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HZSM-5 Catalysed Regiospecific Benzoylation of Activated Aromatic Compounds[#]

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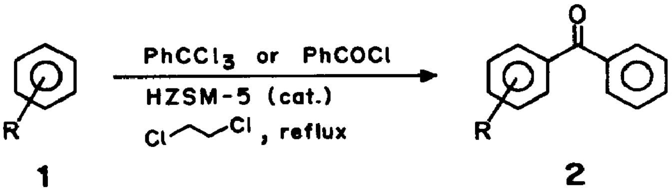
Abstract: *HZSM-5 has been shown to display a remarkable reaction selectivity in the liquid-phase benzoylation of activated arenes to benzophenones in high yields.*

Benzoylation under Friedel-Crafts acylations is an important unit process for the preparation of many industrially valuable chemicals. We have recently established the generation of exceptionally stable phenyldichlorocarbenium ion[1] and its use as an efficient benzoylating agent[2]. The use of Lewis acid catalysts, eg. $AlCl_3$ in the conventional homogeneous Friedel-Crafts acylation of arenes entails problems of corrosivity, work-up and effluent pollution. In the present work, we have attempted to replace traditional Lewis acid catalysts by an acidic zeolite **HZSM-5** to circumvent the problems mentioned above.

Although, in their acid form, zeolites have been widely used as solid catalysts for aromatic hydrocarbon alkylations and alkyl arene isomerisations, much less attention has been given to the possibility of employing them as catalysts for the analogous aromatic acylations[3]. An earlier report mentions the use of highly acidic Ce-Y zeolite for catalysing the acylation of alkyl benzenes with long chain aliphatic carboxylic acids to yield aralkyl ketones[4].

As a part of our comprehensive ongoing programme on zeolites mediated organic reactions and as a logical extension of our work on benzoylation reactions, we wish to report for the first time, a new catalytic method for regiospecific benzoylation of arenes **1** to benzophenones **2** using HZSM-5 as catalyst.



HZSM-5 ($SiO_2/Al_2O_3=40$) was prepared following literature procedure[5]. The catalyst was calcined at 573K before use. In a typical reaction, a mixture of benzotrichloride (1.95 g; 0.01 mol), phenol (0.94 g; 0.01 mol) and HZSM-5 (100 mg) in dichloroethane (25 ml) was refluxed for 5h (the bath temperature was 120° C). The products were analysed by GLC, purified by flash chromatography and characterised[6]. The yields are summarised in **Table-1.**

Table-1: HZSM-5 catalysed benzoylation of aromatic substrates **1** to benzophenones **2**.

Entry	Substrate	Product	Yield(%)^a	
	1	2	$PhCCl_3$	PhCOCl
1	Phenol	4-Hydoxybenzophenone	80	67
2	Anisole	4-Methoxybenzophenone	68	50
3	Catechol	3,4-Dihydroxybenzophenone	15	53
4	o-Nitroaniline	2-Amino-3-nitrobenzophenone	97	84
5	2-Naphthol	1-Benzoyl-2-naphthol	69	82
6	Nerolin	5-Benzoylnerolin	58	34
7	Thiophene	2-Benzoylthiophene	63	36
8	Benzimidazolone	5-Benzoylbenzimidazolone	90	40
9	Acetanilide	Benzanilide	80	65

^{a} Isolated yields.

Notably, activated arenes underwent benzoylation efficiently and the reaction is essentially regiospecific[7]. The yields are generally higher when benzotrichloride is used as the acylating agent(**Table-1**). This is in accordance with our earlier finding that benzotrichloride forms a more electrophilic and reactive carbocation with a Lewis acid[1]. Benzene, halobenzenes and naphthalene failed to undergo benzoylation under the reaction conditions[8]. Interestingly,o-nitroaniline afforded the regiospecific 2-amino-3-nitrobenzophenone in excellent yields whereas acetanilide underwent transacylation to benzanilide. The yield and selectivity remained constant in the temperature range 80°-160°C. The zeolite catalyst was recovered and reused several times with no loss of activity.

Mechanistically, it may be presumed that Lewis acid sites(Al^{3+}) in HZSM-5 can activate benzotrichloride and benzoyl chloride by way of coordination resulting in phenyldichlorocarbenium ion and phenylacylinium ion respectively which in turn react with the aromatic nucleus to produce benzophenones. Presumably, the para selectivity may be explained in terms of reactions occurring inside the cavity of the zeolite whereas the ortho selectivity is indicative of the reactions at the surface of the catalyst[9].

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6. The benzophenones **2** were characterised by IR, ^{1}H-NMR and Mass spectral analyses. Their mixed mps with those of the authentic samples were undepressed.
7. Determined by GLC; column, OV-101 ; temperature, 80°-200°C (20° per min.); the rest is essentially unreacted starting material.
8. Both increase in the temperature(160°C) and catalyst proportions (100% w/w) did not result in any reaction.
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