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An expedient one-pot synthesis of benzophenone Schiff bases from benzene

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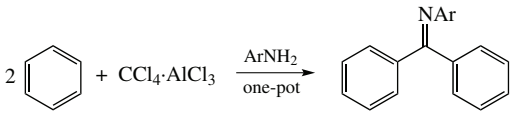
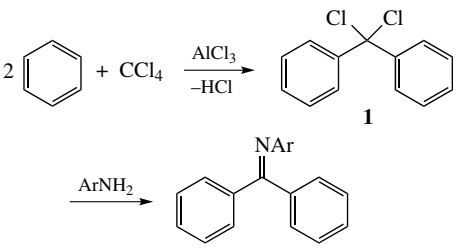
A simple and efficient one-pot synthesis of benzophenone Schiff bases from benzene, CCl_4 and aromatic amines was developed based on the the reaction of benzene with CCl_4·$AlCl_3$ complex. This method affords Ph_2CCl_2 as well as the products of its subsequent reaction with aromatic amines, benzophenone Schiff bases, selectively and in good yields.



Keywords: one-pot synthesis, benzene, Schiff bases, tetrachloromethane, benzophenone, aluminum trichloride.

Benzophenone Schiff bases demonstrate promising activity against different bacterial and fungal strains[1] as well as are used as catalysts and multipurpose reactants.[2] Numerous methods have been developed for their synthesis.[1–3] Among them, the widely used ones originated from ketones and arylamines have definite drawbacks.[3(a)] Unlike the condensation of aldehydes and arylamines, the reactions of ketones require high temperatures as well as use of catalysts and specific techniques. A set of Brønsted or Lewis acids, dehydration agents as well as microwave, infrared or ultrasound irradiation have been employed to carry out the syntheses of ketone Schiff bases.[3(a)] Most of these procedures suffer from low yields, long reaction times, poor functional group tolerance, the need for elevated temperature, expensive substrates, toxic reagents, or have a limited scope. On the other hand, the application of a Lewis acid–base pair like $AlCl_3$–Et_3N provided products in good yields under mild conditions.[3(a)] However, this reaction required large amounts of $AlCl_3$ and Et_3N in a ratio of $[Ph_2C(O)]/[AlCl_3]/[Et_3N]$ 1 : 1.7 : 5.1 and failed to produce anils from sterically crowded anilines. Alternative procedures for the synthesis of Schiff bases were used rarely, notwithstanding their potential advantage.[1,3(b)–(f)] Generally, in more than 150 years since the first Schiff base had been obtained,[4] the development of milder and cheaper methods for their synthesis has remained a challenge.



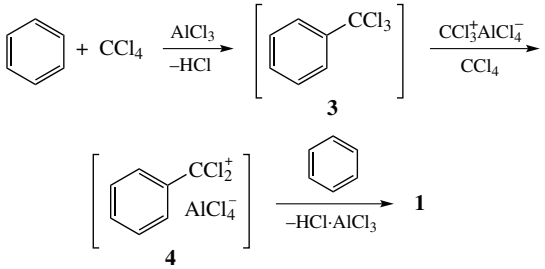
2a Ar = Ph
2b Ar = 4-MeC_6H_4
2c Ar = 4-$MeOC_6H_4$
2d Ar = 4-FC_6H_4
2e Ar = 4-ClC_6H_4
2f Ar = 2-ClC_6H_4
2g Ar = 4-BrC_6H_4
2h Ar = 4-$O_2NC_6H_4$
2i Ar = 2,6-$Me_2C_6H_3$
2j Ar = 2-$O_2NC_6H_4$
2k Ar = 2-Cl-4-MeC_6H_3

Scheme 1

In this work, we have developed a simple one-pot synthesis of benzophenone anils **2a–k** from benzene, CCl_4·$AlCl_3$ complex and aromatic amines (Scheme 1) through *in situ* generated dichlorodiphenylmetane **1**. The reaction can be performed in CH_2Cl_2 or as a solvent-free one.

The reaction of benzene with CCl_4 in the presence of $AlCl_3$ has been known since the early 20th century (Scheme 2).[5] It involves the Friedel–Crafts alkylation of benzene with CCl_3^+ cation, generated from CCl_4 and $AlCl_3$ with formation of benzotrichloride **3**. In turn, compound **3** undergoes the abstraction of Cl^- ion by the electrophile resulting in cation **4** which can alkylate another benzene molecule affording compound **1**.

Willard reported that the exchange of chlorine atom of CCl_4 and $AlCl_3$ labeled with ^{35}Cl occurs even at –20 °C, thus indicating the ionization of CCl_4 to CCl_3^+ cation.[6] Complex $PhCCl_2^+AlCl_4^-$ **4** preceding the formation of dichloride **1** was found to possess definite stability and could be stored for two weeks at 25 °C.[7] The complication arises (see Scheme 2) since the electrophiles, namely $CCl_3^+AlCl_4^-$ if the reaction is carried out in excess CCl_4, or HCl·$AlCl_3$ if CCl_4 is used in the equimolar ratio, can initiate the subsequent transformations of dichloride **1**. Depending on the reaction conditions, this process results in Ph_3CCl,[8(a)] Ph_2CCl_2,[5(b),(c)] Ph_3CH[8(a)] or $PhCCl_3$.[8(b),(c)] If the reaction is carried out in CH_2Cl_2 or $CHCl_3$, the yield of compound **1** decreases due to the side reactions of benzene and CH_2Cl_2[9(a)] or $CHCl_3$,[9(b)] respectively. Several works reported on the use of CS_2 as a solvent.[10] Examples of the preparative use of the reaction of



Scheme 2

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