

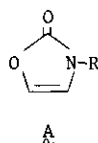
A NEW SYNTHESIS OF 2-OXAZOLONES

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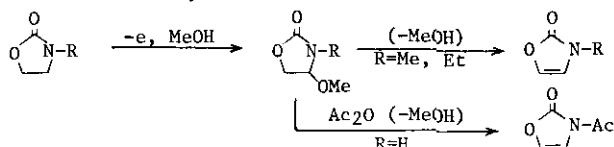
Abstract - 2-Oxazolones were synthesized from 2-oxazolidinones utilizing anodic oxidation as the key step.

2-Oxazolones, **A**, are potential new monomers. 3-Acyl-2-oxazolone was recently shown to undergo smooth free-radical homopolymerization to yield poly-2-oxazolones which can then be converted to poly(1-amino-2-hydroxyethylene).^{1a,b} In addition, 2-oxazolones have been utilized as components for thermal [4+2]^{2a,b} or photo [2+2]³ cycloadditions. The resulting Diels-Alder products and cyclobutane derivatives can be hydrolyzed to the cis- β -aminoalcohols which are potential synthetic intermediates for amino sugars.



Even though the 2-oxazolone skeleton was first reported in 1912,⁴ 4,5-unsubstituted 2-oxazolones were not accessible until the synthesis reported by Hartmann in 1976.⁵ The method involves photochlorination of 2-oxazolidinones in CCl_4 to give a mixture of 4-chloro and 5-chloro-2-oxazolidinones and subsequent thermal dehydrochlorination of the mixture to give 2-oxazolones. In this communication we would like to report an electrochemical approach to 2-oxazolones.

The anodic oxidation of carbamates in methanol has been investigated by Shono and shown to give mainly α -methoxylated products.⁶ The reaction mechanism is believed to involve the electron transfer from the carbamate to the anode as the initiation process. We have found that the anodic oxidation of 2-oxazolidinones in methanol using $\text{Et}_4\text{N}^+\text{OTs}^-$ as a supporting electrolyte yields 4-methoxylated intermediates. The subsequent dealcoholation affords 2-oxazolones.



A typical reaction carried out was as follows: Into a 250 ml undivided electrolysis cell fitted with two carbon electrodes were placed 10.07 g (0.0876 mole) of N-ethyl-2-oxazolidinone, 1.0 g (0.0032 mole) of $\text{Et}_4\text{N}^+\text{OTs}^-$ as a supporting electrolyte and 50 ml of MeOH as a solvent. A constant current (0.5A) was passed through the cell which was externally cooled with H_2O . After two Faradays/mol of electricity was passed, methanol was removed under reduced pressure. The residue was fractionated for isolation of N-ethyl-2-oxazolone (bp 80-83°C/10 mm). N-ethyl-2-oxazolone: $^1\text{Hnmr}$ (CDCl_3) δ 1.30 (t, 3H), 3.60 (q, 2H), 6.54 (d, 1H), 6.74 (d, 1H); 75% overall yield from N-ethyl-2-oxazolidinone. N-methyl-2-oxazolone: mp 78-79°C [lit.⁵ mp 78-80°C]; $^1\text{Hnmr}$ (CDCl_3) δ 3.32 (s, 3H), 6.82 (d, 1H), 7.02 (d, 1H); 80% overall yield from N-methyl-2-oxazolidinone. For the preparation of N-acetyl-2-oxazolone, the residue from the anodic oxidation was treated with an excess of acetic anhydride and heated at 120°C for 6 h. The excess acetic anhydride was then removed under reduced pressure and N-acetyl-2-oxazolone isolated in 50% overall yield from 2-oxazolidinone. N-acetyl-2-oxazolone: bp 90-92°C/10 mm [lit.⁵ 110°C/24 mm], $^1\text{Hnmr}$ (CDCl_3): δ 2.58 (s, 3H), 6.93 (d, 1H), 7.28 (d, 1H).

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