The Reaction of Triphenylphosphine Dibromide with o-t-Butylphenols

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TRIPHENYLPHOSPHINE DIBROMIDE can be used for the conversion of alcohols and phenols into the corresponding alkyl and aryl bromides according to equation (1),[1,2]

$$ROH + Ph_3PBr_2 \rightarrow RBr + Ph_3PO + HBr \quad (1)$$

In attempting to use this procedure for the preparation of some *o*-t-butylbromobenzene derivatives from the corresponding phenols we have made an unexpected observation which defines more precisely both the limitations and the mechanism of this reaction. When 2,6-di-t-butylphenol was heated at 200° with an equimolar quantity of triphenylphosphine dibromide† in a distillation flask a nearly quantitative yield of t-butyl bromide was collected. Steam distillation of the residue revealed that it consisted mainly of *o*-t-butylphenol and triphenylphosphine oxide together with some unreacted starting material. 4-Methyl-2,6-di-t-butylphenol reacted in a similar way to give 4-methyl-2-t-butylphenol and t-butyl bromide as products, and at 240° *o*-t-butylphenol reacted to give phenol, t-butyl bromide, and a small amount of bromobenzene.

The formation of an alkyl bromide in this way appears to be limited to phenols bearing a t-butyl group in the *ortho*-position. Schaefer and Higgins[2] found that *o*-cresol could be converted to *o*-bromotoluene in 72% yield at 340°, and under the conditions of the above experiment (240°) we observed an approximately 10% conversion after four hours. 2,6-Di-isopropylphenol reacted more readily but gave a complex mixture of products. However, since no isopropyl bromide could be detected among these products it appears that the reaction does not involve displacement of an *ortho*-alkyl group.

Previous authors have shown that the reaction between alcohols and this reagent proceeds with formation of an alkoxytriphenylphosphonium bromide intermediate, $ROP^+Ph_3Br^-$, followed by nucleophilic displacement of the oxytriphenylphosphonium group by bromide ion[3]. However, when the alcohol is replaced by a phenol bearing a

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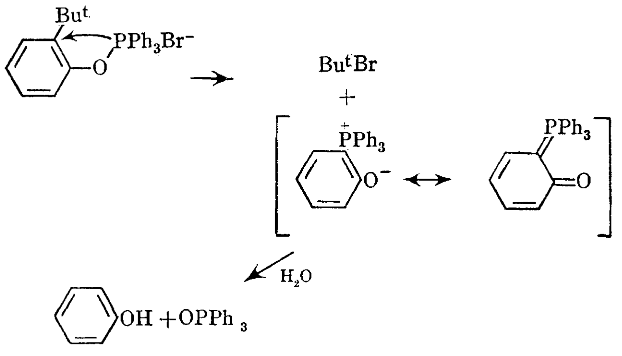
† The reagent used in this work was obtained commercially from Eastman Organic Chemicals, Rochester, New York.



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t-butyl group in the *ortho*- position an alternative pathway involving displacement of the t-butyl group becomes available (see Scheme).

The betaine structure suggested as an intermediate in this pathway is similar to the adduct obtained from the reaction of triphenylphosphine and *p*-benzoquinone,[5] and the concerted nature of the reaction is consistent with the fact that no t-butyl bromide was obtained when we treated *p*-t-butylphenol with triphenylphosphine dibromide. So far attempts to isolate and purify the betaine intermediate have been unsuccessful.

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[1] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, London, 1967, pp. 1247, and references therein.

[2] J. P. Schaefer and J. Higgins, *J. Org. Chem.*, 1967, **32**, 1607.

[3] J. P. Schaefer and D. S. Weinberg, *J. Org. Chem.*, 1965, **30**, 2635, 2639; G. A. Wiley, B. M. Rein, and R. L. Hershkowitz, *Tetrahedron Letters*, 1964, 2509.

[4] F. Ramirez and S. Dershowitz, *J. Amer. Chem. Soc.*, 1956, **78**, 5614.