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A New Approach to the Stereoselective Synthesis of β-Methylchalcones

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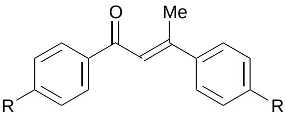
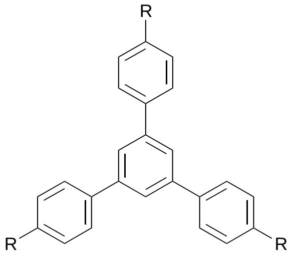
Many β-methylchalcone derivatives are prepared *via* the self condensation of aralkyl ketones mediated by tetrachlorosilane–ethanol under mild conditions.

The present study is concerned with the elaboration of a highly efficient and stereodefined synthesis of β-methylchalcones. Unlike titanium tetrachloride, the reaction of aryl methyl ketone with an equimolar amount of tetrachlorosilane (TCS) in the presence of absolute ethanol and in the absence of catalyst afforded a β-methylchalcone along with a smaller amount of 1,3,5-triarylbenzene, with no polymeric compound being detected[18] (Table 1, entries 1–5). The reaction time required for optimum yields was *ca*. 3 h in most cases.



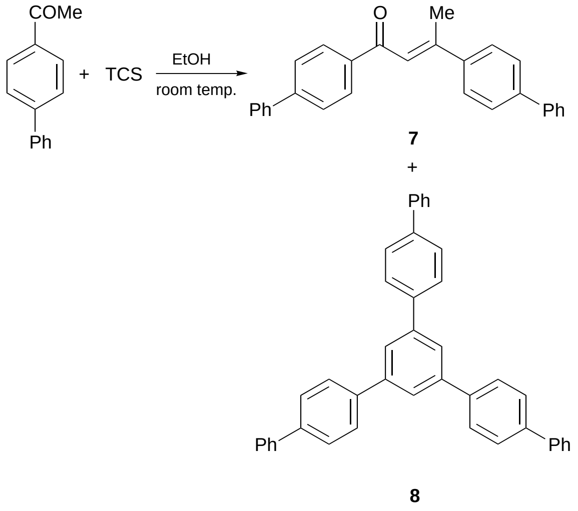
1 R = H
3 R = 4-Cl
5 R = 4-Br
9 R = 4-OMe



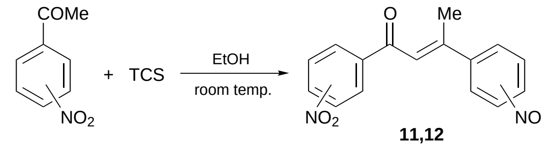
2 R = H
4 R = 4-Cl
6 R = 4-Br
10 R = 4-OMe

With the variation in yields given in Table 1, it can be seen that there are important differences in the behaviour of the TCS–EtOH reagent towards aryl methyl ketones. Substituents such as methoxy and phenyl, which increase the negativity of the acetyl group by resonance or inductive effects, retard the yield of β-methylchalcone as shown in entries 4 and 5 [eqn. (1)].

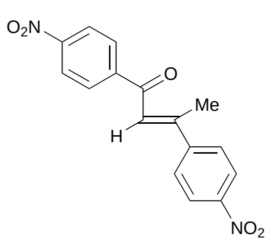
On the other hand, substituted acetophenones having strongly electron withdrawing groups such as nitro groups gave only β-methylchalcones. Thus 3′- or 4′-nitroacetophenone in entries 6 or 7 was treated with a slight excess of tetrachlorosilane in ethanol to afford the β-methylchalcone **11** or **12** respectively in very good yield. Thus the formation of



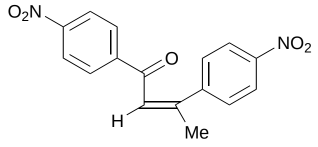
(1)



(2)



(*E*)-**12a**



(*Z*)-**12b**

Table 1 Reaction of aryl methyl ketones with TCS–EtOH

Entry	Substrate	*t*/h	Product	Yield (%)[a]
1	Acetophenone	2	1,3-diphenylbut-2-en-1-one **1** + 1,3,5-triphenylbenzene **2**	62 34
2	4′-Chloroacetophenone	3	1,3-Bis(4-chlorophenyl)but-2-en-1-one **3** + 1,3,5-tris(4-chlorophenyl)benzene **4**	64 28
3	4′-Bromoacetophenone	4	1,3-Bis(4-bromophenyl)but-2-en-1-one **5** + 1,3,5-tris(4-bromophenyl)benzene **6**	65 23
4	4-Acetylbiphenyl	2	1,3-Bis(biphenyl-4-yl)but-2-en-1-one **7** + 1,3,5-tris(biphenyl-4-yl)benzene **8**	59 32
5	4′-Methoxyacetophenone	2	1,3-Bis(4-methoxyphenyl)but-2-en-1-one **9** + 1,3,5-tris(4-methoxyphenyl)benzene **10**	58 37
6	3′-Nitroacetophenone	10	1,3-Bis(3-nitrophenyl)but-2-en-1-one **11**	77
7	4′-Nitroacetophenone	8	1,3-Bis(4-nitrophenyl)but-2-en-1-one **12**	74

[a] Isolated yields after column chromatography.

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a triarylbenzene can be inhibited by slowing the rate of the second aldol condensation with a substituted acetophenone having a strongly electron withdrawing group. Moreover, the reaction in a slight excess of absolute ethanol as solvent ultimately leads to a decrease in the yield of the 1,3,5-triarylbenzene derivatives [eqn. (2)].

The products of the double condensation were obtained either as mixtures of *E*- and *Z*-isomers of the β-methylchalcone (entries 1,2,3 and 7) or exclusively as *E*-isomers (entries 4, 5 and 6). The structural analysis for the *cis*-and *trans*-isomers was carried out by UV absorption and ^{1}H NMR spectral methods. The *E*- and *Z*-isomers exhibit remarkable spectroscopic differences which allow the reported structure assignments.

The reaction rate and stereochemical course of the double condensation of aralkyl ketones were influenced by such factors as the kind of substituent at the aromatic ring and the molar ratio of the reactants. The mild conditions and simplicity of the operation offer distinct advantages over the reported methods. In principle, it is found that β-methylchalcone derivatives can be easily prepared from readily accessible and cheap TCS in the presence of absolute ethanol at room temperature.

Techniques used: IR, UV, GCMS and ^{1}H NMR

References: 24

Table 1: Reaction of aryl methyl ketones with TCS–EtOH

Table 2: Spectral data of the β-methylchalcones

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