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Synthesis of chalcones catalysed by $SOCl_2$/EtOH

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A novel and efficient synthesis chalcones by using $SOCl_2$/EtOH as catalyst was presented. In the presence of thionyl chloride, the aldol condensation of acetophenone and benzaldehyde was catalysed in the anhydrous ethanol in high yields (60–95%) under mild condition.

Keywords: chalcones, thionyl chloride

Chalcones (1,3-diphenyl-prop-2en-1-ones) represent one of the most abundant and ubiquitous groups of natural products.[1] Chalcones and especially chalcones bearing oxygen functions on the aromatic rings are the precursors of the flavonoids.[2] They are biologically active molecules found in many plants and vegetables. Moreover, chalcone derivatives are also used for their excellent second harmonic generation (SHG) properties.[3] Some of these α,β-unsaturated ketones are used as sweeteners, sunscreen agents, photoresists, photographic emulsions and liquid crystal material.[4] The aldol condensation is the most efficient reaction for the preparation of chalcones. The preparation of α,β-unsaturated ketones is catalysed by Lewis acids or by strong alkali in an aqueousoalcoholic medium from benzaldehyde and ketones. The aldol condensation products always contain di-, poly-, self-condensation and undehydrated products (β-hydroxy-ketone).[5] These factors frequently limit the utilisation of this efficient reaction. In order to solve this problem, new and powerful variants of these classical reactions have been developed. Some useful synthetic procedures, for example, using $SnCl_2$,[6] NH_4OAC[7] and KF-Al_2O_3[8] as the catalysts and methods such as Suzuki reaction[2] have been developed.

We previously reported that $SOCl_2$/EtOH reagent could catalyse the tri-condensation of acetophene for the preparation of triarylbenzenes. Recently we found that reagent $SOCl_2$/EtOH is also a good catalyst for catalysing the aldol condensation reaction of acetophenone and benzaldehyde. In this paper, we report a mild and convenient method for the preparation of chalcones by using $SOCl_2$/EtOH as the reagent. In the presence of thionyl chloride, the cross-aldol condensation of acetophenone and benzaldehyde proceeds smoothly in anhydrous ethanol in high yields (60–95%) and only chalcones were obtained. (Scheme1)

Seven chalcones were obtained. All these compounds obtained showed IR, ^{1}H NMR, which data were compatible with their structures. All reactions were optimised for the best yields. The reaction results are summarised in Table 1.

From the results in Table 1, it is obvious that the electronic nature of substrates has a marked effect on the reaction. Strong electron withdrawing groups on the aromatic rings led to increased yields of the reaction (Entry 2, 4) but the electron donating groups decreased yields greatly (Entry 7).

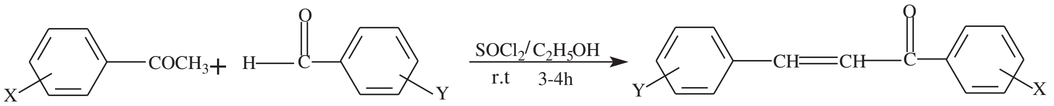
The catalyst system also was changed by using CH_3OH, C_2H_5OH (absolute anhydrous) and Et_2O as the solvents. However, we found that only alcohols could catalyse the reaction. There was no obvious difference in yields between CH_3OH and C_2H_5OH. On the basis of these results, we think the reaction that proceeds via the reaction of the enol sulfite ester of the ketones. The by-product HCl may accelerate the reaction. The detailed mechanistic investigation and further applications of this reaction are under study in our laboratory.

In summary, we have reported a novel and efficient synthesis of chalcones by using $SOCl_2$/EtOH as catalyst. The advantage of this method is easily available and cheap catalyst, single product, simple manipulation and mild conditions. We believe that this reaction expands the application of the thionyl chloride in organic synthesis.

Experimental

Melting points were determined on Kofler micro melting point apparatus without correction. Infrared spectra were record on an FTS-40IR spectrophotometer using KBr pellets. ^{1}H NMR spectra were measured in $CDCl_3$ using TMS as internal standard with a Bruker 250 AC-NMR spectrometer.

General procedure: To a stirred mixture of the acetophenone (11.7ml, 0.1mol), benzaldehyde (0.12mol) and anhydrous ethanol (14.6ml, 0.25mol), thionyl chloride (7.3ml, 0.1mol) was added. The solution turned deep red immediately. When stirred for 20–30min, the mixture became coagulated. After completion of the reaction, saturation Na_2CO_3 was added and the mixture was filtered. The solid



Scheme 1 The synthesis of chalcones

Table 1 The preparation of chalcones

Entry	Compound	Benzaldehyde (Y)	Acetophenone (X)	M.p./°C$^{lit.}$	Yield/%
1	**a**	H	H	56–58 (55–56)[9]	86
2	**b**	H	*p*-NO_2	151–152	92
3	**c**	*p*-$N(CH_3)_2$	H	112–113 (112–114)[9]	80
4	**d**	*o*-NO_2	H	110–112 (111–112)[10]	95
5	**e**	*m*-OCH_3	H	55–56 (54–56)[10]	83
6	**f**	*p*-CH_3	H	86–88 (84–86)[10]	81
7	**g**	*p*-CH_3	*p*-CH_3	95–96 (95–96)[10]	67

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was washed twice successively with water (30ml), anhydrous ethanol (10ml) and ethyl ether (10ml). Some products need recrystallisation. The m.p. are given in the table.

Spectra data of the products

Compound **a:** Chalcone, white powder; IR ν_{max} (KBr, cm^{-1}) 1668, 1602, ^{1}H NMR ($CDCl_3$): 8.03 (m, 2H), 7.82(d, 1H, *J*=16Hz), 7.47–7.71 (m, 9H);

Compound **b:** 4'-Nitrochalcone, yellowish powder; IR ν_{max} (KBr, cm^{-1}) 1662, 1587, 1510, 1336; ^{1}H NMR δ_H ($CDCl_3$) 7.42(m, 1H), 7.48 (m, 3H), 7.54 (d, 1H, *J*=16Hz), 7.61 (m, 1H), 7.64 (m, 2H), 7.81 (d, 1H, *J*=16Hz), 8.06 (m, 2H);

Compound **c**: 4-Dimethylaminochalcone: brown powder; IR ν_{max} (KBr, cm^{-1}) 1649, 1598; ^{1}H NMR δ_H ($CDCl_3$) 3.04(s, 6H), 6.74 (m, 2H), 7.34 (d, 1H, *J*=16Hz), 7.47 (m, 2H), 7.54 (m, 3H), 7.81 (d, 1H, *J*=16Hz), 8.00 (m, 2H);

Compound **d:** 2-Nitrochalcone: white powder; IR ν_{max} (KBr, cm^{-1}) 1656, 1592; ^{1}H NMR δ_H ($CDCl_3$) 7.98 (m, 2H), 7.56–7.54 (m, 4H), 7.51 (m, 3H), 6.89 (d, 1H, *J*=16 Hz), 6.37 (d, 1H, *J*=16Hz)

Compound **e:** 3-Methoxychalcone, yellow powder; IR ν_{max} (KBr, cm^{-1}) 1665, 1595; ^{1}H NMR δ_H ($CDCl_3$) 8.14 (m, 1H), 7.98 (m, 2H), 7.82 (m, 1H), 7.56–7.53(m, 3H), 7.43 (m, 2H), 7.40 (d, 1H, *J*=16 Hz), 7.27 (d, 1H, *J*=16 Hz), 3.89 (s, 3H, OCH3);

Compound **f:** 4-Methylchalcone: yellow solid; IR ν_{max} (KBr, cm^{-1}) 1668, 1596; ^{1}H NMR δ_H ($CDCl_3$) 7.99 (m, 2H), 7.79 (d, 1H, *J*=16 Hz), 7.48–7.52 (m, 7H), 7.27 (m, 1H), 2.40 (s, 3H, CH3);

Compound **g:** 4-Methyl-4'-methylchalcone, yellow powder; IR (KBr, cm^{-1}) 1654, 1596; ^{1}H NMR δ_H ($CDCl_3$) 7.92 (m, 2H), 7.78 (d, 1H, *J*=16 Hz), 7.54–7.45 (m, 3H), 7.38 (m, 2H), 7.20(m, 2H), 2, 42 (s, 3H), 2.37 (s, 3H);

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