The Reaction of Triphenylphosphine Dibromide with Benzoins

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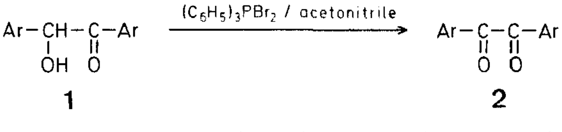
Triphenylphosphine dibromide is a mild and extremely efficacious reagent for the conversion of an alcoholic function to the bromide; even phenolic hydroxy groups are readily replaced[1].

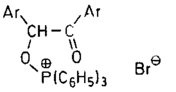
We envisioned that triphenylphosphine dibromide could also act as an oxidizing agent in certain cases in which the carbinolic H-atom of an alcohol is strongly acidic and thus might be readily abstracted from the phosphonium salt initially formed from the reagent and the alcohol. The oxidation reaction would then compete with or even exclude the normal substitution process. This type of reaction was realized with benzoins; treatment of a benzoin (**1**) with triphenylphosphine dibromide in anhydrous acetonitrile resulted in the formation of the corresponding benzil (**2**). The reaction is simple and yields are very good (see Table).



$$\text{Ar}-\underset{\substack{|\\ \text{OH}}}{\text{CH}}-\underset{\substack{\|\\ \text{O}}}{\text{C}}-\text{Ar} \xrightarrow{(C_6H_5)_3PBr_2\ /\ \text{acetonitrile}} \text{Ar}-\underset{\substack{\|\\ \text{O}}}{\text{C}}-\underset{\substack{\|\\ \text{O}}}{\text{C}}-\text{Ar}$$

1 **2**

An S_N2 displacement reaction at the C-atom adjacent to a carbonyl group is generally facilitated. Under our experimental conditions, proton loss from the intermediate



seems to be particularly favoured.

Table. Oxidation of Benzoins with Triphenylphosphine Dibromide

Benzoin	Benzil	% Yield	m. p.
Benzoin	Benzil	90	92–94°
Toluoin	Tolil	96	103–104°
Anisoin	Anisil	98	131–133°
4,4′-Diphenylbenzoin	4,4′-Diphenylbenzil	75[a]	139–142°

[a] 24% starting material recovered, due to low solubility of this benzoin in the reaction medium.

Oxidation of Benzoins; General Procedure:

Bromine was added dropwise to a solution of triphenylphosphine (157 mg, 0.6 mmol) in anhydrous acetonitrile (5 ml) until an orange tinge of the mixture persisted. Benzoin (0.5 mmol) was then introduced in one portion and the stoppered reaction vessel was allowed to stand at room temperature for 20 min. The reaction was quenched with water, the mixture extracted with ether, and the extract evaporated to dryness. Recrystallization of the crude product from methanol afforded the benzil, identified by comparison (I.R., N.M.R., m.p.) with authentic specimens.

In the case of 4,4′-diphenylbenzoin, preparative thick-layer chromatography (silica gel/benzene) was used to isolate the oxidation product.

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