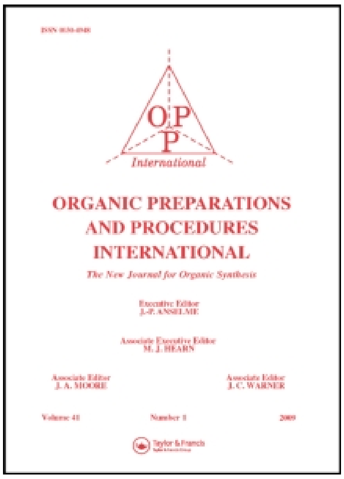

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STUDIES ON POSITIONAL PROTECTIVE GROUPS. VI.[1] THE PREPARATION OF 2,6-DICHLORO- AND 2,6-DIBROMOPHENOL FROM THE CORRESPONDING TETRAHALOGEN SUBSTITUTED BISPHENOL A.

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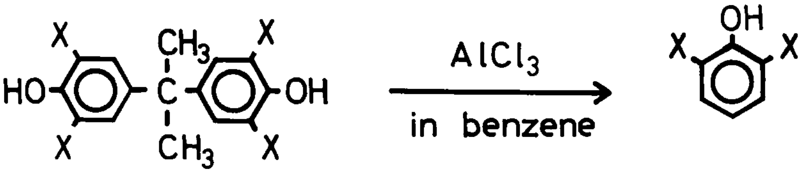
2,6-Dichloro- and 2,6-dibromophenol are easily prepared by the $AlCl_3$ or $AlCl_3$-CH_3NO_2 catalyzed transalkylation of 4-t-butylhalophenols in benzene.[2] When Bisphenol A was treated with $AlCl_3$ catalyst in benzene, phenol was obtained in good yield.[3] This result suggests that Bisphenol A as well as 4-t-butylphenol might be a good starting compound to prepare 2,6-



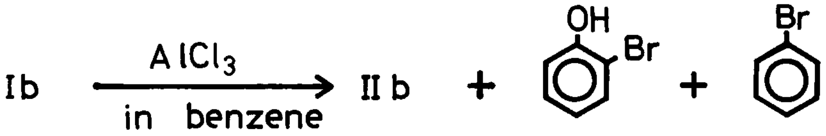
I

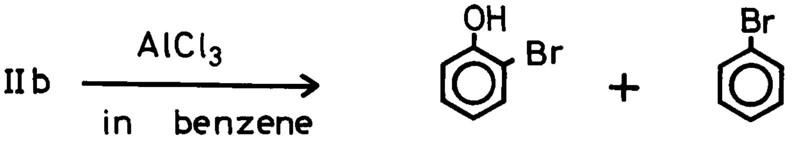
II

a: X = Cl ; b: X = Br

dihalophenols. We now report the preparation of 2,6-dichloro-(IIa) and 2,6-dibromophenol (IIb) 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 IIa 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 IIb 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 (IIb) as reported previously.[2]





2)

EXPERIMENTAL

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

Analytical Procedure.- The analyses were carried out by gas chromatography using a Yanagimoto Gas Chromatograph, Yanaco YR-101: column, 30% high vacum 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°, lit.[4] mp. 162-163°. Ib: mp. 136-137°, lit.[5] mp. 136-137°. 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° 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°, 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 residual organic layer extracted with 10% sodium hydroxide.

2,6-Dibromophenol (IIb).- 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 IIb, mp. 57-59°, accompanied by 6% of 2-bromophenol, bp. 194-195°/ 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.

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* To whom inquiries sould be sent.

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