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THE NEW MICHAEL REACTION

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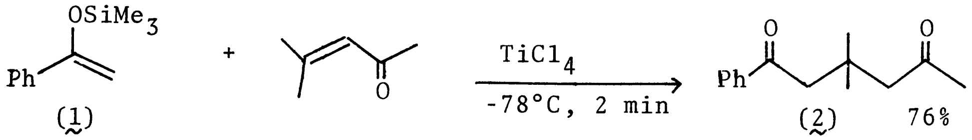
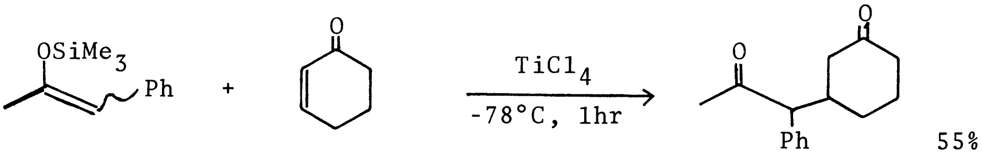
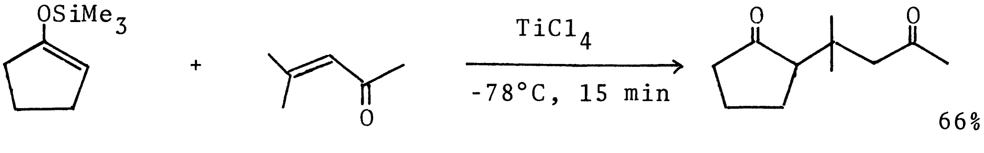
It was found that silyl enol ethers react with α,β-unsaturated ketones and esters in the presence of $TiCl_4$ under mild (-78°C) conditions to give 1,5-dicarbonyl compounds in good yields. Further, it was also found that 1-phenyl-1,5-hexanedione and its monoacetal were obtained by the $TiCl_4$-promoted reaction of methyl vinyl ketone ethylene acetal with α-trimethylsiloxystyrene.

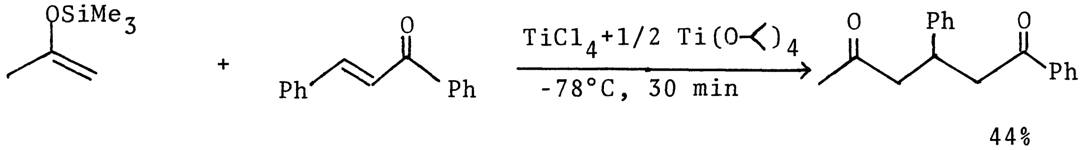
In the preceding papers,[1)] we reported that silyl enol ethers react with various carbonyl compounds and their acetals in the presence of $TiCl_4$ to give cross-aldol products in good yields. On the other hand, it was found by the present experiment that the $TiCl_4$-promoted reaction of α,β-unsaturated ketones with silyl enol ethers results in the formation of 1,5-dicarbonyl compounds (Michael adducts) in good yields in stead of the aldol product. For example, a solution of $TiCl_4$ (2 mmol) in 8 ml of CH_2Cl_2 was cooled to -78°C and stirred under argon atmosphere. A solution of mesityl oxide (2 mmol) in CH_2Cl_2 (3 ml) and a solution of α-trimethylsiloxystyrene (1, 2 mmol) in CH_2Cl_2 (3 ml) were added successively to the above solution. After stirring for 2 min at -78°C, the mixture was quenched with aqueous K_2CO_3 (0.7 g in 15 ml of water) and resulted precipitate was filtered off. The filtrate was extracted with ether and the extract was washed with water and brine. After removal of the solvent, the main product, 3,3-dimethyl-1-phenyl-1,5-hexanedione (2, 76%) was separated by preparative tlc using hexane-ether (2:1) as eluent.

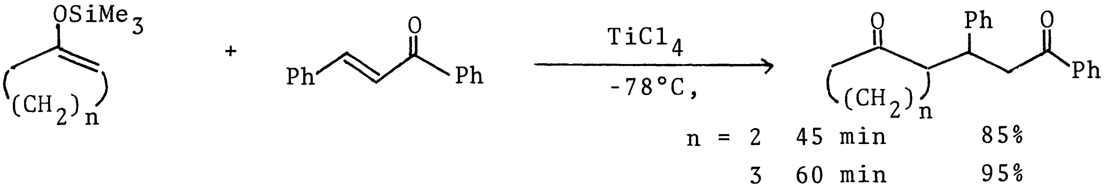


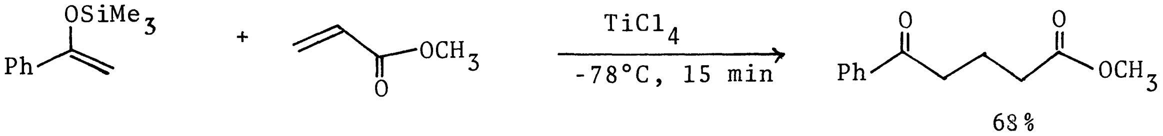
The generality of the reaction between silyl enol ethers and α,β-unsaturated carbonyl compounds is apparent from the results shown in the following equations.





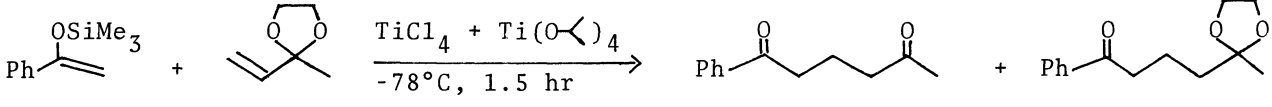






In general, the Michael reaction of α,β-unsaturated carbonyl compound and ketone is carried out under basic condition and the product, 1,5-dicarbonyl compound, frequently tends to further transformation.[2] Moreover, when α,β-unsaturated ketones are used as Michael acceptors, there are many possibilities leading to a variety of side reactions as self-condensation reactions and the Michael reaction followed by aldol reaction.[3] Contrary to these results, by the present method, the Michael reaction proceeds under acidic and very mild (-78°C) conditions, therefore, the side reactions are greatly diminished to result in the formation of 1,5-dicarbonyl compounds in good yields.

In addition, an availability of this acid-catalyzed Michael reaction[4] is shown when α,β-unsaturated acetal is used as Michael acceptor. 1-Phenyl-1,5-hexanedione (4) and its monoacetal (5) were isolated in 37% and 38% yields, respectively, when methyl vinyl ketone ethylene acetal (3)[5] was treated with α-trimethylsiloxystyrene in the presence of equimolar amounts of $TiCl_4$ and $Ti[OCH(CH_3)_2]_4$ according to the procedure described above.



(3) (4) 37% (5) 38%

Further development is now in progress.

References

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