

This article was downloaded by:

On: 27 January 2011

Access details: Access Details: Free Access

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t902189982>

### THE $\text{AlCl}_3$ CATALYZED *t*-BUTYLATION OF HALOBENZENES WITH 2,6-DI-(*t*-BUTYL)-*p*-CRESOL

M. Tashiro<sup>a</sup>; T. Yamato<sup>a</sup>

<sup>a</sup> Research Institute of Industrial Science, Kyushu University, Fukuoka, JAPAN

**To cite this Article** Tashiro, M. and Yamato, T.(1977) 'THE  $\text{AlCl}_3$  CATALYZED *t*-BUTYLATION OF HALOBENZENES WITH 2,6-DI-(*t*-BUTYL)-*p*-CRESOL', Organic Preparations and Procedures International, 9: 3, 151 – 153

**To link to this Article:** DOI: 10.1080/00304947709356871

**URL:** <http://dx.doi.org/10.1080/00304947709356871>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

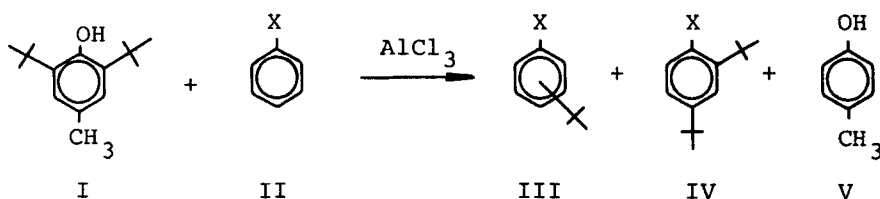
The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

THE  $\text{AlCl}_3$  CATALYZED t-BUTYLATION OF HALOBENZENES WITH 2,6-DI-  
(t-BUTYL)-p-CRESOL<sup>1</sup>

Submitted by M. Tashiro\* and T. Yamato  
(6/6/77)

Research Institute of Industrial Science  
Kyushu University 86  
Hakozaki, Higashi-ku  
Fukuoka 812  
JAPAN

Although  $\text{AlCl}_3\text{-CH}_3\text{NO}_2$  catalyzes t-butylation of alkylbenzenes and anisole with 2,6-di(t-butyl)-p-cresol(I),<sup>2</sup> this system did not effect the t-butylation of halobenzenes(II) with I. The t-butylation of II with I catalyzed by  $\text{AlCl}_3$  is reported now.



a) X = F

b) X = Cl

c) X = Br

Table 1 shows that in contrast to the  $\text{AlCl}_3\text{-CH}_3\text{NO}_2$  catalyst,  $\text{AlCl}_3$  afforded the desired t-butylhalobenzenes(III) in good yields. In addition 2,4-di(t-butyl)fluorobenzene(IVa) was formed in 26% yield as a by-product and this compound was also obtained from IIIa by t-butylation under same conditions. The isomer distribution shows that only 4-t-butylfluorobenzene(IIIa) was obtained without formation of the m-isomer; however, 4-t-butylchloro-(IIIb) and 4-t-butylbromobenzene(IIIc) were formed with small amounts of the corresponding m-isomers, respectively.

Table 1. The  $\text{AlCl}_3$ -catalyzed t-Butylation of II with I<sup>a</sup>

Run	II	Product (%)
1	a	IIIa (71) [100% para] - IVa (26) - V (90)
2	b	IIIb (87) [93% para, 7% meta]      V (85)
3	c	IIIc (84) [91% para, 8% meta]      V (94)

a)  $\text{AlCl}_3/\text{I} = 1.5/1$  mole; react. temp.  $15^\circ$ ; time: 30 min.

## EXPERIMENTAL

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

The t-Butylation of Aromatics.- To a mixture of 2 moles of II and 0.4 mole of I was added gradually 79.2 g (0.6 mole) of  $\text{AlCl}_3$  at  $15^\circ$ . After the reaction mixture was stirred for 30 min, it was quenched with 500 ml of ice water. The organic layer was extracted with three 100 ml portions of ether and the ethereal extract was washed with 10% sodium hydroxide solution, dried over sodium sulfate followed by distillation in reduced pressure to afford III and IVa. After acidification of the sodium hydroxide extract with 10% hydrochloric acid, it was extracted with ether and the ethereal extract was dried over sodium sulfate, then distilled to give V.

IIIa: colorless liquid, bp  $63-64^\circ \text{C}/13 \text{ mmHg}$  (lit.<sup>3</sup>,  $53.6-54.4^\circ \text{C}/10 \text{ mmHg}$ ).  
 PMR ( $\text{CCl}_4$ )  $\delta$ ppm: 1.30 (9H, s, t-Bu), 6.70-7.25 (4H, m, aromatic H)

IIIb: colorless liquid, bp  $57-58^\circ \text{C}/3 \text{ mmHg}$  (lit.<sup>4</sup>,  $209^\circ \text{C}/760 \text{ mmHg}$ ).  
 PMR ( $\text{CCl}_4$ )  $\delta$ ppm: 1.28 (9H, s, t-Bu), 7.08-7.42 (4H, aromatic H).

IIIc: colorless liquid, bp  $67-68^\circ \text{C}/3 \text{ mmHg}$  (lit.<sup>5</sup>,  $104-106^\circ \text{C}/14 \text{ mmHg}$ ).  
 PMR ( $\text{CCl}_4$ )  $\delta$ ppm: 1.30 (9H, s, t-Bu), 6.70-7.25 (4H, m, aromatic H)

IVa: colorless liquid, bp  $105-106^\circ \text{C}/13 \text{ mmHg}$ . PMR ( $\text{CCl}_4$ )  $\delta$ ppm: 1.30 (18H, s, t-Bu), 6.70-7.10 (3H, m, aromatic H).

## REFERENCES

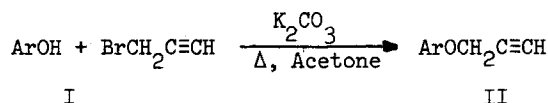
1. Part 6 of the series of "Studies on Friedel-Crafts Chemistry." Part 4: M. Tashiro and T. Yamato, Submitted to J. Org. Chem.
2. M. Tashiro, G. Fukata and T. Yamato, Org. Prep. Proced. Int., 8, 263 (1976).
3. C. Ruchart and S. Eichler, Chem. Ber., 95, 1921 (1962).
4. L. Harvey, G. J. Gleicher and W. D. Totherour, Tetrahedron, 25, 5019 (1969).
5. M. M. Tchitchibabin, S. Elgasine and V. Lengold, Bull. Soc. Chim. France, 43, 238 (1928).

SYNTHESIS OF 3-(2-METHYLPHENOXY)-  
AND 3-(2,6-DIMETHYLPHENOXY)PROPYLENE

Submitted by R. A. Malzahn, C. M. Peek and J. D. Woodyard\*  
(6/27/77)

Department of Chemistry and Killgore Research Center  
West Texas State University  
Canyon, Texas 79016

New compounds IIa and IIb have been prepared from the reaction of 3-bromopropyne with Ia and Ib respectively in refluxing acetone and anhydrous potassium carbonate



a) Ar = 2-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>

b) Ar = 2,6-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>

## EXPERIMENTAL

An F & M gas chromatograph, Model 810, equipped with a flame ionization detector and a 4 ft. by 0.25 in. 10% Carbowax 20 M, was operated at 200° for all vpc analyses. IR spectra were obtained using a Beckman Model 10 grading IR spectrophotometer with potassium bromide cells. Nmr spectra