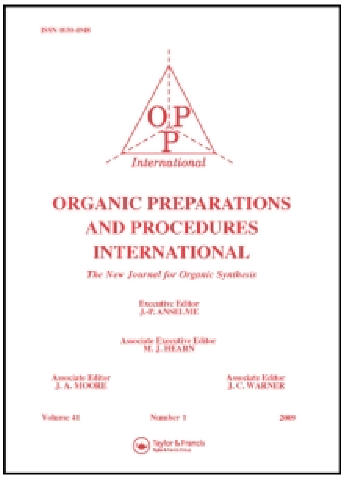


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

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

M. Tashiro[a]; H. Watanabe[a]; O. Tsuge[a]
[a] Research Institute of Industrial Science, Kyushu University, Fukuoka, JAPAN

To cite this Article Tashiro, M. , Watanabe, H. and Tsuge, O.(1975) 'STUDIES ON POSITIONAL PROTECTIVE GROUPS III. A NEW PREPARATIVE METHOD FOR CHLOROPHENOLS WITH THE BROMO GROUP AS A PROTECTIVE GROUP', Organic Preparations and Procedures International, 7: 1, 43 — 46

To link to this Article: DOI: 10.1080/00304947509356814

URL: http://dx.doi.org/10.1080/00304947509356814

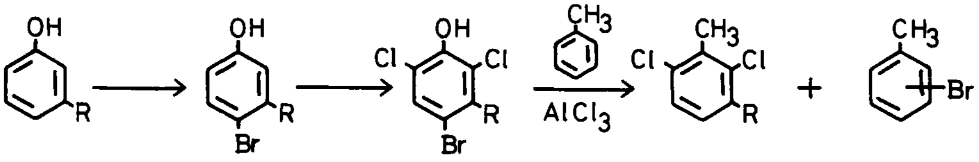
ORGANIC PREPARATIONS AND PROCEDURES INT. 7(1), 43-46 (1975)

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

M. Tashiro*, H. Watanabe and O. Tsuge

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

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.



I II III

$a : R=H \; , \; b : R=CH_3$

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 obtained by the Friedel-Crafts t-butylation of m-cresol (3-methyl-6-t-butylphenol was the main product[3]). 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 toluene[5] 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-methylphenol[7] according to the reported method and purified by recystallization: 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

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 separeted 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. 115-120°/25 mm; mp. 64-65°, lit.[2], mp. 64-65°, 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. 85-90°/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. 84-88°/2 mm, mp. 27-28°, lit.[4], mp. 28.5°.

Anal. Calcd. for $C_7H_6Cl_2O$: 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, $C\underline{H}_3$), 5.9 (iH, s, $O\underline{H}$) and 6.6-7.3 (2H, dd, aromatic protons).

REFERENCE

* To whom inquires should be sent.

1. Part II of this series, M. Tashiro, H. Watanabe and O. Tsuge, Org. Prep. Proced. Int., 6, 117 (1974).
2. M. Tashiro, H. Watanabe and O. Tsuge, ibid., 6, 107 (1974).
3. A. Chichibabin, Compt. Rend., 198, 1239 (1934).
4. F. Raschig, in Beilstein's " Handbuch der Organischen Chemie" , 6, II, 356 (1944).
5. Although benzene could be used in place of toluene as a solvent and acceptor of bromo group, the yields of the products were lower than those obtained with toluene as solvent and acceptor.
6. R. Adams and C. S. Marvel, Org. Synth., Coll. Vol., 1, 128 (1941).
7. R. C. Histon and J. A. Hutchinson, J. Am. Chem. Soc., 54, 1504 (1932).
8. W. H. Hunter and F. E. Joyce, ibid., 39, 2640 (1917).
9. L. C. Raiford and G. Leavell, ibid., 36, 1509 (1914).

(Received December 31, 1974; in revised form February 25, 1975)