SYNTHESIS OF FRAGRANCES STARTING FROM CYCLIC VINYL KETONES

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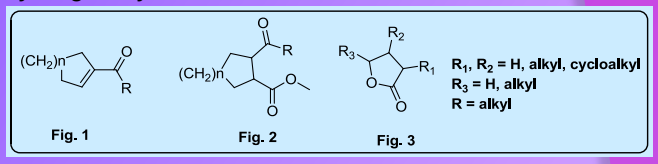
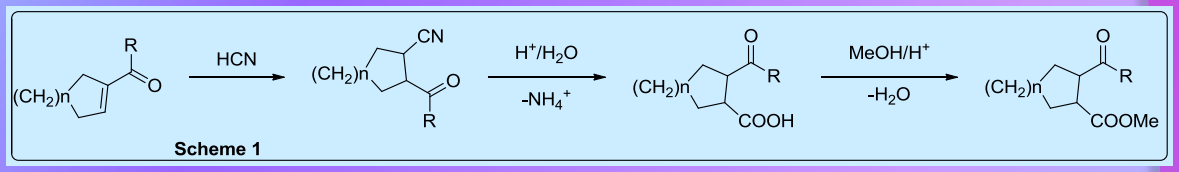
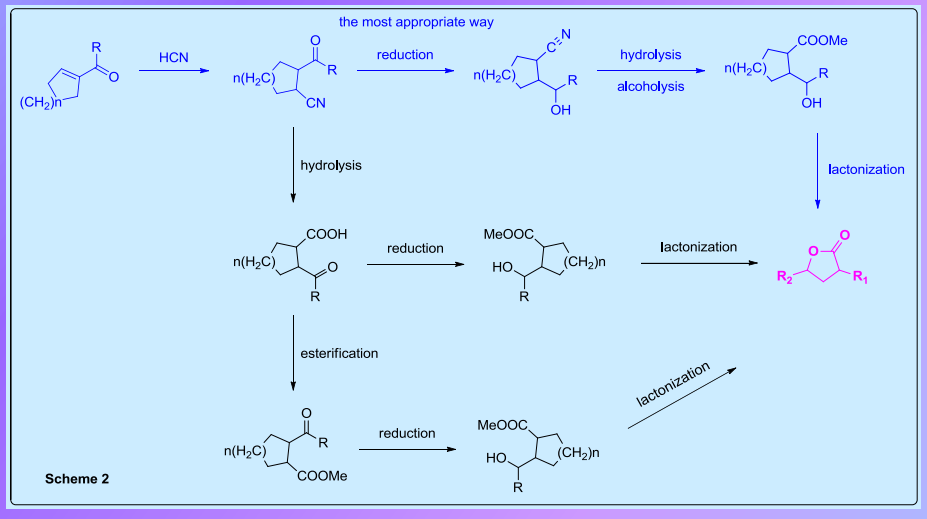
Cyclic vinyl ketones **(Figure 1)** are potential precursors for the synthesis of esters **(Figure 2)** or lactones **(Figure 3)**, which can be used as a fragrance in the cosmetic industry, in the manufacture of soaps, detergents *etc*. The first step of the synthesis starting from vinyl ketones is addition of hydrogen cyanide to activated double carbon-carbon bond in the cyclic vinyl ketones.

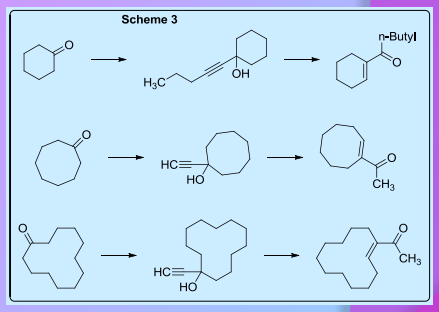


We developed a new process of hydrocyanation of vinyl ketones **(Scheme 1)** for the preparation of keto esters and subsequent lactones. Some vinyl ketones prepared in such procedure are not commercially available.



Three synthetic pathways were studied for the preparation of lactone molecules **(Scheme 2)**. These routes differ in the subsequent transformation of ketonitrile. The method, where the carbonyl group in the ketonitrile is reduced to a secondary alcohol followed by hydrolysis/alcoholysis and subsequent lactonization, seems the most appropriate. Hydrolysis/alcoholysis and subsequent lactonization take place as a one-pot process.





Cyclic ketones were successfully prepared by two-step synthesis **(Scheme 3)**. The first step was the reaction of the corresponding cyclic ketone with 1-alkyne-magnesium halide to form the corresponding alcohol. The second step was Ruppe rearrangement of the alcohol to form a cyclic vinyl ketone. The overall yields of these two step syntheses was 78 – 85%.

Conclusion: Known hydrocyanation processes on similar substrates are often unsuitable for application to industrial scale. The materials used in reactions are expensive and inappropriate (alkali cyanides, solvents as DMF, DMSO, etc.). The advantage of the new process consists of using of cheaper HCN as hydrocyanation agent in combination with a suitable environmental friendly solvent and basic catalyst. This innovative process is simpler and cheaper and provides products in very good yields and purity, which allows further processing in the synthesis of the final products.

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