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ELECTROSYNTHESIS OF HETEROATOM-HETEROATOM BONDS. 5. DIRECT CROSS-COUPLING OF DIALKYLPHOSPHITES WITH AMINES BY AN IODONIUM ION-PROMOTED ELECTROLYTIC PROCEDURE

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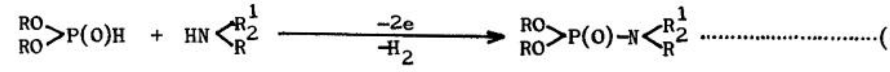
Summary: An efficient direct cross-coupling procedure of dialkylphosphites with amines by an iodonium ion-promoted electrolysis, giving N-substituted dialkyl phosphoramidates, has been proposed.

Our interest in direct formation of S-S,[1] S-N,[2,3] and S-P[4] bonds by electrochemical Procedures has spurred continuing efforts to develope phosphorous nitrogen coupling reactions. The present paper deals with straightforward iodonium ion-promoted electrosynthesis of N-substituted dialkyl phosphoramidates 3[5] from dialkoxyphosphates 1 with amines 2.



$$\begin{matrix}RO\\RO\end{matrix}\!>\!P(O)H + HN\!<\!\begin{matrix}R^1\\R^2\end{matrix} \xrightarrow[-H_2]{-2e} \begin{matrix}RO\\RO\end{matrix}\!>\!P(O)\text{-}N\!<\!\begin{matrix}R^1\\R^2\end{matrix} \quad \cdots\cdots (1)$$

1 2 3

A typical electrolysis procedure is shown as follows: A solution of diethyl phosphite (1, R = Et, 138 mg), diethylamine (2, R = Et, 80 mg), and sodium iodide (20 mg) in acetonitrile (20 ml) containing Et_4NClO_4 (100 mg) as a supporting electrolyte was electrolyzed at a constant voltage of 3V (2.5 F/mol based on 1), at 25-30 °C in an undivided cell equiped with two platinum-foil electrodes. The current density varied from 6 to 0.8 mA/cm^2 during the electrolysis and the workup gave 92% yield of 3. Lack of sodium iodide in the electrolysis media provided trace of 3, indicating that the iodide played an important role in the P-N bond making reaction. Some results of the novel electrosynthesis of the phosphoramidates 3 are listed in Table 1.

Subsequently, our attention was focused on the effect of halide salts in the electrolysis

Table 1. Electrolytic Cross-Coupling of Dialkyl Phosphites 1 with Amines 2

Entry	Phosphite 1 R	Amine 2	Current Density/ (Electricity) mA/cm^2 (F/mol)	Time h	Phosphoramides 3 Yield, %
1	Methyl	Propylamine	9.3–0.4 (2.5)	5.0	79[6]
2	Methyl	Isopropylamine	6.7–0.3 (2.6)	10.3	80[7]
3	Methyl	t-Butylamine	5.0–0.3 (2.5)	10.8	83[8]
4	Methyl	Benzylamine	7.0–1.0 (2.5)	4.6	69[8]
5	Methyl	Diethylamine	9.0–1.8 (2.5)	2.4	81[9]
6	Methyl	Dibutylamine	5.5–1.1 (2.6)	6.0	74[10]
7	Methyl	Morpholine	5.0–0.7 (3.0)	7.0	86[11]
8	Methyl	Piperidine	8.0–1.1 (2.6)	3.5	82[9]
9	Methyl	Pyrrolidine	10.3–6.1 (2.5)	1.8	79[8]
10	Ethyl	Propylamine	7.3–0.8 (2.5)	4.2	88[6]
11	Ethyl	Isopropylamine	7.3–0.8 (2.6)	4.8	79[12]
12	Ethyl	t-Butylamine	6.5–0.4 (2.5)	6.6	79[13]
13	Ethyl	Benzylamine	6.3–1.3 (2.6)	4.7	70[8]
14	Ethyl	Diethylamine	6.0–0.8 (2.5)	4.8	92[14]
15	Ethyl	Dibutylamine	8.3–2.1 (2.5)	2.6	83[10]
16	Ethyl	Morpholine	5.0–0.3 (2.5)	9.7	89[11]
17	Ethyl	Piperidine	5.5–0.6 (2.5)	5.0	91[15]
18	Ethyl	Pyrrolidine	8.3–2.9 (2.6)	3.0	86[8]
19	Isopropyl	Propylamine	7.0–0.8 (2.5)	6.4	74[8]
20	Isopropyl	Isopropylamine	6.7–0.3 (2.5)	11.1	81[16]
21	Isopropyl	t-Butylamine	6.0–0.2 (2.4)	11.7	65[8]
22	Isopropyl	Benzylamine	8.3–0.6 (2.7)	6.4	79[8]
23	Isopropyl	Diethylamine	8.0–2.0 (2.6)	3.8	83[17]
24	Isopropyl	Dibutylamine	6.3–1.0 (2.6)	4.8	70[10]
25	Isopropyl	Morpholine	7.0–0.9 (2.5)	3.8	79[11]
26	Isopropyl	Piperidine	9.0–1.4 (2.7)	3.6	84[8]
27	Isopropyl	Pyrrolidine	8.3–1.2 (2.6)	3.1	90[8]

solution. Previous works reveal that S–N and S–P bonds making reactions take place preferentially in the presence of sodium bromide as a catalytic additive.[2,3] However, in the present electrolysis, the preparation of P–N bond using sodium bromide as well as sodium chloride did not succeed, since the current dropped to zero before the cross-coupling

Table 2. Effect of Alkali Halides on Electrolytic Cross-Coupling of 1 (R = Et) with 2 (R = Et).

Entry	Supporting Electrolyte	Current Density mA/cm^2	Electricity F/mol	Time h	Phosphoramide Yield, %
1	NaI	6.0 - 0.8	2.5	4.8	92
2	LiI	4.4 - 3.4	2.7	3.1	82
3	KI	5.8 - 2.1	2.8	4.2	81
4	NH_4I	8.5 - 5.1	2.5	1.9	85
5	CuI	7.0 - 6.0	2.5	1.9	71
6	NaCl	4.7 - 0	0.8	25	4
7	NaBr	2.5 - 0	1.4	31	35
8	I_2	——	—	24*	21
9	I_2	8.3 - 6.0	2.5	1.6	94

* Stirred without passing electricity.

reaction of 1 with 2 completed (Table 2, entries 6 and 7). But, the surprising feature of salts in the media was observed in the P-N bond making electrolysis as shown in entries 1-5, since the iodide salts-promoted electrolyses could give 3 in 71-92% yields. Addition of iodine also gave a good result (entry 9). The effect of iodine is complex but these data are interesting in finding a characteristic contribution of iodine for the preferential formation of 3.

The oxidation of $(RO)_2P(O)H-R^1_2NH$-Metal I system is generally considered to proceed by discharge of iodide on the anode.[18] Thus, the iodonium ion-promoted reaction is considered tentatively to proceed in the manner as shown in the following equations (2-6).

$$2I^- \xrightarrow{-2e} I_2 \quad (2)$$

$$(RO)_2P(O)H + I_2 \longrightarrow (RO)_2P(O)I + HI \quad (3)$$

$$(RO)_2P(O)I + HNR^1_2 \longrightarrow (RO)_2P(O)NR^1_2 + HI \quad (4)$$

$$R^1_2NH + I^+ \longrightarrow R^1_2NI + H^+ \quad (5)$$

$$R^1_2NI + (RO)_2P(O)H \longrightarrow (RO)_2P(O)NR^1_2 + HI \quad (6)$$

However, there are ambiguous questions of why iodides and iodine are the most influential additives among halide salts in the electrochemical P-N bond formation and also why other halides tend to decrease current during the electrolysis in spite of the presence of Et_4NClO_4 as a supporting electrolyte. We are continuing to study the role of iodine in the electrolysis media.

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