CHEMISTRY LETTERS, pp. 815-816, 1974. Published by the Chemical Society of Japan

REACTION OF HALOANTHRAQUINONES WITH TRI-n-BUTYLPHOSPHINE

Sadao ARAI , Takamichi YAMAGISHI , and Mitsuhiko HIDA

Department of Industrial Chemistry , Faculty of Technology ,
Tokyo Metropolitan University
Fukazawa , Setagaya-ku , Tokyo 158

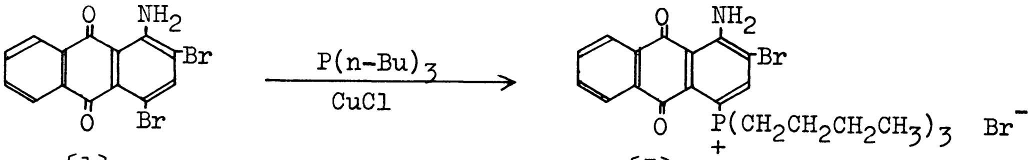
New phosphonium salts were obtained by the reaction of 1-amino-2,4-dibromoanthraquinone or sodium 1-amino-4-bromoanthraquinone-2-sulfonate with tri-n-butylphosphine in the presence of cuprous chloride. In these reactions, the bromine atom of anthraquinone derivatives was substituted by the phosphine to give phosphonium salts containing carbon-phosphorus bond.

In the course of the investigation of the Ullmann condensation reaction of haloanthraquinones, the authors observed that phosphines reacted with haloanthraquinones in the presence of cuprous chloride catalyst. Ramirez found that triphenylphosphine reacted with p-benzoquinone at a carbon atom and with chloranil at an oxygen atom. Both carbon and oxygen attacks were observed in the reaction of triphenylphosphine with 2,5-dichloro-p-benzoquinone.1) The reactions of haloanthraquinones with phosphines, however, have not been reported.

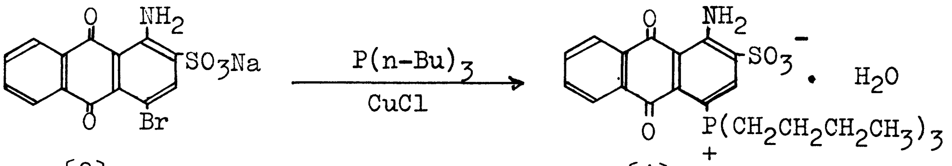
The present study was attempted to clarify the reaction products of haloanthraquinones with tri-n-butylphosphine.

1-Amino-2,4-dibromoanthraquinone[1] and sodium 1-amino-4-bromoanthraquinone-2-sulfonate[2] were used as haloanthraquinones.

A homogeneous mixture of equimolar amounts of cuprous chloride(CuCl) and tri-n-butylphosphine in benzene was added to an ethanol-benzene solution containing equimolar amount of haloanthraquinone, and heated at the boiling point for 10 hr under nitrogen atmosphere. Reaction products [3 from 1 and 4 from 2] were isolated by column chromatography on silica gel and recrystallized (3 from benzene-ethanol and 4 from methanol-water).



[1] [3] 57% , mp 204.0~204.3°C



[2] [4] 72% , mp 219.6~220.0°C

The ir absorption bands of carbonyl groups were remained almost unchanged. Therefore, it was considered that phosphine bonded with carbon of the anthraquinone ring. In nmr spectra of 3 and 4, the ratio of ring protons to alkyl protons was 5:27 and the signal of alkyl protons was split into three peaks, which have signal-strength ratio of 6:12:9. Those three peaks of alkyl protons are assigned to the α-protons, the β- and γ-protons and the δ-protons of n-butyl groups attached to phosphorus atom, respectively. The results of elementary analyses supported that the reaction products (3 and 4) were phosphonium salts.

In conclusion, the obtained results indicated that the products were the phosphonium salts containing carbon-phosphorus bond formed by the substitution of the bromine atom with tri-n-butylphosphine. The product 4 is considered to be an inner salt, since it showed negative Beilstein test.

In the absence of cuprous chloride, the yields of phosphonium salt were very low (3 - 19% : 4 - 3%). The reaction of 1 proceeded almost selectively, but in the reaction of 2, some other products were formed.

Reference

1) F. Ramirez and S. Dershowitz, J. Amer. Chem. Soc., 78, 5614 (1956).

(Received April 23, 1974)