Synthesis and characterization of new heterocyclic compounds from the reaction of 4,7-dioxononanoic acid with 1,2-dinucleophiles

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4,7-Dioxocarboxylic acids have been known for a very long time, however, it was only in 1998 that their spectroscopic data were reported for the first time.[1,2] The chemistry of 4,7-dioxocarboxylic acids has not been explored in detail. These acids can be easily synthesized from furfural, which is a readily available, cheap and versatile organic compound that can be derived from a variety of agricultural byproducts.[3] They are potentially good precursors for the synthesis of 5- and 6- membered heterocyclic compounds with pharmaceutical interest due to the presence of two keto carbonyl groups in a 1,4-relationship as well as a carboxyl carbonyl group and keto carbonyl group in a 1,4-relationship.[4] We have already reported the reaction of 4,7-dioxononanoic acid with hydrazine and here we report the synthesis and characterization of two new heterocyclic compounds (oxazine derivative and a pyrrole derivative) from the reactions of 4,7-dioxononanoic acid with dinucleophiles, phenyl hydrazine and hydroxylamine.[5]

Reactions of 4,7-dioxononanoic acid with hydroxylamine and phenyl hydrazine are shown in Figure 1.

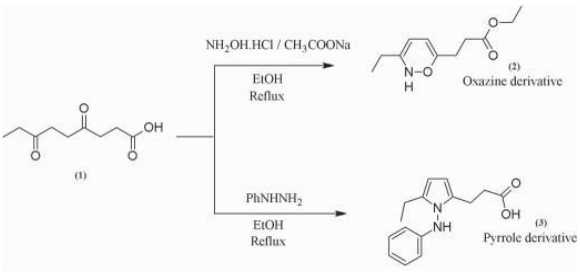

Figure 1: Reactions of 4,7-dioxononanoic acid with hydroxylamine and phenyl hydrazine

The major product **(2)** from the reaction between 4,7-dioxononanoic acid and hydroxylamine showed a single peak in the gas chromatogram and the corresponding mass spectrum showed the molecular ion at 211.1. The resulting strong fragment at 124.0 corresponded to $(M\text{-}CH_2CO_2Et)^+$. The IR spectrum of compound **(2)** showed the ester C=O stretching at 1731.991 cm^{-1}, N-H stretching at 3348.87 cm^{-1} and N-O stretchings at 1463.30 cm^{-1} and 1374.40 cm^{-1} confirming the assigned structure. The UV absorbances of compound **(2)** at 214 and 322 nm were in accordance with a typical oxazine derivative. Similarly the major product **(3)** from the reaction between 4,7-dioxononanoic acid and phenyl hydrazine showed a single peak in the gas chromatogram and the corresponding mass spectrum with the molecular ion at 258.1. The resulting fragments at 199.1 and 93.0 corresponded to $(M\text{-}CH_2COOH)^+$ and $(NHC_6H_5)^+$ respectively. The IR spectrum of compound **(3)** showed the carbonyl stretching of the carboxylic acid at 1707.75 cm^{-1}, N-H stretching at 3324.72 cm^{-1}, C=C aromatic ring stretching at 1602.00 cm^{-1} and 1496.22 cm^{-1} confirming the assigned structure. The OH stretching of the carboxylic acid was not observed, however, TLC using bromocresol green as the indicator, which is specific for carboxylic acid groups, confirmed its presence. The UV absorbances of compound **(3)** at 244 and 280 nm were in accordance with that of a pyrrole derivative.

References:

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