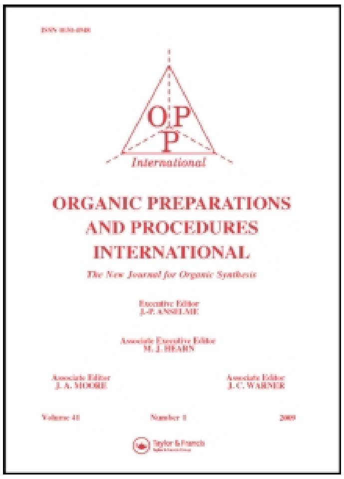

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THE $AlCl_3$ CATALYZED *t*-BUTYLATION OF HALOBENZENES WITH 2,6-DI-(*t*-BUTYL)-*p*-CRESOL

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THE $AlCl_3$ CATALYZED t-BUTYLATION OF HALOBENZENES WITH 2,6-DI-(t-BUTYL)-p-CRESOL[1]

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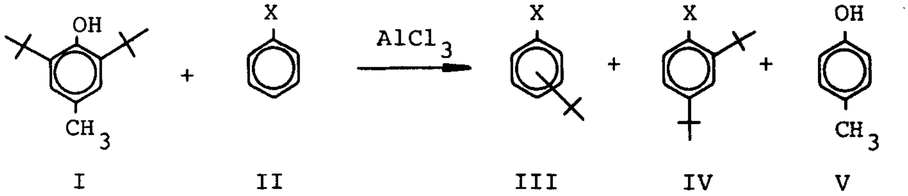
Although $AlCl_3$-CH_3NO_2 catalyzes t-butylation of alkylbenzenes and anisole with 2,6-di(t-butyl)-p-cresol(I),[2] this system did not effect the t-butylation of halobenzenes(II) with I. The t-butylation of II with I catalyzed by $AlCl_3$ is reported now.



a) X = F b) X = Cl c) X = Br

Table 1 shows that in contrast to the $AlCl_3$-CH_3NO_2 catalyst, $AlCl_3$ 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 Alcl$_3$-catalyzed *t*-Butylation of II with I[a]

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) $AlCl_3$/I = 1.5/1 mole; react. temp. 15°; 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°, 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 $AlCl_3$ at 15°. 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° C/13 mmHg (lit.[3], 53.6-54.4°C/10 mmHg). PMR (CCl_4) δppm: 1.30 (9H, s, *t*-Bu), 6.70-7.25 (4H, m, aromatic H)

IIIb: colorless liquid, bp 57-58° C/3 mmHg (lit.[4], 209° C/760 mmHg). PMR (CCl_4) δppm: 1.28 (9H, s, *t*-Bu), 7.08-7.42 (4H, aromatic H).

IIIc: colorless liquid, bp 67-68° C/3 mmHg (lit.[5], 104-106°C/14 mmHg). PMR (CCl_4) δppm: 1.30 (9H, s, *t*-Bu), 6.70-7.25 (4H, m, aromatic H)

IVa: colorless liquid, bp 105-106° C/13 mmHg. PMR (CCl_4) δppm: 1.30 (18H, s, *t*-Bu), 6.70-7.10 (3H, m, aromatic H).

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

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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

$$\underset{\text{I}}{\text{ArOH}} + \text{BrCH}_2\text{C}\equiv\text{CH} \xrightarrow[\Delta,\ \text{Acetone}]{\text{K}_2\text{CO}_3} \underset{\text{II}}{\text{ArOCH}_2\text{C}\equiv\text{CH}}$$

a) Ar = 2-$CH_3C_6H_4$ b) Ar = 2,6-$(CH_3)_2C_6H_3$

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