

## Preparation of *p*-1, 1, 3, 3-Tetramethylbutylphenol by Using Nafion-H Catalyst

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**Abstract:** *p*-1, 1, 3, 3-Tetramethylbutylphenol was prepared by the alkylation of the phenol with Nafion catalyst in extremely high yield. Various reaction conditions were investigated, including the reaction temperature, reaction time, ratio of the starting material, amount of the Nafion catalyst and the recycle times of the catalyst.

**Keywords:** Nafion-H catalyst, Friedel-Crafts alkylation, synthesis.

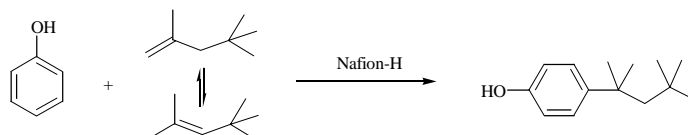
Nafion-H resin is a kind of solid superacid catalyst with the structure of perfluorinated alkyl sulfuric acid. Due to the easy separation after the reaction and highly catalytic activity, it has been widely used in the organic synthesis instead of the triflic acid and concentrated sulfuric acid. For example, it shows highly activity towards Friedel-Crafts alkylation and acylation reactions<sup>1-3</sup>. In order to increase the surface area of the catalyst, the Nafion resin/silica composite catalyst has also been studied and it shows highly catalytic activity<sup>4-6</sup>.

*p*-1, 1, 3, 3-Tetramethylbutylphenol is a key intermediate in the preparation of polyethylene glycol surfactants, for example, Triton-100. It can also be used in the preparation of the fluorescent brightener which was applied in the plastic industry. Normally, the *p*-1, 1, 3, 3-tetramethylbutylphenol was prepared by the alkylation of phenol with Lewis acid<sup>7</sup> or concentrated sulfuric acid<sup>8</sup> catalysis. In this way, a large amount of the waste acid could be generated and the catalyst can not be reused. If the ion exchange resin, for example, Amberlite-15, was used as the acid catalyst<sup>9</sup>, above deficiencies can be avoided. However, mild yield and less regioselectivity were obtained.

In this paper, we wish to report the synthesis of the *p*-1, 1, 3, 3-tetramethylbutylphenol by alkylation of phenol with the mixture of 2, 4, 4-trimethyl-1-pentene and 2, 4, 4-trimethyl-2-pentene which were prepared by the dehydration of *t*-butanol with concentrated sulfuric acid. Nafion-H was used as the catalyst in this reaction (**Scheme 1**). This is an atomic economic reaction. All atoms in the starting material were consumed and quantitatively transferred into the product.

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**Scheme 1** Alkylation of phenol with the Nafion-H catalyst

A typical procedure is as follows: phenol, alkene and a certain amount of the catalyst were placed in a round bottom flask which was heated in an oil bath. The reaction mixture was stirred and monitored by the gas chromatography (Column: PEG-20M). After reaction was completed, the Nafion-H catalyst was filtered off and after cooling the filtrate was solidified. The crude product was recrystallized from petroleum ether (mp 82-83°C). Nafion-H catalyst was washed with petroleum ether for three times and was stored in the petroleum ether for further use. The effect of temperature, reaction time, molar ratio of phenol to diisobutene and the amount of the catalyst were summarized in **Table 1-4**.

**Table 1** Effect of temperature

Reaction Temperature	Conversion of diisobutene (%)	<i>o:p</i> ratio	Isolation Yield (%)
110 °C	97.6	1:29	83
100 °C	96.1	1:37	88
90 °C	93.0	1:43	87
80 °C	91.8	1:32	87
70 °C	82.5	1:28	80

The molar ratio of phenol to diisobutene is 1.2:1. The reaction time is 5 hours. 7% (w/w) Nafion was used. Isolation yield was calculated based on diisobutene.

**Table 2** Effect of the reaction time

Reaction time (minutes)	Conversion of diisobutene (%)	<i>o:p</i> ratio	Isolation Yield (%)
220	88	1:30	76
240	90	1:34	81
270	93	1:36	83
300	93	1:43	87
330	95	1:24	84

The reaction temperature is 90 °C. The molar ratio of phenol to diisobutene is 1.2:1. 7% (w/w) Nafion was used. Isolation yield was calculated based on diisobutene.

**Table 3** Effect of ratio of phenol to diisobutene

Molar ratio of phenol to diisobutene	Conversion of diisobutene (%)	<i>o:p</i> ratio	Isolation Yield (%)
1.2:1	93	1:43	87
1:1	89	1:47	85
1:1.2	73*	1:43	86*

The reaction temperature is 90 °C. The reaction time is 5 hours. Isolation yield was calculated based on diisobutene. \*Based on the conversion of phenol.

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Table 4 Effect of the amount of the catalyst

Catalyst amount (w/w %)	Conversion of diisobutene (%)	<i>o:p</i> ratio	Isolation Yield (%)
9	92	1:36	88
7	89	1:47	85
5	80	1:55	79

The reaction temperature is 90 °C. The molar ratio of the phenol to diisobutene is 1:1. The reaction time is 5 hours. Isolation yield was calculated based on diisobutene.

The catalyst Nafion-H has been recycled for 8 times, the catalytic activity and the conversion yield did not change, only the color of the catalyst changed into slightly brown. The conclusion can be made that the Nafion-H is a highly active catalyst for the phenol alkylation reaction in the absence of any solvents.

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