Heterogenous Catalysis by Solid Superacids; 11[1]. Perfluorinated Resinsulfonic Acid (Nafion-H)[2] Catalyzed Friedel-Crafts Acylation of Benzene and Substituted Benzenes

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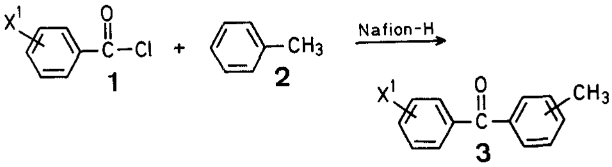
Friedel-Crafts acylation reactions generally require molar amounts of the catalyst, which form complexes with both the acylating agent and the carbonyl product. Work up, consequently, is needed to decompose these complexes and the catalyst is usually non-recoverable. There is, therefore, substantial interest to catalyze these reactions with solid acids which form no stable complexes with carbonyl compounds. So far, however, only extremely reactive aromatics, such as thiophenes and substituted thiophenes, have been successfully acylated using catalysts such as sulfonated polystyrene resins[3].

We describe now the convenient and efficient method of Nafion-H[2] (a solid perfluorinated resinsulfonic acid) catalyzed acylation of benzene and substituted benzenes with aroyl chlorides and anhydrides.

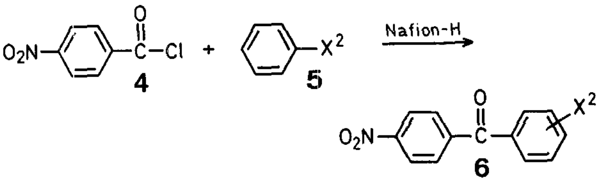
The acylation reactions were carried out by heating under reflux a stirred mixture of the corresponding benzoyl chloride, arene and the solid Nafion-H catalyst. Product benzophenones were simply isolated by filtering the hot reaction mixture and distilling off the solvent. The solid benzophenones were recrystallized in the usual way. The reactions are very clean, with HCl, the only by-product, escaping during the reaction.



The reaction is general for aroyl halides (see Table 1) and aromatics generally undergoing Friedel-Crafts acylations. Toluene (**2**) with aroyl chlorides (**1**) gave the corresponding ketones (**3**) in 80% or higher yield.

The amount of the catalyst used relative to the aroyl halide was between 10% and 30%. Optimum yields of ketones were obtained with 30% of the catalyst (Table 1), whereas 10% gave only slightly lower yields. Higher catalyst concentrations significantly decrease the yields due to absorption of an appreciable amount of the product and starting material on the catalyst.

The aroylation reaction was further studied by reacting various substituted benzenes (**5**) with *p*-nitrobenzoyl chloride (**4**) under similar conditions. The yields of **6** are comparable for toluene, *m*-xylene, and mesitylene, and somewhat lower for benzene and chlorobenzene (Table 2). No attempt was made, however, to optimize the yields of reactions other than those with toluene. Benzoylation of anisole was complicated by accompanying demethylation under the reaction conditions. In a control experiment, formation of a mixture of cresols was observed on heating anisole under reflux over Nafion-H.



Benzoylation of toluene was also studied using benzoic anhydride; 48 mmol of methylbenzophenones were obtained when 100 mmol of toluene were heated under reflux with 50 mmol of benzoic anhydride and 1 g Nafion-H for 2 h, corresponding to 96% yield.

The isomeric composition of the methylbenzophenones resulting from toluene were determined by G.L.C.[4,6]. The results (Table 1) show that the reactions give predominantly *ortho-para* substitution, in accordance with a typical electrophilic aromatic substitution pathway. The *ortho*: *para* ratio is in general higher than that obtained under usual solution Friedel-Crafts conditions using $AlCl_3$ as the catalyst[4]. It is difficult, however, to properly assess the selectivity of the reactions and the exact nature of the electrophile involved because of the heterogenous nature of the reaction. Comparing the reactions with those carried out with trifluoromethanesulfonic acid and aroyl halides[5], it is reasonable to assume that mixed anhydrides are the involved acylating agents formed on Nafion-H at some stage of the reaction.

Attempted acetylation of aromatics with acetyl chloride under similar conditions assumes a different path and results in preferential formation of ketene. We believe the intermediate mixed anhydride in this case undergoes facile thermal elimination to give ketene and further products thereof. Although the formation of ketene has been previously proposed by Effenberger and Epple[5] in the reaction of acetyl chloride with trifluoromethanesulfonic acid, attempts to directly observe this reaction failed. We have obtained diketene in the reaction of acetyl chloride over Nafion-H and identified it by infrared and N.M.R. spectroscopy.

We also investigated the Nafion-H catalyzed acetylation of aromatics with acetic acid, acetic anhydride, and their mixtures. Neither acetic acid nor acetic anhydride alone proved to be an effective acetylating agent under the reaction conditions. An equimolar mixture of the two, however, turned out to be efficient in acetylating reactive alkylbenzenes. Thus, upon heating under reflux a mixture of 0.1 mol arene, 0.1 mol acetic acid, 0.1 mol acetic anhydride, and 1 g

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Nafion-H, toluene was acetylated to the extent of only 3%, *m*-xylene up to 21% and mesitylene up to 72%.

Table 1. Acylation of Toluene (**2**) with Aroyl Chlorides (**1**) to Methylbenzophenones (**3**)

X^1	Yield[a] [%] of **3**	Isomer Distribution[b] *o*:*m*:*p*	*o*:*p* ratio
H	81	22.4:3.1:74.5	3.33
4-H_3C	83	28.7:3.1:68.2	2.34
2-F	87	16.7:2.9:80.4	4.81
3-F	82	19.5:3.4:77.1	3.95
4-F	87	21.5:3.4:75.1	3.49
3-Cl	82	22.6:1.1:76.3	3.38

[a] Yield based on aroyl chloride; identity and purity of products confirmed by G.L.C.

[b] Determined by G.L.C. as described previously[4,6].

Table 2. Reaction of Various Aromatics (**5**) with *p*-Nitrobenzoyl Chloride (**4**) to give 4-nitrobenzophenones (**6**)

X^2 in **5**	Reaction temperature	Yield[a] [%] of **6**
H	80°	63
H_3C	110°	83
1,3-di-H_3C	138°	83
1,3,5-tri-H_3C	163°	88
Cl	132°	73

[a] Yield based on aroyl chloride; identity and purity of products confirmed by G.L.C.

General Procedure for Preparation of Benzophenones:

A mixture of aroyl chloride (15 mmol), aromatic hydrocarbon (30 mmol), and Nafion-H catalyst (~1 g, 30% based on the aroyl chloride) is heated under reflux until there was no further evolution of hydrogen chloride gas (usually 8–10 h). The reaction mixture is filtered while hot, and the solid catalyst washed with hot chloroform (2 × 10 ml). The filtrate is worked up by distilling off solvent and benzophenones remaining are either crystallized from ethyl alcohol or chromatographed over alumina with benzene as eluent. (All products were known compounds and gave the correct physical and spectral characteristics.)

The used Nafion-H catalyst can be readily regenerated in the following way: After filtration, the catalyst is washed subsequently with acetone and deionized water, then is dried overnight at 105°. Repeating the preparation of benzophenones with the regenerated catalyst gives identical results with those using freshly activated catalyst.

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[1] Part 10; G. A. Olah, D. Meidar, *Synthesis* **1978**, 671.

[2] Nafion is the trade name of the DuPont Company for a commercially available perfluorinated resinsulfonic acid. The active H-form was generated from the commercial potassium salt by treatment with nitric acid, washing with water and drying at 105°.

[3] T. R. Norton, *U. S. Patent* 2711414 (1955); *C. A.* **50**, 5759 (1956).

[4] G. A. Olah, S. Kobayashi, *J. Am. Chem. Soc.* **93**, 6964 (1971).

[5] F. Effenberger, G. Epple, *Angew. Chem.* **84**, 295 (1972); *Angew. Chem. Int. Ed. Engl.* **11**, 300 (1972).

[6] N. V. Veber, N. G. Sidorova, *Zh. Org. Khim.* **7**, 1417 (1971); Engl. Edit. 1466.

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