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# Microwave-Assisted Nafion-H Catalyzed Friedel–Crafts Type Reaction of Aromatic Aldehydes with Arenes: Synthesis of Triarylmethanes

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**Abstract** A new solid acid Nafion-H, a perfluorinated sulfonic acid resin, catalyzed microwave-assisted synthesis of triarylmethanes is described. Various benzaldehydes react readily with arenes to provide the corresponding triarylmethanes in good to excellent yields. The reactions were carried out under solvent free conditions under microwave irradiation in a pressure vessel. The solvent free microwave irradiation methods appears to be an environmentally friendly synthetic protocol providing products in significantly shorter reaction times over traditional heating methods carried out in a pressure tube.

**Keywords** Nafion-H · Microwave irradiation · Arylation · Triarylmethanes · Benzaldehyde

## 1 Introduction

Over the past two decades, microwave-assisted organic synthesis has emerged as an important area that has attracted significant attention as indicated by extensive number of publications [1–3]. It is a convenient and time saving method, which promotes the application of environmentally benign approaches such as solvent free and heterogeneous catalytic reaction conditions [4, 5].Triarylmethanes constitute an important class of compounds that are ubiquitous in materials, medical, and dyestuff fields [6]. Acid-catalyzed condensation of benzaldehyde with benzene is known since 1886 [7]. This classic reaction readily occurs under highly acidic conditions for example over 2 equivalent of $AlCl_3$ at 60 °C [8] to give a number of products such as triphenylmethane, diphenylmethane, triphenylmethanol and anthracene in yields varying from 30 to 60% [9]. Further work showed that substituted triphenylmethanes and anthracenes were formed by the reactions of other aromatic aldehydes with aromatic hydrocarbons such as toluene and xylenes in presence of excess $AlCl_3$ [10–13]. The initial step in these reactions was considered to be the decarbonylation of the aldehydes, the reverse of a Gattermann–Koch reaction [14–17], rather than a transformylation reaction. The aldehyde derived from a transformylation reaction was not detected. The carbon monoxide produced by the decarbonylation was presumed to react with the aromatic hydrocarbons in some unspecified way to produce the triarylmethanes and anthracenes. To ascertain the mechanism, a number of aromatic aldehydes with a variety of arenes and Lewis and Brønsted acid catalysts were examined [18]. In many reactions, triarylmethanes were observed that did not contain the aromatic moiety corresponding to the original aldehydes. This might be interpreted as evidence for initial formation of the "other aldehydes" by transformylation, followed by subsequent addition reactions to produce the triarylmethanes.

To establish the mechanism, different acids were studied at room temperature [19]. For example in 100% $H_2SO_4$ ($H_0 = -12$) [20] benzaldehyde did not react with benzene at room temperature. In trifluoromethanesulfonic acid ($H_0 = -14$) however, the reaction is complete in 30 h, giving a 90% yield of triphenylmethane at room temperature. Addition of 1% $SbF_5$ to trifluoromethanesulfonic acid ($H_0 = -16$) enhanced the reaction rate, and the reaction was completed in 18 h at room temperature. In stronger acid, $CF_3SO_3H_2{}^+B(OSO_2CF_3)_4^-$ ($H_0 = -18$), the reaction

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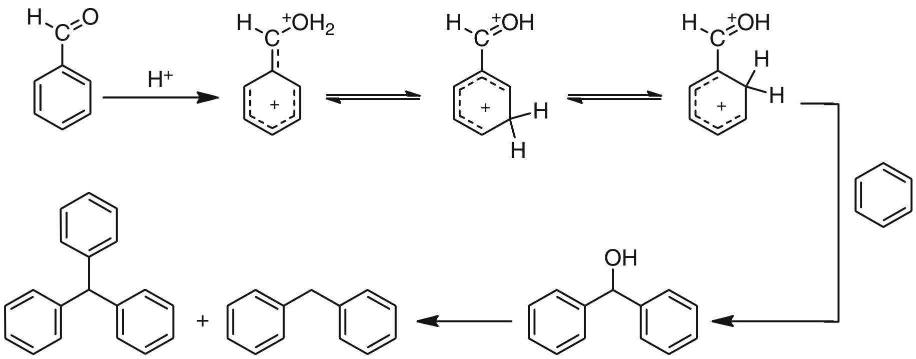
**Scheme 1** Mechanism for the superacid-catalyzed condensation reaction of benzaldehyde with benzene



was instantaneous with 83% yield of the isolated product. Similar studies are reported in liquid Brønsted superacids using isomeric pyridine and quinoline carboxaldehydes as well as aromatic dialdehydes [21, 22]. This study suggests that the monoprotonated aromatic aldehydes are not strong enough to react with aromatics. In O-protonated benzaldehyde the carboxonium ion is stabilized both by the oxygen and by the phenyl group, resulting in a weak carbon electrophile (Scheme 1). To decrease the neighbouring group participation, further protonation or protosolvation is required that will increase the electrophilic reactivity of the carbonyl carbon. Further protonation of protonated benzaldehyde can take place either on oxygen or on carbon on the phenyl ring.

In this article, we describe a novel, environmentally benign approach for the synthesis of a wide variety of triarylmethanes using the heterogeneous strong solid acid, Nafion-H under microwave irradiation. The combination of microwave irradiation and solid superacid catalyst, Nafion-H (estimated $H_0 \geq -12$ [23]), decreases the reaction time significantly. In order to evaluate the effect of the microwave on the reaction rates, yields and conditions, the reaction was carried out under classical heating conditions as well.

## 2 Experimental

### 2.1 Materials

The Nafion-H catalysts were prepared from commercial (DuPont) Nafion-K resin according to the procedure described in [23]. The different aromatic aldehydes and arenes were supplied by Aldrich and used as received.

### 2.2 General Method for Thermal and Microwave Induced Condensation Reactions

The thermally heated reactions were carried out in a 15 mL pressure tube loaded with Nafion-H (200 mg, ~0.2 mmol protonic site), benzaldehyde derivative (50 mg, ~0.5 mmol) and benzene (4 mL). The resulting suspension was magnetically stirred at a controlled temperature. After cooling, the solid resin sulfonic acid was filtered off, water was introduced to the reaction mixture followed by extraction using dichloromethane. The combined organic phase was dried over anhydrous $Na_2SO_4$ and the solvent evaporated to obtain the product/products.

The microwave-induced reactions were carried out in a 7 mL pressure resistant Pyrex glass tube equipped with a rubber septum and an aluminium cap. The capped reaction tube with the above mentioned suspension was introduced into the cavity of the microwave apparatus (CEM Discover, 2.45 GHz, CEM Corporation, NC, USA) and magnetically stirred at a constant temperature (150 °C) controlled by an IR sensor. The pressure of the reaction vessel with various reactants used hovered between 2 and 7 bars. The product isolation was identical to that of the thermal method.

### 2.3 Analysis

The products are all well known [and were identified on the basis of their $^1H$ and $^{13}C$ NMR (Varian 400 MHz) and mass spectra (Thermo Finigan GC coupled with a mass spectrometer) as well as with comparison with the literature data [22]. The isomer distribution of the product was determined by $^1H$ NMR and gas chromatographic analysis

**Scheme 2** Reaction of benzaldehyde derivatives with aromatics over Nafion-H catalyst

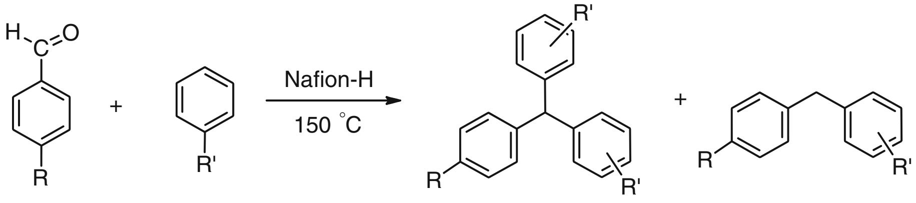
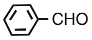
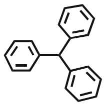
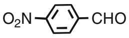
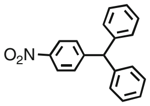
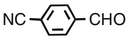
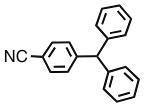
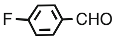
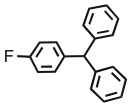
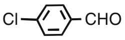
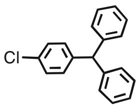
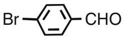
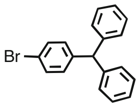
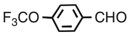
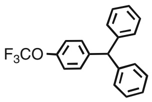
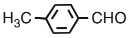
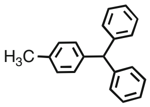
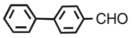
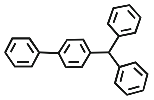


**Table 1** Microwave and conventionally heated reaction of benzaldehyde derivatives with benzene

| Entry | Aldehyde | Product | Microwave[a] Heating |  | Classical |  |
|---|---|---|---|---|---|---|
|  |  |  | Time (min) | Yield (%) | Time (min) | Yield (%) |
| 1 |  |  | 70 | 92 | 720 | 97 |
| 2 |  |  | 30 | 100 | 600 | 100 |
| 3 |  |  | 190 | 100 | 1920 | 100 |
| 4 |  |  | 70 | 79 | 480 | 74 |
| 5 |  |  | 30 | 94 | 300 | 92 |
| 6 |  |  | 25 | 94 | 240 | 94 |
| 7 |  |  | 30 | 94 | 600 | 94 |
| 8 |  |  | 90 | 21 | 1080 | 26 |
| 9 |  |  | 70 | 26 | 720 | 45 |

Conditions: 150 °C, 0.5 mmol aldehyde, 2 mL benzene, 0.4 g Nafion-H

[a] 50–150 W, 2–7 bar pressure

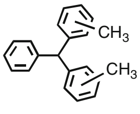
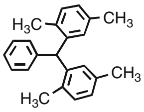
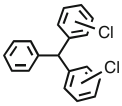
Thermo Finigan GC (DB-5 capillary column, with helium as the carrier gas).

## 3 Results and Discussion

Our goal was to develop an efficient and at the same time, environmentally friendly method for the synthesis of triarylmethanes. The condensation of benzaldehydes with arenes over Nafion-H catalyst was developed under microwave irradiation. For comparison, the reaction has been carried out using traditional heating methods using an oil bath. The reactions were carried out under solvent free conditions using excess of aromatics. Different aromatics and benzaldehydes were used for the arylation reactions. The Friedel–Crafts arylation of arenes can produce several products and in some cases isomeric products (Scheme 2).

Wide ranges of triarylmethanes were prepared using benzene as the reactant with different benzaldehydes (Table 1). All reactions were driven to 100% conversion.

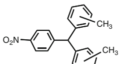
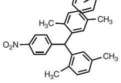
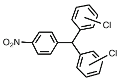
**Table 2** Microwave and conventionally heated reaction of benzaldehyde with aromatics

| Entry | Aromatic | Product | Microwave[a] | | Classical | |
|---|---|---|---|---|---|---|
| | | | Heating | | | |
| | | | Time (min) | Yield (%) | Time (min) | Yield (%) |
| 1 | Toluene |  | 25 | 70 (oo:op:pp = 15:17:68) | 240 | 82 (oo:op:pp = 3:27:70) |
| 2 | *p*-Xylene |  | 10 | 30 | 120 | 68 |
| 3 | Chlorobenzene |  | 160 | 62 (oo:op:pp = 19:32:49) | 2700 | 46 (oo:op:pp = 8:28:64) |

Conditions: 150 °C, 0.5 mmol benzaldehyde, 2 mL aromatics, 0.4 g Nafion-H

[a] 50–150 W, 5–7 bar

**Table 3** Microwave and conventionally heated reaction of *p*-nitro-benzaldehyde with aromatics

| Entry | Aromatic | Product | Microwave[a] | | Classical | |
|---|---|---|---|---|---|---|
| | | | Heating | | | |
| | | | Time (min) | Yield (%) | Time (min) | Yield (%) |
| 1 | Toluene |  | 30 | 95 (oo:op:pp = 15:17:68) | 270 | 90 (oo:op:pp = 3:21:76) |
| 2 | *p*-Xylene |  | 15 | 66 | 120 | 82 |
| 3 | Chlorobenzene |  | 155 | 100 (oo:op:pp = 4:35:61) | 2520 | 100 (oo:op:pp = 5:35:60) |

Conditions: 150 °C, 0.5 mmol *p*-nitro-benzaldehyde, 2 mL aromatics, 0.4 g Nafion-H

[a] 50–150 W, 5–7 bar

In most cases the formation of triarylmethanes was preferred, with benzene, however, diarylmethane was also formed (Entries 4, 8 and 9).

In any case, microwave or classical heating result in comparable yields for the respective triarylmethanes derivatives. However, benzaldehyde containing weakly electron donating groups such as a phenyl or a methyl group (Entry 8 and 9, Table 1) result in lower product yields under microwave irradiation 21%/26% and 26%/45%, respectively. Using benzaldehydes with strongly electron-withdrawing groups such as nitro- or cyano-, quantitative yields can be achieved. However, the longest reaction time was observed with cyanobenzaldehyde. Among halobenzaldehydes, the chloro- and bromo-derivatives gave higher yields than the fluoro-derivatives. Microwave mediated heating results in much faster reaction times compared to regular heating.

Arylation of benzaldehyde has been performed with toluene, *p*-xylene and chlorobenzene (Table 2) in order to evaluate effect of the nature of the reactants.

The different aromatics have different effects on the product yields: alkylbenzene derivatives gave higher yields for microwave-irradiated reactions and halogen ones gave higher yields with classical heating. An isomeric mixture of three triarylmethanes was obtained (Table 2) in case of mono-substituted aromatics, corresponding to the *ortho–ortho′* (oo), *ortho–para′* (op) and *para–para′* (pp) positional isomers as expected. With the conventional heating the *para–para′* products were the most preferred. With the microwave irradiation, the isomeric distribution moved toward the formation of *ortho–ortho′* products indicating higher reactivity.

The study was also extended to *p*-nitro-benzaldehyde (Table 3).

In the case of *p*-nitro-benzaldehyde, the best result was obtained with electron deficient chlorobenzene, but the reaction took the longest time. Benzaldehyde and *p*-nitrobenzaldehyde gave similar oo:op:pp ratios with similar reaction times as well. The similarity concerning isomer distribution and reaction time appears to be related the nature of the reacting arene.

## 4 Conclusion

A novel effective solid superacid-catalyzed, economic and environmentally benign method for triarylmethane synthesis has been developed. The combination of microwave irradiation and Nafion-H catalyst greatly reduce the reaction time compared to the classical heating methods. The short reaction time, solvent free condition, ease of product isolation, and the safe nature of the catalyst make the process an attractive alternative for the synthesis of triarylmethanes in a practical way.

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