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

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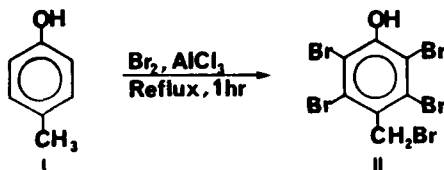
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ONE-STEP PREPARATION OF 4-BROMOMETHYL-2,3,5,6-TETRABROMOPHENOL

Submitted by Wenjeng Guo* and George Wu
(04/15/86)

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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



In the present work, *p*-cresol is smoothly brominated at reflux in bromine as solvent³ 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 CCl₄, 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 bromine³ 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°.

¹H NMR: δ 4.75 (s, 2H, CH₂), 6.25 (s, 1H, OH).

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