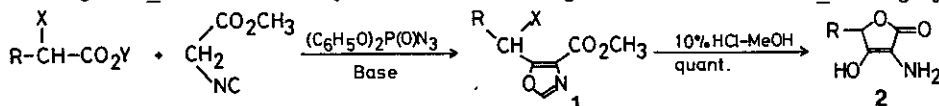


A NEW EFFICIENT SYNTHESIS OF AMINO SUGARS UTILIZING RING CLEAVAGE OF OXAZOLE SKELETONS

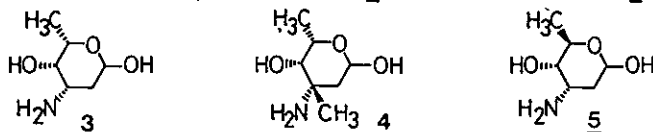
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Recent publication from our laboratories has disclosed¹⁾ that optically active 5-substituted 4-methoxycarbonyloxazoles **1** can be efficiently prepared from optically active carboxylic acids and methyl isocyanoacetate by the direct C-acylation using diphenyl phosphorazidate (DPPA, (C₆H₅O)₂P(O)N₃), and the oxazole rings of **1** were cleaved by acid treatment to give amino reductones **2** in high yield.

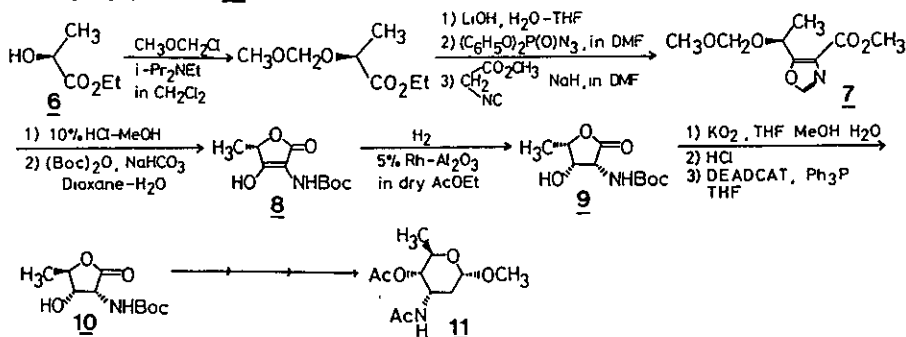


As an application of this oxazole synthesis followed by the ring cleavage, we achieved a facile stereoselective synthesis of L-daunosamine **3**,²⁾ the amino sugar component of the antitumor antibiotics daunomycin and adriamycin, and a derivative of L-vancosamine **4**,³⁾ a branched amino sugar component of the glycopeptide antibiotics vancomycin and sporaviridin.

The enantiomer **5** of L-ristosamine, an amino sugar component of the antibiotics ristomycin, has also been prepared from a common key intermediate **9**, a Boc derivative of **2**.



Ethyl L-lactate **6** was efficiently converted²⁾ to 2-tert-butoxycarbonylamino-2,5-dideoxy-L-lyxono-1,4-lactone **9**, which is a common key intermediate, through the oxazole **7** and the amino reductone **8**. Hydrolysis of **9** with potassium superoxide in THF-MeOH-H₂O (4:1:1) and subsequent acidification, followed by Mitsunobu reaction, afforded the D-ribonolactone **10** in high yield. Reduction of **10**, introduction of C-1 unit by the Wittig reaction, followed by acid treatment, gave D-ristosamine as its N,O-diacetyl methyl glycoside **11**.



- 1) Y. Hamada and T. Shioiri, *Tetrahedron Lett.*, **23**, 235, 1226 (1982)
- 2) Y. Hamada, A. Kawai, and T. Shioiri, *Tetrahedron Lett.*, **25**, 5409 (1984)
- 3) Y. Hamada, A. Kawai, and T. Shioiri, *Tetrahedron Lett.*, **25**, 5413 (1984)