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A NEW METHOD FOR ENOL ACETYLATION

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Abstract : Saturated and conjugated ketones react with chlorotrimethylsilane and acetic anhydride to furnish the enol acetates in excellent yield.

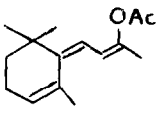
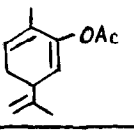
Enol acetylation of ketones is a reaction of great preparative value especially for 17α-hydroxy corticoids including cortisone[1]. Earlier methods of enol acetylation[2] describe chiefly the use of acetic anhydride-perchloric acid[3] (thermodynamic control) or p-toluene sulphonic acid and isopropenyl acetate-acid catalysis[4] (Kinetic control).

It was argued that chlorotrimethylsilane (CTMS) would split acetic anhydride to generate trimethylsilyl acetate, acylonium ($CH_3C^+=O$) and chloride ions and that there may exist some amount of naked acylonium ions besides the formation of acetyl chloride. Our surmise was indeed proved to be correct when several of the saturated and conjugated ketones listed in Table 1 reacted with CTMS/Ac_2O or CTMS/Ac_2O and sodium iodide to furnish the enol acetates in excellent yield. Support for the presence of bare acylonium ion was forthcoming through an experiment carried out by treating ketone at entry 1 with acetic anhydride and acetyl chloride when no enol acetylation was observed at r.t.

From Table 1 it is evident that our method of enol acetylation will be a useful addition to the existing ones.

In a typical experiment a solution of the substrate (0.25m mol) in 1.0 ml of Ac_2O is treated with chlorotrimethylsilane (1.0m mol) and NaI (1.0m mol) added whereever mentioned in Table 1. The reaction mixture is kept at r.t. or heated if the reaction is slow as indicated by TLC monitoring of the reaction.

Table 1[a,b]

Entry	Substrate	Reaction conditions	Product	Yield (%) (Isolated)
1	Cholest-4-en-3-one	CTMS/Ac_2O; r.t. 30 min.	Cholesta-3,5-diene-3-ol acetate	90
2	Cholest-5-en-3-one	do	do	90
3	Cholestan-3-one[c]	CTMS/Ac_2O; 100°C, 2h	Cholest-2-en-3-ol acetate	85
4	Progesterone[d]	CTMS/Ac_2O/NaI; r.t. 1h	Pregna-3,5,17(20)-triene-3,20-diol diacetate	82
5	Cholestan-7-one[c]	CTMS/Ac_2O; 100°C, 2h	Chloest-7-en-7-ol acetate	90
6	Androst-5-en-3-ol-17-one[d]	CTMS/Ac_2O/NaI; 100°C, 8h	Androsta-5,16-diene-3,17-diol diacetate	50
7	β-Ionone[c]	CTMS/Ac_2O; r.t. 2h		70
8	Carvone[c]	CTMS/Ac_2O; 100°C, 4h		70

[a] All compounds mentioned in Table 1 gave satisfactory IR, NMR and Mass spectral data.

[b] Enol acetylation of all the ketones listed in Table 1 was tried with Ac_2O/AcCl/NaI, however in each case poor yield of the enol acetates was obtained and extreme decomposition was observed.

[c] The reaction time was reduced to one half in the presence of sodium iodide.

[d] In case of entry 4 & 6 there was no reaction without sodium iodide. Chlorotrimethylsilane and sodium iodide react to give iodotrimethylsilane[5].

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