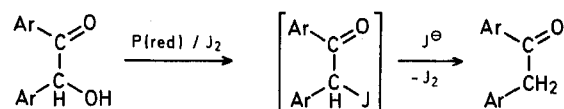


Conversion of an alcohol to iodide by the red phosphorus/iodine couple is a common practice. Under these conditions,  $\alpha$ -ketols should yield  $\alpha$ -iodoketones; but these compounds would suffer reduction by the iodide ion *in situ* to provide the ketones directly. The carbonyl group serves to activate the neighboring iodine atom toward electrophilic attack and supports the negative charge which develops along the reaction pathway. Surprisingly, it does not appear that such a simple extension has been reported, although benzilic acid affords diphenylacetic acid on exposure to a similar reagent system<sup>1</sup>.



The purpose of this communication is to demonstrate that benzoin is easily reduced to desoxybenzoin by a mixture of red phosphorus and iodine in very good yields. The reaction proceeds under notably mild conditions and dispenses with strongly acidic medium (*e.g.* HJ<sup>2</sup>).

**Table** Reduction of Benzoin with Red Phosphorus and Iodine

| Benzoin | Desoxybenzoin<br>Yield (%) | M. p.    |
|---------|----------------------------|----------|
|         | 90                         | 58–60°   |
|         | 85                         | 98–100°  |
|         | 83                         | 109–111° |
|         | 80                         | 112–114° |

#### Reduction of Benzoin; General Procedure.

A mixture of red phosphorus (0.372 g, 12 meq.) and iodine (4.57 g, 36 meq.) in carbon disulfide (30 ml) was stirred for 10 min. The benzoin (10 mmol) was added as such or together with benzene (10 ml), then after a few min pyridine (0.80 g, 10 mmol). The dark brown reaction mixture was allowed to stand for 3.5 h at room temperature, poured into aqueous thiosulfate. The liquid was decanted from a small amount of residue, separated into layers, and the aqueous phase was extracted with benzene (25 ml). The combined organic solutions were dried (MgSO<sub>4</sub>) and evaporated to give a crude product. Filtration through a short alumina column followed by crystallization afforded the pure ketone, identified by spectral comparison.

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#### Synthesis of Desoxybenzoin. Deoxygenation with the Red Phosphorus/Iodine System

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One of the most economical access to ketones of the type R—CO—CH<sub>2</sub>R is the sequential self-condensation of aldehydes (aromatic) or esters and deoxygenation of the resultant symmetrical  $\alpha$ -ketols. For accomplishing the latter step, zinc in acetic acid is generally used.

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<sup>1</sup> C. S. Marvel, F. D. Hager, E. C. Caudle, *Org. Syn.* **1**, 224 (1941).

<sup>2</sup> W. Reusch, R. LeMahieu, *J. Amer. Chem. Soc.* **86**, 3068 (1964).