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NAFION-H CATALYZED CONDENSATION OF ACETOPHENONE DERIVATIVES. A PREPARATIVE ROUTE OF 1,3,5-TRIARYLBENZENES [1]

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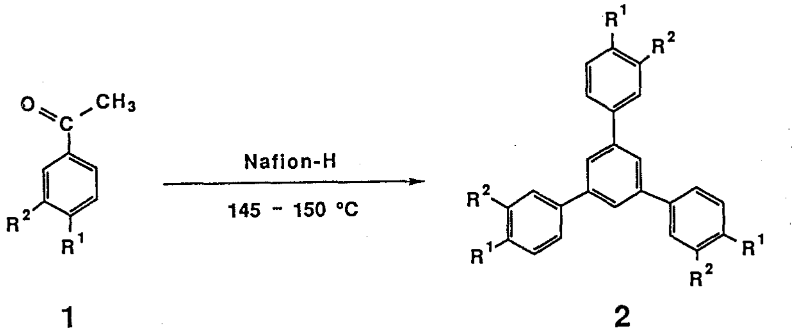
Solid superacids, Nafion-H catalyst, 1,3,5-triarybenzenes

Nafion-H, a perfluorinated resinsulfonic acid, catalyzes condensation of acetophenones to provide 1,3,5-triarylbenzenes under relatively mild conditions. Reaction are clean, and water formed as by-product does not deactivate the catalyst. However, ortho-substituted acetophenones and 2-acetylthiophene gave no condensation product.

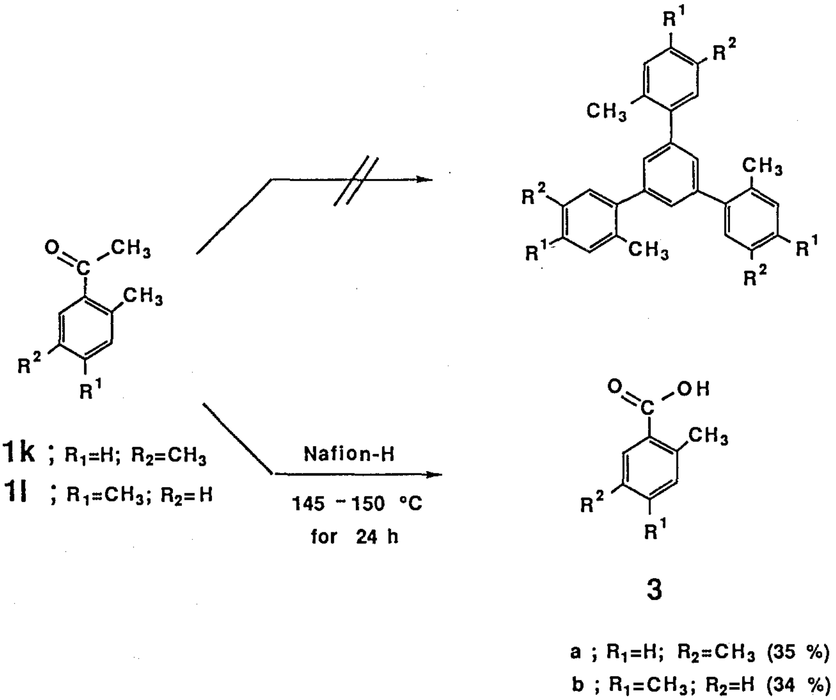
The acid-catalyzed condensation of acetophenone derivatives to the corresponding 1,3,5-triarylbenzenes has been studied using various acid catalysts [2–5]. Generally, elevated temperatures (> 250 ° C), prolonged reaction times, and excess of protonic and Lewis acids are, however, required for this condensation reaction.

Over the years we have shown that Nafion-H [6], a superacidic perfluororesinsulfonic acid is a convenient catalyst for a variety of acid-catalyzed synthetic transformations. The selectivity, high catalytic activity, and its ease of reaction frequently make Nafion-H the acid catalyst of choice.

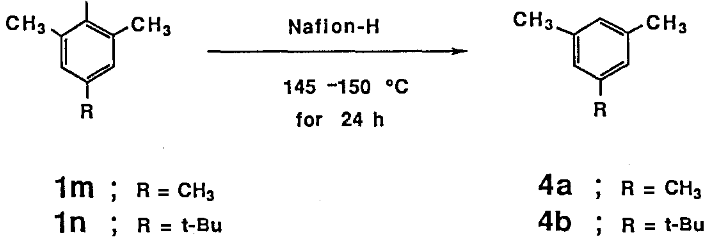
Recently, the convenient condensation of acetone to mesitylene in the presence of Nafion-H catalyst was reported by one of us [7]. We now report the condensation of acetophenones **1a–1n** under Nafion-H catalysis. Nafion-H catalyzed condensation reaction of acetophenone derivatives **1a–j** was carried out at 145–150 ° C to provide the corresponding 1,3,5-triarylbenzenes **2a–2g** and **2i** in 30–75% yields (table 1, scheme 1), but in the case of **1h** and **1j** only resinous materials were obtained.



Scheme 1.



Scheme 2.



Scheme 3.

Table 1
Nafion-H catalyzed condensation of acetophenone derivatives to give 1,3,5-triarylbenzenes

	R^1	R^2	Reaction time [h]	Yield[a] [%]	m.p. [°C]	
					found	reported
a.	H	H	24	57 (73)[b]	174–176	175–176 [8]
b.	CH_3	H	24	43 (75)[b]	172–175	172–174 [8]
c.	CH_2CH_3	H	24	37 (46)[b]	112–114	114 [3]
d.	t-Bu	H	24	31	294–297	294 [3]
e.	OCH_3	H	24	34 (67)[b]	145–146	145 [8]
f.	Br	H	12	73	262–266	159–262 [8]
g.	Cl	H	12	63	244–246	246 [3]
h.	NO_2	H	24	0[c]	–	–
i.	H	Br	24	74	164–167	163–165 [8]
j.	OCH_3	OCH_3	24	0[c]	–	–

[a] Yield of product isolated by recrystallization and characterized by I.R. and ^{1}H-N.M.R. spectroscopy.

[b] The product yields were determined by G.L.C. analyses.

[c] Resinous materials were obtained.

However, ortho-substituted acetophenones **1k–1n** and 2-acetyl thiophene gave no condensation product after a long period of heating; **1k** and **1l** gave only oxidized products (**3**) (scheme 2) and **1m** and **1n** deacylated products (**4**) (scheme 3).

The major advantage in the above method with Nafion-H is the simple workup procedure, wherein the product **2** is isolated by filtration from the catalyst after adding methanol to the reaction mixture and purified by recrystallization.

General procedure for the Nafion-H catalyzed condensation of acetophenones

A mixture of acetophenone (**1**) (42 mmol), and Nafion-H (500 mg, 10 wt%) was heated at 145–150 °C under nitrogen atomosphere for the reaction time listed in table 1. The reaction was monitored by G.L.C. analysis (OV 1 column). The reaction mixture was cooled to room temperature followed by addition of 20 mL of methanol. The insoluble materials were filtered and washed with dichloromethane (in this step Nafion-H was recovered). The filtrate was condensed to give the crude products, which on recrystallization, gave the respective 1,3,5-triarylbenzenes (**2**).

Regeneration of Nafion-H catalyst

The catalyst was washed successively with acetone and deionized water, then dried overnight at 105 °C. The obtained catalyst had the same catalytic activity as the fresh catalyst.

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