



Comparative study on the rate of reaction of maleic anhydride, maleic acid and fumaric acid with α -Oxoketene N, S-acetals towards analogous Nenitzescu reaction

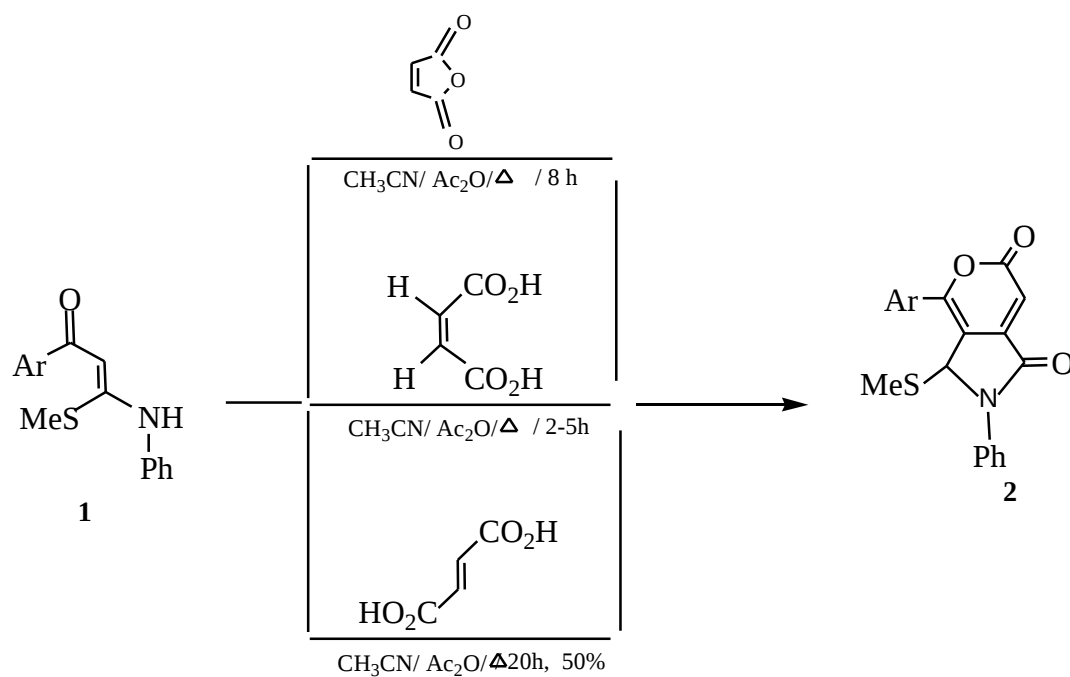
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ABSTRACT

We have earlier reported the synthesis of various pyrano[3,4-c]pyrroles from the reaction of respective α -oxoketene N, S- and N, N-acetals with maleic anhydride in the presence of acetic anhydride in refluxing acetonitrile¹. It is expected that maleic acid and fumaric acid would also react with the α -oxoketene N, S- and N, N-acetals in the same reaction conditions to afford corresponding pyrano[3,4-c]pyrroles as they also possess the activated olefinic bond in their structure. We expected a difference in the reactivity of maleic anhydride, maleic acid and fumaric acid because the anhydrides are considered to be more reactive than their respective acids. With this view in mind we attempted to study the rates of the reaction of these molecules with α -oxoketene N, S-acetals in the presence of acetic anhydride in refluxing acetonitrile. The results of this study are described in the following paragraph.

It was found that the rate of the reaction was found to be the fastest in case of maleic acid and the slowest in case of maleic anhydride. This is evident from the reaction time taken by the three compounds for completion of the reaction. The reaction with maleic acid takes 2-5 hours whereas that with maleic anhydride takes 8 hours. The reaction with fumaric acid completes only 50% even after refluxing for 20 hours (scheme). The least reactivity of fumaric acid is expected as it has the thermodynamically more stable trans-geometry. This extra stability makes the initial nucleophilic addition of the N, S-acetals to the very strong olefinic bond of fumaric acid very very slow. The reversal of reactivity in case of maleic anhydride and maleic acid can be explained as follows. Presence of acetic anhydride plays the trick here. It converts the maleic acid into its double mixed anhydride. The olefinic bond in the double mixed anhydride is now more electrophilic than that in case of maleic anhydride. Therefore, the initial nucleophilic addition of the N, S-acetals to the olefinic bond is more favoured in case of maleic acid and hence the increase in the rate of the reaction.



Scheme

REFERENCE

- [1] Gupta, Akhilesh Kumar, Ila, H. ; Junjappa, H. , *Synthesis*, 284 (1988)