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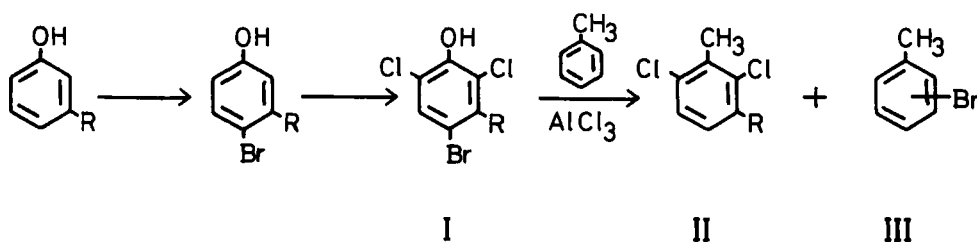
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STUDIES ON POSITIONAL PROTECTIVE GROUPS III.
 A NEW PREPARATIVE METHOD FOR CHLOROPHENOLS
 WITH THE BROMO GROUP AS A PROTECTIVE GROUP.¹

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The aluminum chloride catalyzed transbromination of bromophenols as a side reaction during the transalkylation of alkylbromophenols has been previously reported.² This result seemed to suggest that the group might serve as a protective group for the preparation of certain aromatic compounds.



a : R = H , b : R = CH₃

An attempt to prepare 2,6-dichloro-3-methylphenol (IIb) from 4-t-butyl-2,6-dichloro-3-methylphenol by the transalkylation did not seem to be a practical method because the starting compound 3-methyl-4-t-butylphenol could not be

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obtained by the Friedel-Crafts t-butylation of m-cresol (3-methyl-6-t-butylphenol was the main product³). Although the formation of IIb from 3,5-dichloro-4-hydroxy-2-methylbenzenesulfonic acid by the desulfonation was reported as a private communication,⁴ a detailed procedure is not available.

We now describe a new method for the preparation of 2,6-dichloro- (IIa) and 2,6-dichloro-3-methylphenol (IIb) from 2,6-dichloro-4-bromo- (Ia) and 2,6-dichloro-4-bromo-3-methylphenol (Ib) by transbromination in toluene⁵ at 50° for 2 hr. The expected products, IIa and IIb were isolated in 78 and 70% respectively with concurrent formation of a mixture of bromotoluenes (III).

EXPERIMENTAL

All the melting and boiling points are uncorrected. IR spectra were measured as KBr pellets on a Nippon Bunko IR-S spectrophotometer and mass spectra were obtained on a Hitachi RMS-4 mass spectrometer with a direct inlet (ionization energy 70 eV). NMR spectra were determined at 60 MHz with a Hitachi R-20 NMR spectrometer with TMS as internal reference.

Material.- 4-Bromo-2,6-dichloro- (Ia) and 4-bromo-2,6-dichloro-3-methylphenol (Ib) were prepared from 4-bromo-⁶ and 4-bromo-3-methylphenol⁷ according to the reported method and purified by recrystallization: Ia: mp. 64-65°, lit.⁸, mp. 66.5°, Ib: mp. 73-74°, lit.⁹, mp. 65°.

Aluminum chloride was purified by sublimation just prior to use.

Preparation of IIa.- A solution of 10 g (41 mmol) of Ia and

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10 g (75 mmol) of AlCl_3 in 135 ml of toluene was shaken at 50° for 2 hr. and the reaction mixture was quenched with 100 ml of hydrochloric acid (1:1). The organic layer was separated and extracted with 10% sodium hydroxide and the aqueous extract was acidified with 10% hydrochloric acid. After extraction with diethyl ether and drying (sodium sulfate), the ethereal extract was evaporated and the residue distilled to afford 5.2 g (78%) of IIa, bp. $115\text{-}120^\circ/25$ mm; mp. $64\text{-}65^\circ$, lit.², mp. $64\text{-}65^\circ$, its infrared spectrum was identical with that of an authentic sample.²

Distillation of the residual organic layer extracted with 10% aqueous sodium hydroxide gave 5.4 g (74%) of III, bp. $85\text{-}90^\circ/25$ mm.

Preparation of IIb.- A solution of 12 g (47 mmol) of Ib and 11.3 g (85 mmol) of AlCl_3 in 160 ml of toluene was shaken at 50° for 2 hr., the reaction mixture was then treated and worked up as described above.

Distillation afforded 5.8 g (70%) of IIb and 6.0 g (72%) of III. IIb: bp. $84\text{-}88^\circ/2$ mm, mp. $27\text{-}28^\circ$, lit.⁴, mp. 28.5° .

Anal. Calcd. for $\text{C}_7\text{H}_6\text{Cl}_2\text{O}$: C, 47.49; H, 3.42.

Found: C, 47.47; H, 3.47.

IR cm^{-1} : 3360 (νOH). Mass spectrum m/e : 177 (M^+).

NMR spectrum (CCl_4): δ 2.3 (3H, s, CH_3), 5.9 (1H, s, OH) and 6.6-7.3 (2H, dd, aromatic protons).

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