It would appear that expulsion of triethylboron tosylate from I to give II results in the spontaneous β-elimination of adenine before reduction of the free carbonyl function takes place. However, in the presence of >6 equiv of LTBH, association of a second triethyl borohydride species at the α-face may occur and promote a more closely "concerted" sequence. The hydride shift from C3′ to C2′ with Walden displacement of tosylate may be accompanied by hydride transfer from a second boron to C3′ with inversion of the boronate-substituted carbon or by rapid reduction of a transient trigonal boron–carbonyl complex at the α-face.

A sequence postulated for the ribonucleotide reductase mediated deoxygenation is initiated by abstraction of H3′, departure of O2′ (possible loss of the 3′-hydroxyl proton to give a 3′-ketone[3c]), external hydrogen transfer to C2′ at the α-face, and return of the originally abstracted H3′ to C3′ from the β-face.[3] Our present rearrangement includes certain features of that sequence, but the [1,2]-hydride shift to C2′ on the β-face and hydride transfer to C3′ at the α-face result in inversion of both chiral centers in contrast to the double-retention stereochemistry of the enyzmatic process.

Our new conversion provides convenient access to inverted deoxypentofuranosyl compounds that are difficult to obtain by conventional methods.[9,13] Compound **4a** is the core nucleoside of an unusual plant bacteriocin, agrocin 84.[14] This rearrangement provides other useful carbohydrate derivatives by efficient synthetic routes. Details of its application with other nucleoside bases and anomers and the experimental and spectral data will be reported.

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Supplementary Material Available: Spectroscopic and analytical data for compounds **2a,b**, **3**, **4a,b**, and **6a,b** (2 pages). Ordering information is given on any current masthead page.

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Regiospecific Metal-Catalyzed Ring Expansion of Aziridines to β-Lactams

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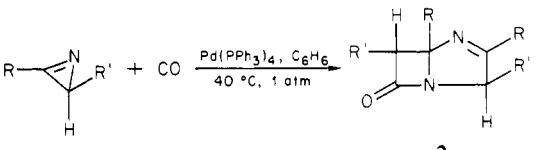
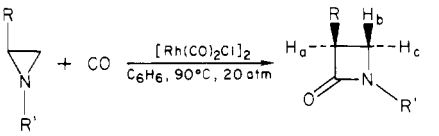
Three-membered ring compounds undergo interesting cleavage reactions in the presence of transition-metal complexes.[1] Of particular and practical value are those processes in which the metal complex functions as a catalyst and not as a stoichiometric reagent. In 1981, one of us[2] reported a novel approach to the synthesis of bicyclic β-lactams. Exposure of an azirine (**1**) to carbon monoxide and a catalytic amount of tetrakis(triphenylphosphine)palladium(0), at 40 °C and 1 atm, afforded the heterocycles **2** in reasonable yields. Attempts to synthesize monocyclic



1 2

β-lactams from azirines by metal-catalyzed carbonylation (and reduction) failed. It seemed conceivable that the desired monocyclic β-lactams could be prepared by the carbonylation of aziridines, the saturated three-membered ring heterocycles, under appropriate conditions. In fact, the mechanism first proposed for the formation of **2** from **1** involved the generation of a fused aziridine which then could be carbonylated to **2**. However, neither monocyclic nor bicyclic aziridines react with carbon monoxide under conditions used for the conversion of **1** to **2**.[3] While this result was disappointing in terms of monocyclic β-lactam formation, we knew that, in some cases, rhodium(I) and palladium(0) can effect the same kinds of reactions with one or the other metal complex being superior for a particular transformation (e.g., formation of vinyl isocyanates from aziridines).[3] We now wish to report the direct, regiospecific, rhodium-catalyzed carbonylation of aziridines to β-lactams.

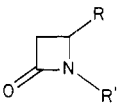
Treatment of *N-tert*-butyl-2-phenylaziridine (**3**, R = Ph, R′



3 4

= $(CH_3)_3C$) with carbon monoxide in benzene, using chlorodicarbonylrhodium(I) dimer as the catalyst (20:1 ratio of **3**/catalyst), at 90 °C and 20 atm, afforded the β-lactam **4**, R = Ph, R′ = $(CH_3)_3C$, in quantitative yield. The β-lactam was identified on the basis of analytical (Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 77.08; H, 8.44; N, 6.95) and spectral data. In particular the infrared carbonyl stretching frequency occurred at 1740 cm^{-1}, and the proton magnetic resonance spectrum displayed a typical 12-line AMX spectrum for the three protons attached to the carbon atoms of the heterocyclic ring. Carbon-13 magnetic resonance and mass spectral data are also in accord with the assigned structure (see Table I for pertinent nuclear magnetic resonance and mass spectral data).

β-Lactams were also formed in quantitative yields with **3**, R = Ph, *p*-BrC_6H_4, *p*-PhC_6H_4 and R′ = *tert*-butyl or 1-adamantyl, as reactants (aziridines were prepared by standard literature methods).[4] In all instances, the reaction was completely regiospecific with none of the isomeric β-lactam **5** being detected.



5

Note that, in order for reaction to occur under the described conditions, the R′ group must not contain acidic hydrogens on carbon adjacent to the heterocyclic nitrogen atom. If it does (e.g., R′ = $PhCH_2$) then ring cleavage of **3** occurs to give a complex mixture of products. However, one can achieve the synthesis of the desired benzylic compound by simply carbonylating *N*-(trimethylsilyl)-**2**-phenylaziridine to **4**, R = Ph, R′ = $Si(CH_3)_3$ and exposing the latter to benzyl chloride and tetrabutylammonium fluoride. This result is of relevance to the synthesis of nocardicin type antibiotics.[5] Another rhodium(I) complex, 1,5-cyclooctadienerhodium(I) chloride dimer, is also an effective catalyst for converting **3** to **4**. However, the dimer of 1,5-hexadiene-

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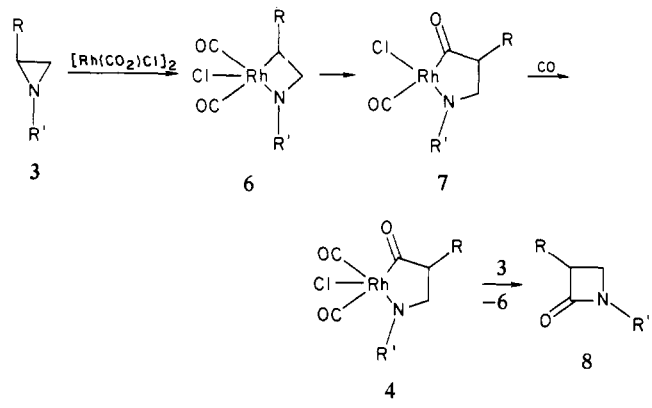
Table I. β-Lactams (4) Obtained by the Rhodium(I)-Catalyzed Carbonylation of Aziridines

4: R, R'	^{1}H NMR, ppm[a]	^{13}C NMR, ppm[a,b]	MS, m/e
Ph, $C(CH_3)_3$	1.36 (s, 9 H, $C(CH_3)_3$), 3.07 (dd, 1 H, H_b, J_{AB} = 2, J_{BC} = 6 Hz), 3.52 (dd, 1 H, H_c, J_{ac} = 5 Hz), 4.06 (dd, 1 H, H_a), 7.23 (s, 5 H, Ph)	27.78 (q, CH_3), 44.70 (t, CH_2), 52.28 (s, $C(CH_3)_3$), 53.24 (d, *CH*Ph), 128.79, 127.26 (d each, CH of Ph), 136.39 (s, quaternary carbon of Ph), 167.14 (s, CO)	203, $[M]^+$
Ph, 1-adamantyl	1.68-2.05 (m, 15 H, adamantyl protons), 3.11 (dd, 1 H, H_b, J_{ab} = 2, J_{bc} = 5.5 Hz) 3.55 (dd, 1 H, H_c, J_{ac} = 5.0 Hz), 4.06 (dd, 1 H, H_a), 7.23 (s, 5 H, Ph)	29.06 (d), 36.21 (t), 40.83 (t) (secondary and tertiary adamantyl carbons), 43.75 (t, CH_2), 52.06 (d, *CH*Ph), 53.97 (s, quaternary C of adamantane group), 127.29, 128.75 (d each, CH of Ph), 136.45 (s, quaternary carbon of Ph), 167.12 (s, CO)	281, $[M]^+$
p-PhC_6H_4, $C(CH_3)_3$	1.33 (s, 9 H, $C(CH_3)_3$), 3.13 (dd, 1 H, H_b, J_{ab} = 2, J_{bc} = 5.5 Hz), 3.53 (dd, 1 H, H_c, J_{ac} = 6 Hz), 4.10 (dd, 1 H, H_a), 7.16-7.56 (m, 9 H, aromatic ring protons)	27.77 (q, CH_3), 44.63 (t, CH_2), 51.94 (d, *CH*Ph), 53.28 (s, $C(CH_3)_3$), 127.01, 127.26, 127.51, 127.66, 128.76 (d each, aromatic CH), 135.31, 140.26, 140.78 (s each, quaternary carbons of p-PhC_6H_4), 167.05 (s, CO)	279, $[M]^+$
p-PhC_6H_4, 1-adamantyl	1.70-2.05 (m, 15 H, adamantyl protons), 3.15 (dd, 1 H, H_b, J_{ab} = 2, J_{bc} = 5.5 Hz), 3.56 (dd, 1 H, H_c, J_{ac} = 5 Hz), 4.10 (dd, 1 H, H_a), 7.15-7.65 (m, 9 H, aromatic ring protons)	29.04 (d), 36.19 (t), 40.82 (t) (secondary and tertiary adamantyl carbons), 43.63 (t, CH_2), 51.72 (d, *CH*Ph), 54.00 (s, quaternary C of adamantane group), 127.01, 127.25, 127.50, 127.68, 128.75 (d each, aromatic CH), 135.44, 140.25, 140.81 (s each, quaternary carbons of p-PhC_6H_4), 167.03	357, $[M]^+$
p-BrC_6H_4, $C(CH_3)_3$	1.38 (s, 9 H, $C(CH_3)_3$), 3.06 (dd, 1 H, H_b, J_{ab} = 2, J_{bc} = 5.5 Hz), 3.53 (dd, 1 H, H_c, J_{ac} = 5.0 Hz), 4.05 (dd, 1 H, H_a), 7.00-7.60 (m, 4 H, aromatic protons)		283, 281, $[M]^+$

[a] $CDCl_3$ with tetramethylsilane as internal standard. [b] Multiplicity of signals observed when C-13 spectra were recorded in the partially decoupled mode.

Scheme I



rhodium(I) chloride and rhodium acetate are incapable of catalyzing the desired transformation.

A possible mechanism for the formation of β-lactams is outlined in Scheme I. Oxidative addition of rhodium(I) to the more substituted carbon-nitrogen bond of the aziridine would give the rhodium(III) complex **6**. Ligand migration to **7** and subsequent carbonylation would give **8**. The β-lactam would then be formed by reductive elimination of **8**, with or without the assistance of another molecule of the aziridine. Analogy to the proposed mechanism is found in the elegant work done on the stoichiometric rhodium(I)-induced cleavage and carbonylation of certain polycyclic hydrocarbons such as cubane[6] and the photolytic reaction of chromium carbene complexes with imines to give β-lactams.[7] Unfortunately, the latter reaction, as well as the use of cyclopentadienyliron dicarbonyl complexes to prepare β-lactams[8] are both *stoichiometric* methods and not catalytic as in the present case.

The following procedure is typical: a mixture of **3**, R = Ph, R' = $C(CH_3)_3$ (1.00 g, 5.71 mmol), and $[Rh(CO)_2Cl]_2$ (0.11 g, 0.28 mmol) in dry benzene (30 mL) was stirred under carbon monoxide for 2 days at 20 atm and 90 °C. The solvent was removed by rotary evaporation, and the analytically pure β-lactam was obtained by silica gel chromatography using ethyl acetate-hexane as the eluant.

In conclusion, aziridines can be carbonylated to β-lactams in a completely regiospecific manner. This constitutes the first example of direct ring expansion and carbonylation of an aziridine.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council for support of this work.

Registry No. 3 (R = Ph; R' = $C(CH_3)_3$), 18366-49-9; **3** (R = Ph; R' = 1-adamantyl), 87461-58-3; **3** (R = p-PhC_6H_4; R' = $C(CH_3)_3$), 87451-10-3; **3** (R = p-PhC_6H_4; R' = 1-adamantyl), 87451-11-4; **3** (R = p-BrC_6H_4; R' = $C(CH_3)_3$), 87451-12-5; **4** (R = Ph; R' = $C(CH_3)_3$), 87451-13-6; **4** (R = Ph; R^1 = 1-adamantyl), 87451-14-7; **4** (R = p-PhC_6H_4; R' = $C(CH_3)_3$), 87451-15-8; **4** (R = p-PhC_6H_4; R' = 1-adamantyl), 87451-16-9; **4** (R = p-BrC_6H_4; Rr' = $C(CH_3)_3$), 87451-17-0; $[Rh(CO)_2Cl]_2$, 14523-22-9; 1,5-cyclooctadienerhodium(I) chloride dimer, 12092-47-6.

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Photophysics of the Second Excited Singlet States of Xanthione and Related Thiones in Perfluoroalkane Solvents

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Xanthione and related molecules have been adopted as model compounds for the study of the remarkable photophysics and spectroscopy of aromatic thiones in a variety of media.[2-5] On the basis of measurements of low quantum yields of net photodecomposition (ϕ_d) it has been assumed that xanthione itself does

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