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NAFION-H CATALYZED TERT-BUTYLATION OF AROMATIC COMPOUNDS WITH 2,6-DI(TERT-BUTYL)-p-CRESOL [1]

Takehiko YAMATO *[1], Chieko HIDESHIMA [1], Akira MIYAZAWA [1],
Masashi TASHIRO [2], G.K. Surya PRAKASH [3] and George A. OLAH [3]

[1] *Department of Industrial Chemistry, Faculty of Science and Engineering, Saga University, Saga 840, Japan*

[2] *Research Institute of Advanced Molecular Science, and Department of Molecular Science and Technology, Graduate School of Engineering, Kyushu University 86, 6-1 Kasuga-kohen, Kasuga-shi, Fukuoka 816, Japan*

[3] *Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90089-1661, U.S.A.*

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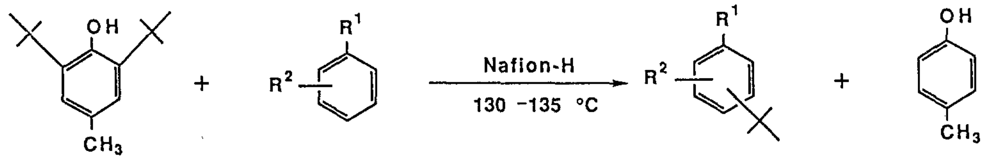
Convenient and high yield tert-butylation of aromatic compounds can be achieved by the Nafion-H, a superacidic perfluorinated resinsulfonic acid, catalyzed irreversible trans-tert-butylation from 2,6-ditert-butyl-p-cresol.

Tert-butylation of aromatic compounds is of particular importance since tert-butyl group can be successively employed as an effective protecting group in achieving selective aromatic substitution [2]. We previously reported a convenient and high yield (96–99%) tert-butylation procedure for aromatic compounds by the aluminum chloride-nitromethane catalyzed irreversible transalkylation from 2,6-di(tert-butyl)-p-cresol [3–6]. In this reaction, however, to obtain optimum yields more than the molar equivalent of catalyst is required, since the hydroxyl group is easily complexed with $AlCl_3$.

On the other hand, we have shown that Nafion-H [7], a superacidic perfluoro-resinsulfonic acid is a convenient catalyst for de-tert-butylation of a variety of the corresponding aromatic compounds [7]. We report now a much improved, convenient way to carry out the trans-tert-butylation of aromatic compounds with 2,6-di(tert-butyl)-p-cresol in the presence of Nafion-H as a catalyst.

Heating a solution of 2,6-di(tert-butyl)-p-cresol in a variety of aromatic compounds at 130–135 °C in the presence of Nafion-H (~ 10% by weight with respect to the 2,6-di(tert-butyl)-p-cresol effects smooth conversion to the corresponding tert-butylated aromatic compounds and p-cresol (scheme 1). The results are summerized in table 1.



1 2 3 4

Scheme 1.

The isomeric composition of the products (3) were determined by G.L.C. and the results (table 2) show that the reactions give predominantly para substitution, in accordance with a typical electrophilic aromatic substitution pathway. The para: meta ratio is in general same as that obtained under usual solution Friedel-Crafts conditions using $AlCl_3$ as the catalyst [3].

Table 1
Nafion-H catalyzed trans-tert-butylation of aromatic compounds with 2,6-di-tert-butyl-p-cresol [a]

R^1	R^2	Reaction time [h]	Yield [%] [b] tert-butylated compounds(3)	m.p. or b.p./Torr (°C)		Yield [%] [b] p-cresol(4)
				found	reported	
CH_3	H	3	83	77/10	192.2/760 [7]	95
C_2H_5	H	3	73	60/4	120–122/30 [7]	99
n-C_3H_7	H	3	72	128/30	116/15 [8]	96
i-C_3H_7	H	3	79	119/30	109/15 [8]	96
t-C_4H_9	H	3	77	69–71	72–75 [9]	95
CH_3	2-CH_3	3	81	85/3	102–104/16 [10]	93
CH_3	3-CH_3	3	67	113/37	92–95/12 [11]	95
OCH_3	H	1.5	93	100/16	96–97/13 [12]	99

[a] [Aromatic compound]/[2,6-di-tert-butyl-p-cresol] = 5 : 1, catalyst 10 wt%. Reaction was carried out under reflux.

[b] Yield of isolated product.

Table 2
The isomer distribution of products(3). [a]

R^1	R^2	ortho	meta	para
CH_3	H	0	11	89
C_2H_5	H	0	8	92
n-C_3H_7	H	0	11	89
i-C_3H_7	H	0	0	100
t-C_4H_9	H	0	11	89
CH_3	2-CH_3	4-t-butyl-		100
CH_3	3-CH_3	5-t-butyl-		100
OCH_3	H	0	2	98

[a] Isomer distribution were determined by G.L.C. analyses.

The workup of the reaction mixture is extremely simple, involving filtration of the solid catalyst (which can be reused after simple regeneration), extracting p-cresol into a solution of 10% NaOH, neutralizing the basic solution with acid to afford p-cresol. The organic layer is evaporated and the residue is distilled under reduced pressure to give the product. The present method provides excellent yields, easy workup procedure for the isolation of the product, and ready regeneration of the catalyst without loss of activity. Moreover, only a catalytic amount of catalyst is needed instead of usual stoichiometric quantity of $AlCl_3$ [3–6].

General procedure for Nafion-H-catalyzed trans-tert-butylation

Into a solution of 10 mmol of 2,6-di(tert-butyl)-p-cresol in 50 mmol of aromatic compounds was added 1 g of Nafion-H and heated at 130–135 °C with stirring till completion of the reaction, as monitored by G.L.C. analysis (OV 1 column, reaction time listed in table 1). The reaction mixture was cooled to room temperature, and the catalyst was filtered off. The filtrate was extracted with 10% NaOH (3 × 25 mL), and the basic aqueous solution was neutralized with 10% HCl, extracted with ether and the ether layer washed with saturated NaCl solution. Evaporation of the ether after drying over anhydrous sodium sulfate gave p-cresol. The organic layer was condensed to give the residue, which was distilled under reduced pressure to afford the corresponding tert-butylated aromatic compounds.

Regeneration of Nafion – H catalyst

After filtration the catalyst was washed with acetone and deionized water, dried overnight at 105 °C. Repeating the reaction with the regenerated catalyst gave identical results with those of freshly activated catalyst.

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