



Synthesis of Benzophenones Using Silica-Gel Supported Lewis acid Catalyst.

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Abstract : Liquid phase benzylation of activated as well as deactivated aromatics was carried out using silica gel supported FeCl_3 and benzotrichloride as a benzylation agent. The catalyst was prepared by co-grinding FeCl_3 with silica gel in an agate mortar. The catalyst has a good shelf life of at least two months.

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Benzylation under Friedel-Crafts conditions is an industrially important process. Recently the generation of exceptionally stable phenyl dicarbenium ion¹ and its use as a benzylation agent² was established. The use of Lewis acid catalysts e.g. AlCl_3 in the conventional homogeneous Friedel-Crafts acylations³ and also in a benzylation process with benzotrichloride as a benzylation agent² entails problems of corrosion, work-up, pollution due to effluents. Solid acids are known⁴ to overcome the above mentioned problems. This approach has not been exploited much apart from a single report of use of Zeolite as a catalyst for benzylation using benzotrichloride⁴ capable of bringing about benzylation of activated aromatics only.

In our laboratory we have successfully developed a co-grinding method for preparation of evenly supported oxidants⁶. Therefore we decided to extend the same methodology to adsorb FeCl_3 on silica gel support. The catalyst (silferc) was prepared by co-grinding FeCl_3 and silica gel (SRL 230-400 mesh) in appropriate amounts in an agate mortar and activating it at 80°C for three hours to obtain brown free flowing powder. The uniform adsorption was confirmed by carrying out SEM-EDAX study. The catalyst was used after activation.

Typically benzylation was carried out by stirring the catalyst (Silferc 6g, FeCl_3 content 1g i.e. 6.16 mmol) with benzotrichloride (7.8g, 40mmol) and aromatic substrate (20mmol) in ethylene dichloride at reflux temperature. Though the yields of benzophenones were less, compared to that obtained with reported methods^{2,4,5}, the unreacted benzotrichloride could be recovered and recycled. The reaction work-up involved mere filtration and washing with hot solvent. The products were purified by column chromatography by using silica gel (SRL 60-120 mesh) as a stationary phase and benzene as eluent. The catalyst showed a good shelf life of at least two months. The amount of catalyst required was small (Silferc 6g, FeCl_3 content 1g i.e. 6.16 mmol). It is noteworthy that the catalysts with similar activity can be prepared even in large quantity in a ball mill. Thus the catalyst provides a cheaper and more convenient method for preparation of benzophenones¹⁰ from activated and even deactivated aromatics without any handling problems.

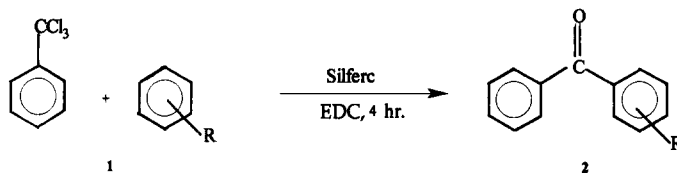


Table: Benzoylation of different aromatics using Silferc catalyst.

Sr.No.	R	Isolated Yield(%) Silferc	Physical const.°C M.P. (Lit)
1.	-H	72	48(48.5) ³
2.	-CH ₃	61	59(59) ⁹
3.	-OCH ₃	50	61(61) ⁸
4.	-Cl	32	75(76) ⁷
5.	-Br	34.3	82(82.5) ⁷

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10. The benzophenones **2** were characterised by recording FTIR and ¹H NMR spectra. FTIR and ¹H NMR were recorded using Jasco-300E FTIR spectrophotometer and Bruker AMX500, 500MHz spectrometer respectively.

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