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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. VI. THE PREPARATION OF 2,6-DICHLORO- AND 2,6-DIBROMOPHENOL FROM THE CORRESPONDING TETRAHALOGEN SUBSTITUTED BISPHENOL

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M. Tashiro^a; H. Watanabe^a; K. Oe^a

^a Research Institute of Industrial Science, Kyushu University, Higashi-ku, Fukuoka, Japan

To cite this Article Tashiro, M. , Watanabe, H. and Oe, K.(1975) 'STUDIES ON POSITIONAL PROTECTIVE GROUPS. VI. THE PREPARATION OF 2,6-DICHLORO- AND 2,6-DIBROMOPHENOL FROM THE CORRESPONDING TETRAHALOGEN SUBSTITUTED BISPHENOL A', *Organic Preparations and Procedures International*, 7: 4, 189 – 192

To link to this Article: DOI: 10.1080/00304947509355144

URL: <http://dx.doi.org/10.1080/00304947509355144>

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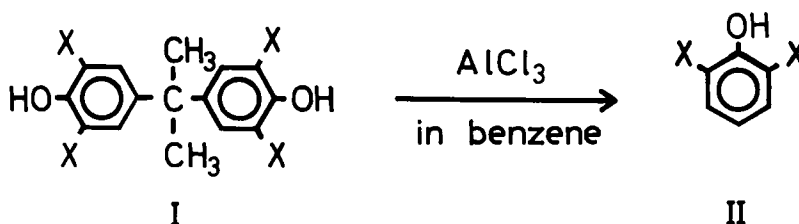
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STUDIES ON POSITIONAL PROTECTIVE GROUPS. VI.¹ THE PREPARATION OF 2,6-DICHLORO- AND 2,6-DIBROMOPHENOL FROM THE CORRESPONDING TETRAHALOGEN SUBSTITUTED BISPHENOL A.

M. Tashiro*, H. Watanabe and K. Oe

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

2,6-Dichloro- and 2,6-dibromophenol are easily prepared by the AlCl_3 or $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ catalyzed transalkylation of 4-t-butylhalophenols in benzene.² When Bisphenol A was treated with AlCl_3 catalyst in benzene, phenol was obtained in good yield.³ This result suggests that Bisphenol A as well as 4-t-butylphenol might be a good starting compound to prepare 2,6-

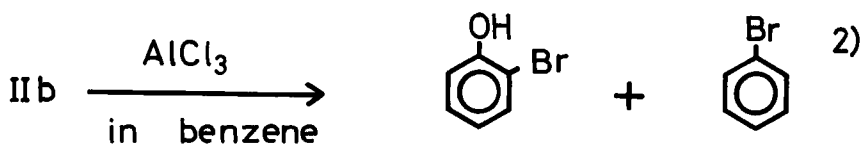
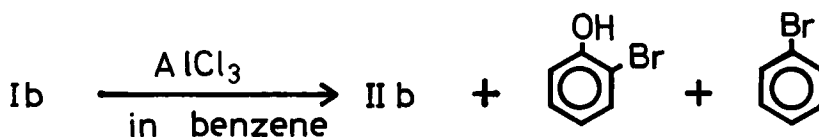


a: X = Cl ; b: X = Br

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dihalophenols. We now report the preparation of 2,6-dichloro- (II a) and 2,6-dibromophenol (II b) from 3,3',5,5'-tetrachloro- (Ia) and -tetrabromo-bisphenol A (Ib) by the treatment with AlCl_3 in benzene.

Treatment of Ia with AlCl_3 catalyst in benzene at 50° for 5 hr gave the expected II a in 85% yield; however, 2,2-diphenylpropane, which would also be expected to form, was not isolated but a small amount of unexpected diphenylmethane and the unidentified arylalkanes were detected by VPC analysis. In case of Ib, not only the expected II b but also 2-bromophenol and bromobenzene were obtained in 67%, 6% and 5% of yields respectively. The last two might be formed from the transbromination of the former (II b) as reported previously.²



EXPERIMENTAL

All melting and boiling points are uncorrected. IR spectra were measured as KBr pellets on a Nippon Bunko IR-A spectrophotometer.

THE PREPARATION OF 2,6-DICHLORO- AND 2,6-DIBROMOPHENOL

Analytical Procedure.- The analyses were carried out by gas chromatography using a Yanagimoto Gas Chromatograph, Yanaco YR-101: column, 30% high vacuum silicon grease, 75 cm; increase rate of column temperature, 12° /min, carrier gas, hydrogen, 30 ml/min.

From the areas of individual peaks, mole % figures were calculated for each product after the relative response data had been determined by the internal standard method. Nitrobenzene was used as an internal standard.

Materials.- Bisphenol A of commercial grade was used without further purification. 3,3',5,5'-tetrachloro- (Ia) and -tetrabromo-bisphenol A (Ib) were prepared from Bisphenol A according to the reported method and purified by recrystallization: Ia: mp. 161-162 $^{\circ}$, lit.⁴ mp. 162-163 $^{\circ}$. Ib: mp. 136-137 $^{\circ}$, lit.⁵ mp. 136-137 $^{\circ}$. Aluminum chloride was purified by sublimation just prior to use.

2,6-Dichlorophenol (II a).- To a solution of 29.4 g (0.1 mole) of Ia in 250 ml of benzene was added 29.2 g (0.22 mole) of $AlCl_3$, and the reaction mixture was shaken at 50 $^{\circ}$ for 5 hr and quenched with 200 ml of dilute 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 distilled to afford 24.4 g (86%) of II a, mp. 64-65 $^{\circ}$, its IR spectrum was identical with that of an authentic sample.²

Small amounts of diphenylmethane and the other unidentified arylalkanes were detected by the VPC analysis of the

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residual organic layer extracted with 10% sodium hydroxide. 2,6-Dibromophenol (II b).— Similarly a solution of 47.2 g (0.1 mole) of Ib and 29.2 g (0.22 mole) of AlCl_3 in 250 ml of benzene was shaken at 50° for 2 hr, and then it was treated and worked up as described above affording 34.3 g (67%) of II b, mp. $57-59^\circ$, accompanied by 6% of 2-bromophenol, bp. $194-195^\circ / 760$ mmHg. The IR spectra of the both compounds were identical with these of the authentic samples.²

Besides diphenylmethane and the unidentified arylalkanes described above, bromobenzene was detected in about 5% yield by the VPC analysis of the residual organic layer extracted with 10% sodium hydroxide.

Acknowledgement.— The authors are particularly indebted to Prof. O. Tsuge for his continuing interest and encouragement.

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* To whom inquiries should be sent.

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(Received June 10, 1975; in revised form September 9, 1975)