

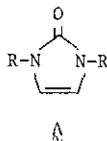
A NEW SYNTHESIS OF 2-IMIDAZOLONES

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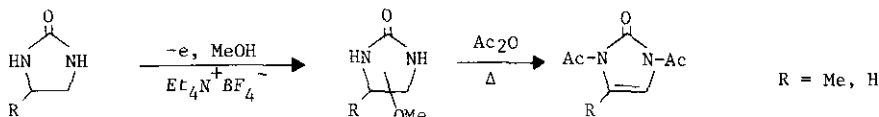
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**Abstract** — 2-Imidazolones were synthesized from ethylene ureas utilizing anodic oxidation as the key step.

2-Imidazolones  $\Delta$  are important building blocks for pharmaceutical chemicals.<sup>1a-c</sup> 4,5-Unsubstituted 2-imidazolones are also new components for thermal [4+2]<sup>2,3</sup> and photo [2+2]<sup>3</sup> cycloadditions. The resulting Diels-Alder products and cyclobutane derivatives can be hydrolyzed to the *cis*-1,2-diamines. 4,5-Unsubstituted 2-imidazolone was first prepared by Fenton and Wilks from the condensation of dehydroxymaleic acid with urea.<sup>4</sup> It can also be prepared by photochlorination of ethylene urea followed by treatment with Zn<sup>5</sup> or by the reduction of hydantoin with diisobutylaluminum hydride.<sup>3</sup> In this communication, we would like to report a new approach based on electrochemical oxidation.



The anodic oxidation of carbamates and amides in methanol has been investigated by Shono and shown to give mainly  $\alpha$ -methoxylated products.<sup>6</sup> The reaction mechanism is believed to involve the electron transfer from the carbamate or amide to the anode as the initiation process. The anodic oxidation of urea compounds has not been reported before. We have found that the anodic oxidation of ethylene ureas in methanol using Et<sub>4</sub>N<sup>+</sup>BF<sub>4</sub><sup>-</sup> as a supporting electrolyte yields  $\alpha$ -methoxylated intermediates. Treatment of the crude mixture with acetic anhydride at 100°C gives the corresponding N,N'-diacetyl-imidazolones in 40-50% overall yields from ethylene ureas. A typical reaction carried out was as follows:



Into a 250 ml undivided electrolysis cell fitted with two platinum (2 x 2 cm<sup>2</sup>) electrodes were placed 8.6 g (0.1 mole) of ethylene urea, 0.32 g (0.003 mole) of tetraethylammonium tetrafluoroborate as a supporting electrolyte and 100 ml of MeOH as a solvent. A constant current (0.5A)

was passed through the cell which was externally cooled with H<sub>2</sub>O.<sup>7</sup> After two Faradays/mol of electricity had passed, the methanol was removed under reduced pressure. The residue<sup>8</sup> was treated with excess acetic anhydride, a catalytic amount of sodium acetate and heated at 110-120°C. The progress of the reaction was monitored by GLC. The desired N,N'-diacetyl-2-imidazolone was isolated by distillation or sublimation as long needles after removing the acetic anhydride. N,N'-diacetyl-2-imidazolone: mp 104-105°C [lit.<sup>9</sup> mp 105-106°C]; <sup>1</sup>Hnmr (CDCl<sub>3</sub>) 2.60 (s, 6H) 6.98 (s, 2H); 40% overall yield from ethylene urea; N,N'-diacetyl-5-methyl-2-imidazolone: mp 78-79°C [lit.<sup>1a</sup> mp 78-80°C]; <sup>1</sup>Hnmr (CDCl<sub>3</sub>) 2.30 (d, 3H), 2.57 (s, 3H), 2.60 (s, 3H), 6.68 (d, 1H); 50% overall yield from 5-methyl ethylene urea.

#### References and Notes

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- Oxidation potential (E<sub>ox</sub>) of ethylene urea: 1.80; oxidation potential (E<sub>ox</sub>) of 5-methyl ethylene urea: 1.76.
- $\alpha$ -Methoxylated intermediates were used for the next step without any purifications. The presence of methoxyl group was confirmed by <sup>1</sup>Hnmr.
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