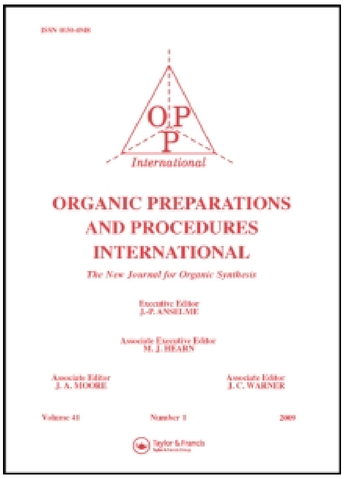

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$AlCl_3$-CH_3NO_2 CATALYZED t-BUTYLATION OF BIPHENYL, NAPHTHALENE AND SOME PHENOL DERIVATIVES WITH 2,6-DI(t-BUTYL)-p-CRESOL†

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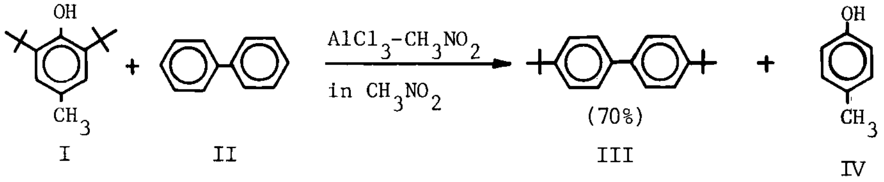
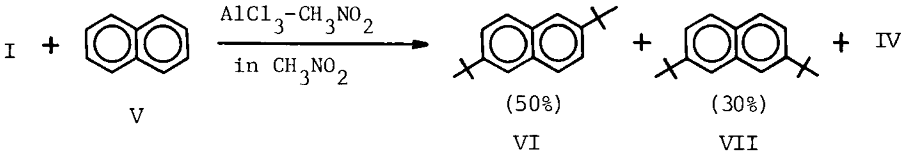
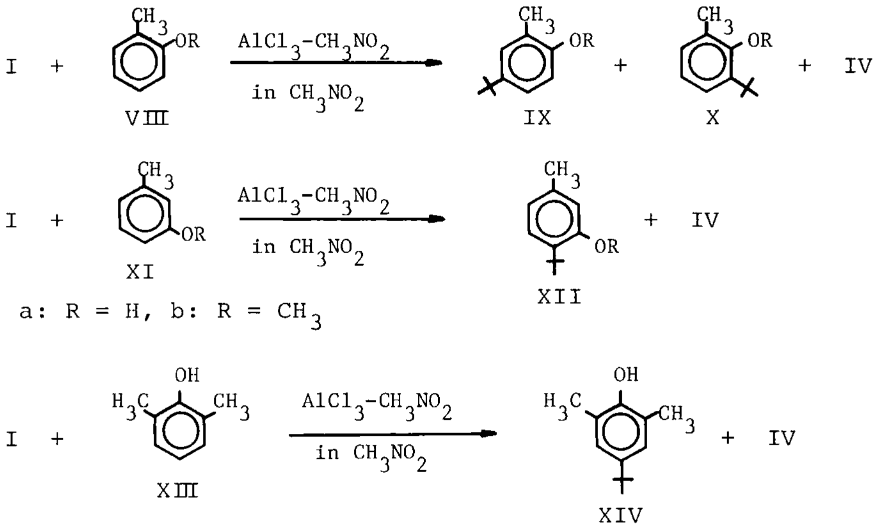
The convenient and high yield t-butylation of aromatic compounds such as alkylbenzenes,[1,2,4] and halobenzenes,[3] by the irreversible aluminum chloride-nitromethane or aluminum chloride catalyzed trans t-butylation with 2,6-di(t-butyl)-p-cresol(I).





We now report the $AlCl_3$-CH_3NO_2 catalyzed t-butylation of biphenyl(II), [5] naphthalene(V)[5] and some phenol derivatives (VIII, XI and XIII) with I. On the $AlCl_3$-CH_3NO_2 catalyzed t-butylation of II and V in nitromethane with I at 15° for 5 min gave the expected 4,4'-di(t-butyl)phenyl(III), 2,6-di(t-butyl)-(VI) and 2,7-di(t-butyl)naphthalene(VII) in 70, 50 and 30% yields, respectively. p-Cresol(IV) was formed as a by-product in almost quantitative yield. The separation of VI and VII was easily carried out since the latter is preferentially soluble in nitromethane.

Similarly $AlCl_3$-CH_3NO_2 catalyzed *t*-butylation of *o*-cresol (VIIIa), 2-methoxytoluene(VIIIb), *m*-cresol(XIa), 3-methoxytoluene (XIb), 2,6-dimethylphenol(XIII) afforded the corresponding *t*-butyl derivatives as shown in Table 1.



These data show that the use of nitromethane as solvent is beneficial since phenols react with $AlCl_3$ to afford the corresponding aluminum phenolates. In contrast to VIIIb , XIb gave XIIb in only poor yields in nitromethane. However, when XIb was used in place of nitromethane as a solvent, XIIb was obtained in good yield. Although nitromethane and carbon tetrachloride could be used instead of nitromethane in all above reactions, these solvents were not practical since boiling point of the former complicates the separation of the products and the solubility of $AlCl_3$ in the latter is insufficient to give homogenous reaction mixture.

TABLE 1. The $AlCl_3$-CH_3NO_2 Catalyzed t-Butylation of Phenol Derivatives with I *a)*

Run	Substance	Temp.(°C)	Product (%)
1	VIIIa	15	IXa(85.5)*b)*, Xa(9.5)*b)*, IV(87)
2	VIIIb	-5	IXb(100), IV(70)
3*c)*	XIa	15	XIIa(64)
4*d)*	XIb	15	XIIb(83), IV(90)
5	XIII	5	XIV(100), IV(81)

a) Reaction time is 30 min, Substance/I = 2 mol/mol, $AlCl_3$/I = 1.5 mol/mol. The solvent is nitromethane. *b)* Yields determined by GC analysis. *c)* The yield of IV was not determined since the separation of IV and recovered XIa was very difficult by distillation. *d)* XIb was used as a solvent.

EXPERIMENTAL

All melting points are uncorrected. IR spectra were measured as KBr pellets or as liquid film on NaCl plates on a Nippon Bunko IR-S spectrometer and NMR spectra were determined at 60 MHz with a Hitachi R-20 NMR spectrometer with TMS as an internal references. Nitromethane may explode under certain conditions. Caution sould be exercized.

t-Butylation of Biphenyl.- To a solution of 72 g (0.5 mole) of II, 143.2 g (0.65 mole) in 200 ml of nitromethane was added a solution of 115.5 g (0.845 mole) of aluminum chloride in 200 ml of nitromethane over a period of 5 min at 15°C. The reaction mixture then was poured into a large amount of ice-water. The organic layer was extracted with ether, dried over sodium sulfate and evaporated in vacuo to leave the residue which was washed with 10% sodium hydroxide solution (500 ml) to afford 93.1 g (70%) of 4,4'-di(t-butyl)biphenyl (III), mp. 128-129°, lit.[6] mp. 128°, colorless needles from ethanol; ir(KBr) 3030, 2960, 1490, 1360, 1260, 1120, 820 cm^{-1}, pmr (CCl_4) δ 1.31 (s, 18H, t-CH_3), 7.38 (s, 8H, aromatic protons).

Anal. Calcd for $C_{20}H_{26}$: C, 90.16; H, 9.84.

Found: C, 90.01; H, 9.87.

Acidification of the basic aqueous extract with 10% HCl afforded *p*-cresol(IV) in almost quantitative yield.

t-Butylation of Naphthalene.- To a solution of 6.4 g (50 mmoles) of V and 14.3 g (65 mmoles) of I in 30 ml of nitromethane was added a solution of 12.9 g (98 mmoles) of aluminum chloride in 24 ml of nitromethane over a period of 5 min at 15°. The reaction mixture was quenched with ice-water and the resulting precipitate was collected by filtration . Recrystallization from benzene afforded 6.0 g (50%) of 2,6-di(*t*-butyl)naphthalene (VI) as colorless needles, mp. 147-148°, lit.[7] mp. 145-146°. IR: 3040, 1600, 1460, 880, 805 cm^{-1}; pmr(CCl_4): δ 1.40 (s, 18H, *t*-C*H*$_3$), 7.20-7.80 (m, 6H, aromatic protons).

Anal. Calcd for $C_{18}H_{24}$: C, 89.94; H, 10.06.

Found: C, 89.35; H, 10.14.

The filtrate was extracted with ether, washed with 10% sodium hydroxide solution, dried over sodium sulfate and evaporated *in vacuo* to give 3.5 g (30%) of 2,7-di(*t*-butyl)-naphthalene(VII) as colorless needles (from benzene), mp. 102-103°, lit.[6] mp. 103-104°. IR: 3040, 2950, 1600, 1460, 1360, 900, 840 cm^{-1}; pmr(CCl_4): δ 1.44 (s, 18H, *t*-C*H*$_3$), 6.56-7.37 (m, 6H, aromatic protons).

Anal. Calcd for $C_{18}H_{24}$: C, 89.94; H, 10.06.

Found: C, 89.25; H, 10.12.

t-Butylation of *o*-Cresol(VIIIa).- To a solution of 5.4 g (50 mmoles) of VIIIa, 5.5 g (25 mmoles) of I in 15 ml of nitromethane was added at 15° a solution of 5.0 g (38 mmoles) of $AlCl_3$ in 10 ml of nitromethane. After the reaction mixture was stirred for 30 min, it was treated and worked up as described above to afford 7.78 g (95%) of a mixture of 4-t-butyl- (IXa)[8] and 6-t-butyl-o-cresol(Xa)[8] with 2.34 g (86.6%) of IV. The boiling point of the mixture is 122-124°/13 mm. The distribution of IXa and Xa (Table 1) was determined by GC analysis.

t-Butylation of 2-Methoxytoluene(VIIIb).- To a solution of 2.44 g (20 mmoles) of VIIIb, 2.20 g (10 mmoles) of I in 10 ml of nitromethane was added at -5° a solution of 2.66 g (20 mmoles) of $AlCl_3$ in 5 ml of nitromethane. After the reaction mixture was stirred for 30 min, it was worked up as described above to give 3.54 g (100%) of IXb, bp. 107-109°/15 mm, lit.[9] bp. 82°/2.5 mm; IR: 3030, 2960, 1505, 1150, 1040, 805 cm^{-1}; pmr (CCl_4): δ 1.27 (s, 9H, t-CH_3), 2.18 (s, 3H, CH_3), 3.74 (s, 3H, OCH_3), 6.51-7.10 (m, 3H, aromatic protons).

t-Butylation of m-Cresol (XIa).- To a solution of 5.4 g (50 mmoles) of XIa, 5.5 g (25 mmoles) of I in 15 ml of nitromethane was added at 15° a solution of 5 g (38 mmoles) of $AlCl_3$ in 10 ml of nitromethane. The reaction mixture was treated and worked up as described above to give 5.21 g (63.5%) of XIIa as a colorless liquid, bp. 118-119°/14 mm, lit.[10] bp. 121-122°/15 mm; IR: 3550, 3040, 2960, 1620, 1410, 1300, 1190, 1140, 1090, 955, 810 cm^{-1}; pmr(CCl_4): δ 1.35 (s, 9H, t-CH_3), 2.18 (s, 3H, CH_3), 4.48 (s, 1H, OH), 6.20-7.30 (m, 3H, aromatic protons).

t-Butylation of 3-Methoxytoluene(XIb).- To a solution of 15.25 g (125 mmoles) of 3-methoxytoluene, 5.5 g (25 mmoles) of I in 20 ml of nitromethane was added at 15° a solution of 5 g (38 mmole) of $AlCl_3$ in 10 ml of nitromethane. The reaction mixture was treated and worked up as described above to afford 8.58 g

(96.4%) of XIIb[11] as a colorless liquid, bp. 106-108°/14 mm; IR: 3040, 2960, 2880, 1610, 1300, 1260, 1180, 1100, 1050, 810, cm^{-1}; pmr(CCl_4) δ 1.32 (s, 9H, t-CH_3), 2.27 (s, 3H, CH_3), 3.75 (s, 3H, OCH_3), 6.40-7.10 (m, 3H, aromatic protons).

t-Butylation of 2,6-Dimethylphenol (XIII).- To a solution of 2.44 g (20 mmoles) of XIII and 2.80 g (13 mmoles) of I in 10 ml of nitromethane was added a solution of 2.64 g (20 mmoles) of $AlCl_3$ in 5 ml of nitromethane. The reaction mixture was worked up as described above to give 3.55 g (100%) of XIV as colorless prisms (from petroleum ether), mp. 72.5-73.5°, lit.[12] mp. 72.5-73.5°.

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