Cyclopentanes from *N*-Aminoglyconolactams: Reaction Mechanism and Improved Access to Diazocyclopentanones

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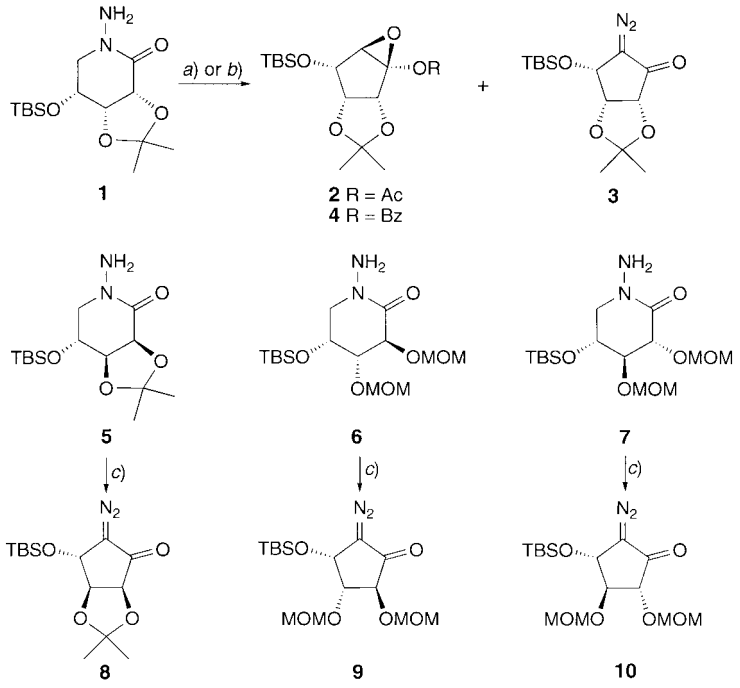
One of the two mechanisms to rationalize the $Pb(OAc)_4$ oxidation of **1** to **2** and **3** postulates the intermediate generation of a carbene **25** *via* the acetoxy-diazepinone **22** and the oxadiazoline **23** (*Scheme 2*). This mechanism was excluded on the basis of the oxidation of the diazepinone **32** that was synthesized in six steps from the ribonolactone **26**. Oxidation of **32** with $Pb(OAc)_4$ provided the unstable acetoxy-diazepinone intermediate **22**, its C(5) epimer, and the stable 5-*O*-acetyl-1,5-ribonolactone **33**; the ^{1}H-NMR spectra of the products of the oxidation of **32** and the decomposition of **22** showed no evidence for the formation of the acetoxy epoxide **2** and the diazo ketone **3**, excluding **22** as intermediate in the oxidation of **1**. To increase the yield of the diazo-cyclopentanones, we oxidized the acetohydrazide **34**, the 4-toluenesulfonohydrazide **44**, and the *N*,*O*-diacetate **46** with $Pb(OAc)_4$. Oxidation of the acetohydrazide **34** with $Pb(OAc)_4$ led to a higher yield of the diazo ketone **3** (40%) than oxidation of the *N*-amino-ribonolactam **1** without affecting the yield of **2**. Oxidation of the 4-toluenesulfonohydrazide **44** gave mostly the product **45** of *C*-acetoxylation, while the analogous oxidation of **46** gave the acetoxy lactone **33**; neither **2** nor **3** could be detected among the products, excluding **46** as intermediate of the oxidation of **34**. Oxidation of the *N*-acetamido-lyxonolactam **47** with $Pb(OAc)_4$ provided the diazo ketone **8** (77 *vs.* 37% from **5**); higher yields of diazo ketones resulted also from the oxidation of the acetohydrazides **48** and **49**.

Introduction. – Oxidation of the *N*-aminoribonolactam **1** (*Scheme 1*) with $Pb(OAc)_4$ led to the acetoxy epoxide **2** (49%) and the diazo ketone **3** (29%); similarly, $Pb(OBz)_4$ transformed **1** into the benzoyloxy epoxide **4** (33%) and **3** (42%) [1]. Oxidation of the related *N*-aminolyxonolactam **5**, *N*-aminoarabinonolactam **6**, and *N*-aminoxylonolactam **7** provided the corresponding diazo ketones **8** (37%), **9** (22%), and **10** (25%), respectively, as major products, besides a multitude of side-products. The synthetic potential of the acetoxy epoxide **2** was illustrated by an efficient synthesis of mannostatin A.

Two mechanisms were discussed for this novel transformation of **1** to **2** and **3** (*Scheme 2*) [1]. According to both hypotheses, **1** is first transformed into **17** by *N*-acetoxylation (→ **11**), elimination (→ **12**), isomerization (→ **13**), addition of an AcO group (→ **14**), and a second *N*-acetoxylation (→ **15**) and elimination to form **16**; ring opening of this highly electrophilic acyl derivative leads to the azo compound **17**. According to the first mechanism, **17** is transformed into the diazo anhydride **18**. Intramolecular nucleophilic addition to the acyloxycarbonyl group forms the diastereoisomeric intermediates **19** and **20**. The isomer **19** forms the acetoxy epoxide **2** by nucleophilic substitution; competing elimination of the acyloxy group may also lead (*via* a diastereoisomer of **21**) to the diazo ketone **3**. The diastereoisomeric intermediate **20** can only undergo elimination to **21**, deprotonation of **21** providing **3**. A comparison of the oxidation of **1** with $Pb(OBz)_4$ and with $Pb(OAc)_4$ in toluene shows that $Pb(OBz)_4$ leads to a higher proportion of the diazo ketone **3** relative to the acyloxy

Scheme 1



a) $Pb(OAc)_4$, toluene, 23°, 2 h; 49% of **2**, 29% of **3**. *b*) $Pb(OBz)_4$, toluene, 23°, 2 h; 33% of **4**, 42% of **3**. *c*) $Pb(OAc)_4$, toluene, 23°, 1 h; 37% of **8**, 22% of **9**, 25% of **10**. MOMO = Methoxymethoxy, TBSO = (*t*-Bu)Me_2SiO.

epoxide (**4/3** 3 : 4 *vs.* **2/3** 5 : 3); this correlates with the relative leaving-group quality of the BzO and AcO groups, and a higher propensity of the benzoylated analogue of **19** towards elimination. According to the second mechanism, *N*-acylation of **17** gives a cyclic *N*-acyl diazo compound **22** that cyclizes to the oxadiazoline **23**. This oxadiazoline is transformed *via* the carbonyl ylide **24** and the carbene **25** to the acetoxy epoxide **2**, while the diazo ketone **3** is formed *via* **18** and **19/20**. The first mechanism appeared more probable, and we wondered if the second one might be excluded by showing that the intermediate **22** is not a precursor of **2**. We also wished to improve the yields of the diazo ketones, which are versatile and promising synthetic intermediates in their own right.

Results and Discussion. – *Synthesis and Oxidation of the* N*-Acyl Hydrazone* **32**. The above-mentioned diazepinone intermediate **22** (*Scheme 2*) should also result from the $Pb(OAc)_4$ oxidation of the *N*-acyl hydrazone **32** (*Scheme 3*); this kind of transformation, is, indeed, well-documented by *Iffland et al.*, and by *Hoffmann* and *Luthardt*[1]) [3]. We, therefore, decided to prepare the *N*-acyl hydrazone **32**, and to examine its reaction with $Pb(OAc)_4$.

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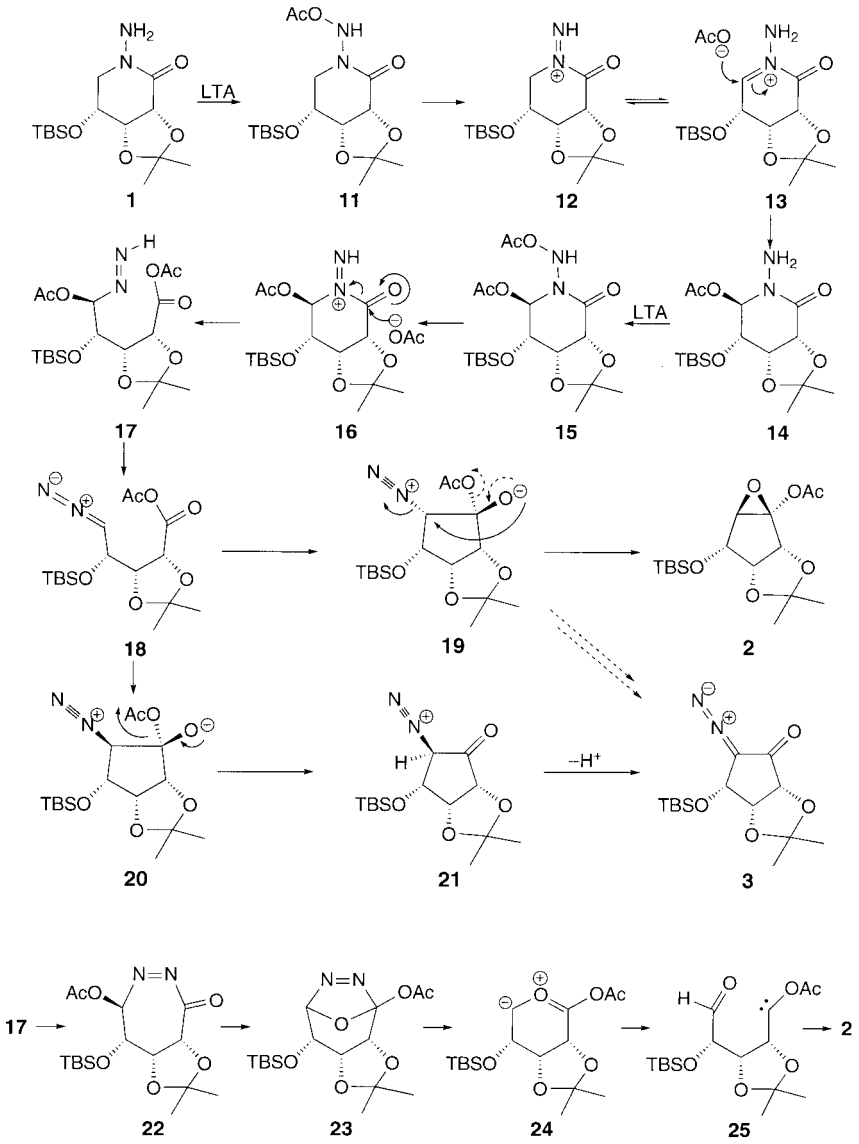
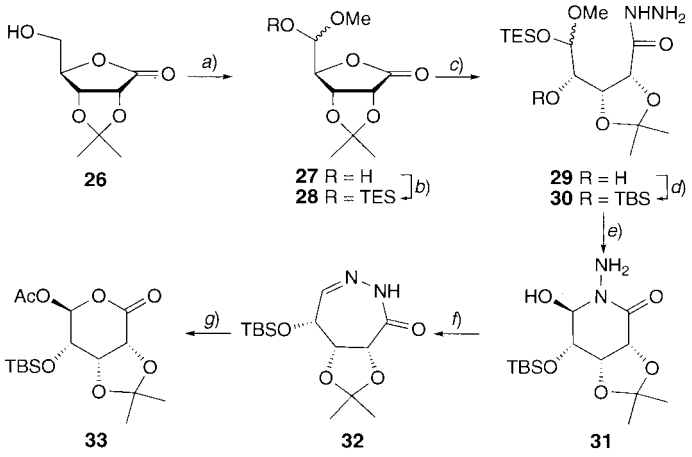
[1]) On the basis of *Iffland*'s hydrazone oxidation, *Freeman* [2] realized a synthesis of cyclopropyl acetates by $Pb(OAc)_4$ oxidation of 3-methyl-5-phenyl-2-pyrazoline.

Scheme 2. *Hypothetical Reaction Mechanisms for the Transformation of* **1** *to the Acetoxy Epoxide* **2** *and the Diazo Ketone* **3**



The synthesis of **32** was based on a report by *Walker* and *Hogenkamp* [4] according to which *Pfitzner–Moffatt* oxidation of the ribonolactone **26** with *N*,*N*′-dicyclohexylcarbodiimide (DCC), pyridine, CF_3COOH (TFA), and DMSO, followed by addition of oxalic acid in MeOH, leads to the corresponding aldehyde and its hydrate. However, the ^{1}H-NMR spectrum of the crude product obtained according to this procedure revealed predominantly the formation of the diastereoisomeric hemiacetals **27**

Scheme 3



a) 1. DCC, DMSO, pyridine, TFA, 23°, 1.5 h; 2. $(COOH)_2 \cdot 2\,H_2O$, MeOH, 23°, 0.5 h. *b*) TESCl, pyridine, CH_2Cl_2, 0°, 3 h; 65% from **26**. *c*) $NH_2NH_2 \cdot H_2O$, $CHCl_3$, 23°, 24 h. *d*) TBSOTf, pyridine, CH_2Cl_2, 0°, 1.5 h; 53% from **28**. *e*) AcOH, MeOH, 23°, 48 h, 50°, 8 h; 56%. *f*) Mol. sieves (4 Å), toluene, reflux, 22 h; 60%. *g*) $Pb(OAc)_4$, CH_2Cl_2, 23°, 12 h; 28%. DCC = *N*,*N*′-Dicyclohexylcarbodiimide, TBSO = (*t*-Bu)Me_2SiO, TESO = Et_3SiO, Tf = CF_3SO_2.

(*Scheme 3*). *O*-Triethylsilylation[2]) of the crude hemiacetals led to a mixture of the diastereoisomeric acetals **28** that were isolated in a yield of 65%. Treatment of **28** with $NH_2NH_2 \cdot H_2O$ gave a mixture of the ring-opened hydrazides **29**. Protection as the (*t*-Bu)Me_2Si (TBS) ethers provided a 6:4 mixture of the diastereoisomeric hydrazides **30** (53% from **28**) that were separated by flash chromatography (FC). Treatment of the mixture **30** under acidic conditions provided the *N*,*O*-hemiacetal **31** (56%) rather than the expected diazepinone **32** that was obtained only upon heating **31** for 22 h in toluene in the presence of molecular sieves (4 Å)[3]). Molecular sieves proved crucial, and several portions had to be added to complete the transformation of **31** into **32**, which was isolated as white crystals in a yield of 60%.

Oxidation of **32** with $Pb(OAc)_4$ in CH_2Cl_2 at room temperature for 12 h, followed by usual workup, gave a crude product without loss of material. Its ^{1}H-NMR spectrum showed no signals for either the acetoxy epoxide **2** or the diazo ketone **3**, and the only product that could be isolated by chromatography was the acetoxy lactone **33**. Oxidation of **32** with $Pb(OAc)_4$ in toluene at room temperature for 1 h, followed by usual workup, led similarly without loss of material to a 4:2:1 mixture of three products: according to ^{1}H-NMR analysis, the desired intermediate **22**, its C(5)-epimer, and the lactone **33**. No signals of either **2** or **3** could be detected. The major product is characterized by a *d* at 5.81 ($J = 10.0$, H−C(5)), a *d* at 4.86 ($J = 6.5$, H−C(2)), a *dd* at 4.42 ($J = 6.5$, 4.5, H−C(3)), and a *dd* at 3.81 ppm ($J = 10.0$ and 4.5, H−C(4)). The

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[2]) The hemiacetals were originally protected by trimethylsilylation. Treating the resulting mixed acetals with $NH_2NH_2 \cdot H_2O$ led to a complex mixture, indicating that the Me_3SiO (TMSO) group is insufficiently stable to the conditions of hydrazinolysis.

[3]) See [5] for analogous transformations to pyridazinones.

second major product showed a br. *s* at 6.04 (H–C(5)), a *d* at 4.65 ($J = 7.0$, H–C(2)), a *dd* at 4.57 ($J = 7.0$ and 4.5, H–C(3)), and a br. *d* at 4.35 ppm ($J = 4.5$, H–C(4)). The stability of the products was evaluated by periodically taking ^{1}H-NMR spectra. Signals of the first product, **22**, disappeared within 24 h at room temperature, those of the second product disappeared more slowly, and only **33** remained after 4 days. It was isolated by FC in a yield of 17%.

The isolation of the acetoxy lactone **33**, the formation of **22**[4]) and its C(5)-epimer, and the absence of signals for **2** or **3** in the crude products resulting from $Pb(OAc)_4$ oxidation of the diazepinone **32** constitute strong evidence against the alternative mechanism involving **22** as intermediate. This is also in agreement with the observation that the transformation of Δ^3-1,3,4-oxadiazolines to the corresponding ylides requires higher temperatures (> 80°) [7]. The formation of the acetoxy lactone **33** from *N*-acyl diazo compounds is precedented [8].

The ^{1}H-NMR spectra of crude **27** showed two MeO *s* at 3.40 and 3.37 ppm (60 : 40). An IR band for **28** at 1793 cm^{-1} and the ^{13}C=O *s* at 174.26 ppm evidence a 1,4-lactone, the isopropylidene Me groups (*s*) resonate at 1.47 and 1.37 ppm, and two *m* at 1.05–0.85 and at 0.75–0.50 ppm indicate the Et_3Si group. The mixed acetal moiety of the diastereoisomers **28** is characterized by two *d* at 4.80 and 4.79 ppm, and two *d* at 96.61 and 96.13 ppm.

The hydrazide moiety of the major isomer **30** is evidenced by a br. *s* at 7.53, a br. *d* at 3.70 ppm, and an IR band at 1682 cm^{-1}. The mixed acetal moiety gives rise to a MeO *s* at 3.38 ppm, a *t* at 0.98 ppm and a *q* at 0.69 ppm, a H–C(1) *d* at 5.22 ppm, and a ^{13}C(1) *d* at 99.52 ppm. The minor isomer **30** shows very similar data.

Cyclization of **30** to the *N*-amino-5-hydroxyribonolactam **31** is evidenced by a new IR band at 1651 cm^{-1}, the disappearance of the MeO and Et_3Si signals, the replacement of the br. *s* at 7.53 and the br. *d* at 3.70 ppm for the hydrazide group by a br. *s* at 4.52–4.20 ppm, and a br. OH *s* at 3.82 ppm. The coupling constants for the ring C–*H ds* are similar to those of **45** (*Scheme 5*, and *Table* in *Exper. Part*), suggesting the same configuration and a similar conformation.

Elemental analysis and the mass spectrum of **32** evidence the empirical formula $C_{14}H_{26}N_2O_4Si$. The formation of the *N*-acylhydrazone **32** from **31** was revealed by the disappearance of the OH and *exo*-NH_2 signals. A strong IR band at 1679 cm^{-1} and the shoulder at 1639 cm^{-1} indicate a C=O and a C=N group, as confirmed by a ^{13}C *s* at 168.61 and a br. *d* at 163.38 ppm. The br. *s* at 8.09 and the *d* at 7.44 ppm revealed an *N*-acylhydrazone substructure.

The empirical formula $C_{16}H_{28}O_7Si$ of **33** is based on elemental analysis and the HR-ESI-MS. NMR Data evidence a (*t*-Bu)Me_2Si and an isopropylidene group. Two ^{13}C=O resonate as two *s* at 167.84 and 167.41 ppm. The ^{1}H *s* at 2.15 ppm and the ^{13}C *q* at 20.96 ppm show that one of them is part of an AcO group. A strong, broad IR band at 1769 cm^{-1} results from the overlap of the AcO and the 1,5-lactone C=O bands [9]. A ^{1}H-NMR spectrum in $CDCl_3$ showed overlapping signals at 4.67 ppm (2 H), but a ^{1}H-NMR spectrum in C_6D_6 was well-resolved and showed that **33** possesses the same configuration and conformation as **31** and **45** (*Table* in *Exper. Part*).

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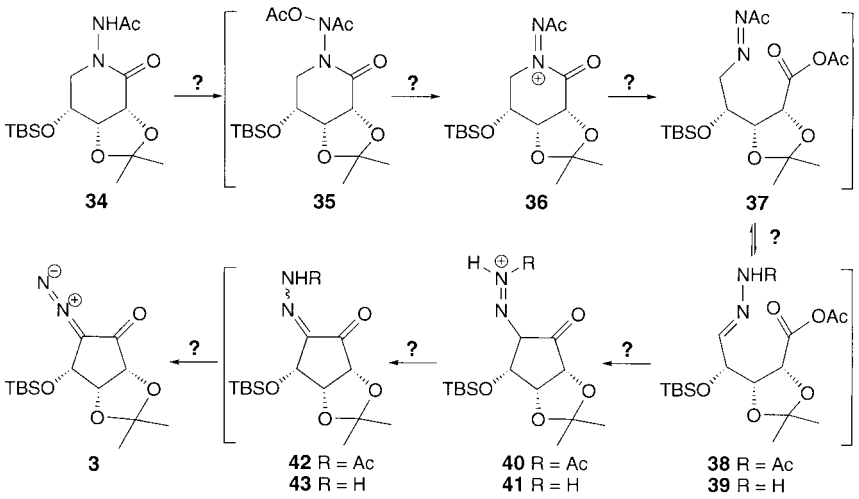
4) The transformation of acyclic *N*-acyl hydrazones with $Pb(OAc)_4$ to Δ^3-1,3,4-oxadiazolines is well-documented [6]

Synthesis and Oxidation of N′*-Acetyl-*N*-aminoribonolactams*; *Improved Access to Carbohydrate-Derived Diazo-cyclopentanones.* According to the reaction mechanism formulated in *Scheme 2*, nucleophilic addition of acetate (or AcOH) to the intermediate **16** leads *via* ring opening and elimination of acetate to an intramolecular acylation of the diazo anhydride **18**. Suppressing the oxidation of **12** to **16**, or enhancing the electrophilic character of **12**, *e.g.*, by *N*-acylation or *N*-sulfonylation, might lead to an analogous nucleophilic addition of acetate (or AcOH) to **12** (or a derivative of **12**), followed by ring opening, formation of a hydrazone, and intramolecular *C*-acylation. A hypothetical reaction mechanism is formulated in *Scheme 4* for the *N*′-acetyl-*N*-aminolactam **34**. *N*-Acetoxylation to **35** and elimination of acetate generates **36**, an analogue of **12** with enhanced electrophilic character. Ring opening to **37** and tautomerisation yields the *N*-acetylated hydrazone **38**, or the deacetylated **39**. Intramolecular *C*-acylation to **40** or **41**, followed by tautomerization, should lead to **42** or **43**; a final oxidation step [10] (with, in the case of **42**, concomitant deacetylation) will then lead to **3**.

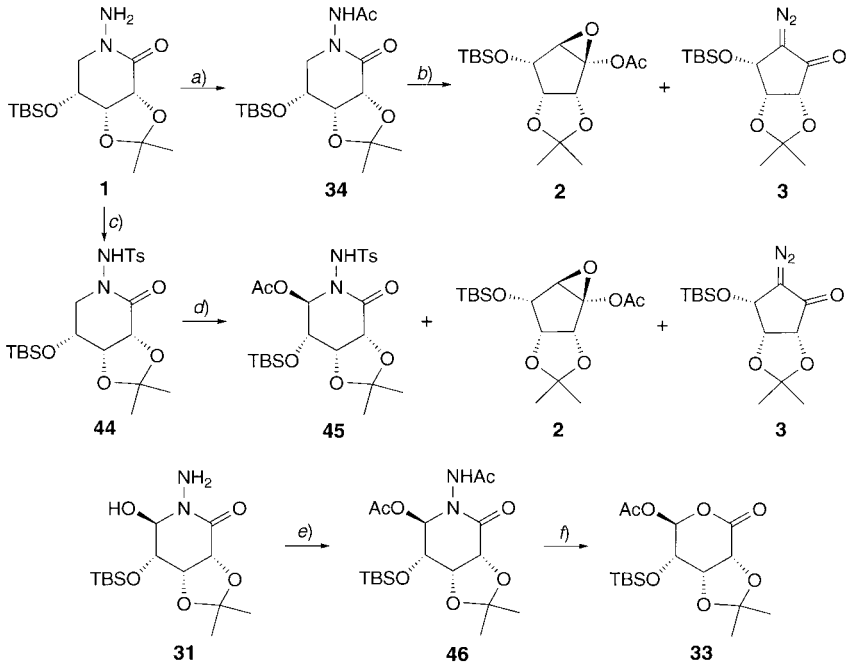
Scheme 4



The *N*-amino-ribonolactam **1** was acetylated (Ac_2O/MeOH) to provide **34** in a yield of 99%; **1** was similarly tosylated (TsCl/pyridine) to yield 90% of the 4-toluenesulfonohydrazide **44** (*Scheme 5*). Oxidation of the acetohydrazide **34** with $Pb(OAc)_4$ gave the acetoxy epoxide **2** (43%) and the diazo ketone **3** (40%). The higher yield of **3** and the ratio **2**/**3** 1:1, as compared to **2**/**3** 5:3 from the oxidation of **1** evidence the value of the hypothesis and, within its framework, a competing *N*-deacylation of the intermediate **36**. Oxidation of the 4-toluenesulfonohydrazide **44** with $Pb(OAc)_4$ yielded 25% of **2**, 14% of **3**, and 50% of the *C(5)*-acetoxylated **45**. In this case, the ratio **2**/**3** 5:3 was not affected, but the yields were considerably lowered in favor of **45**. Although **45** resisted further oxidation with $Pb(OAc)_4$, this result prompted us to check if the analogous acetate **46** is an intermediate in the oxidation of **34** to the acetoxy epoxide **2** and the diazo ketone **3**. The acetate **46** was readily prepared in a yield of 58%

from **31** (*Schemes 3* and *5*). It reacted slowly with $Pb(OAc)_4$ to yield 57% of the acetoxy lactone **33**; neither **2** nor **3** were detected in the crude product. Although these observations do not falsify the reaction mechanism proposed for the oxidation of **1**, they suggest that the oxidation of **1** to **16** may not occur *via* **14**; thus, *C*-acetoxylation of **11** could directly lead to **15**.

Scheme 5

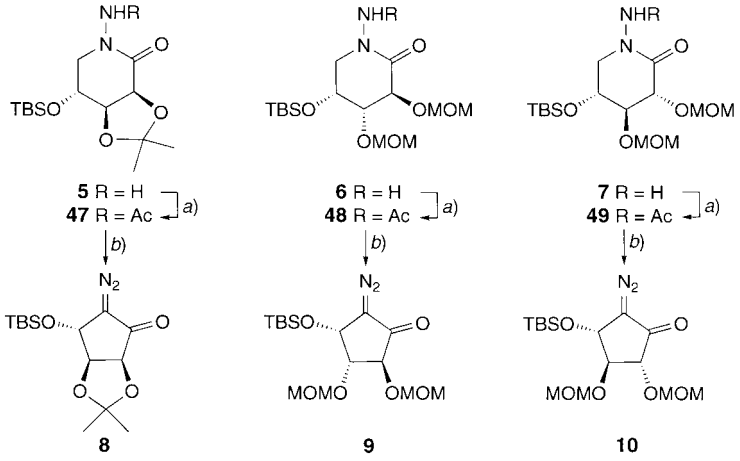


a) Ac_2O, MeOH, 23°, 1 h; 99%. *b*) $Pb(OAc)_4$, toluene/CH_2Cl_2, 23°, 2 h; 43% of **2**, 40% of **3**. *c*) TsCl, pyridine, CH_2Cl_2, 23°, 3 h; 90%. *d*) $Pb(OAc)_4$, toluene/CH_2Cl_2, 23°, 2 h; 25% of **2**, 14% of **3**, 50% of **45**. *e*) Ac_2O, pyridine, 0°, 3 h, 23°, 24 h; 58%. *f*) $Pb(OAc)_4$, toluene/CH_2Cl_2, 23°, 12 h; 57%.

Oxidation of the *N*-acetate **34** resulted in a higher amount of the diazo ketone **3** (40%) and in a higher combined yield (83%) of the cyclopentanes **2** and **3**. We, therefore, also subjected the *N*′-Ac derivates of the *N*-amino lactams **5**–**7** to the action of $Pb(OAc)_4$. The *N*′-acetylated **47**, **48**, and **49** were prepared in high yields by *N*-acetylation of **5**–**7**. As expected, their oxidation with $Pb(OAc)_4$ gave the corresponding diazo ketones **8**–**10** (*Scheme 6*). Compared to the results of the oxidation of **5**–**7**, the yield of **8**–**10** increased considerably, from 37 to 77% for the *N*-amino-D-lyxonolactam-derived diazo ketone **8**, from 22 to 39% for the *N*-amino-D-arabinonolactam derived **9**, and from 25 to 46% for the *N*-amino-D-xylonolactam derived **10**, respectively.

Acetylation of **1** to **34** is evidenced by the replacement of the NH_2 *s* by a broad *s* at 9.04 ppm, and, additionally, a *s* at 2.00 ppm, a new ^{13}C *s* at 167.25 (or 167.23) ppm, and a ^{13}C *q* at 21.08 ppm, typical for an NHAc moiety. The 4-toluenesulfonohydrazide **44** is recognized by a new broad *s* at 7.90 ppm and the *s* at 2.41 ppm, by the ^{13}C *q* at 22.03 ppm

Scheme 6



a) Ac_2O, MeOH, 23°, 1–3 h; 99% of **47**, 99% of **48**, 94% of **49**. *b*) $Pb(OAc)_4$, toluene, 23°, 1–2 h; 77% of **8**, 39% of **9**, 46% of **10**.

besides the aromatic ^{13}C's signals showing a Ts group, and by $[M+Na]^+$ (493, 100%). The structure of the oxidation product **45** was established by X-ray crystal-structure analysis[5]) (*Fig.*). The AcO group is oriented *trans* to the (*t*-Bu)Me_2SiO group at C(4), in keeping with *J*(4,5) (*Table* in *Exper. Part*). The *O*,*N*-di-acetylation of **31** to **46** is evidenced by IR bands at 1757, 1731, and 1707 cm^{-1}, two *s* at 2.12 and 2.01 ppm, a *q* at 21.13 ppm, and three *s* at 169.88, 169.42, and 167.75 ppm. The *trans*-arrangement of AcO–C(5) and (*t*-Bu)Me_2SiO–C(4) in **46** is confirmed by a comparison of the *J*(4,5) value to that of **45** (*Table* in *Exper. Part*). Similarly to **34**, the structures of the

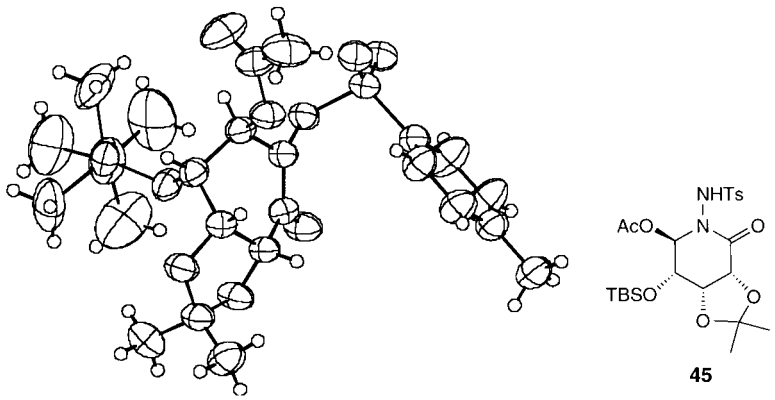


Figure. *Crystal structure of the 5-acetoxy*-N-*(tosylamino)ribonolactam* **45**

[5]) The crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-239384. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

acetohydrazides **47**–**49** are evidenced by a br. *s* between 9.5 and 8.2 ppm for a NH group, a *s* around 2.00 ppm, two ^{13}C *s* around 167–170 ppm, and a ^{13}C *q* around 21 ppm.

We thank Dr. *B. Schweizer* for the crystal-structure determination, Dr. *B. Bernet* for checking the *Exper. Part*, and the *Swiss National Science Foundation*, *F. Hoffman-La Roche AG*, Basel, and *OxfordGlycosciences*, Abingdon GB, for generous support.

Experimental Part

General. Unless specified otherwise, reactions were carried under N_2. Solvents were removed under reduced pressure (rotatory evaporator). CH_2Cl_2 was distilled over CaH_2 and toluene over Na immediately before use. Org. phases were dried with $MgSO_4$. TLC: *Merck* silica gel *60F-254* plates; detection with UV and/or by heating with Mostain (400 ml of 10% H_2SO_4 soln., 20 g of $(NH_4)_6\,Mo_7O_{24}\cdot 6\,H_2O$, 0.4 g of $Ce(SO_4)_2$). M.p.: uncorrected. Optical rotations $[\alpha]_D^{25}$ were determined at 589 nm.

*(1*R*/1*S*)-3,4-*O*-Isopropylidene-*L*-riburono-5,2-lactone Methyl Triethylsilyl Acetals* (**28**). A soln. of **26** (1.88 g, 10 mmol) in DMSO (40 ml) was treated sequentially with DCC (6.25 g, 30 mmol), pyridine (0.4 ml, 5 mmol), and TFA (0.37 ml, 5 mmol), stirred at r.t. for 1.5 h, and diluted with AcOEt (100 ml). The mixture was treated dropwise with a soln. of oxalic acid dihydrate (3.2 g, 25 mmol) in MeOH (10 ml) and stirred at r.t. for 0.5 h. After the addition of brine (60 ml), the mixture was filtered. The org. layer was extracted with AcOEt (2×60 ml), washed with brine (2×60 ml), and a mixture of brine (60 ml) and sat. $NaHCO_3$ soln. (3 ml, adjusting the mixture to pH of *ca.* 7), dried, and evaporated. A cooled (0°) soln. of the residue (3.46 g of crude **27**) in CH_2Cl_2 (20 ml) was treated with Et_3SiCl (3.5 ml, 20 mmol) and pyridine (5 ml), stirred for 3 h, treated with H_2O, and extracted with CH_2Cl_2 (3×50 ml). The combined org. layers were dried and evaporated. FC (cyclohexane/AcOEt 20:1) gave **28** (2.08 g, 65% from **26**). R_f (cyclohexane/AcOEt 4:1) 0.63. IR ($CHCl_3$): 2957*m*, 2914*w*, 2878*w*, 1793*s*, 1457*w*, 1414*w*, 1375*m*, 1332*w*, 1238*m*, 1214*m*, 1173*s*, 1151*s*, 1130*s*, 1069*vs*, 1003*s*, 977*s*, 855*s*, 784*m*, 729*s*. ^{1}H-NMR ($CDCl_3$, 300 MHz, 2:1 mixture of diastereoisomers): signals of both isomers: 1.47, 1.37 (2*s*, Me_2C); 1.05–0.85 (*m*, (*Me*CH_2)$_3$Si); 0.75–0.50 (*m*, (MeCH_2)$_3$Si); signals of the major isomer: 4.87 (*d*, $J=5.9$, H–C(4)); 4.80 (*d*, $J=2.2$, H–C(1)); 4.63 (*d*, $J=5.9$, H–C(3)); 4.48 (*d*, $J=2.2$, H–C(2)); 3.43 (*s*, MeO); signals of the minor isomer: 4.88 (*d*, $J=5.9$, H–C(4)); 4.79 (*d*, $J=2.2$, H–C(1)); 4.68 (*d*, $J=5.6$, H–C(3)); 4.33 (*d*, $J=2.5$, H–C(2)); 3.33 (*s*, MeO). ^{13}C-NMR ($CDCl_3$, 75 MHz, 2:1 mixture of diastereoisomers): signals of both isomers: 112.94 (*s*, Me_2C); 26.74 (*q*, *Me*C); 6.70 (*t*, (*Me*CH_2)$_3$Si); 4.87 (*q*, (MeCH_2)$_3$Si); signals of the major isomer: 173.98 (*s*, C=O); 96.61 (*d*, C(5)); 82.07, 75.78, 75.31 (3*d*, C(2), C(3), C(4)); 56.10 (*q*, MeO); 25.44 (*q*, *Me*C); signals of the minor isomer: 174.26 (*s*, C=O); 96.13 (*d*, C(5)); 83.00, 75.71, 75.39 (3*d*, C(2), C(3), C(4)); 56.34 (*q*, MeO); 25.50 (*q*, *Me*C). ESI-MS: 687 (45, $[2\,M+Na]^+$), 387 (39, $[M+MeOH+Na]^+$), 371 (33, $[M+K]^+$), 355 (100, $[M+Na]^+$).

*(1*R*/1*S*)-2-*O*-[(*tert*-Butyl)dimethylsilyl]-3,4-*O*-isopropylidene-*L*-riburonohydrazide Methyl Triethylsilyl Acetals* (**30**). A soln. of **28** (800 mg, 2.4 mmol) in $CHCl_3$ (5 ml) was treated with $NH_2NH_2\cdot H_2O$ (150 µl, 3 mmol), stirred at r.t. for 24 h, washed with brine (10 ml), dried, and evaporated. A cooled (0°) soln. of the residue (805 mg of crude **29**) in CH_2Cl_2 (10 ml) was treated with pyridine (2 ml) and TBSOTf (1.15 ml, 5 mmol), stirred for 1.5 h, treated with brine (15 ml), stirred at r.t. for 0.5 h, and extracted with CH_2Cl_2 (3×15 ml). The combined org. layers were dried and evaporated. FC (cyclohexane/AcOEt 6:1 → 4:1) gave the major and the minor diastereoisomers of **30** (430 and 180 mg, resp.; 53% from **28**).

Data of **30** (major isomer a): Oil. R_f (cyclohexane/AcOEt 2:1) 0.55. $[\alpha]_D^{25}=+6.5$ ($c=0.55$, $CHCl_3$). IR ($CHCl_3$): 3452*w*, 3334*w*, 2956*s*, 2932*m*, 2879*m*, 2857*m*, 1682*s*, 1625*m*, 1493*m*, 1473*m*, 1462*m*, 1413*w*, 1384*m*, 1255*m*, 1155*m*, 1135*m*, 1067*s*, 1004*m*, 837*m*, 827*m*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.53 (br. *s*, NH); 5.22 (*d*, $J=7.2$, H–C(1)); 4.60 (*dd*, $J=8.1, 2.5$, H–C(3)); 4.44 (*d*, $J=8.1$, H–C(4)); 3.95 (*dd*, $J=7.2, 2.5$, H–C(2)); 3.70 (br. *d*, $J=2.8$, NH_2); 3.38 (*s*, MeO); 1.55, 1.31 (2*s*, Me_2C); 0.98 (*t*, $J\approx 8.0$, (*Me*CH_2)$_3$Si); 0.85 (*s*, Me_3C); 0.69 (*q*, $J\approx 8.0$, (MeCH_2)$_3$Si); 0.06, 0.05 (2*s*, Me_2Si). ^{13}C-NMR ($CDCl_3$, 75 MHz): 171.20 (*s*, C=O); 108.13 (*s*, Me_2C); 99.52 (*d*, C(1)); 78.51 (*d*, C(4)); 74.85, 74.67 (2*d*, C(2), C(3)); 55.99 (*q*, MeO); 26.43, 23.72 (2*q*, *Me*$_2$C); 26.03 (*q*, *Me*$_3$C); 18.48 (*s*, Me$_3$*C*); 7.00 (*q*, (*Me*CH_2)$_3$Si); 5.50 (*t*, (MeCH_2)$_3$Si); −4.02, −4.77 (2*q*, Me_2Si). ESI-MS: 979 (21, $[2\,M+Na]^+$), 947 (24, $[2\,M-MeOH+Na]^+$), 745 (100), 517 (14, $[M+K]^+$), 501 (57, $[M+Na]^+$), 479 (26, $[M+H]^+$). Anal. calc. for $C_{21}H_{46}N_2O_6Si_2$ (478.78): C 52.68, H 9.68, N 5.85; found: C 52.93, H 9.76, N 5.75.

Data of **30** (minor isomer b): Oil. R_f (cyclohexane/AcOEt 2:1) 0.30. $[\alpha]_D^{25}=-25.9$ ($c=0.5$, $CHCl_3$). IR (neat): 3452*w*, 3327*w*, 2953*m*, 2933*w*, 2879*w*, 2856*w*, 1683*m*, 1626*w*, 1496*w*, 1473*w*, 1462*w*, 1413*w*, 1381*w*, 1372*w*, 1244*m*, 1215*m*, 1168*m*, 1153*m*, 1114*m*, 1072*s*, 1004*s*, 897*m*, 833*s*, 778*s*, 727*s*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.66

(br. *s*, NH); 4.92 (*d*, *J* = 4.0, H–C(1)); 4.50–4.42 (*m*, H–C(3), H–C(4)); 4.05 (*dd*, *J* = 4.0, 1.2, H–C(2)); 3.71 (br. *s*, NH_2); 3.40 (*s*, MeO); 1.60, 1.34 (2*s*, Me_2C); 0.97 (*t*, *J* = 7.8, $(MeCH_2)_3Si$); 0.87 (*s*, Me_3C); 0.66 (*q*, *J* = 7.8, $(MeCH_2)_3Si$); 0.084, 0.075 (2*s*, Me_2Si). ^{13}C-NMR ($CDCl_3$, 75 MHz): 171.68 (*s*, C=O); 108.58 (*s*, Me_2C); 99.13 (*d*, C(1)); 77.81 (*d*, C(4)); 75.44, 74.01 (2*d*, C(2), C(3)); 55.00 (*q*, MeO); 26.78, 25.11 (2*q*, Me_2C); 26.36 (*q*, Me_3C); 18.65 (*s*, Me_3C); 7.06 (*q*, $(MeCH_2)_3Si$); 5.34 (*t*, $(MeCH_2)_3Si$); −4.06, −4.35 (2*q*, Me_2Si). ESI-MS: 479 (34, $[M+H]^+$), 365 (80), 129 (100). Anal. calc. for $C_{21}H_{46}N_2O_6Si_2$ (478.78): C 52.68, H 9.68, N 5.85; found: C 52.78, H 9.76, N 5.74.

*(*5R*)-*4-O-*[(*tert*-Butyl)dimethylsilyl]-5-*C-*hydrazino-2,3-*O-*isopropylidene-*D-*ribono-1,5-lactam* (**31**). *a*) A soln. of **30** (major isomer a; 330 mg, 0.71 mmol) in MeOH (5 ml) was treated with AcOH (0.12 ml) and stirred at r.t. for 48 h and at 50° for 8 h. Removal of the solvents by co-evaporation with toluene and FC (cyclohexane/AcOEt 1:1 → 1:3) gave **31** as a solid (132 mg, 56%).

b) A soln. of **30** (mixture of two diastereoisomers; 2.39 g, 5 mmol) in MeOH (50 ml) was treated with AcOH (0.9 ml, 15 mmol) and stirred at 50° for 8 h. Removal of the solvents by co-evaporation with toluene and FC (cyclohexane/AcOEt 1:1 → 1:3) gave **31** as a solid (860 mg, 52%).

Data of **31**: R_f (cyclohexane/AcOEt 1:1) 0.12. IR (neat): 3324*w* (br.), 2951*w*, 2929*w*, 2897*w*, 2857*w*, 1651*m*, 1472*w*, 1462*w*, 1381*m*, 1374*m*, 1252*m*, 1208*m*, 1149*m*, 1099*m*, 1070*s*, 980*m*, 938*m*, 910*m*, 884*m*, 867*m*, 834*s*, 776*s*. ^{1}H-NMR ($CDCl_3$, 300 MHz): see the *Table*; additionally, 4.52–4.20 (*m*, NH_2); 3.82 (br. *s*, HO–C(5)); 1.46, 1.39 (2*s*, Me_2C); 0.89 (*s*, Me_3C); 0.12 (*s*, Me_2Si). ^{13}C-NMR ($CDCl_3$, 75 MHz): see the *Table*; additionally, 167.94 (*s*, C=O); 110.96 (*s*, Me_2C); 26.46, 24.86 (2*q*, Me_2C); 25.83 (*q*, Me_3C); 18.23 (*s*, Me_3C); −4.41, −4.85 (2*q*, Me_2Si). MALDI-MS: 355 (100, $[M+Na]^+$), 333 (16, $[M+H]^+$). HR-MALDI-MS: 355.1656 (100, $[M+Na]^+$, $C_{14}H_{28}N_2NaO_5^+$; calc. 355.1660).

Table 1. *Selected ^{1}H- and ^{13}C-NMR Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *of* **31**–**34**, and **44**–**46** *in $CDCl_3$*

	31	**32**	**33**[a])	**34**	**44**	**45**	**46**
H–C(2)	4.62–4.52	4.70–4.63	4.38	4.52	4.16	4.26	4.77
H–C(3)	4.62–4.52	4.70–4.63	4.23	4.45	4.37	4.60	4.67
H–C(4)	4.06	4.53	3.84	4.35	4.14	4.18	4.15
H–C(5)	5.02	7.44	6.59	3.45	3.79	6.23	6.05
H′–C(5)	–	–	–	3.83	3.86	–	–
J(2,3)	[b])	[b])	8.1	5.9	7.5	8.7	8.4
J(3,4)	2.5	1.5	3.7	2.2	3.1	3.4	3.4
J(4,5)	5.0	3.7	4.7	4.2	3.4	4.0	4.4
J(4,5′)	–	–	–	9.3	6.9	–	–
J(5,5′)	–	–	–	11.0	12.7	–	–
C(2)	73.73[d])	85.55[c])	73.36[d])	76.53[d])	76.36[d])	72.91[d])	72.97[d])
C(3)	72.72[d])	77.35	72.65[d])	74.08[d])	73.02[d])	72.32[d])	72.88[d])
C(4)	67.76	70.31[c])	66.03	65.81	65.32	64.87	65.82
C(5)	86.23	163.68[c])	92.72	51.92	54.59	88.41	85.22

[a]) In C_6D_6. [b]) Not assigned. [c]) Broad signal. [d]) The assignments may be interchanged.

*4-*O*-*[(*tert*-Butyl)dimethylsilyl]-5-deoxy-5-hydrazono-2,3-*O-*isopropylidene-*D-*ribono-1,5*[1]*-lactam* (**32**). A soln. of **31** (132 mg, 0.4 mmol) in toluene (8 ml) was treated with molecular sieves (4 Å; 1 g), boiled under reflux for 18 h, treated with more molecular sieves (4 Å; 1 g), and again boiled under reflux for 4 h. Filtration and evaporation gave 115 mg of residue, which was purified by FC (cyclohexane/AcOEt 3:1) to afford **32** (75 mg, 60%). White crystals M.p. 135.5–137° (hexane). R_f (cyclohexane/AcOEt 1:1) 0.73. $[\alpha]_D^{25} = -231.1$ (*c* = 1.6, $CHCl_3$). IR ($CHCl_3$): 3400*m*, 3018*m*, 2955*m*, 2931*s*, 1679*s*, 1639*w*, 1603*w*, 1471*w*, 1463*w*, 1384*m*, 1378*m*, 1363*m*, 1260*s*, 1163*m*, 1113*s*, 1063*s*, 1006*w*, 977*m*, 937*w*, 912*w*, 888*m*, 861*m*, 839*s*, 806*m*. IR (neat): 3203*w* (br.), 3092*w*, 2931*w*, 2857*w*, 1667*s*, 1636*m*, 1472*w*, 1463*w*, 1383*m*, 1375*m*, 1361*m*, 1251*m*, 1211*s*, 1162*m*, 1134*m*, 1113*s*, 1058*s*, 1007*w*, 979*m*, 936*w*, 889*m*, 862*s*, 836*vs*, 774*s*, 733*s*, 674*m*. ^{1}H-NMR ($CDCl_3$, 300 MHz): see the *Table*; additionally, 8.09 (br. *s*, NH); 1.54, 1.34 (2*s*, Me_2C); 0.90 (*s*, Me_3C); 0.104, 0.099 (2*s*, Me_2Si). ^{13}C-NMR ($CDCl_3$, 75 MHz): see the *Table*; additionally, 168.61 (*s*, C=O); 163.68 (br. *d*, C=N); 111.28 (*s*, Me_2C); 25.83 (*q*, Me_3C);

25.54, 24.38 (2*q*, *Me*$_2$C); 18.35 (*s*, Me$_3$*C*); −4.61 (*q*, Me$_2$Si). MALDI-MS: 337 (61, [*M* + Na]$^+$), 315 (100, [*M* + H]$^+$). HR-MALDI-MS: 315.1734 (100, [*M* + H]$^+$, $C_{14}H_{27}NaN_2O_4^+$; calc. 315.1735). Anal. calc. for $C_{14}H_{26}N_2O_4Si$ (314.46): C 53.47, H 8.33, N 8.91; found: C 53.55, H 8.30, N 8.70.

*(5*S*)-5-C-Acetoxy-4-*O*-[(*tert*-butyl)dimethylsilyl]-2,3-*O*-isopropylidene-*D*-ribono-1,5-lactone* (**33**). A soln. of Pb(OAc)$_4$ (133 mg, 0.2 mmol) in CH_2Cl_2 (5 ml) was treated with a soln. of **32** (32 mg, 0.1 mmol) in CH_2Cl_2 (5 ml). The mixture was stirred at r.t. for 12 h, treated with H_2O, and extracted with Et_2O (25 ml and 2 × 10 ml). The combined org. layers were dried and evaporated. FC (cyclohexane/AcOEt 10 : 1 → 4 : 1) gave **33** (10 mg, 28%) Oil. R_f (cyclohexane/AcOEt 2 : 1) 0.40. $[\alpha]_D^{25} = +56.6$ ($c = 0.25$, $CHCl_3$). IR ($CHCl_3$): 2954*m*, 2931*m*, 2859*w*, 1779*s* (br.), 1472*w*, 1463*w*, 1377*m*, 1258*m*, 1162*s*, 1108*s*, 1081*m*, 1014*s*, 990*m*, 940*w*, 840*m*. IR (neat): 2952*w*, 2931*w*, 2858*w*, 1769*s* (br.), 1473*w*, 1463*w*, 1376*m*, 1252*m*, 1210*m*, 1154*s*, 1104*s*, 1076*m*, 1012*s*, 990*s*, 940*m*, 837*s*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 6.37 (*d*, *J* = 3.9, H−C(5)); 4.67 (*d*, *J* = 2.1, H−C(2), H−C(3)); 4.17 (*dt*, *J* = 4.0, 2.0, H−C(4)); 2.15 (*s*, AcO); 1.54, 1.42 (2*s*, Me$_2$O); 0.90 (*s*, Me$_3$C); 0.13, 0.12 (2*s*, Me$_2$Si). ^{1}H-NMR (C_6D_6, 300 MHz): see the *Table*; additionally, 3.84 (*dd*, *J* = 4.7, 3.7, irrad. at 6.59 → *d*, *J* = 3.6, H−C(4)); 1.54 (*s*, AcO); 1.41, 1.13 (2*s*, Me$_2$C); 0.91 (*s*, Me$_3$C); 0.06, 0.00 (2*s*, Me$_2$Si). ^{13}C-NMR ($CDCl_3$, 75 MHz): 167.84, 167.41 (2*s*, 2 C=O); 111.71 (*s*, Me$_2$*C*); 92.86 (*d*, C(5)); 72.65, 71.79 (2*d*, C(2), C(3)); 64.88 (*d*, C(4)); 26.10, 24.83 (2*q*, *Me*$_2$C); 25.68 (*q*, *Me*$_3$C); 20.96 (*q*, *Me*C=O); 18.24 (*s*, Me$_3$*C*); −4.32, −5.05 (2*q*, Me$_2$Si). ^{13}C-NMR (C_6D_6, 75 MHz): see *Table*; additionally, 167.67, 166.20 (2*s*, 2 C=O); 111.72 (*s*, Me$_2$*C*); 26.40, 25.05 (2*q*, *Me*$_2$C); 25.87 (*q*, *Me*$_3$C); 20.29 (*q*, *Me*C=O); 18.46 (*s*, Me$_3$*C*); −4.24, −4.94 (2*q*, Me$_2$Si). HR-ESI-MS: 383.1485 (100, [*M* + Na]$^+$, $C_{16}H_{28}NaO_7Si^+$; calc. 383.1497). Anal. calc. for $C_{16}H_{28}O_7Si$ (360.48): C 53.31, H 7.83; found: C 53.13, H 7.96, N 0.08.

N-*Acetamido-5-amino-4-*O*-[(*tert*-butyl)dimethylsilyl]-5-deoxy-2,3-*O*-isopropylidene-*D*-ribono-1,5-lactam* (**34**). A soln. of **1** (680 mg, 2.15 mmol) in MeOH (10 ml) was treated with Ac_2O (0.44 ml, 4.3 mmol) and stirred at r.t. for 1 h. Co-evaporation with toluene and crystallization (cyclohexane/Et_2O) gave **34** (760 mg, 99%). White crystals. M.p. 233–235°. R_f (CH_2Cl_2/MeOH/Et_3N 200 : 10 : 1.5) 0.34. $[\alpha]_D^{25} = -30.9$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3394*w*, 3252*w* (br.), 2955*m*, 2932*m*, 2859*m*, 1712*m*, 1674*s*, 1471*m*, 1421*w*, 1384*m*, 1375*m*, 1259*s*, 1165*m*, 1135*m*, 1093*m*, 1054*m*, 994*m*, 882*m*, 839*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): see the *Table*; additionally, 9.04 (br. *s*, NH); 2.00 (*s*, AcN); 1.45, 1.40 (2*s*, Me$_2$C); 0.90 (*s*, Me$_3$C); 0.14, 0.12 (2*s*, Me$_2$Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see the *Table*; additionally, 167.25, 167.23 (2*s*, 2 C=O); 111.52 (*s*, Me$_2$*C*); 27.11, 25.49 (2*q*, *Me*$_2$C); 26.06 (*q*, *Me*$_3$C); 21.08 (*q*, *Me*C=O); 18.51 (*s*, Me$_3$*C*); −4.38, −4.43 (2*q*, *Me*$_2$Si). MALDI-MS: 739 (100, [2 *M* + Na]$^+$), 381 (63, [*M* + Na]$^+$). HR-MALDI-MS: 381.1814 (63, [*M* + Na]$^+$, $C_{21}H_{34}N_2NaO_6SSi^+$; calc. 381.1816). Anal. calc. for $C_{16}H_{30}N_2O_5Si$ (358.51): C 53.60, H 8.43, N 7.81; found: C 53.64, H 8.37, N 7.54.

*5-Amino-4-*O*-[(*tert*-butyl)dimethylsilyl]-5-deoxy-2,3-*O*-isopropylidene-{[(4-methylphenyl)sulfonyl]amino}-*D*-ribono-1,5-lactam* (**44**). A cooled (0°) soln. of **1** (158 mg, 0.5 mmol) in CH_2Cl_2 (2 ml) was treated with a soln. of pyridine (0.5 ml) and TsCl (143 mg, 0.75 mmol) in CH_2Cl_2 (2 ml). The mixture was stirred at r.t. for 3 h, treated with H_2O, and extracted with CH_2Cl_2 (3 × 15 ml). The combined org. layers were dried and evaporated. FC (cyclohexane/AcOEt 4 : 1) gave **44** (212 mg, 90%). White foam. R_f (cyclohexane/AcOEt 2 : 1) 0.33. $[\alpha]_D^{25} = -7.8$ (c = 0.34, $CHCl_3$). IR ($CHCl_3$): 3249*w*, 3031*m*, 2955*m*, 2933*m*, 2860*m*, 1688*s*, 1598*w*, 1472*m*, 1385*s*, 1352*s*, 1257*s*, 1187*m*, 1169*s*, 1091*s*, 981*m*, 959*m*, 895*m*, 839*s*, 813*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): see the *Table*; additionally, 7.90 (br. *s*, NH); 7.73 (*d*, *J* = 8.4, 2 arom. H); 7.27 (*d*, *J* = 8.4, 2 arom. H); 2.41 (*s*, *Me*C_6H_4); 1.40, 1.32 (2*s*, Me$_2$C); 0.88 (*s*, Me$_3$C); 0.12, 0.11 (2*s*, Me$_2$Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see the *Table*; additionally, 167.27 (*s*, C=O); 145.18, 132.29 (2*s*); 129.74 (2*d*); 128.53 (2*d*); 111.74 (*s*, Me$_2$*C*); 26.49, 24.96 (2*q*, *Me*$_2$C); 25.99 (*q*, *Me*$_3$C); 22.03 (*q*, *Me*C_6H_4); 18.40 (*s*, Me$_3$*C*); −4.31, −4.59 (2*q*, Me$_2$Si). MALDI-MS: 493 (100, [*M* + Na]$^+$), 471 (28, [*M* + H]$^+$). Anal. calc. for $C_{21}H_{34}N_2O_6SSi$ (470.66): C 53.59, H 7.28, N 5.95, S 6.81; found: C 53.62, H 7.42, N 5.84, S 6.67.

Oxidation of **34** *with Pb(OAc)$_4$.* A soln. of Pb(OAc)$_4$ (1.06 g, 2.4 mmol) in CH_2Cl_2 (3 ml) was added dropwise to a soln. of **34** (288 mg, 0.8 mmol) in toluene (40 ml). The mixture was stirred at r.t. for 2 h, treated with H_2O, and extracted with Et_2O (3 × 30 ml). The combined org. layers were dried and evaporated. FC (cyclohexane/AcOEt 5 : 1) gave **2** (119 mg, 43%) and **3** (100 mg, 40%).

Oxidation of **44** *with Pb(OAc)$_4$.* A soln. of Pb(OAc)$_4$ (178 mg, 0.4 mmol) in CH_2Cl_2 (2 ml) was added dropwise to a soln. of **44** (94 mg, 0.2 mmol) in toluene (10 ml). The mixture was stirred at r.t. for 2 h, treated with H_2O (10 ml), and extracted with Et_2O (3 × 15 ml). The combined org. layers were dried and evaporated. FC (cyclohexane/AcOEt 5 : 1) gave **45** (53 mg, 50%), **2** (17 mg, 25%), and **3** (9 mg, 14%).

*Data of (*5R*)-5-O-Acetyl-5-amino-4-*O*-[(*tert*-butyl)dimethylsilyl]-2,3-*O*-isopropylidene-*N*-{[(4-methylphenyl)sulfonyl]amino}-*D*-ribono-1,5-lactam* (**45**). White crystals. M.p. 205–206° (hexane/CH_2Cl_2). R_f (cyclohexane/AcOEt 2 : 1) 0.34. $[\alpha]_D^{25} = +92.1$ ($c = 0.34$, $CHCl_3$). IR ($CHCl_3$): 3259*w*, 3028*w*, 2982*w*, 2956*w*, 2932*m*, 2886*w*, 2861*w*, 1757*m*, 1718*m*, 1597*w*, 1471*w*, 1462*w*, 1426*m*, 1383*m*, 1377*m*, 1358*m*, 1307*w*, 1290*w*, 1257*m*, 1234*m*, 1194*s*,

1170*vs*, 1104*m*, 1091*m*, 1080*m*, 1020*s*, 994*w*, 975*m*, 959*w*, 920*m*, 862*w*, 841*m*, 813*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see the *Table*; additionally, 7.85 (*s*, NH); 7.74 (*d*, $J = 8.1$, 2 arom. H); 7.28 (*d*, $J = 8.1$, 2 arom. H); 2.43 (*s*, *Me*C_6H_4); 2.22 (*s*, AcO); 1.45, 1.32 (2*s*, Me_2C); 0.85 (*s*, Me_3C); 0.15, 0.07 (2*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see the *Table*; additionally, 168.53, 168.33 (2*s*, 2 C=O); 145.13, 132.80 (2*s*); 129.61 (2*d*); 128.53 (2*d*); 111.93 (*s*, Me_2C); 25.74 (*q*, Me_3C); 25.74, 24.44 (2*q*, Me_2C); 21.94 (*q*, *Me*C_6H_4); 20.84 (*q*, *Me*C=O); 18.11 (*s*, Me_3C); −4.43, −5.17 (2*q*, Me_2Si). MALDI-MS: 551 (22, $[M + Na]^+$), 491 (20), 441 (28), 307 (100). Anal. calc. for $C_{23}H_{36}N_2O_8SSi$ (528.70): C 52.25, H 6.86, N 5.30, S 6.07; found: C 52.40, H 6.91, N 5.29, S 5.96.

Crystal Structure of **45**. Recrystallization of **45** in hexane/CH_2Cl_2 gave crystals suitable for X-ray analysis: $C_{23}H_{36}N_2O_8SSi$ (528.70); monoclinic $P2_1$; $a = 10.0022$ (5) Å, $b = 13.2022$ (7) Å, $c = 11.3778$ (6) Å, $\beta = 111.803$ (2)°; $V = 1394.97$ (13) Å^3; $D_{calc.} = 1.316$ Mg/m^3; $Z = 2$. 2787 reflections were measured on a *KappaCCD* diffractometer with MoK_α radiation (graphite monochromator, $\lambda = 0.71073$ Å) at 298 K. $R = 0.059$, $R_w = 0.105$. The structure was solved by direct methods with SIR-97. The non-H-atoms were refined anisotropically with SHELXS-97.

*(5*R*)*-N-*Acetamido-5*-O-*acetyl-5-amino-4*-O-*[(*tert*-butyl)dimethylsilyl]-2,3*-O-*isopropylidene*-D-*ribono-1,5-lactam* (**46**). A cooled (0°) soln. of **31** (34 mg, 0. 1 mmol) in CH_2Cl_2 (1 ml) was treated with pyridine (0.1 ml) and Ac_2O (40 µl, 0.4 mmol), stirred for 3 h, warmed to r.t., stirred for 24 h, treated with H_2O, and extracted with CH_2Cl_2 (3 × 10 ml). The combined org. layers were dried ($MgSO_4$) and evaporated. FC (cyclohexane/AcOEt 1:2) gave **46** (24 mg, 58%). White crystals. M.p. 167–168° ($CHCl_3$). R_f (cyclohexane/AcOEt 1:4) 0.30. $[\alpha]_D^{25} = +69.2$ ($c = 0.95$, $CHCl_3$). IR ($CHCl_3$): 3385*m*, 3026*m*, 2954*m*, 2932*m*, 2859*w*, 1757*m*, 1731*s*, 1707*s*, 1485*w*, 1472*w*, 1463*w*, 1425*w*, 1383*m*, 1375*m*, 1255*m*, 1203*s*, 1164*m*, 1106*s*, 1081*m*, 1017*m*, 974*m*, 863*w*, 840*s*. ^{1}H-NMR ($CDCl_3$, 300 MHz): see the *Table*; additionally, 7.74 (*s*, NH); 2.12 (*s*, AcO); 2.01 (*s*, AcN); 1.53, 1.39 (2*s*, Me_2C); 0.88 (*s*, Me_3C); 0.12, 0.11 (2*s*, Me_2Si). ^{13}C-NMR ($CDCl_3$, 75 MHz): see the *Table*; additionally, 169.88, 169.42, 167.75 (3*s*, 3 C=O); 111.65 (*s*, Me_2C); 26.16, 24.65 (2*q*, Me_2C); 26.02 (*q*, Me_3C); 21.13 (*q*, 2 *Me*C=O); 18.40 (*s*, Me_3C); −4.09, −4.91 (2*q*, Me_2Si). HR-MALDI-MS: 439.1865 (100, $[M + Na]^+$, $C_{18}H_{32}O_7N_2NaSi^+$; calc. 439.1871). Anal. calc. for $C_{18}H_{32}O_7N_2Si$ (416.55): C 51.90, H 7.74, N 6.73; found: C 51.93, H 7.62, N 6.67.

Oxidation of **46** *with Pb(OAc)$_4$*. A suspension of $Pb(OAc)_4$ (443 mg, 1.0 mmol) in toluene (22 ml) was treated with a soln. of **46** (142 mg, 0.34 mmol) in CH_2Cl_2 (8 ml), stirred at r.t. for 12 h, treated with H_2O, and extracted with Et_2O (3 × 20 ml). The combined org. layers were dried and evaporated. FC (cyclohexane/AcOEt 4:1) gave **33** (72 mg, 57%) Syrup.

N-*Acetamido-5-amino-4*-O-*[(*tert*-butyl)dimethylsilyl]-5-deoxy-2,3*-O-*isopropylidene*-D-*lyxono-1,5-lactam* (**47**). A soln. of **5** (68 mg, 0.215 mmol) in MeOH (2 ml) was treated with Ac_2O (22 µl, 0.215 mmol) and stirred at r.t. for 3 h. Co-evaporation with toluene and FC (cyclohexane/AcOEt 1:2) gave **47** (76 mg, 99%). White crystals. M.p. 187–188° ($CHCl_3$). R_f (cyclohexane/AcOEt 1:2) 0.23. $[\alpha]_D^{25} = -17.8$ ($c = 0.55$, $CHCl_3$). IR ($CHCl_3$): 3393*w*, 3252*w* (br.), 3026*w*, 3015*m*, 2955*m*, 2932*m*, 2903*w*, 2859*m*, 1711*s*, 1673*vs*, 1471*m*, 1421*w*, 1385*m*, 1375*m*, 1348*w*, 1291*w*, 1259*m*, 1163*w*, 1128*m*, 1102*s*, 1044*w*, 1000*w*, 937*w*, 908*w*, 892*w*, 839*s*, 809*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 9.46 (*s*, NH); 4.54 (*d*, $J = 6.2$, H–C(2)); 4.26 (br. *t*, $J \approx 5.6$, H–C(3)); 4.20–4.14 (*m*, H–C(4)); 4.10 (*dd*, $J = 12.4$, 2.5, H–C(5)); 3.33 (*dd*, $J = 12.8$, 3.7, H′–C(5)); 2.00 (*s*, AcN); 1.50, 1.38 (2*s*, Me_2C); 0.85 (*s*, Me_3C); 0.093, 0.087 (2*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 169.39, 167.22 (2*s*, 2 C=O); 111.68 (*s*, Me_2C); 76.94 (*d*, C(2)); 74.36 (*d*, C(3)); 67.27 (*d*, C(4)); 54.06 (*d*, C(5)); 27.26, 25.88 (2*q*, Me_2C); 25.88 (*q*, Me_3C); 21.13 (*q*, *Me*C=O); 18.18 (*s*, Me_3C); −4.59, −4.64 (2*q*, Me_2Si). MALDI-MS: 381 (100, $[M + Na]^+$), 359 (17, $[M + H]^+$). HR-MALDI-MS: 381.1812 (100, $[M + Na]^+$, $C_{21}H_{34}N_2NaO_6SSi^+$; calc. 381.1816). Anal. calc. for $C_{16}H_{30}N_2O_5Si$ (358.51): C 53.60, H 8.43, N 7.81; found: C 53.49, H 8.48, N 7.58.

N-*Acetamido-5-amino-4*-O-*[(*tert*-butyl)dimethylsilyl]-5-deoxy-2,3-bis*-O-*(methoxymethyl)*-D-*arabinono-1,5-lactam* (**48**). A soln. of **6** (114 mg, 0.31 mmol) in MeOH (2 ml) was treated with Ac_2O (65 µl, 0.62 mmol) and stirred at r.t. for 1 h. Co-evaporation with toluene and FC (cyclohexane/AcOEt 1:2) gave **48** (126 mg, >99%). Colourless oil. R_f (cyclohexane/AcOEt 1:2) 0.20. $[\alpha]_D^{25}$ −103.6 ($c = 0.42$, $CHCl_3$). IR ($CHCl_3$): 3394*w*, 3259*w*, 2955*m*, 2931*m*, 2898*m*, 2858*m*, 1710*m*, 1671*s*, 1472*m*, 1441*w*, 1368*m*, 1255*m*, 1140*s*, 1106*s*, 1039*vs*, 919*m*, 868*m*, 838*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.29 (*s*, NH); 5.00 (*d*, $J = 6.5$, MeOC*H*); 4.76 (*s*, MeOCH_2); 4.75 (*d*, $J = 6.8$, MeOC*H*); 4.38 (*d*, $J = 7.1$, H–C(2)); 4.35 (*ddd*, $J = 5.6$, 4.0, 1.9, H–C(4)); 3.95 (*dd*, $J = 7.1$, 1.9, H–C(3)); 3.72 (*dd*, $J = 11.5$, 4.0, H–C(5)); 3.53 (*dd*, $J = 11.5$, 5.3, H′–C(5)); 3.43, 3.39 (2*s*, 2 MeO); 2.02 (*s*, AcN); 0.89 (*s*, Me_3C); 0.12, 0.10 (2*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 169.39, 168.02 (2*s*, 2 C=O); 97.36, 96.37 (2*t*, 2 MeOCH_2); 75.83 (*d*, C(2)); 73.25 (*d*, C(3)); 66.35 (*d*, C(4)); 56.21, 55.94 (2*q*, 2 *Me*OCH$_2$); 54.34 (*t*, C(5)); 25.83 (*q*, Me_3C); 21.10 (*q*, *Me*C=O); 18.22 (*s*, Me_3C); −4.62, −4.78 (2*q*, Me_2Si). ESI-MS: 445 (18, $[M + K]^+$), 429 (100, $[M + Na]^+$), 407 (7, $[M + H]^+$). Anal. calc. for $C_{17}H_{34}N_2O_7Si$ (406.55): C 50.22, H 8.43, N 6.89; found: C 50.47, H 8.55, N 6.79.

N-*Acetamido-5-amino-4*-O-*[(*tert-*butyl)dimethylsilyl]-5-deoxy-2,3-bis*-O-*(methoxymethyl)*-D-*xylono-1,5-lactam* (**49**). A soln. of **7** (56 mg, 0.15 mmol) in MeOH (1.5 ml) was treated with Ac_2O (23 µl, 0.22 mmol) and stirred at r.t. for 3 h. Co-evaporation with toluene and FC (cyclohexane/AcOEt 1:2) gave **49** (57 mg, 94%). White crystals. M.p. 85.5–87°. R_f (hexane/AcOEt 1:4) 0.30. $[\alpha]_D^{25} = +33.0$ ($c = 0.51$, $CHCl_3$). IR ($CHCl_3$): 3309*w*, 2956*m*, 2932*m*, 2897*m*, 2859*m*, 1716*s*, 1681*s*, 1472*m*, 1464*m*, 1442*w*, 1423*w*, 1390*w*, 1368*w*, 1259*m*, 1153*s*, 1104*s*, 1081*m*, 1037*vs*, 1007*m*, 917*m*, 839*s*. ^{1}H-NMR (300 Hz, $CDCl_3$): 8.81 (*s*, NH); 4.96 (*d*, $J = 6.5$), 4.85 (*d*, $J = 6.5$), 4.80 (*d*, $J = 6.5$), 4.75 (*d*, $J = 6.5$) (2 MeOCH_2); 4.16 (*d*, $J = 7.8$, H–C(2)); 4.06 (*td*, $J \approx 7.8$, 5.0, H–C(4)); 3.79 (*t*, $J \approx 7.5$, H–C(3)); 3.69 (*dd*, $J = 11.8$, 4.7, H–C(5)); 3.44, 3.40 (2*s*, 2 MeO); 3.35 (*dd*, $J = 11.8$, 8.1, H′–C(5)); 1.99 (*s*, AcN); 0.86 (*s*, Me_3C); 0.10, 0.09 (2*s*, Me_2Si). ^{13}C-NMR ($CDCl_3$): 169.07, 168.42 (2*s*, 2 C=O); 97.38 (*t*, 2 MeO*C*H_2); 79.70, 74.71 (2*d*, C(2), C(3)); 68.82 (*d*, C(4)); 56.46, 56.24 (2*q*, 2 *Me*OCH_2); 54.38 (*t*, C(5)); 25.88 (*q*, *Me*$_3$C); 21.00 (*q*, *Me*C=O); 18.12 (*s*, Me$_3$*C*)); –4.49, –4.64 (2*q*, Me_2Si). HR-MALDI-MS: 429.2025, (100, $[M + Na]^+$, $C_{17}H_{34}N_2NaO_7Si^+$; calc. 429.2028). Anal. calc. for $C_{17}H_{34}N_2O_7Si$ (406.55): C 50.22, H 8.43, N 6.89; found: C 50.20, H 8.41, N 6.69.

Oxidation of **47** *with Pb(OAc)$_4$.* A soln. of **47** (36 mg, 0.1 mmol) in toluene (5 ml) was treated with a suspension of $Pb(OAc)_4$ (134 mg, 0.3 mmol) in toluene (5 ml), stirred at r.t. for 1 h, treated with H_2O, and extracted with Et_2O (3 × 5 ml). The combined org. layers were dried and evaporated. FC (cyclohexane/AcOEt 10:1) gave the diazo ketone **8** (24 mg, 77%).

Oxidation of **48** *with Pb(OAc)$_4$.* A soln. of **48** (92 mg, 0.23 mmol) in toluene (8 ml) was treated with a suspension of $Pb(OAc)_4$ (335 mg, 0.75 mmol) in toluene (6 ml), stirred at r.t. for 2 h, treated with H_2O, and extracted with Et_2O (3 × 10 ml). The combined org. layers were dried and evaporated. FC (cyclohexane/AcOEt 8:1) gave the diazo ketone **9** (32 mg, 39%).

Oxidation of **49** *with Pb(OAc)$_4$.* A soln. of **49** (354 mg, 0.87 mmol) in toluene (20 ml) was treated with a suspension of $Pb(OAc)_4$ (1.16 g, 2.61 mmol) in toluene (25 ml), stirred at r.t. for 2 h, treated with H_2O, and extracted with Et_2O (3 × 40 ml). The combined org. layers were dried and evaporated. FC (cyclohexane/AcOEt 15:1 → 8:1) gave the diazo ketone **10** (146 mg, 46%).

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Received May 28, 2004