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# Dediazoniation of Arenediazonium Salts with Trivalent-Phosphorus Compounds. Tool for Examination of the Reactivity of Phosphorus-Centered Radicals

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## ABSTRACT

*Trialkyl phosphites (***1***), dialkyl phenylphosphinites (***2***), and alkyl diphenylphosphonites (***3***) as well as 2-phenyl-1,3,2-dioxaphospholan (***4a***) and 2-phenyl-1,3,2-dioxaphosphorinan (***4b***) give rise to dediazoniation of arenediazonium salt (***5***) in an alcoholic solvent under an argon atmosphere at 20°C. The reaction proceeds via a radical-chain mechanism initiated by single-electron transfer (SET) from the trivalent-phosphorus compounds to* **5***, as a result of which, an aryl radical Ar· and a cation radical* **15** *are generated from the former and the latter, respectively. The aryl radical Ar· participates in this chain process by abstracting a hydrogen from the solvent alcohol, yielding the corresponding arene ArH. The cation radical* **15** *undergoes both an ionic reaction with the solvent alcohol and a radical coupling with Ar·, giving the phosphoranyl radical* **16** *and the phosphonium ion* **17***, respectively, as intermediates. The phosphoranyl intermediate* **16** *decomposes through either the SET process to* **5** *or by β-scission, yielding the oxidation product (phosphate, phosphonate, or phosphinate from* **1***,* **2***, or* **3***, respectively, or phosphonates from* **4***). The phosphonium intermediate* **17** *affords the arylated product (phosphonate, phosphinate, or phosphine oxide from* **1***,* **2***,* **3***, respectively, or the phosphinate from* **4***). Among the trivalent-phosphorus compounds tested,* **1** *gives the arylated product in the highest yield. This observation, together with the literature data of ESR for structurally related phosphoranyl radicals, indicates that the radical coupling of* **15** *with Ar· is facilitated by the high spin density on its central phosphorus atom.*

Radical reactions constitute one of the most important fields in organic chemistry. A huge number of studies have been devoted to elucidate both reactivities and physical properties of carbon-centered radicals as well as radicals centered on a nitrogen, oxygen, or sulfur atom. On the other hand, the chemistry of phosphorus-centered radicals is not entirely clear. In particular, trivalent-phosphorus cation radicals have been studied mainly to describe their physical properties [1], whereas much poorer information about their chemical properties has so far been presented. This is partly due to difficulty of producing these cation radicals selectively. In fact, anodic oxidation [2] or γ-irradiation [3] of trivalent-phosphorus compounds gives several kinds of radical species in addition to the cation radicals [4].

A trivalent-phosphorus cation radical reacts with a nucleophile to give a phosphoranyl radical [5,6]. Therefore, a reaction system in which such cation radicals are selectively generated in the presence of a nucleophile may be useful for examination of the reactivity of both trivalent-phos-

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phorus cation radicals and phosphoranyl radicals. An acridinium salt in the photoexcited state causes a selective one-electron oxidation of an alkyl diphenylphosphinite (**3**) [7] or a triphenylphosphine (**14**) [8]. However, this photoreaction is feasible only with trivalent-phosphorus compounds that have relatively low oxidation potentials. Diazonium salts are more powerful one-electron oxidants and oxidize phosphites [9,10], phosphonites [10], phosphinites [10], and phosphines [9] to the corresponding cation radicals. Thus, diazonium salts can produce trivalent-phosphorus cation radicals with largely different structures, and subsequently, the corresponding phosphoranyl radicals can be formed when the reactions are carried out in a nucleophilic solvent such as an alcohol.

A preliminary study on the dediazoniations of arenediazonium fluoroborates (**5**) with trialkyl phosphites (**1**), dialkyl phenylphosphonites (**2**), and **3** in an alcoholic solvent has shown that the trivalent-phosphorus compounds are converted to two kinds of products during the reaction, namely, the oxidation products (**6**, **9**, and **11** from **1**, **2**, and **3**, respectively) and the arylated products (**7**, **10**, and **12** from **1**, **2**, and **3**, respectively) (Scheme 1) [10]. Based on these results, we propose that a trivalent-phosphorus cation radical initially generated undergoes both an ionic reaction with a solvent alcohol and a radical reaction with Ar·, giving the oxidation and the arylated products, respectively. The relative ease of these reactions depends on the spin density on the central phosphorus atom in the cation radical.

In this article, we present clearer evidence for the proposed mechanism. We also discuss the reactivity of a phosphoranyl radical that is produced by the reaction of the cation radical with a solvent alcohol.

## *RESULTS*

### *General*

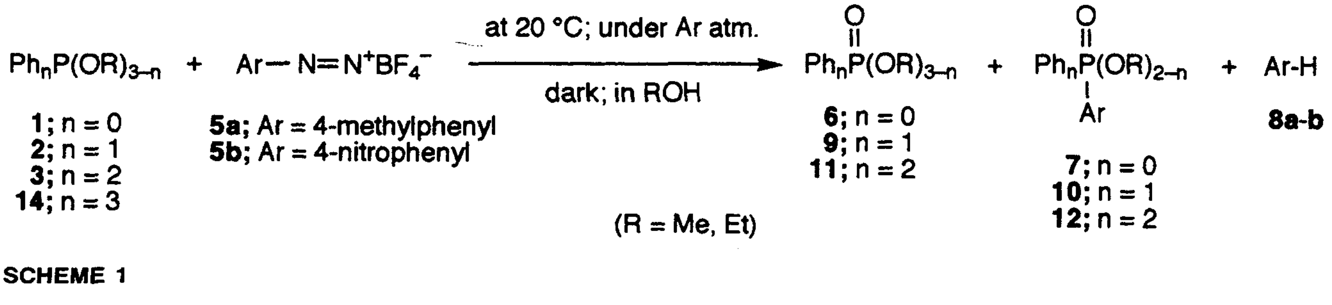
A trivalent-phosphorus compound ($1.00 \times 10^{-1}$ M) was reacted with an equimolar amount of a diazonium salt under an argon atmosphere in the dark at 20°C for 15 minutes unless otherwise noted. The reaction mixture was analyzed by gas chromatography (GC) and gas chromatography mass spectroscopy (GCMS) as well as by $^1$H and $^{31}$P NMR spectroscopy to identify the products. The yields of the products were determined by GC. $^{31}$P NMR spectroscopy suggested that a low material balance sometimes observed by GC analysis results from the formation of nonvolatile materials. Most of these were not identified.

### *Reactions of Phosphites* (**1**) *with 4-Methylbenzenediazonium Fluoroborate* (**5a**)

When trimethyl phosphite (**1a**) was reacted with **5a** in methanol, trimethyl phosphate (**6a**) and dimethyl 4-methylphenylphosphonate (**7a**), the oxidation and the arylated products respectively, from **1a**, were obtained, along with toluene (**8a**) (Table 1, Scheme 2). The reaction of **1a** in ethanol gave the phosphates and the phosphonates in which one or more methoxyl ligands had been replaced by ethoxyl groups; that is, the products from **1a** in this reaction were ethyl dimethyl phosphate (**6b**), diethyl methyl phosphate (**6c**), triethyl phosphate (**6d**), **7a**, ethyl methyl 4-methylphenylphosphonate (**7b**), and diethyl 4-methylphenylphosphonate (**7c**) (no **6a** was detected). When the reaction was carried out in ethanol-acetonitrile mixture, the extent of the transesterification increased with an increasing content of ethanol in the solvent (Figure 1). Appreciable transesterification took place neither in the starting materials nor in the products.

Toluene **8a** was detected in more than a stoichiometric amount when a 0.2- or 0.1-equivalent amount of **1a** was reacted with **5** (entries 2 and 3, respectively). Under the aerobic conditions, the formation of **7a** and **8a** was suppressed (entry 4).

In the reaction of triethyl phosphite (**1b**) with **5a** in ethanol, the oxidation product **6d** and the arylated product **7c** were formed from **1b**. The reaction of **1b** in methanol or in methanol-acetonitrile afforded the mixtures of phosphates, **6a**, **6b**, **6c**, and **6d**, and of phosphonates, **7a**, **7b**, and **7c**, the yields of the transesterified products being higher with higher content of methanol in the sol-



**SCHEME 1**

**TABLE 1** Reaction of Trialkyl Phosphite **1** with Diazonium Salt **5a**[a]

| | | | *Yield/%*[b] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | *Phosphate* | | | | *Phosphonate* | | | | |
| *Entry* | **1** | *Solvent* | **6a** | **6b** | **6c** | **6d** | **7a** | **7b** | **7c** | **8a** | **A/O**[c] |
| 1 | **1a** | MeOH | 80.5 | — | — | — | 17.2 | — | — | 30.3 | 0.21 |
| 2[d] | | | 12.5[e] | — | — | — | 9.1[e] | — | — | 34.6 | 0.73 |
| 3[f] | | | 0 | — | — | — | 5.6[e] | — | — | 33.3 | — |
| 4[g] | | | 52.3 | — | — | — | 6.9 | — | — | 12.9 | 0.13 |
| 5 | | EtOH | 0 | 14.9 | 14.7 | 31.9 | 2.4 | 2.5 | 2.4 | —[h] | 0.11 |
| 6 | | EtOH–MeCN (1:1) | 0 | 16.7 | 10.8 | 14.8 | 1.8 | 1.6 | 1.5 | —[h] | 0.12 |
| 7 | | EtOH–MeCN (1:9) | 8.6 | 30.4 | 8.3 | 7.7 | 2.0 | 0.4 | 1.0 | —[h] | 0.062 |
| 8 | | EtOH–MeCN (1:99) | 19.2 | 32.6 | 0 | 0 | 1.3 | 0 | 1.2 | —[h] | 0.048 |
| 9 | **1b** | EtOH | — | — | — | 79.2 | — | — | 8.2 | —[h] | 0.10 |
| 10 | | MeOH | 4.0 | 23.6 | 37.6 | 22.7 | 1.9 | 3.0 | 5.0 | 37.8 | 0.11 |
| 11 | | MeOH–MeCN (1:1) | 0 | 11.4 | 35.7 | 24.4 | 1.0 | 2.0 | 5.2 | 32.2 | 0.12 |
| 12 | | MeOH–MeCN (1:9) | 0 | 2.2 | 41.0 | 31.4 | 0.3 | 0.3 | 4.9 | —[h] | 0.074 |
| 13 | | MeOH–MeCN (1:99) | 0 | 0 | 35.6 | 31.9 | 0 | 0 | 5.1 | —[h] | 0.076 |

[a] Initial concentrations of **1** and **5a**, both 1.00 × 10$^{-1}$ M; reaction time, 15 minutes; in the dark at 20°C under an argon atmosphere unless otherwise noted.

[b] Based on **5a** used otherwise indicated; determined by GC.

[c] The ratio of total yield of phosphonates to that of phosphates.

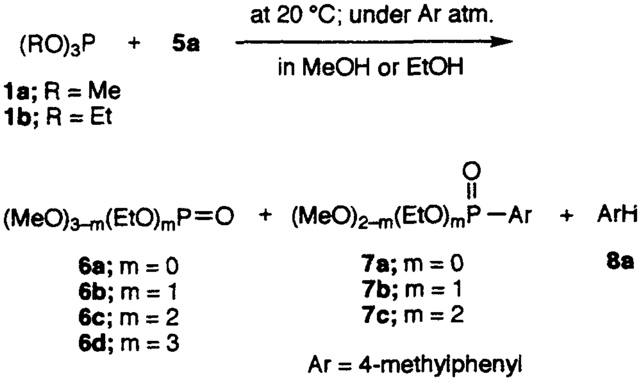
[d] Initial concentration of **1a**, 2.00 × 10$^{-2}$ M.

[e] Based on **1a** used.

[f] Initial concentration of **1a**, 1.00 × 10$^{-2}$ M.

[g] Under an oxygen atmosphere.

[h] Not determined.



**SCHEME 2**

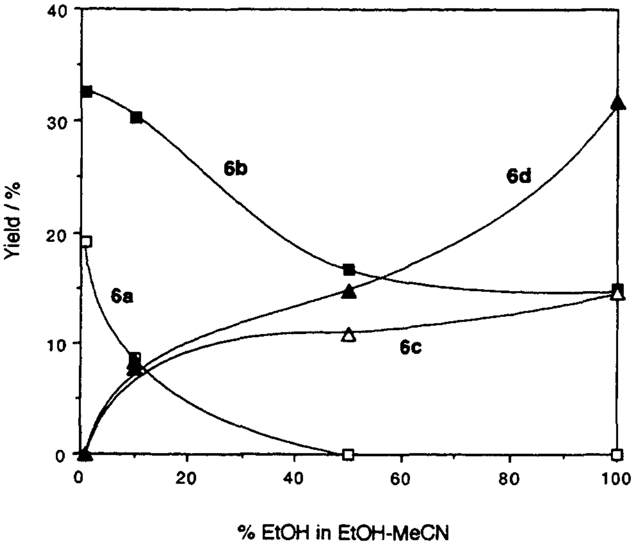


**FIGURE 1** Dependency of yields of **6a** (□), **6b** (■), **6c** (△), and **6d** (▲) on the ethanol content in the reaction of **1a** with **5a** in ethanol-acetonitrile mixture.

vent (Figure 2). Replacement of methoxyl ligands by ethoxyl groups in the solvent was more facile than of ethoxyl ligands by methoxyl groups (see Figures 1 and 2).

### *Reactions of* **1** *with 4-Nitrobenzenediazonium Fluoroborate* (**5b**)

When **1a** was reacted with diazonium salt **5b** in methanol, **6a**, dimethyl 4-nitrophenylphosphonate (**7a**′), and nitrobenzene (**8b**) were obtained (Table 2). The reaction of **1b** with **5b** in methanol gave the mixtures of phosphates, **6a**, **6b**, **6c**, and **6d**, and of phosphonates, **7a**′, ethyl methyl 4-nitrophenylphosphonate (**7b**′), and diethyl 4-nitrophenylphosphonate (**7c**′), along with **8b**. The ratio of total yield of the arylated products to that of the oxidation products **A/O** increased with an increasing ratio of the starting materials **1**/**5b**.

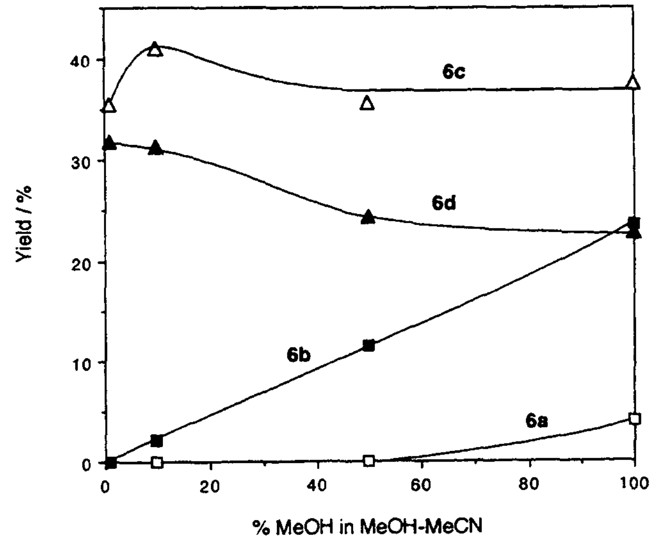


**FIGURE 2** Dependency of yields of **6a** (□), **6b** (■), **6c** (△), and **6d** (▲) on the methanol content in the reaction of **1b** with **5a** in methanol-acetonitrile mixture.

### *Reactions of Phosphonites* (**2**) *with Diazonium Salt* **5a**

The reaction of dimethyl phenylphosphonite (**2a**) with **5a** in methanol gave dimethyl phenylphosphonate (**9a**) and methyl (4-methylphenyl)-phenylphosphinate (**10a**), the oxidation and the arylated products, respectively, from **2a**, as well as **8a** (Table 3). The reaction of diethyl phenylphosphonite (**2b**) in ethanol afforded diethyl phenylphosphonate (**9c**), ethyl (4-methylphenyl)phenylphosphinate (**10b**), and **8a**. Exchange of alkoxyl ligands was again observed when the phosphonite had different alkoxyl groups from that in the solvent alcohol (Scheme 3). The extent of the transesterification increased with an increasing content of the alcohol in alcohol-acetonitrile mixture. No attempt was made to determine the yield of **8a**.

When the reaction of **2b** with **5a** was carried out in tetrahydrofuran (THF), the reaction mixture became highly viscous within 10 minutes obviously due to polymerization of THF. The polymer formed was not characterized (see the Discussion section). The addition of a small amount of methanol into the THF solution allowed the dediazoniation of **5a** to take place without appreciable polymerization of THF (entries 27–29 and 35–37).

### *Reactions of Phosphinites* (**3**) *with Diazonium Salt* **5a**

Table 4 summarizes the results from the reactions of methyl (**3a**) or ethyl phenylphosphinites (**3b**) with **5a** in methanol or ethanol. The oxidation products, methyl (**11a**) and/or ethyl diphenylphosphinates (**11b**), and the arylated product, (4-methylphenyl)diphenylphosphine oxide (**12**), were obtained along with **8a** (Scheme 4). The yields of the transesterified products increased with an increasing amount of alcohol in the solvent. The yield of **8a** was not determined.

### *Reactions of Cyclic Phosphonites* (**4**) *with Diazonium Salt* **5a**

2-Phenyl-1,3,2-dioxaphospholan (**4a**) and 2-phenyl-1,3,2-dioxaphosphorinan (**4b**) were reacted with **5a** in methanol. The corresponding oxidation products, 2-oxo-2-phenyl-1,3,2-dioxaphospholan (**13a**) and 2-oxo-2-phenyl-1,3,2-dioxaphosphorinan (**13b**), respectively, were formed as well as dimethyl phenylphosphonate (**9a**) (Table 5, Scheme 5). The arylated product, methyl (4-methylphenyl)-

**TABLE 2** Reaction of Trialkyl Phosphite **1** with 4-Nitrobenzenediazonium Fluoroborate **5b**[a]

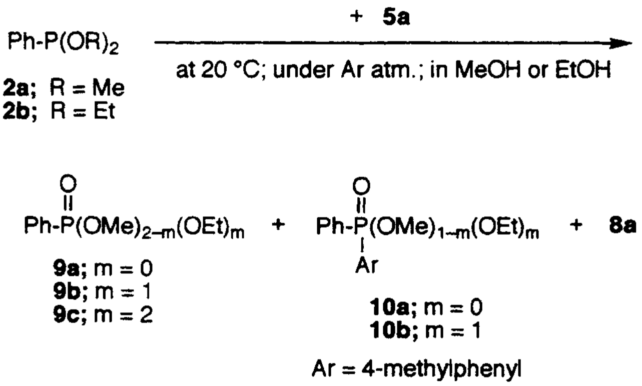
| | | | *Yield/%*[b] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | *Phosphate* | | | | *Phosphonate* | | | | |
| *Entry* | **1** | **1/5b**[c] | **6a** | **6b** | **6c** | **6d** | **7a′** | **7b′** | **7c′** | **8b** | **A/O**[d] |
| 14 | **1a** | 0.3 | 19.8 (66.1) | — | — | — | 3.2 (10.8) | — | — | 75.6 | 0.16 |
| 15 | | 0.5 | 34.1 (68.1) | — | — | — | 5.3 (10.6) | — | — | 60.6 | 0.16 |
| 16 | | 1.0 | 56.2 (56.2) | — | — | — | 11.0 (11.0) | — | — | 46.1 | 0.20 |
| 17 | | 2.0 | 89.0 (44.5) | — | — | — | 23.0 (11.5) | — | — | 13.2 | 0.26 |
| 18 | **1b** | 0.3 | 11.3 (37.6) | 7.4 (24.5) | 1.0 (3.3) | 0 (0) | 1.1 (3.5) | 0.7 (2.4) | 0.4 (1.2) | 71.4 | 0.12 |
| 19 | | 0.5 | 23.8 (47.6) | 13.9 (7.0) | 2.5 (5.0) | 1.9 (3.8) | 3.3 (6.5) | 1.5 (2.9) | 0.4 (0.7) | 59.6 | 0.12 |
| 20 | | 1.0 | 43.3 (43.3) | 11.6 (11.6) | 2.8 (2.8) | 2.9 (2.9) | 7.1 (7.1) | 2.0 (2.0) | 0.8 (0.8) | 41.7 | 0.16 |
| 21 | | 2.0 | 64.8 (32.4) | 34.6 (17.3) | 6.6 (3.3) | 4.6 (2.3) | 21.8 (10.9) | 7.6 (3.8) | 2.6 (1.3) | 16.1 | 0.29 |

[a] Initial concentration of **5b**, $1.00 \times 10^{-1}$ M; in MeOH; reaction time, 15 minutes; in the dark at 20°C under an argon atmosphere.
[b] *Based on* **5b** *used; determined by GC. The values in parentheses denote yields based on* **1** *used.*
[c] The ratio of the initial amount of **1** to that of **5b**.
[d] The ratio of total yield of phosphonates to that of phosphates.

**TABLE 3** Reaction of Dialkyl Phosphonite **2** with Diazonium Salt **5a**[a]

| | | | *Yield/%*[b] | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | *Phosphonate* | | | *Phosphinate* | | |
| *Entry* | **2** | *Solvent* | **9a** | **9b** | **9c** | **10a** | **10b** | **A/O**[c] |
| 22 | **2a** | MeOH | 79.9 | — | — | 1.7 | — | 0.021 |
| 23 | | EtOH | 7.4 | 28.7 | 37.8 | 0.7 | 3.3 | 0.054 |
| 24 | | EtOH–MeCN (1:1) | 10.5 | 38.4 | 23.0 | 1.5 | 1.8 | 0.050 |
| 25 | | EtOH–MeCN (1:9) | 18.7 | 32.7 | 4.5 | 1.4 | 0 | 0.025 |
| 26 | | EtOH–MeCN (1:99) | 29.7 | 18.6 | 0.8 | 0.8 | 0 | 0.016 |
| 27 | | EtOH–THF (1:1) | 11.5 | 32.9 | 27.1 | 0.9 | 2.2 | 0.043 |
| 28 | | EtOH–THF (1:9) | 28.5 | 28.7 | 8.6 | 0.6 | 0.7 | 0.020 |
| 29 | | EtOH–THF (1:99) | 37.3 | 10.4 | 0.5 | 0.4 | 0 | 0.083 |
| 30 | **2b** | EtOH | — | — | 61.4 | — | 4.7 | 0.077 |
| 31 | | MeOH | 26.3 | 38.2 | 20.7 | 1.6 | 3.7 | 0.062 |
| 32 | | MeOH–MeCN (1:1) | 7.7 | 35.8 | 27.7 | 1.0 | 4.7 | 0.080 |
| 33 | | MeOH–MeCN (1:9) | 2.1 | 29.5 | 21.6 | 1.2 | 3.1 | 0.081 |
| 34 | | MeOH–MeCN (1:99) | 1.3 | 29.7 | 26.8 | 0.3 | 1.3 | 0.028 |
| 35 | | MeOH–THF (1:1) | 11.4 | 29.1 | 20.3 | 0.3 | 0.6 | 0.015 |
| 36 | | MeOH–THF (1:9) | 2.8 | 17.2 | 30.9 | 0.3 | 1.3 | 0.031 |
| 37 | | MeOH–THF (1:99) | 0 | 5.4 | 27.0 | 0 | 0.3 | 0.0093 |

[a] Initial concentrations of **2** and **5a**, both $1.00 \times 10^{-1}$ M; reaction time, 15 minutes; in the dark at 20°C under an argon atmosphere. [b] Based on **5a** used otherwise indicated; determined by GC. The yield of **8a** was not determined.
[c] The ratio of total yield of phosphinates to that of phosphonates.



$$\text{Ph-P(OR)}_2 \xrightarrow[\text{at 20 °C; under Ar atm.; in MeOH or EtOH}]{+\ \mathbf{5a}}$$

**2a**; R = Me
**2b**; R = Et

$$\text{Ph-}\overset{\text{O}}{\overset{\|}{\text{P}}}\text{(OMe)}_{2-m}\text{(OEt)}_m + \text{Ph-}\overset{\text{O}}{\overset{\|}{\underset{\text{Ar}}{\underset{|}{\text{P}}}}}\text{(OMe)}_{1-m}\text{(OEt)}_m + \mathbf{8a}$$

**9a**; m = 0
**9b**; m = 1
**9c**; m = 2

**10a**; m = 0
**10b**; m = 1

Ar = 4-methylphenyl

**SCHEME 3**

phenylphosphinate (**10a**), was also obtained. The yield of **8a** produced was not determined.

## *DISCUSSION*

### *Dediazoniation of* 5 *with Trivalent-Phosphorus Compounds*

Dediazoniation of arenediazonium salts with trialkyl phosphites (**1**) or triphenylphosphine (**14**) in an alcoholic solvent proceeds according to a radical-chain process initiated by single-electron transfer (SET) from the former to the latter, as a result of which the aryl radical Ar· and the cation radicals **15a** and **15d**, respectively, are generated (Scheme 6) [9]. Such a chain character of the reaction has again been confirmed in this work. Thus, **8a** is formed in more than a stoichiometric amount when the initial amount of **1a** is smaller than that of **5a**. The aerobic conditions suppress the formation of **7a** and **8a**, indicating that radical species are involved in this reaction (Table 1).

Further evidence for the SET mechanism is that solvent THF polymerizes during the reaction of **2** with **5a**. Thus, Ar· initially generated abstracts a hydrogen from THF to afford tetrahydrofuranyl radical, which is oxidized by **5** to an oxonium ion to initiate the cationic polymerization (Scheme 7). Cationic polymerization of THF promoted by a free-radical initiator is well known [11,12]. As expected, added methanol traps the oxonium ion, allowing the dediazoniation of **5** to proceed with little, if any, polymerization of THF [11].

In summary, there is no doubt that trivalent-phosphorus compounds, **1**, **2**, and **3**, donate an electron to **5**, generating **15a**, **15b**, and **15c**, respectively, under the reaction conditions.

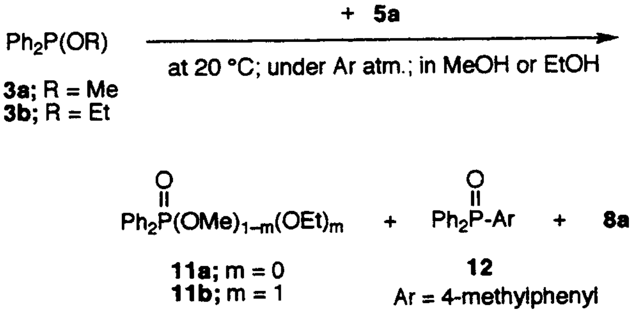
### *Reaction of Cation Radicals* 15

The trivalent-phosphorus compounds are converted to two kinds of the products, the oxidation product (**6**, **9**, and **11** from **1**, **2**, and **3**, respectively) and the arylated product (**7**, **10**, and **12** from **1**, **2**, and **3**, respectively). The formation of the oxidation product is well accounted for by nucleophilic attack of the solvent alcohol on the cation radical **15**; this process affords phosphoranyl radical **16**, which is eventually converted to the oxidation

TABLE 4 Reaction of Alkyl Phosphinite **3** with Diazonium Salt **5a**[a]

| | | | *Yield/%*[b] | | | |
|---|---|---|---|---|---|---|
| | | | *Phosphinate* | | *Phosphine Oxide* | |
| *Entry* | **3** | *Solvent* | **11a** | **11b** | **12** | **A/O**[c] |
| 38 | **3a** | MeOH | 52.0 | — | 1.7 | 0.033 |
| 39 | | EtOH | 5.7 | 45.2 | 3.9 | 0.077 |
| 40 | | EtOH–MeCN (1:1) | 9.6 | 49.6 | 0.9 | 0.015 |
| 41 | | EtOH–MeCN (1:9) | 22.7 | 28.2 | 0.7 | 0.014 |
| 42 | | EtOH–MeCN (1:99) | 39.1 | 15.9 | 0.4 | 0.0073 |
| 43 | **3b** | EtOH | — | 52.3 | 4.2 | 0.080 |
| 44 | | MeOH | 37.4 | 16.1 | 3.4 | 0.064 |
| 45 | | MeOH–MeCN (1:1) | 26.1 | 19.2 | 0.8 | 0.018 |
| 46 | | MeOH–MeCN (1:9) | 22.5 | 28.2 | 0.6 | 0.012 |
| 47 | | MeOH–MeCN (1:99) | 21.9 | 30.1 | 1.2 | 0.023 |

[a] Initial concentrations of **3** and **5a**, both 1.00 × $10^{-1}$ M; reaction time, 15 minutes; in the dark at 20°C under an argon atmosphere.
[b] Based on **5a** used otherwise indicated; determined by GC. Diphenylphosphinic fluoride (>10%) was detected. The yield of **8a** was not determined.
[c] The ratio of yield of phosphine oxide to total yield of phosphinates.



**SCHEME 4**

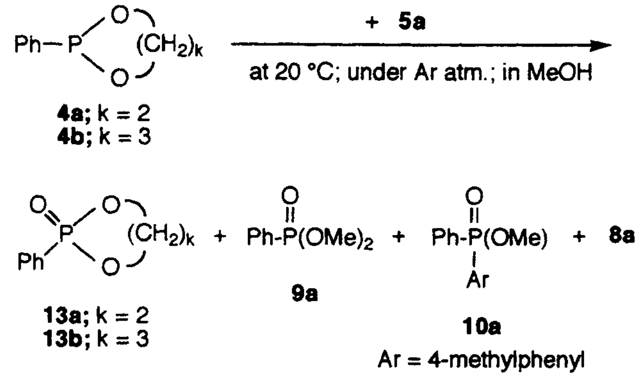
product (Scheme 8) [5,6]. Highly likely, the arylated product results also from **15**, since the aerobic conditions suppress the formation of this product. Thus, **15** may also undergo radical coupling with Ar· to give phosphonium ion **17**, a precursor of the arylated product.

Phosphoranyl radicals with and without aryl ligand(s) exhibit small and large $a_P$-values in their ESR spectra, respectively, indicating low and high spin densities on the central phosphorus atoms in the former and the latter, respectively [13]. That is, the unpaired electron developed on the phosphorus in a phosphoranyl radical delocalizes well into adjacent aryl ligand(s) if available. The unpaired electrons in cation radicals **15b** and **15c** would likewise delocalize into their phenyl ligands, whereas the unpaired electron in **15a** would be dominantly developed on the central phosphorus atom. As a result, **15a** would exhibit the highest reactivity with respect to radical coupling with Ar· among **15a–c**. Table 6 shows that the ratio of the yield of the arylated product to that of the oxidation product **A/O** is largest in the reaction of **1**.

TABLE 5 Reaction of Cyclic Phosphonites **4** with Diazonium Salt **5a** in MeOH[a]

| | | | *Yield/%*[b] | | | | |
|---|---|---|---|---|---|---|---|
| | | | *Phosphonate* | | | *Phosphinate* | |
| *Entry* | **4** | **4/5a**[c] | **13a** | **13b** | **9a** | **10a** | **9a/13**[d] |
| 48 | **4a** | 0.5 | 14.9 | — | 6.1 | 2.3 | 0.409 |
| 49 | | 1.0 | 17.6 | — | 7.9 | 1.9 | 0.449 |
| 50 | | 2.0 | 21.7 | — | 10.2 | 0.9 | 0.470 |
| 51 | **4b** | 0.5 | — | 11.2 | 22.6 | 2.8 | 2.018 |
| 52 | | 1.0 | — | 12.1 | 18.7 | 2.0 | 1.545 |
| 53 | | 2.0 | — | 14.0 | 13.2 | 0.8 | 0.943 |

[a] Initial concentration of **4**, 1.00 × $10^{-1}$ M; reaction time, 15 minutes; in the dark at 20°C under an argon atmosphere.
[b] Based on **4** used; determined by GC. The yield of **8a** was not determined.
[c] The ratio of the initial amount of **4** to that of **5a**.
[d] The ratio of the yield of **9a** to that of **13**.



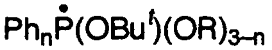
**SCHEME 5**

**TABLE 6** Yield Ratio of the Oxidation and the Arylated Products[a]

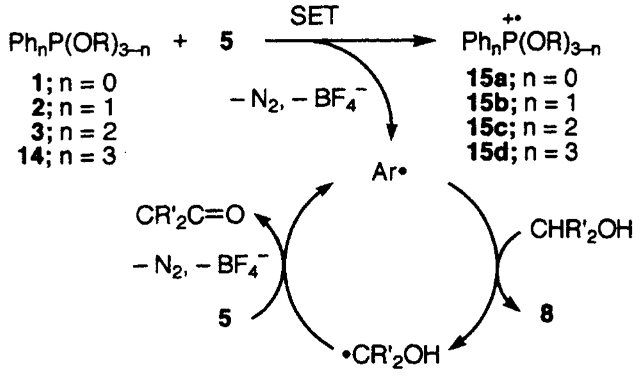
| Entry | Trivalent Phosphorus | Yield/%[b] O[c] | Yield/%[b] A[d] | A/O[e] | $a_P$-Value/G[f] |
|---|---|---|---|---|---|
| 1 | **1a** | 80.5 | 17.2 | 0.21 | 890 (**18**)[g] |
| 10 | **1b** | 87.9 | 9.4 | 0.11 | — |
| 22 | **2a** | 79.9 | 1.7 | 0.021 | 9.25 (**19**)[h] |
| 31 | **2b** | 85.2 | 5.3 | 0.062 | — |
| 38 | **3a** | 52.0 | 1.7 | 0.033 | 23.0 (**20**)[h] |
| 44 | **3b** | 53.5 | 3.4 | 0.064 | — |
| 49 | **4a** | 25.5 | 1.9 | 0.075 | — |
| 52 | **4b** | 30.8 | 2.0 | 0.065 | — |

[a] Initial concentrations of trivalent-phosphorus compound and **5a**, both 1.00 × $10^{-1}$ M; reaction time, 15 minutes; in the dark at 20°C in MeOH under an argon atmosphere unless otherwise noted.
[b] Based on **5a** used otherwise indicated; determined by GC.
[c] Total yield of the oxidation products.
[d] Total yield of the arylated products.
[e] The ratio of total yield of the arylated products to that of the oxidation products.
[f] Values for the related phosphoranyl radicals designated in parentheses.
[g] From Ref. [13].
[h] From Ref. [14].

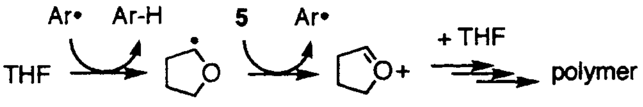
Correlations of **A**/**O** with the reported $a_P$-values for phosphoranyl radicals **18**, **19**, and **20** [13,14], the structures of which are related to **15a**, **15b**, and **15c**, respectively, are seen for the reactions of the methyl or the ethyl esters in methanol or ethanol (Fig. 3) [15]. Presently, it is not clear why the reactions of the methyl esters in methanol are much more sensitive to the change in the spin density than the other reactions.


$\mathrm{Ph_n\dot{P}(OBu^t)(OR)_{3-n}}$

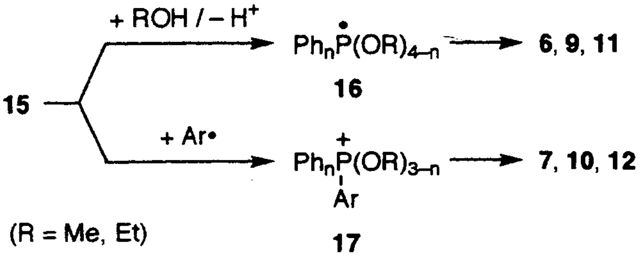
**18**; n = 0
**19**; n = 1
**20**; n = 2



**SCHEME 6**



**SCHEME 7**



**SCHEME 8**

Rationalization of observed results precludes a mechanism in which Ar· attacks the phosphorus atom in the starting trivalent-phosphorus compound, and the resulting phosphoranyl radical decomposes to the observed arylated product. This mechanism predicts that a trivalent-phosphorus compound from which a more stable phosphoranyl radical results would afford the arylated product in a higher yield [16]. The results are contrary to this prediction; while a phosphoranyl radical with the higher number of phenyl ligands should be more stable, the arylated product is obtained in the highest yield from the reaction with the compound **1** that has no phenyl group.

The last columns in Tables 1, 3, and 4 show a general tendency that the product ratio **A**/**O** becomes smaller with a decreasing content of alcohol in alcohol-acetonitrile or alcohol-THF mixture. Acetonitrile or THF is a better hydrogen donor than alcohols toward a free radical. Accordingly, the higher content of acetonitrile or THF results in more efficient conversion of Ar· to ArH, making the radical coupling of Ar· with **15** less favorable [17]. Phosphite **3a** reacts with **5a** in acetonitrile to give

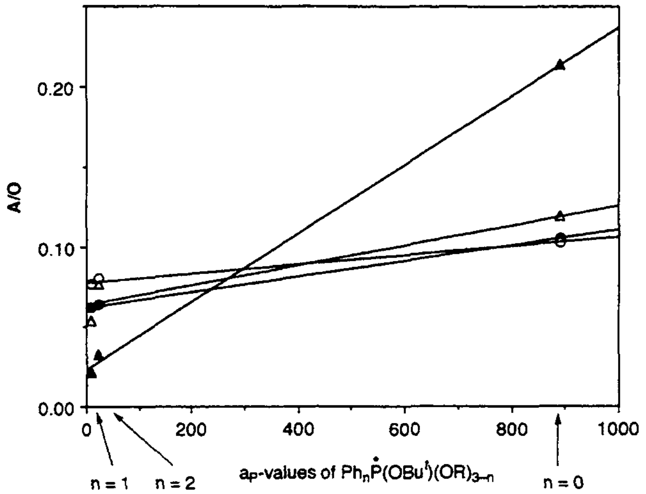


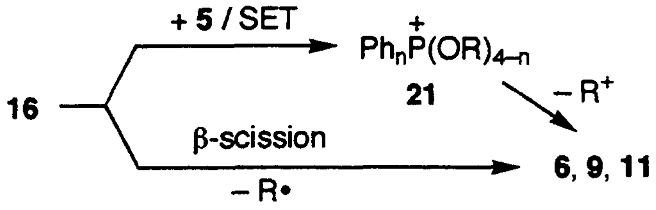
**FIGURE 3** Correlations between the yield ratios **A/O** and $a_P$-values of the related phosphoranyl radicals for the reactions of **1a** in methanol (▲), of **1a** in ethanol (●), of **1b** in methanol (△), and of **1b** in ethanol (○).

only a small amount of **11a** ($^{31}$P NMR assay), which results probably from the ionic reaction of **15** with a trace amount of water in the solvent. In this reaction, phosphonium ion **17**, which would result from the radical coupling of **15** with Ar·, is detectable by $^{31}$P NMR spectroscopy only in a trace amount. This fact indicates that Ar· abstracts a hydrogen from acetonitrile too rapidly to undergo a radical coupling with **15** in acetonitrile.

It is thus concluded that **15** undergoes both an ionic reaction with the solvent alcohol and a radical coupling with Ar· to give the oxidation and the arylated products via **16** and **17**, respectively (Scheme 8) [10]. The latter reaction is facilitated by high spin density on the central phosphorus atom in **15**. Hereafter, we term the reaction sequences leading to the former and the latter reactions as the "ionic path" and the "radical path," respectively, to avoid tedious expressions in the remainder of this article.

### *Reaction of Phosphoranyl Radicals* 16

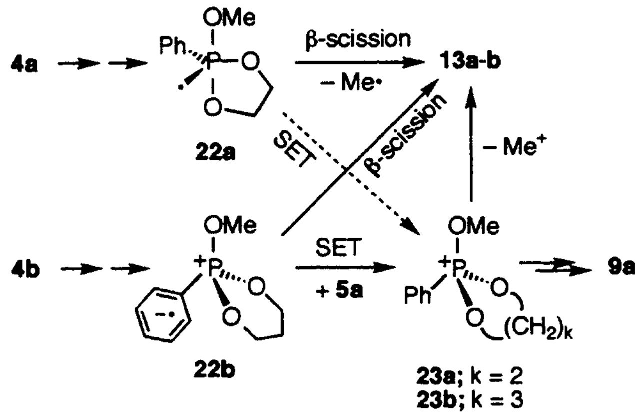
When a phosphonium ion that has more than one alkoxyl ligand decomposes to the corresponding neutral oxo-compound in alcohol, successive replacement of its alkoxyl ligands by the alkoxyl from the solvent takes place through successive phosphonium-phosphorane equilibria [9,18]. In other words, the formation of the products that have experienced such transesterification is evidence for a phosphonium ion intermediacy. The transesterification is in fact observed during the radical path that includes phosphonium intermediate **17**; the reaction of **1a** or **2a** in ethanol or the reaction of **1b** or **2b** in methanol gives a mixture of the arylated products in which the original alkoxyl ligands of the substrate have been successively replaced by the alkoxyl group from the solvent (Tables 1, 3, and 4).



**SCHEME 9**

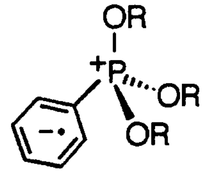
The transesterification is also observed during the ionic path that includes phosphoranyl intermediate **16**. Thus, the transesterified products are obtained in the reaction of **1a**, **2a**, or **3a** in ethanol or of **1b**, **2b**, or **3b** in methanol (Tables 1, 3, and 4). The degree of transesterification is higher when an alcohol-acetonitrile or alcohol-THF mixture contains a higher concentration of the alcohol. In addition, methoxyl ligands in the reactant are more easily replaced by ethoxyl groups from the solvent than ethoxyl ligands by methoxyl groups from the solvent; that is, replacement by an alkoxyl group with higher nucleophilicity is more facile. These findings indicate clearly an intermediacy of phosphonium ion **21** during the ionic path (Scheme 9). Therefore, **16** must undergo SET to produce **21** during this reaction path. Table 2 shows that the product ratio **A/O** increases with an increasing ratio of the initial amount of **1** to that of **5b**, **1/5b**; a smaller amount of **5b** makes the ionic path less favorable. This observation suggests that a surplus of **5** causes SET from **16** to produce **21**. Comparison of half-wave redox potentials of phosphoranyl radicals [19] and diazonium salts [20] suggests that this SET process is highly exothermic. β-Scission of **16** could afford the transesterified oxidation products, **6b**, **9b**, and **11b**, from the reactions of **1**, **2**, and **3** in ethanol, respectively, but this mode of decomposition does not account for the formation of "more transesterified" products, **6c**, **6d**, and **9c**. The formation of these products is clear evidence for SET from **16**.

Nevertheless, if **16** decomposes only through SET, no oxidation product would be formed when the ratio **1/5** is larger than unity because, with this ratio of the starting materials, there is no **5** left available for the second SET. The fact is that the oxidation products are produced even when the initial amount of **1** is higher than that of **5** (Table 2), which means that there is another pathway in which **16** is converted to the oxidation products without the aid of an oxidant. Thus, β-scission of **16** takes place in competition with SET (Scheme 9). β-Scission with liberation of a methyl or ethyl radical is not unusual, although such a radical is



SCHEME 10

relatively unstable [21]. It has been also reported that a phenyl ligand on a phosphoranyl radical remarkably accelerates the rate of β-scission [14,22]. This mechanism predicts that β-scission becomes more predominant as **1**/**5** increases, making the ratios of the yields of the transesterified products smaller. This is what we have observed (Table 2, entries 18–21).



(R = Me, Et)

**16b**

The results from the dediazoniations of **5a** with cyclic phosphonites **4a** and **4b** help us to inspect the mechanism proposed here. According to this mechanism, phosphoranyl radicals **22a** and **22b** are generated from **4a** and **4b**, respectively, during the ionic path (Scheme 10). Phosphoranyl radical **22b** that has a six-membered ring is likely to adopt tetrahedral geometry the same as its acyclic analog **16b** [13,14], since there is no strain in this structure. Therefore, **22b** behaves like **16b** and decomposes through either SET or β-scission. Phosphonium ion **23b**, formed through SET, undergoes transesterification with the alkoxyl from the solvent methanol. That is, SET from **22b** eventually produces **9a** in which the ring structure has been replaced by methoxyl groups, as well as **13b**. Meanwhile, β-scission of **22b** would afford **13b** without ring-opening (vide infra). Relative ease of SET and β-scission is therefore represented by the ratio of the products **9a**/**13b**. As expected, **9a**/**13b** decreases with increase in the ratio of the initial amounts of the starting materials **4b**/**5a** (Table 5); SET from **22b** becomes less favorable with a decreasing amount of **5a**. On the other hand, **13a** is formed as a major oxidation product in the reaction of **4a**, indicating that SET is only a minor pathway for the decompostion of **22a**. Phosphoranyl radical **22a** adopts a trigonal-bipyramidal (TBP) geometry in which the ring bridges the apical and equatorial sites [23]. It seems likely that β-scission of **22a** occurs with liberation of a methyl radical from an apical position without ring-opening, giving **13a** [24]. It is not certain whether β-scission is apical [25] or equatorial [26] site selective, but a phosphoranyl radical originating from a phosphite with a five-membered ring is known to undergo β-scission without ring-opening [25,26]. Reluctance of **22a** to undergo SET is probably due to the additional energy required for the structural change during its conversion to a tetrahedral intermediate, **23a**.

In conclusion, phosphoranyl radical **16** initially produced during the ionic path decomposes to the product through either SET to **5** or β-scission by liberating a methyl or ethyl radical. A previous report as to the photoreaction of isopropyl diphenylphosphinite with acridinium iodide has demonstrated that a phosphoranyl radical with an isopropoxyl ligand decomposes exclusively through SET, an iodine atom being an electron acceptor. Importantly, the β-scission of this phosphoranyl radical could liberate an isopropyl radical that is more stable than a methyl or ethyl radical [7]. Thus, β-scission of a phosphoranyl radical can take place only when an electron acceptor is absent in the reaction mixture.

## *EXPERIMENTAL*

### *Instruments*

The GC analysis was performed with a Shimadzu GC-12A gas chromatograph. Mass spectra were obtained on a Shimadzu GCMS-QP2000A gas chromatograph mass spectrometer equipped with a Shimadzu GC-MSPAC 200S data processor. $^{1}$H and $^{31}$P NMR spectra were recorded on a Varian XL 200 NMR spectrometer.

### *Materials*

Trimethyl (**1a**) and triethyl phosphite (**1b**) were commercially available (Tokyo Chemical Industry Co., Tokyo, Japan) and distilled prior to use.

Dimethyl (**2a**) and diethyl phenylphosphonite (**2b**) [27] were prepared by addition of an ether solution (20 mL) containing equimolar amounts (0.080 mol) of methanol or ethanol, respectively, and pyridine to an ether solution (20 mL) of dichlorophenylphosphine (0.040 mol), contained in an ice bath, through an addition funnel. The precipitate was filtered off, and the organic layer was concentrated in vacuo. Distillation of crude materials gave

**TABLE 7** $^{31}P$ NMR Chemical Shifts of Products from Dediazoniation of **5** with **1**, **2**, **3**, and **4**[a]

| *Compound* | $\delta^b$ | *Compound* | $\delta^b$ |
|---|---|---|---|
| **6a** | 3.5 | **9a** | 23.5 |
| **6b** | 2.3 | **9b** | 22.0 |
| **6c** | 1.1 | **9c** | 20.5 |
| **6d** | −0.2 | **11a** | 34.5 |
| **7a** | 24.2 | **11b** | 33.5 |

[a] In $CD_3OD$.
[b] From $H_3PO_4$ in ppm.

the phosphonites **2a** and **2b** (2.8 g, 35% and 5.2 g, 25%, respectively). **2a**; bp 49–50°C (0.5 torr). $^{31}P$ NMR (in $CD_3OD$, $\delta$ from $H_3PO_4$) 161.9. **2b**: bp 40–41°C (0.5 torr).

2-Phenyl-1,3,2-dioxaphospholan (**4a**) and 2-phenyl-1,3,2-dioxaphosphorinan (**4b**), were obtained by condensation of 1,2-ethanediol and 1,3-propanediol, respectively, with dichlorophenylphosphine, as described in the literature [28]. Crude materials were purified by distillation. **4a**: 10%, bp 52–53°C (0.5 torr); MS $m/z$ 168, 140, 124, 91. **4b**: 22%, bp 61–62°C (0.5 torr) (Ref. [28] 78–80°C (1.0 torr)); MS $m/z$ 182, 141, 124, 105.

Procedures for the preparation of methyl (**3a**) and ethyl diphenylphosphinite (**3b**) have been previously reported [29]. Diazonium salts **5a** and **5b** were prepared as described in the literature [30].

### *General Procedure*

To the solution of 0.10 mmol of diazonium salt **5** in 0.75 mL of an appropriate solvent contained in a reaction vessel equipped with a septum and filled with argon gas was introduced a 0.25 mL solution containing 0.10 mmol of a trivalent-phosphorus compound. After a 15 minute reaction period, the reaction mixture was analyzed by GC and GCMS. Dodecane was used as an internal standard for determination of the yields of the products. For NMR analysis, the reaction was carried out in a deuterated solvent in an NMR tube. The observed signals were assigned, based on the comparison with the reported data [31]. $^{31}P$ NMR chemical shifts thus obtained in the reaction mixtures are summarized in Table 7.

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