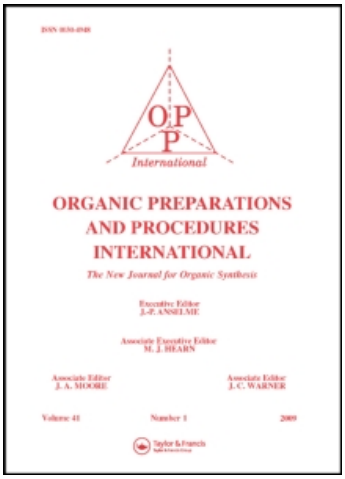

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ONE-STEP PREPARATION OF 4-BROMOMETHYL-2,3,5,6-TETRABROMOPHENOL

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ONE-STEP PREPARATION OF 4-BROMOMETHYL-2,3,5,6-TETRABROMOPHENOL

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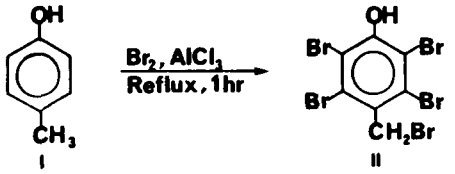
4-Bromomethyl-2,3,5,6-tetrabromophenol (II) is an important starting material for the synthesis of flame retardants containing both bromine and phosphorus atoms.[1] The existing method for its preparation is a multi-step route involving electrophilic attack by bromine on the aromatic nucleus, followed by photobromination of the methyl group.[2]



I II

In the present work, p-cresol is smoothly brominated at reflux in bromine as solvent[3] in the presence of aluminum chloride to yield the title compound; under the same conditions, o and m-cresols are brominated on the aromatic rings but not on the methyl groups. At the present time, it is not clear why p-cresol undergoes bromination at the aromatic ring as well as methyl group.

EXPERIMENTAL SECTION

Capillary melting point is uncorrected. The ^1H nmr was taken on a Varian EM-360L nmr spectrometer in CCl_4, using TMS as internal standard.

4-Bromomethyl-2,3,5,6-tetrabromophenol (II).- Aluminum chloride (1 g) was added to 200 ml of bromine (620 g, 3.88 mol) in a 500 ml three-neck flask equipped with a mechanical stirrer, a dropping funnel, a reflux condenser and a thermometer. After 30 min. stirring at 10-15°, 27 g (0.25 mol) of p-cresol was slowly added at such a rate as to maintain the temperature at 10-15°. When the addition was completed (about 1 hr), the reaction mixture was refluxed at 60° for 1 hr. Then 200 ml of water was slowly added with

stirring and then the excess bromine[3] was removed by distillation until a temperature of 100° was reached. The aqueous slurry was filtered by suction and the solid collected was washed twice with water and dried at 110° to give 120.1 g (96%) of 4-bromomethyl-2,3,5,6-tetrabromophenol, mp. 181-182°, lit.[2,4] 183-184°, 182°.

^{1}H NMR: δ 4.75 (s, 2H, CH_2), 6.25 (s, 1H, OH).

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2. J. M. Brittain, P. B. D. de la Mare and P. A. Newman, J. Chem. Soc., Perkin II, 32 (1981).

3. Bromine serves both as reagent and as solvent; the excess bromine may be recovered and reused.

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[2-CARBOXY-2'-CHLORO-4,4',5,5'-TETRA(BENZYLOXY)]AZOBENZENE FROM THE BENZYNE DECOMPOSITION OF 2-CARBOXY-4,5-DIBENZYLOXYBENZENEDIAZONIUM CHLORIDE†

Submitted by Frank W. Muellner, Ashraf N. Abdel-Sayed and Ludwig Bauer*
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Of the many by-products reported from reactions involving benzynes generated from anthranilic acids via o-carboxybenzenediazonium salts, few