Pd(dba)_2$ in DMF (10 mL) was heated under a carbon monoxide atmosphere (see Table I for reaction time and temperature). The reaction mixture was poured into 50 mL of salt water and extracted with ether (2 × 50 mL), and the ether extract was dried (Na_2SO_4) and concentrated by rotary evaporation. Pure aza-β-lactam was obtained by aluminum oxide preparative thin-layer chromatography (*note*: do not use silica gel, as the aza-β-lactam decomposes on this adsorbent) with 4:1 hexane–ethyl acetate as the developing solvent mixture.

General Procedure for the Carbonylation of Diaziridines with Cobalt Carbonyl. A mixture of 1.5–2.5 mmol of diaziridine and 0.75–1.25 mmol of $Co_2(CO)_8$ (2:1 ratio of 1–$Co_2(CO)_8$) in benzene (10–15 mL) was refluxed, under a carbon monoxide atmosphere, for the period indicated in Table I. The solution was cooled and filtered through a small amount of alumina to remove most of the cobalt, and crude **3** was obtained by concentration of the filtrate. Pure aza-β-lactam was then isolated by preparative thin-layer chromatography (Al_2O_3) with 3:1 pentane–ether as eluant.

Elemental analyses for **3** are as follows. Anal. Calcd for **3**(R = *n*-C_7H_{15}, R′ = H, R″ = R‴ = CH_3), $C_{11}H_{22}N_2O$: C, 66.62; H, 11.18; N, 14.13. Found: C, 66.26; H, 10.87; N, 13.87. Calcd for **3**(R = CH_3, R′ = H, R″ = CH_3, R‴ = Ph), $C_{10}H_{12}N_2O$: C, 68.16; H, 6.86; N, 15.90. Found: C, 67.90; H, 6.88; N, 15.82. Calcd for **3**(R = $(CH_3)_2CHCH_2$, R′ = H, R″ = CH_3, R‴ = $CH_2CH{=}CH_2$), $C_{10}H_{18}N_2O$: C, 65.90; H, 9.95; N, 15.37. Found: C, 65.53; H, 10.47; N, 14.90. Calcd for **3**(R = R′ = $(CH_2)_5$, R″ = CH_3, R‴ = C_6H_{11}), $C_{14}H_{24}N_2O$: C, 71.14; H, 10.24; N, 11.85. Found: C, 71.11; H, 10.07; N, 12.03. Calcd for **3**(R = R′ = $(CH_2)_5$, R″ = CH_3, R‴ = $CH_2C_{10}H_7$-1), $C_{19}H_{22}N_2O$: C, 77.52; H, 7.53; N, 9.52. Found: C, 77.87; H, 7.45; N, 9.56. Calcd for **3**(R = R′ = $(CH_2)_5$, R″ = R‴ = CH_3), $C_9H_{16}N_2O$: C, 64.25; H, 9.59; N, 16.65. Found: C, 64.07; H, 9.81; N, 16.70. Calcd for **3**(R = R′ = $(CH_2)_5$, R″ = CH_3, R‴ = *n*-$C_{12}H_{25}$), $C_{20}H_{38}N_2O$: C, 74.48; H, 11.88; N, 8.69. Found: C, 74.86; H, 11.53; N, 8.94. Calcd for **3**(R = R′ = $(CH_2)_4$, R″ = CH_3, R‴ = *n*-C_4H_9), $C_{11}H_{20}N_2O$: C, 67.31; H, 10.27; N, 14.27. Found: C, 67.55; H, 9.93; N, 14.18.

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Registry No. 1 (R = *n*-C_7H_{15}, R′ = H, R″ = R‴ = Me), 125023-24-7; 1 (R = Me, R′ = H, R″ = Me, R‴ = Ph), 51456-64-5; 1 (R = *i*-Bu, R′ = H, R″ = Me, R‴ = $CH_2CH{=}CH_2$), 125023-25-8; 1 (R = R′ = $(CH_2)_5$, R″ = Me, R‴ = C_6H_{11}), 125023-26-9; 1 (R = R′ = $(CH_2)_5$, R″ = Me, R‴ = $CH_2C_{10}H_7$-1), 125048-80-8; 1 (R = R′ = $(CH_2)_5$, R″ = R‴ = Me), 125023-27-0; 1 (R = R′ = $(CH_2)_5$, R″ = Me, R‴ = *n*-$C_{12}H_{25}$), 125023-28-1; 1 (R = R′ = $(CH_2)_4$, R″ = Me, R‴ = *n*-Bu), 125023-29-2; **3** (R = *n*-C_7H_{15}, R′ = H, R″ = R‴ = Me), 125023-31-6; **3** (R = R″ = Me, R′ = H, R‴ = Ph), 125023-32-7; **3** (R = *i*-Bu, R′ = H, R″ = Me, R‴ = $CH_2CH{=}CH_2$), 125023-33-8; **3** (R = R′ = $(CH_2)_5$, R″ = Me, R‴ = C_6H_{11}), 125023-34-9; **3** (R = R′ = $(CH_2)_5$, R″ = Me, R‴ = $CH_2C_{10}H_7$-1), 125023-35-0; **3** (R = R′ = $(CH_2)_5$, R″ = R‴ = Me), 125023-36-1; **3** (R = R′ = $(CH_2)_5$, R″ = Me, R‴ = *n*-$C_{12}H_{25}$), 125023-37-2; **3** (R = R′ = $(CH_2)_4$, R″ = Me, R‴ = *n*-Bu), 125023-38-3; $H_3C(CH_2)_{11}NH_2$, 124-22-1; $H_3C(CH_2)_3NH_2$, 109-73-9; $MeNHOSO_3H$, 3400-11-1; cyclohexanone, 108-94-1; cyclohexylamine, 108-91-8; *N*-cyclohexylcyclohexylimine, 10468-40-3; 1-cyclohexyl-3,3-pentamethylenediaziridine, 54862-83-8; 1-naphthylmethylamine, 118-31-0; *N*-cyclohexyl-1-naphthylmethylimine, 125023-30-5; cyclopentanone, 120-92-3; *N*-cyclopentylbutylimine, 6407-38-1; 1,3-diazetidin-2-one, 5265-50-9.

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