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Diphosphorus tetraiodide effects reductive ring-closure of a variety of 2-ene-1,4-diones into furans within a few minutes at room temperature.

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Diphosphorus tetraiodide has recently found a number of useful synthetic applications including the deoxygenation of epoxides [1,2], sulfoxides [3,4], selenoxides [3], and heteroaromatic *N*-oxides [5,6]; the conversion of aldoximes [1] and nitroalkanes [3] to nitriles; the synthesis of iodoalkanes from alcohols [7]; the deprotection of acetals and ketals [8]; the conversion of  $\alpha,\omega$ -diols into iodoalcohols [9], and the reduction of benzyl alcohols to the parent hydrocarbons [10]. This versatile reagent, which can be easily handled and stored, is now commercially available.

In this paper we report the remarkable propensity of diphosphorus tetraiodide for effecting reductive ring-closure of a variety of 2-ene-1,4-diones **1** into furans **2** within a few minutes at room temperature (Table). The efficacy of diphosphorus tetraiodide in this transformation contrasts sharply with the corresponding sluggishness of trialkylphosphites. The latter have been reported to give furans from 2-ene-1,4-diones by tedious procedures requiring prolonged periods of reflux (22 hours at 150° [11] or 2-3 hours at 216° [12]).

At room temperature trimethylphosphite reacts [11] with *cis*- or *trans*-1,2-dibenzoyl ethylene **1e** or **1f** to give initially an ylide **3**, (after 2 or 10 hours) which finally rearranges to an enol phosphonate methyl ether **4** (after 18 hours or 6 days) [11]. Diphosphorus tetraiodide, on the

other hand, rapidly gives the furan under mild conditions, obviates laborious procedures for product isolation, and provides a direct route to **2** from the readily available **1**.

The present furan synthesis occurs in solvents such as dry methylene chloride and benzene, but proceeds most conveniently in commercial chloroform containing 1% of ethanol. All the tabulated reactions are carried out at room temperature, and the yields refer to chromatographically pure products. The furans **2a** to **2e** are readily recognizable by the characteristic nmr singlet at  $\delta$  6.7-6.8 of their heteroaromatic ring protons.

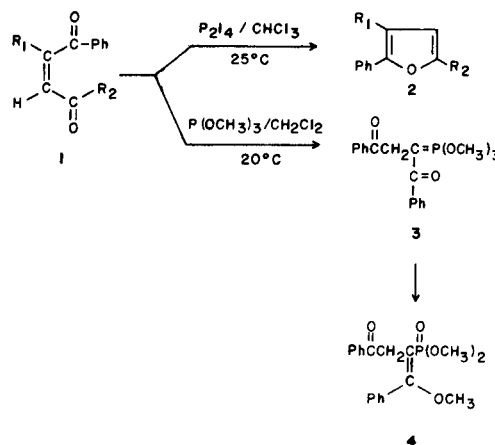


Table  
Preparation of Furans

Substrate	R <sub>1</sub>	R <sub>2</sub>	Product	Time (minutes)	Yield %	Mp (°C) [a]	Molecular Formula or Lit mp	<sup>1</sup> H-NMR ( $\delta$ )
<b>1a</b>	Ph	<i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl	<b>2a</b>	20	70	102-103	C <sub>22</sub> H <sub>13</sub> ClO [b]	6.84 (s, 1H), 7.30-7.80 (m, 14H)
<b>1b</b>	Ph	<i>p</i> -C <sub>6</sub> H <sub>4</sub> Br	<b>2b</b>	30	67	106-108	107-108 [12]	6.80 (s, 1H), 7.25-7.70 (m, 14H)
<b>1c</b>	Ph	<i>p</i> -C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	<b>2c</b>	20	75	104-105	103-105 [12]	2.38 (s, 3H), 6.78 (s, 1H), 7.20-7.80 (m, 14H)
<b>1d</b>	Ph	<i>p</i> -C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>	<b>2d</b>	25	76	96-97	94-96 [12]	3.85 (s, 3H), 6.72 (s, 1H), 6.92-7.85 (m, 14H)
<b>1e</b>	H	Ph	<b>2e</b>	30	55	87-88	88-89 [11]	6.80 (s, 2H), 7.26-7.92 (m, 10H)
<b>1f</b>	<i>trans</i> isomer of <b>1e</b>		<b>2e</b>	30	55	87-88	88-89 [11]	6.80 (s, 2H), 7.26-7.92 (m, 10H)

[a] Recrystallized from methanol. [b] Calcd.: C, 79.88; H, 4.57; Cl, 10.72. Found: C, 79.89; H, 4.59; Cl, 10.8.

Preparation of 2-Ene-1,4-diones **1a** to **1d**.

The general procedure is based on the method of Japp and Klingemann [14]. A solution of benzil (0.05 mole) in 10% methanolic potassium hydroxide (150 ml) was treated at room temperature with the corresponding substituted acetophenone (0.05 mole), whereupon the solution darkened immediately and the product, which precipitated after a few minutes, was collected and washed with methanol (yield 75-90%).

Preparation of Furans **2a** to **2e**. General Procedure.

To a stirred solution of the 2-ene-1,4-dione **1** (1 mmole) in chloroform (10 ml) was added in one portion a suspension of diphosphorus tetraiodide (0.5 mmole) in chloroform (5 ml). The reaction was allowed to proceed at room temperature and monitored by tlc. After 20-30 minutes, the mixture was diluted with chloroform and washed with aqueous sodium thio-sulfate (3 × 15 ml). The organic layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure to give an oil which solidified when triturated with methanol. The crude product was purified by thick layer chromatography using *n*-hexane as the eluent.

## Dedication.

This work is respectfully dedicated to Professor Stanley Wawzonek, State University of Iowa, on the occasion of his retirement in June, 1984.

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