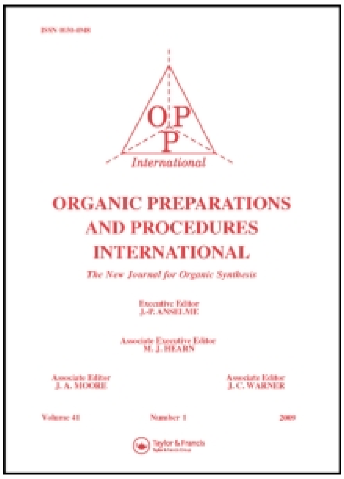

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THE t-BUTYLATION OF AROMATIC COMPOUNDS WITH 2,6-DI(t-BUTYL)-p-CRESOL. THE SELECTIVE SEPARATION OF p-XYLENE FROM C_8 AROMATICS

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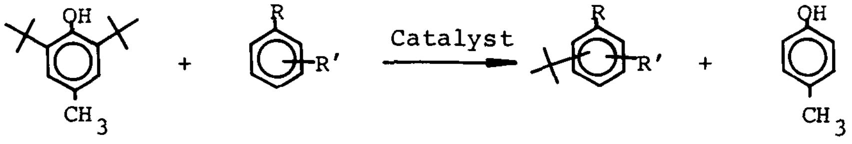
The transalkylation of some t-butylbenzenes has been applied to the preparation of other t-butylbenzenes.[1-4] However, the aromatics used as an acceptor of t-butyl group must be used in large excess in order to obtain high yields of the desired t-butylbenzenes since the transalkylation is generally reversible.



I II III IV

a: R = CH_3, R' = H
b: R = C_2H_5, R' = H
c: R = n-C_3H_7, R' = H
d: R = i-C_3H_7, R' = H
e: R = CH_3, R' = 2-CH_3
f: R = CH_3, R' = 3-CH_3
g: R = CH_3, R' = 4-CH_3
h: R = OCH_3, R' = H

We now report the convenient and high yield (96-99%) t-butylation of aromatic compounds (II) by the irreversible aluminum chloride-nitromethane catalyzed translakylation of 2,6-di(t-butyl)-p-cresol (I); the t-butylation of IIg was not observed. IV was obtained in high yields (90-99%) in all cases. The isomers distribution of the product (III) is summarized in Table 1.

Table 1.- The Isomer Distribution (vpc) of Products (III)

Run	III	ortho	meta	para
1	a	0	7.0	93.0
2	b	0	7.0	93.0
3	c	0	6.4	93.6
4	d	0	7.0	93.0
5	h	0	0	100
6	e		4-*t*-butyl-	100
7	f		5-*t*-butyl-	100

This suggested that the $AlCl_3$-CH_3NO_2 catalyzed *t*-butylation of the mixture of C_8-aromatics such as xylenes and ethylbenzene with I as a method of the selective separation of IIc from the mixture and the results are summarized in Table 2.

Table 2.- The $AlCl_3$-CH_3NO_2 Catalyzed *t*-Butylation of the Mixture of II and III with I at 15°.$^{a)}$

	Reactant(%)$^{b)}$				I/II	Product(%)					
Run	IIe	IIf	IIg	IIb	(mole/mole)	IIg$^{c)}$	IIIe	IIIf	IIIg	IIIb	IV
1	10	0	90	0	0.055	95	95	0	+	0	92
2$^{d)}$	50	0	50	0	0.275	97	99				87
3$^{d)}$	0	50	50	0	0.275	94	0	98	0	0	91
4	5	5	90	0	0.055	95	44	47	1	0	88
5	0	0	90	10	0.055	95	0	0	+	98	94
6	5	5	85	5	0.090	95	34	34	++	20	93

a) Catalyst/I = 1.5 mole/mole; time: 1 minute. b) Total mole of II was kept as one mole. c) The purity of IIg was higher than 99%. d) Reaction time: 30 min.

As shown in Table 2, IIg did not react but the corresponding *t*-butylxylenes (IIIe and IIIf) and *t*-butylethylbenzene (IIIb) were obtained in good yields in all cases. The boiling points of IIg is somuch lower that those of IIIb, IIIe and IIIf that the separation of IIg by distillation from the reaction mixture is very easy and IV was easily removed with 10% sodium hydroxide solution.

The formation of small amounts of IIIg observed for the one minute reaction suggests that IIIg is unstable under the condition used and that IIg is regenerated. The very much shorter reaction time recommends this reaction as a more convenient separation of *p*-xylene from the mixture of C_8-aromatics than previously reported methods.[5-10]

EXPERIMENTAL

The isomers distribution of III was determined by gas chromatography using a Yanagimoto Gas Chromatography, Yanagimoto G8 YR-101; column,$_o$30% high vacuum silicon grease, 2 m; temperature is 110 carrier gas, helium 50 ml/min.

The *t*-Butylation of Aromatics.- To a mixture of 5 equivalents of II and 1 equivalent of I was added 1.5 equivalent of catalyst[16] in one portion at room temperature. After the reaction mixture was stirred for 1 min.(unless otherwise indicate), it was quenched with 10% HCl. The organic layer was extracted with three 100 ml portions of ether and the ethereal extract was washed with 10% sodium hydroxide, dried over sodium sulfate followed bydistillation in reduced pressure to afford III. After acidification of the sodium hydroxide extract with 10% HCl, it was extracted with ether and the ethereal extract was dried over sodium sulfate, then distilled to give IV.

IIIa: bp 77°/10 mm, lit.[11], bp 192.2°/760 mm. IIIb: bp 120-122°/30 mm, lit.[11], bp 212.1°/760 mm. IIIc" bp 106-109°/18 mm, lit.[12], bp 116-15 mm. IIId: bp 106-109°/15 mm, lit.[12], bp 109°/15 mm. IIIe: bp 102-104°/16 mm, lit.[13], bp 83-85°/3 mm. IIIf: bp 92-95°/12 mm, lit.[14], bp 102-104°/30 mm. IIIh: bp 96-97°/13 mm, lit.[15], bp 99-100°/15.5 mm.

General Procedure of Separation of p-Xylene.- To a solution of 12.2 g (55 mmoles) of I in a mixture of II (total amount: 1 mole) was added $AlCl_3$-CH_3NO_2 catalyst (10.9 g/20 ml) in one portion. After one minute with stirring, it was quenched with 100 ml of water and the organic layer was worked up as described above. Distillation under reduced pressure afforded IIg (bp 31-32°/13 mm), III and V (bp of III: 87-93°/13 mm).

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