

[Chem. Lett., 1992, 2265-2268]

[Lab. of Pharm. Synthetic Chemistry]

Enantiospecific Synthesis of (3S, 4S)-Statine and Its Analogue from D-Glucosamine as a Chiral Pool.

KATSUO SHINOZAKI, KAZUHIRO MIZUNO, HIROHISA ODA, YUKIO MASAKI*

The C(6)-carbon degradation and elimination of C(4)-hydroxy group of D-glucosamine were achieved in 8-steps and 30 % overall yield to furnish (4R, 5S)-5-vinyl-2-oxazolidinone-4-carbaldehyde dimethyl acetal, which was utilized as a key intermediate for enantiospecific synthesis of biologically important threo β -hydroxy- γ -amino acids, natural (3S, 4S)-statine and (3S, 4S)-AHPPA.

[Synthesis, 1992, 1119-1124]

[Lab. of Pharm. Synthetic Chemistry]

Preparation of Nitroalkenes : Substitution Reaction via Addition-Elimination Using β -Nitrovinyl Sulfoxides.

MANABU NODE, AKICHIKA ITOH*, KIYOHARU NISHIDE, HITOSHI ABE,

TAKEO KAWABATA, YUKIO MASAKI, KAORU FUJI

Nitroalkenes were prepared by the substitution reaction of β -nitrovinyl sulfides and sulfoxides [1-ethylsulfinyl-2-nitrocyclohex-1-ene, -cyclohept-1-ene and (E)-2-ethylsulfinyl-1-nitroprop-1-ene] with a variety of carbon nucleophiles (i.e. alkylmetal reagents and enolates of carbonyl compounds), via an addition-elimination sequence. The sulfoxide as a leaving group was suitable for the reaction with an enolate of carbonyl compounds. This method was useful for the synthesis of nitroalkenes [2-nitrocyclohex-1-enyl (hept-1-enyl)- and 2-nitro-1-methylvinyl-substituted cyclohexanone, γ -butyrolactones, δ -valerolactones, 2-pyrrolidinones and piperidinones].

[J. Am. Chem. Soc., 114, 6505-6512 (1992)]

[Lab. of Pharm. Physical Chemistry]

Plasma-Induced Free Radicals of Polycrystalline myo-Inositol Studied by Electron Spin Resonance. Orbital Rehybridization-Induced Effect of Hydroxylalkyl Radicals on Their Reactivities in Crystalline State.

MASAYUKI KUZUYA*, NAHOKO NODA, SHIN-ICHI KONDO,

KAEI WASHINO, AKIHIRO NOGUCHI

We report the first detailed ESR study of plasma-induced carbohydrate radicals in powdered myo-inositol. On the basis of the ESR kinetics, it was found that plasma irradiation produced the hydroxylalkyl radicals at all four possible sites. A striking difference in the reactivity (stability) of the hydroxylalkyl radicals was observed. We rationalize the observed anomalies in terms of the conformation of O-H bond at C1 (=C3). The difference in radical reactivity is a general phenomenon with broad implications for carbohydrate radicals, providing a pioneering concept to facilitate assignment of the carbohydrate radical structure in the crystalline state.