Synthesis of 1,4-Dioxa-2λ⁵-phosphorinanes by Insertion of Triphenylalkylidenephosphoranes into the Peroxide Bond of 1,2-Dioxetanes: Thermolysis, Hydrolysis, and Wittig Olefination

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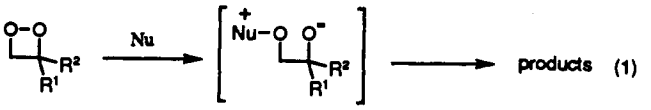
Abstract: The reaction of the methyl-substituted 1,2-dioxetanes **1–3** with triphenylalkylidenephosphoranes **4–7** was investigated. By nucleophilic attack of the negatively charged phosphorane carbon atom at the peroxide bond of the 1,2-dioxetanes, the dipolar phosphonium alkoxides **8–13** were formed, which were in equilibrium with the ring-closed 2,2,2-triphenyl-1,4-dioxa-2λ⁵-phosphorinanes **14–19**. Hydrolysis of the phosphonium alkoxides **8–12** afforded the phosphine oxides **21–25** by benzene elimination. For the phenyl-substituted phosphonium alkoxide **13**, hydrolysis led to the benzyl ether **26**, while deprotonation at the α carbon atom resulted in the corresponding ylide, which on air oxidation led to benzoate **27** and triphenylphosphine oxide. In the presence of benzaldehyde, the ylide derived from phosphonium alkoxide **8** was trapped in the form of the novel 3-hydroxy enol ether **28** through stereoselective Wittig olefination, which establishes the phosphonium alkoxides **8–13** as potentially useful *in situ* building blocks.

Introduction

Since their discovery in 1969,[1] numerous chemical transformations of the labile 1,2-dioxetanes have been documented.[2] Among the long-known reactions figure the reductions with lithium aluminium hydride[3] and mercaptans,[4] the insertion reactions with phosphines,[5] arsines, and stibines,[6] and the deoxygenation reactions with sulfides[7] and sulfoxylates.[8] Only recently has the general scope of S_N2 reactivity been established for 1,2-dioxetanes, namely for 3,3-disubstituted derivatives. Carbanions[9] and heteroatom[10] as well as π nucleophiles, e.g., enamines,[11] olefins, and enol ethers[12] undergo nucleophilic substitution at the sterically more exposed site of the peroxide bond in the 3,3-disubstituted dioxetanes (eq 1) to afford a variety of products derived from the intermediary nucleophile–dioxetane adducts.

On the other hand, when trivalent phosphaalkenes are oxidized by molecular oxygen, the corresponding ketone and a polymeric material of the phosphorus-containing moiety are formed. The oxidation mechanism was shown to involve first the oxidation of the phosphorus atom and subsequent formation of a dioxaphosphetane, which cleaves to the ketone and the phosphinidene oxide. Further oxidation of the latter furnishes the phosphinidene dioxide.[13] However, upon protection of the phosphorus lone pair of the phosphaalkene by coordination to a metal fragment, the oxidation by *m*-chloroperbenzoic acid results in a stable oxaphosphirane complex, as was confirmed by X-ray crystallography[14] (eq 2).



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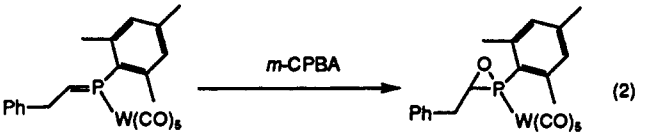

(2)

Reactions of pentavalent phosphorus ylides with *organic peroxides* have, to our knowledge, not been performed until now. The propensity of such ylides for oxidation is manifested in the reaction with singlet oxygen,[15] ozone,[16] and potassium peroxymonosulfate,[17] in which carbonyl products and the corresponding phosphine oxides are obtained.

The reaction of trimethylmethylenephosphorane with the parent oxirane and oxetane[18] afforded five- and six-membered ring insertion products, which contain a pentacoordinated phosphorus functionality. For these strained cyclic ethers, nucleophilic attack by the negatively charged carbon atom of the phosphorus ylide

† Undergraduate research participant, March to May, 1992.

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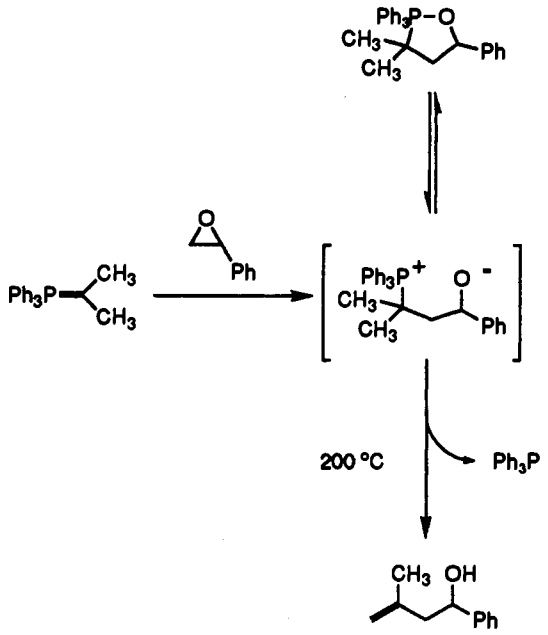
Scheme 1



takes place at the epoxide or oxetane carbon atoms, and subsequent cyclization of the zwitterionic intermediates generates the cyclic phosphoranes (Scheme 1). For example, substituted 1,2λ⁵-oxaphospholanes were obtained in the reaction of triphenylisopropylidenephosphorane with styrene epoxide,[19] while spirocyclic phosphoranes resulted from the reaction of 1-methyl-1-methylene-1λ⁵-phospholane with the parent oxirane.[18]

In view of the aforementioned, reaction of the 1,2-dioxetanes with the phosphorus ylides was expected. In contrast, however, to reaction with the strained cyclic ethers, nucleophilic attack of the phosphorus ylides should occur, as established for all nucleophiles examined so far, at the peroxide bond of the 1,2-dioxatenes to generate a zwitterionic phosphonium alkoxide. The latter may cyclize to the 2,2,2-triphenyl-1,4-dioxa-2λ⁵-phosphorinanes as insertion products. Indeed, herein we present our results which establish this novel transformation of 1,2-dioxetanes with phosphorus ylides.

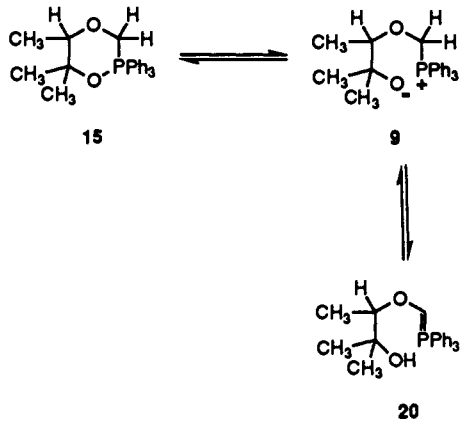
Results

The reactions of dioxetanes **1–3** with the phosphoranes **4–7** were carried out at low temperatures (−78 to −10 °C) in dry ether or toluene under a nitrogen gas atmosphere for the rigorous exclusion of moisture and air (Scheme 2). Under these conditions, the phosphorinanes **14–19** were formed quantitatively, as established by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy directly on the reaction mixture. An exception is the reaction of 3,3-dimethyldioxetane (**1**) with triphenylbenzylidenephosphorane (**7**), in which besides ca. 70% of the phosphorinane **19**, also ca. 30% of the phosphonium alkoxide **13** was detected in the crude product mixture. All reactions of 3,3-dimethyldioxetane (**1**) with the phosphoranes **4–7** were finished within 1 min at −78 °C, as was established by the lack of the peroxide test (KI/HOAc) and the disappearance of the intense color of the ylides.

Triphenylmethylenephosphorane (**4**) gave along with the methyl-substituted dioxetanes **1–3** at −78 °C in dry ether the phosphorinanes **14–16**. The reaction times for complete conversion of the dioxetanes **1–3** at −78 °C were determined iodometrically to follow the order **1** (ca. 1 min) < **2** (ca. 10 min) ≪ **3** (6000 min).

When the reaction of dioxetane **1** with phosphorane **4** was run in toluene at −10 °C, the only observed product was the phosphonium alkoxide **8**. No phosphorinane **14** could be detected at this temperature, as confirmed by ^{31}P NMR spectroscopy at −10 °C.

At −40 °C, the phosphorinanes **14–19** persisted, but upon standing at room temperature for several days, they underwent P–O bond heterolysis to yield quantitatively the corresponding open-chain phosphonium alkoxides **8–13** (Scheme 2), as established by ^{1}H, ^{13}C, and ^{31}P NMR monitoring directly on the reaction mixture. In the case of the 1,4-dioxa-2λ⁵-phosphorinane **15**, besides the phosphonium alkoxide **9**, also the tautomeric oxymethylidenephosphorane **20** was observed by NMR spectroscopy (doublet α carbon at δ 17.9, $^1J_{PC}$ = 124.1 Hz) in a ratio of 43:57 (eq 3).



15 **9** **20** (3)

^{13}C and ^{31}P NMR spectroscopy provided definitive and direct evidence for the open-chain phosphonium alkoxides **8–13** and the cyclic phosphorinanes **14–19**. The carbon–phosphorus coupling and the multiplicities of the carbon atoms were used to assign and differentiate between the phosphonium alkoxide (**8–13**) and the phosphorinane (**14–19**) structures. While the phosphorinanes **14–19** exhibited a phosphorus–carbon, two-bond coupling for the C-6 atom of the phosphorinane ring (the $^2J_{PC}$ coupling constants were 10.4–11.2 Hz for **14–17** and **19** and 2.5 Hz for **18**), the open-chain phosphonium alkoxides **8–13** did not show this coupling. Furthermore, the resonances at δ −38.6 to −43.8 in the ^{31}P NMR spectra for the phosphorinanes **14–19** are characteristic for pentavalent phosphorus compounds. For comparison, the phosphorus atom in the five-membered ring system 1,2λ⁵-oxaphospholane, obtained in the reaction of styrene epoxide with triphenylisopropylidenephosphorane, exhibits a ^{31}P NMR resonance at δ −49.2.[19]

Moreover, the ring-opening process could also be monitored by ^{31}P NMR spectroscopy, in which the resonances of the phosphonium alkoxides **8–13** appeared in the range between δ 24 and 31. These values are typical for tetravalent phosphorus compounds with four alkyl and aryl substituents at the phosphorus atom (e.g., triphenylmethylphosphonium iodide shows a ^{31}P NMR resonance at δ 21.9). Finally, the P–O–C stretching frequency at 1115 cm^{-1} in the IR spectra of the phosphorinanes **14–19** disappeared upon thermal transformation to the phosphonium alkoxides **8–13**.

These findings provide clear evidence for the P–O bond heterolysis during the ring-opening of the phosphorinanes **14–19** to the phosphonium alkoxides **8–13** (eq 3). To prove the reversibility of this process, a solution of the phosphonium alkoxide **8** in deuteriochloroform was cooled to −50 °C for several days. The ring reclosure to the phosphorinane **14** was confirmed by direct spectral measurements as described above.

Due to the extreme hygroscopic nature of the phosphonium alkoxides **8–13** and the phosphorinanes **14–19**, no satisfactory elemental analyses could be obtained for these new compounds. Thus, for the purpose of chemical characterization, deliberate

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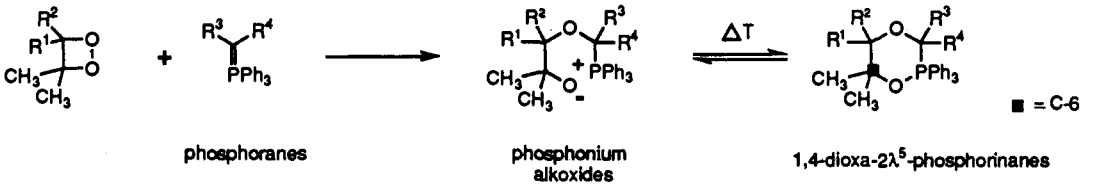
Scheme 2

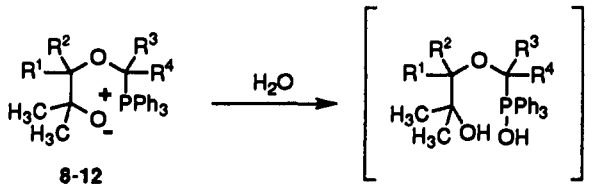


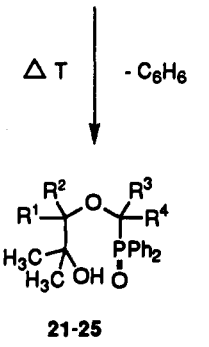
	R^1	R^2
1	H	H
2	CH_3	H
3	CH_3	CH_3

	R^3	R^4
4	H	H
5	CH_3	H
6	CH_3	CH_3
7	Ph	H

	R^1	R^2	R^3	R^4	
8	H	H	H	H	14
9	CH_3	H	H	H	15
10	CH_3	CH_3	H	H	16
11	H	H	CH_3	H	17
12	H	H	CH_3	CH_3	18
13	H	H	Ph	H	19

Scheme 3



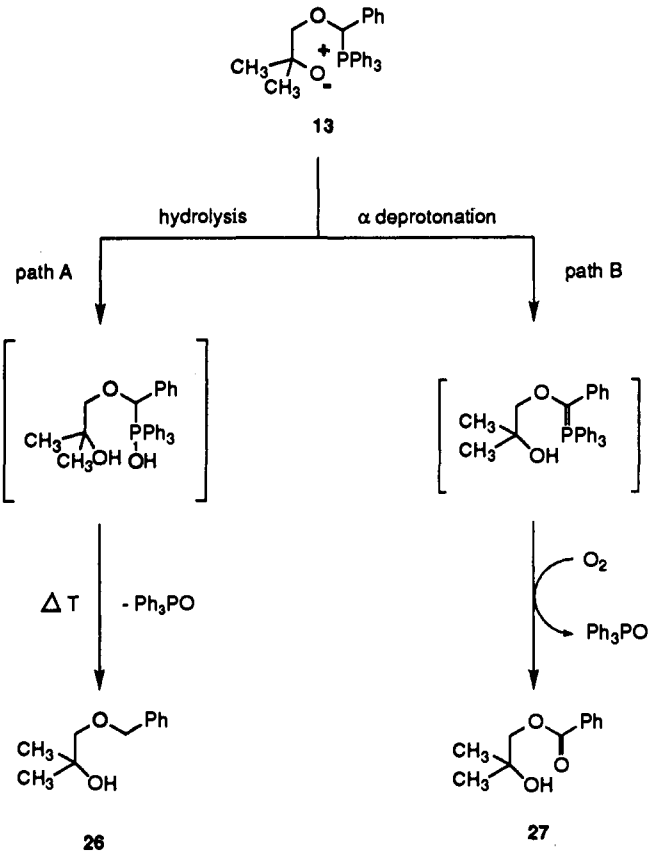


	R^1	R^2	R^3	R^4
8, 21	H	H	H	H
9, 22	CH_3	H	H	H
10, 23	CH_3	CH_3	H	H
11, 24	H	H	CH_3	H
12, 25	H	H	CH_3	CH_3

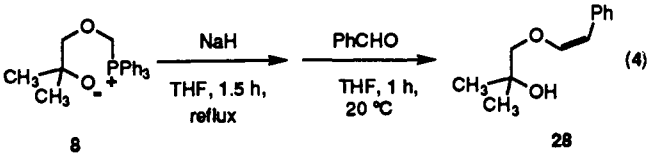
hydrolysis of the phosphonium alkoxides **8–13** was performed under controlled conditions. With sodium hydroxide in a 2:1 methanol/water mixture, the phosphine oxides **21–25** (Scheme 3) were isolated in 66–93% yields, purified by column chromatography, and fully characterized. Instead of aqueous NaOH (alkaline conditions), for practical reasons the hydrolysis of the mixture of phosphonium alkoxide **13** and phosphorinane **19** was performed in water (neutral conditions) at room temperature. Column chromatography on silica gel afforded 80% of a 49:51 mixture of the known 1-(benzyloxy)-2-methylpropan-2-ol (**26**) and 2-hydroxy-2-methylpropyl benzoate (**27**), as displayed in Scheme 4. Additionally, 85% of triphenylphosphine oxide and 17% of 2-methylpropane-1,2-diol were isolated. The diol is presumably the hydrolysis product of the benzoate **27**, while the triphenylphosphine oxide results from autoxidation of the intermediary ylide (Scheme 4, path B).

To confirm the intervention of such ylides, a Wittig olefination experiment was conducted. For this purpose the phosphonium alkoxide **8** was refluxed with sodium hydride in dry tetrahydrofuran under a nitrogen gas atmosphere, followed by the addition of benzaldehyde. Indeed, a 47% yield of 2-methyl-1-((2-phenylethenyl)oxy)propan-2-ol (**28**) was obtained after column chromatography on silica gel (eq 4). This trapping reaction not only establishes the intermediacy of the ylide, but also the synthetic potential of the phosphonium alkoxides for the preparation of

Scheme 4



hydroxy enol ethers becomes evident, especially since exclusively the *Z* isomer is formed.



Discussion

In view of our previous work on 1,2-dioxetanes,[2] the formation of the phosphonium alkoxides **8–13** and the 1,4-dioxa-2λ⁵-phosphorinanes **14–19** can most reasonably arise from nucleophilic attack of the negatively charged ylide carbon atom at the peroxide

bond of the dioxetanes **1–3**. This S_N2 process affords the phosphonium alkoxides **8–13**, which are in equilibrium with their phosphorinanes **14–19** (Scheme 2). In such a nucleophilic attack, the phosphorane carbon lone pair (HOMO) is for stereoelectronic reasons obliged to approach the dioxetane along the direction of the σ^* orbital (LUMO) of the peroxide bond.

The approach of the attacking phosphorane should be sterically impeded when the C-4 atom of the dioxetane ring bears bulky substituents. Hence, a slower reaction rate would be expected for substrates with substituents at the C-4 position of the dioxetane ring. Indeed, for the reaction of the 3,3-dimethyl- (**1**), trimethyl- (**2**), and tetramethyldioxetane (**3**) with triphenylmethylenephosphorane (**4**), the relative rates were found to be 1:10:6000. Clearly, this dramatic rate effect speaks for the proposed S_N2 mechanism (Scheme 2). In contrast to the 1,2-dioxetanes **1–3**, the degree of substitution at the ylide carbon atom had essentially no effect on the overall reactivity of the phosphoranes **4–7**. Apparently electronic and steric factors are balanced in such a way that rate effects are not displayed in the phosphorinane formation.

When the reaction of phosphorane **4** with 3,3-dimethyldioxetane (**1**) was carried out at −10 °C, the only observed product was the phosphonium alkoxide **8** (Scheme 2); no phosphorinane **14** could be detected by ^{31}P NMR spectroscopy. Moreover, the authentic phosphorinane **14** was converted completely to the phosphonium alkoxide **8** only after several days at room temperature. It is thus unlikely that the phosphorinane **14** is formed first through direct insertion of the phosphorane **4** into the peroxide bond of the dioxetane **1** and is subsequently ring-opened to the phosphonium alkoxide **8**. A similar situation applies to all the other phosphorinanes except **19**, derived from the reaction (Scheme 2) of 3,3-dimethyldioxetane (**1**) with triphenylbenzylidenephosphorane (**7**), for which ca. 30% of the phosphonium alkoxide **13** persist even at −78 °C. Presumably, steric interactions between the phenyl ring at the C-3 position and those of the phosphorus atom are responsible, since such steric buttressing is expected to promote the ring-opening of **19** to **13** even at low temperatures.

Such temperature-dependent, reversible formation of pentavalent phosphorus species is known for the reaction of triphenylmethylenephosphorane (**4**) with methanol and ethanol.[20] At low temperatures, the alcohols add to the double bond of the phosphorane to yield the pentavalent triphenylmethylalkoxyphosphoranes. At room temperature, the process is reversed, and ylide and alcohol are regenerated. P–O bond heterolysis is also postulated in the pyrolysis of 1,2λ^5-oxaphospholanes, which affords triphenylphosphine and the homoallylic alcohol (Scheme 1),[19] and in the fragmentation of 1,3-dioxa-2λ^5-phospholanes to epoxides and triphenylphosphine oxide.[5] Furthermore, the reaction of 1,2-dioxetanes with other π nucleophiles, e.g., the electron-rich enol ethers, was proposed to proceed through an 1,6 dipole derived from the nucleophilic attack of the π bond on the peroxide bond of the dioxetane.[12]

All the phosphonium alkoxides led to the respective phosphine oxides **21–25** on hydrolysis (Scheme 3). It has been established[21,22] in the hydrolysis of phosphonium hydroxides that the phosphorus substituent is cleaved which can best stabilize the incipient negative charge. Therefore, for these phosphonium alkoxides, the phenyl group is preferentially released from the pentavalent phosphorus intermediate in the form of benzene (Scheme 3). However, for the phenyl derivative **13**, a mixture of benzyl ether **26**, benzoate **27**, and triphenylphosphine oxide was obtained (Scheme 4). In the phosphonium alkoxide **13**, the negative charge is better stabilized at the benzyl site, and hydrolysis results in benzyl ether **26** and triphenylphosphine oxide (path A, Scheme 4). Furthermore, since the phenyl ring at the α carbon atom also facilitates deprotonation, an alternative reaction pathway (path B, Scheme 4) constitutes generation of the ylide, which on autoxidation affords the benzoate **27** and triphenylphosphine oxide.

In summary, the nucleophilic attack of the alkylidenephosphoranes **4–7** on the peroxide bond of the 1,2-dioxetanes **1–3** affords first the phosphonium alkoxides **8–13**, which are in equilibrium with their ring-closed isomers, namely the phosphorinanes **14–19** (Scheme 2). Subsequent hydrolysis of the phosphonium alkoxides **8–12** gives the phosphine oxides **21–25** (Scheme 3). For the phenyl substituted phosphonium alkoxide **13**, hydrolysis yields the benzyl ether **26**. Additionally, deprotonation at the α position results in the corresponding ylide and its subsequent air oxidation to the benzoate **27** (Scheme 4). In the presence of benzaldehyde, the ylide obtained by sodium hydride deprotonation of phosphonium alkoxide **8** can be trapped in the form of the novel hydroxy enol ether **28** through Wittig olefination (eq 4). The latter transformation constitutes a direct stereoselective synthesis of such otherwise cumbersome to prepare enol ethers.

Experimental Section

General Aspects. Melting points were taken on a Reichert Thermovar Kofler apparatus and are uncorrected. ^1H NMR spectra were recorded on Bruker AC 200 (200 MHz) and Bruker AC 250 (250 MHz) instruments, TMS as internal standard; ^{13}C NMR spectra on Bruker AC 200 (50 MHz) and Bruker AC 250 (63 MHz) instruments, $CDCl_3$ as internal standard; ^{31}P NMR spectra on a Bruker AMX 400 (163 MHz) instrument, 85% H_3PO_4 as external standard. ^1H, ^{13}C, and ^{31}P NMR spectra of the thermolabile phosphorinanes **14–19** were recorded at −20 to −30 °C, and those of all other products were recorded at room temperature. ^{13}C NMR resonances of the phenyl rings always appeared in the regions of 125 and 150 ppm and are listed only when a reliable structural assignment could be made. The first entry in the parentheses refers to the multiplicity of the carbon atom, and the second indicates the carbon–phosphorus coupling. Infrared spectra were recorded on a Perkin-Elmer 1420 ratio recording infrared spectrophotometer. Combustion analyses were carried out by the Microanalytical Division of the Institute of Inorganic Chemistry, University of Würzburg. Column chromatography was done on silica gel (63–200 μm) from Woelm, absorbant/substrate ratio of ca. 100:1. Thin-layer chromatography (TLC) used Polygram SIL G/UV_{254} (40 × 80 mm) from Machery and Nagel; peroxides were detected by 10% aqueous KI solution, other products by means of a 5% ethanolic solution of molybdophosphoric acid.

Dioxetanes **1–3** were synthesized according to literature methods[3] from the corresponding β-bromo hydroperoxides. Triphenylalkylidenephosphoranes **4–7** were obtained by deprotonation of the corresponding triphenylalkylphosphonium halides with sodium amide.[23] Due to the moisture sensitivity of the phosphorus ylides and the products, all reactions of the triphenylalkylidenephosphoranes **4–7** with dioxetanes **1–3** were carried out under rigorous exclusion of water and air under a nitrogen gas atmosphere. All solvents were purified and dried according to literature procedures.

Caution! β-Bromo hydroperoxides and the 1,2-dioxetanes **1–3** may decompose spontaneously when allowed to warm up over 0 °C. Dioxetane **1** in particular must be handled with extreme care, since it may detonate even at lower temperatures.

General Procedure for the Reaction of Dioxetanes 1–3 with Triphenylalkylidenephosphoranes 4–7. A solution of 1.70–2.90 mmol of the phosphoranes **4–7** in 20–40 mL of dry ether or toluene was prepared under a nitrogen gas atmosphere and cooled to −78 °C. The dioxetanes **1–3** were dissolved in 10–20 mL of dry ether or toluene and added to the phosphorane solution. Stirring was continued at −78 °C until a negative peroxide test (KI/HOAc) was obtained. Ether was removed at −50 °C, toluene between −20 and −10 °C under oil pump vacuum (ca. 0.01 Torr). Crystalline products were purified by dissolving in *n*-pentane/methylene chloride mixtures at room temperature and recrystallization at −50 °C. Oily crude product mixtures could not be purified further and were used as such for hydrolysis.

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Reaction of Triphenylmethylenephosphorane (4) with 3,3-Dimethyldioxetane (1). According to the general procedure, 596 mg (2.16 mmol) of triphenylmethylenephosphorane (**4**) and 190 mg (2.16 mmol) of 3,3-dimethyldioxetane (**1**) in 40 mL of dry ether were allowed to react at −78 °C for 1 min. After evaporation of the solvent, the white crystalline product was recrystallized from *n*-pentane/methylene chloride to yield 712 mg (91%) of white plates.

6,6-Dimethyl-2,2,2-triphenyl-1,4-dioxa-2λ⁵-phosphorinane (14): mp 162–163 °C dec; IR (CCl_4) 3080, 3000, 1555, 1485, 1450, 1385, 1200, 1115 cm^{-1}; ^1H NMR (toluene-d_8, 200 MHz) δ 0.89 (s, 6H, CH_3), 3.36 (s, 2H, C[5]H_2), 4.87 (br s, 2H, C[3]H_2), 7.0–7.9 (m, 15H, arom H); ^{13}C NMR (toluene-d_8, 50 MHz) δ 27.2 (q, CH_3), 70.8 (td, $^1J_{PC}$ = 111.7 Hz, C-3), 74.3 (td, $^3J_{PC}$ = 10.0 Hz, C-5), 76.3 (sd, $^2J_{PC}$ = 11.2 Hz, C-6); ^{31}P NMR (toluene-d_8, 163 MHz) δ −38.9.

Reaction of Triphenylmethylenephosphorane (4) with Trimethyldioxetane (2). According to the general procedure, 600 mg (2.17 mmol) of phosphorane **4** and 222 mg (2.17 mmol) of dioxetane **2** in 30 mL of dry ether were allowed to react for 10 min at −78 °C. After evaporation of the solvent, the colorless crude product was dissolved in *n*-pentane/methylene chloride at room temperature and recrystallized at −50 °C to yield 740 mg (90%) of a colorless microcrystalline powder.

5,6,6-Trimethyl-2,2,2-triphenyl-1,4-dioxa-2λ⁵-phosphorinane (15): mp 169–171 °C dec; IR (CCl_4) 3000, 2970, 1640, 1445, 1200, 1190, 1130, 1110, 1040 cm^{-1}; ^1H NMR (toluene-d_8, 200 MHz) δ 0.56 (s, 3H, CH_3), 0.94 (*d*, 3H, $^3J_{HH}$ = 6.4 Hz, CH_3), 1.00 (s, 3H, CH_3), 3.71 (q, 1H, $^3J_{HH}$ = 6.4 Hz, C[5]H), AB system (δ_A = 4.45, dd, 1H, $^2J_{HH}$ = 12.9 Hz, $^2J_{PH}$ = 8.8 Hz; δ_B = 4.80, dd, 1H, $^2J_{HH}$ = 12.9 Hz, $^2J_{PH}$ = 4.5 Hz, CH_2), 7.0–7.2 and 7.6–7.8 (m, 15H, arom H); ^{13}C NMR (toluene-d_8, 50 MHz) δ 17.1 (q, CH_3), 23.5 (q, CH_3), 26.7 (q, CH_3), 72.1 (td, $^1J_{PC}$ = 112.7 Hz, C-3), 79.1 (dd, $^3J_{PC}$ = 8.9 Hz, C-5), 80.1 (sd, $^2J_{PC}$ = 11.1 Hz, C-6); ^{31}P NMR (toluene-d_8, 163 MHz) δ −43.8.

Reaction of Triphenylmethylenephosphorane (4) with Tetramethyldioxetane (3). According to the general procedure, 600 mg (2.17 mmol) of phosphorane **4** and 252 mg (2.17 mmol) of dioxetane **3** in 40 mL of dry ether were allowed to react for 100 h at −78 °C. After evaporation of the solvent at −50 °C, 639 mg (75%) of a yellowish oil remained that could not be brought to crystallization.

5,5,6,6-Tetramethyl-2,2,2-triphenyl-1,4-dioxa-2λ⁵-phosphorinane (16): IR (CCl_4) 3180, 3100, 3020, 1620, 1500, 1450, 1375, 1200, 1115 cm^{-1}; ^1H NMR (toluene-d_8, 200 MHz) δ 0.84 (s, 6H, CH_3), 1.28 (s, 6H, CH_3), 4.70 (br s, 2H, CH_2), 7.0–7.2 and 7.6–7.8 (m, 15H, arom H); ^{13}C NMR (toluene-d_8, 50 MHz) δ 23.2 (q, CH_3), 26.2 (q, CH_3), 67.4 (td, $^1J_{PC}$ = 119.3 Hz, C-3), 74.3 (sd, $^3J_{PC}$ = 3.6 Hz, C-5), 84.1 (sd, $^2J_{PC}$ = 12.1 Hz, C-6); ^{31}P NMR (toluene-d_8, 163 MHz) δ −38.8.

Reaction of Triphenylethylidenephosphorane (5) with 3,3-Dimethyldioxetane (1). According to the general procedure, 264 mg (0.909 mmol) of phosphorane **5** and 80.1 mg (0.909 mmol) of dioxetane **1** in 20 mL of dry toluene were allowed to react at −78 °C for 1 min. After evaporation of the solvent at −10 °C, 330 mg (96%) of phosphorinane **17** was obtained as a colorless oil, which could not be induced to crystallize.

3,6,6-Trimethyl-2,2,2-triphenyl-1,4-dioxa-2λ⁵-phosphorinane (17): ^1H NMR (toluene-d_8, 200 MHz) δ 0.92 (s, 3H, CH_3), 1.20 (s, 3H, CH_3), 2.04 (dd, 3H, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 17.7 Hz, CH_3), AB system (δ_A = 3.38, δ_B = 3.83, 2H, $^2J_{HH}$ = 11.7 Hz, CH_2), 4.88 (m, 1H, CH), 7.3–7.5 and 7.9–8.1 (m, 15H, arom H); ^{13}C NMR (toluene-d_8, 50 MHz) δ 25.9 (q, CH_3), 27.1 (qd, $^2J_{PC}$ = 5.5 Hz, CH_3), 28.7 (q, CH_3), 68.4 (td, br, C-5), 69.0 (dd, $^1J_{PC}$ = 55.5 Hz, C-3), 78.0 (sd, $^2J_{PC}$ = 11.2 Hz, C-6); ^{31}P NMR (d_8-toluene, 163 MHz) δ −38.8.

Reaction of Triphenylisopropylidenephosphorane (6) with 3,3-Dimethyldioxetane (1). According to the general procedure, a solution of 240 mg (0.788 mmol) of phosphorane **6** in 20 mL of dry toluene was cooled to −78 °C, and 69.5 mg (0.788 mmol) of dioxetane **1** was added. After 1 min, the peroxide and the red color of the ylide had completely disappeared, and the solvent was removed at −10 °C to afford 297 mg (96%) of phosphorinane **18** as a colorless oil.

3,3,6,6-Tetramethyl-2,2,2-triphenyl-1,4-dioxa-2λ⁵-phosphorinane (18): ^1H NMR (toluene-d_8, 200 MHz) δ 1.43 (br s, 6H, CH_3), 1.51 (s, 6H, CH_3), 3.24 (d, 2H, $^4J_{PH}$ = 2.2 Hz, [C-3]H_2), 7.40–7.60 and 8.00–8.25 (m, 15 H, arom. H); ^{13}C NMR (toluene-d_8, 50 MHz) δ 27.1 (qd, $^3J_{PC}$ = 5.4 Hz, CH_3), 27.9 (qd, $^2J_{PC}$ = 15.5 Hz, CH_3), 69.5 (t, C-5), 70.2 (sd, $^1J_{PC}$ = 39.5 Hz, C-2), 74.3 (sd, $^2J_{PC}$ = 2.5 Hz, C-6); ^{31}P NMR (toluene-d_8, 163 MHz) δ −38.8.

Reaction of Triphenylbenzylidenephosphorane (7) with 3,3-Dimethyldioxetane (1). According to the general procedure, 700 mg (1.99 mmol) of triphenylbenzylidenephosphorane (**7**) was dissolved in 20 mL of dry toluene and cooled to −78 °C. To this solution was added 175 mg (1.99 mmol) of dioxetane **1**, and the mixture was stirred for 1 min until a negative peroxide test (KI/HOAc) indicated full conversion of the peroxide. The solvent was evaporated at −10 °C and oil pump vacuum (0.01 Torr) to afford 858 mg (98%) of a colorless oil. ^1H and ^{31}P NMR spectroscopy showed a mixture of phosphonium alkoxide **13** and the phosphorinane **19** in a ratio of ca. 30:70.

1-((1′-Triphenylphosphonio-1′-phenylmethyl)oxy)-2-methylpropan-2-olate (13): ^1H NMR (toluene-d_8, 200 MHz) δ 1.34 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), AB system (δ_A = 3.66, d, 1H; δ_B = 3.92, d, 1H, *J* = 7.6 Hz, CH_2), 4.45 (br s, 1H, CH), 6.9–7.2 and 7.6–7.9 (m, 20H, arom H); ^{13}C NMR (toluene-d_8, 50 MHz) δ 27.5 (br q, CH_3), 70.4 (s, C-2), 73.4 (dd, $^1J_{PC}$ = 80.5 Hz, C-1′) 80.0 (t, C-1); ^{31}P NMR (toluene-d_8, 163 MHz) δ 27.0.

6,6-Dimethyl-2,2,2,3-tetraphenyl-1,4-dioxa-2λ⁵-phosphorinane (19): ^1H NMR (toluene-d_8, 200 MHz) δ 1.18 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 3.18–3.25 (m, 2H, CH_2), 3.37 (dd, 1H, J_1 = 10.9 Hz, J_2 = 2.7 Hz, CH), 6.9–7.2 and 7.6–7.9 (m, 20H, arom H); ^{13}C NMR (toluene-d_8, 50 MHz) δ 27.2 (qd, $^3J_{PC}$ = 6.7 Hz, CH_3), 27.4 (qd, $^3J_{PC}$ = 3.4 Hz, CH_3), 70.0 (sd, $^2J_{PC}$ = 10.4 Hz, C-6), 75.0 (dd, $^1J_{PC}$ = 115.6 Hz, C-3), 80.9 (t, C-5); ^{31}P NMR (toluene-d_8, 163 MHz) δ −38.6.

Thermolysis of 6,6-Dimethyl-2,2,2-triphenyl-1,4-dioxa-2λ⁵-phosphorinane (14). A sample of 50.0 mg (0.137 mmol) of phosphorinane **14** was dissolved in 0.8 mL of deuteriochloroform under a nitrogen gas atmosphere and kept at ambient temperature for 3 days. The ring-opening process was monitored by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. The solvent was then removed at 20 °C/0.01 Torr to yield 47.8 mg (96%) of phosphonium alkoxide **8** as a colorless oil.

1-((1′-Triphenylphosphoniomethyl)oxy)-2-methylpropan-2-olate (8): IR (CCl_4) 3040, 2960, 1600, 1495, 1450, 1350, 1140 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.07 (s, 6H, CH_3), 3.37 (s, 2H, C[1]H_2), 4.29 (d, 2H, $^2J_{PH}$ = 5.4 Hz, C[1′]H_2), 7.3–7.5 and 7.7–7.9 (m, 15H, arom H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 25.6 (q, CH_3), 69.5 (s, C-2), 69.7 (td, $^1J_{PC}$ = 86.7 Hz, C-1′), 82.3 (td, $^3J_{PC}$ = 9.3 Hz, C-1), 116.7 (sd, $^1J_{PC}$ = 85.0 Hz, *ipso*-C), 128.2 (dd, $^3J_{PC}$ = 12.1 Hz, *m*-C), 131.9 (dd, $^2J_{PC}$ = 10.3 Hz, *o*-C); 135.2 (dd, $^4J_{PC}$ = 2.9 Hz, *p*-C); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 24.4.

Thermolysis of 5,6,6-Trimethyl-2,2,2-triphenyl-1,4-dioxa-2λ⁵-phosphorinane (15). A sample of 114 mg (0.300 mmol) of phosphorinane **15** was dissolved in 0.8 mL of deuteriochloroform under a nitrogen gas atmosphere and kept at ambient temperature for 36 h. In the ^1H, ^{13}C, and ^{31}P NMR spectra, besides the phosphonium alkoxide **9**, the ylide **20** was observed in a ratio of 43:57.

3-((1′-Triphenylphosphoniomethyl)oxy)-2-methylbutan-2-olate (9): ^1H NMR ($CDCl_3$, 200 MHz) δ 1.00 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH_3), 1.18 (s, 6H, CH_3), 3.34 (q, 1H, $^3J_{HH}$ = 6.4 Hz, CH), AB system (δ_A = 4.11, dd, 1H, $^2J_{HH}$ = 12.8 Hz, $^2J_{PH}$ = 8.7 Hz; δ_B = 4.48, dd, 1H, $^2J_{HH}$ = 12.8 Hz, $^2J_{PH}$ = 4.2 Hz, CH_2), 7.4–8.0 (m, 15H, arom H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.1 (q, CH_3), 23.4 and 25.8 (q, CH_3), 67.9 (td, $^1J_{PC}$ = 72.2 Hz, C-1′), 71.8 (s, C-2), 86.7 (dd, $^3J_{PC}$ = 8.5 Hz, C-3), 117.0 (sd, $^1J_{PC}$ = 84.5 Hz, *ipso*-C), 130.3 (dd, $^3J_{PC}$ = 12.3 Hz, *m*-C), 134.0 (dd, $^2J_{PC}$ = 9.8 Hz, *o*-C), 135.1 (d, *p*-C); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 25.3.

Triphenyl((3′-hydroxy-3′-methylbut-2′-oxy)methylidene)phosphorane (20): ^1H NMR ($CDCl_3$, 200 MHz) δ 0.93 (d, 3H, $^3J_{HH}$ = 6.5 Hz, CH_3), 1.03 (s, 6H, CH_3), 4.26 (q, 1H, $^3J_{HH}$ = 6.5 Hz, C[2′]H), 4.82 (d, 1H; $^2J_{PH}$ = 4.9 Hz, C[1]H), 7.4–8.0 (m, 15H, arom H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 16.6 (q, CH_3), 17.9 (dd, $^1J_{PC}$ = 124.1 Hz, C-1), 21.4 (q, CH_3), 27.6 (q, CH_3), 74.1 (s, C-3), 86.7 (dd, $^3J_{PC}$ = 8.5 Hz, C-2), 128.3 (dd, $^3J_{PC}$ = 11.5 Hz, m-C), 130.3 (sd, $^1J_{PC}$ = 79.7 Hz, *ipso*-C), 131.3 (dd, $^2J_{PC}$ = 9.8 Hz, *o*-C), 133.9 (d, *p*-C); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 17.2

Thermolysis of 5,5,6,6-Tetramethyl-2,2,2-triphenyl-1,4-dioxa-2λ⁵-phosphorinane (16). A sample of 50.0 mg (0.127 mmol) of phosphorinane **16** was dissolved in 0.8 mL of deuteriochloroform and kept at ambient temperature for 24 h. The formation of the phosphonium alkoxide **10** was monitored by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. The solvent was then removed at 20 °C/0.01 Torr to afford 49.3 mg (99%) of a colorless oil.

3-((1′-Triphenylphosphoniomethyl)oxy)-2,3-dimethylbutan-2-olate (10): IR (CCl_4) 3060, 3020, 2960, 2920, 1580, 1430, 1360, 1210, 1180, 1120 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.02 (s, 6H, CH_3), 1.17 (s, 6H, CH_3), 4.04 (d, 2H, $^2J_{PH}$ = 8.0 Hz, CH_2), 7.3–7.9 (m, 15H, arom H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 15.1 (q, CH_3), 24.0 (q, CH_3), 60.1 (td, $^1J_{PC}$ = 83.6 Hz, C-1′), 74.1 (s, C-2), 84.2 (sd, $^3J_{PC}$ = 8.7 Hz, C-3); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 25.2.

Thermolysis of 3,6,6-Trimethyl-2,2,2-triphenyl-1,4-dioxa-2λ⁵-phosphorinane (17). A sample of 70.0 mg (0.185 mmol) of phosphorinane **17** was dissolved in 0.8 mL of deuteriochloroform and kept at ambient temperature for 3 days. The conversion of phosphorinane **17** into the phosphonium alkoxide **11** was monitored by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. The solvent was then evaporated at 20 °C/0.01 Torr to afford 67.1 mg (96%) of a colorless oil.

1-((1′-Methyl-1′-triphenylphosphoniomethyl)oxy)-2-methylpropan-2-olate (11): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.09 (s, 3H, CH_3), 1.13 (s, 3H, CH_3), 1.49 (dd, 3H, $^3J_{HH}$ = 9.8 Hz, $^3J_{PH}$ = 11.0 Hz, CH_3), AB system (δ_A = 3.10, 1H, d; δ_B = 3.49, 1H, d, $^2J_{HH}$ = 9.8 Hz, C[1]H_2], 4.30 (m, 1H, C[1′]H), 7.3–7.4 and 7.7–7.8 (m, 15H, arom H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 27.6 (br q, CH_3), 30.3 (q, CH_3), 70.1 (s, C-2), 76.5 (dd, $^1J_{PC}$ = 90.5 Hz, C-1′), 80.6 (td, $^3J_{PC}$ = 9.1 Hz, C-1); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 28.7.

Thermolysis of 3,3,6,6-Tetramethyl-2,2,2-triphenyl-1,4-dioxa-2λ⁵-phosphorinane (18). A sample of 50.0 mg (0.127 mmol) of phosphorinane **18** was dissolved in 0.8 mL of deuteriochloroform and kept at ambient temperature for 2 days. The conversion of phosphorinane **18** into the phosphonium alkoxide **12** was monitored by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. The solvent was then evaporated at 20 °C/0.01 Torr to afford 48.1 mg (96%) of a colorless oil.

1-((1′,1′-Dimethyl-1′-triphenylphosphoniomethyl)oxy)-2-methylpropan-2-olate (12): ^{1}H NMR (toluene-d_8, 200 MHz) δ 1.25 (d, 6H, $^3J_{PH}$ = 1.0 Hz, CH_3), 1.30 (s, 6H, CH_3), 3.55 (br s, 2H), 7.25–7.50 and 7.75–7.95 (m, 15 H, arom. H); ^{13}C NMR (toluene-d_8, 50 MHz) δ 26.9 (q, CH_3), 27.4 (qd, $^2J_{PC}$ = 15.4 Hz, CH_3), 70.1 (td, $^3J_{PC}$ = 10.0 Hz, C-1), 72.5 (s, C-2), 75.5 (sd, $^1J_{PC}$ = 122.7 Hz, C-1); ^{31}P NMR (toluene-d_8, 163 MHz) δ 30.5.

Reaction of Triphenylmethylidenephosphorane (4) with 3,3-Dimethyldioxetane (1) at −10 °C. A sample of 600 mg (2.17 mmol) of phosphorane **4** was dissolved in 15 mL of dry toluene and cooled to −10 °C, and 191 mg (2.17 mmol) of dioxetane **1** was added. The yellow color of the solution disappeared immediately, and no peroxide could be detected (KI/HOAc) after 1 min. The solvent was removed at room temperature to yield 676 mg (85%) of a brownish oil. ^{1}H, ^{13}C, and ^{31}P NMR spectral data established the product to be identical with phosphonium alkoxide **8**, obtained in the thermolysis of the phosphorinane **14**.

General Procedure for the Hydrolysis of the Phosphonium Alkoxides 8–12 to the Phosphine Oxides 21–25. A sample of 0.166–2.89 mmol of the phosphonium alkoxides **8–12** was dissolved in 5–10 mL of methanol, and 5 mL of 2 N NaOH was added. The mixture was heated to 60 °C for 30 min, and the solution was concentrated at 20 °C/0.01 Torr to a volume of 10 mL. Extraction with methylene chloride (3 × 20 mL) was followed by drying over $MgSO_4$ and evaporation of the solvent (20 °C/15 Torr). The crude product was purified by silica gel chromatography by eluting with methylene chloride/methanol mixtures to afford the phosphine oxides **21–25**.

Hydrolysis of Phosphonium Alkoxide 8. According to the general procedure, 82.0 mg (0.225 mmol) of the phosphonium alkoxide **8** was allowed to react under the above conditions. Silica gel chromatography eluting with 20:1 methylene chloride/methanol gave 64.0 mg (93%) of the phosphine oxide **21** as a colorless oil.

Diphenyl((2′-hydroxy-2′-methylpropoxy)methyl)phosphine Oxide (21): R_f 0.25 (40:1 methylene chloride/methanol); IR (CCl_4) 3250, 3070, 2980, 2900, 2850, 2820, 1425, 1390, 1340, 1145, 1085, 1060, 870 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.11 (s, 6H, CH_3), 3.44 (s, 2H, C[1′]H_2), 4.35 (d, 2H, $^2J_{PH}$ = 5.3 Hz, C[1]H_2), 7.4–7.6 and 7.8–7.9 (m, 10H, arom H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 25.9 (q, CH_3), 70.2 (td, $^1J_{PC}$ = 86.5 Hz, C-1), 70.3 (s, C-2), 82.7 (td, $^3J_{PC}$ = 8.9 Hz, C-1′), 128.6 (dd, $^2J_{PC}$ = 11.8 Hz, *m*-C), 131.0 (sd, $^1J_{PC}$ = 120.1 Hz, *ipso*-C), 131.5 (dd, $^3J_{PC}$ = 7.9 Hz, *o*-C), 132.3 (d, *p*-C); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 28.3. Anal. Calcd for $C_{17}H_{21}O_3P$ (304.4): C, 67.08; H, 6.97. Found: C, 66.68; H, 6.93.

Hydrolysis of Phosphonium Alkoxide 9. According to the general procedure, 106 mg (0.280 mmol) of the phosphonium alkoxide **9** was allowed to react under the above conditions. Silica gel chromatography eluting with 20:1 methylene chloride/methanol gave 74.0 mg (83%) of the phosphine oxide **22** as a colorless oil.

Diphenyl((3′-hydroxy-3′-methylbut-2′-oxy)methyl)phosphine Oxide (22): R_f 0.62 (20:1 methylene chloride/methanol); IR (CCl_4) 3410, 3040, 2950, 2900, 2840, 1420, 1380, 1180, 1110, 1020, 935 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.98 (s, 6H, CH_3), 1.03 (d, $^2J_{HH}$ = 6.4 Hz, 3H, CH_3), 2.92 (br s, 1H, OH), 3.26 (q, 1H, $^2J_{HH}$ = 6.4 Hz, CH), AB system (δ_A = 4.09; δ_B = 4.41, dd, $^2J_{HH}$ = 12.9 Hz, $^2J_{PH}$ = 12.9 Hz, 2H, CH_2), 7.4–7.6 and 7.7–7.8 (m, 10H, arom H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.0, 23.6 and 25.6 (q, CH_3), 67.8 (td, $^1J_{PC}$ = 88.0 Hz, C-1), 72.6 (s, C-3′), 86.3 (dd, $^3J_{PC}$ = 9.8 Hz, C-2′), 128.5 (dd, $^2J_{PC}$ = 11.7 Hz, *m*-C), 130.4 (sd, $^1J_{PC}$ = 125.4 Hz, *ipso*-C), 131.3 (dd, $^3J_{PC}$ = 9.4 Hz, *o*-C), 132.3 (dd, $^4J_{PC}$ = 2.3 Hz, *p*-C); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 29.9. Anal. Calcd for $C_{18}H_{23}O_3P$ (318.4): C, 67.90; H, 7.30. Found: C, 68.05; H, 7.52.

Hydrolysis of Phosphonium Alkoxide 10. According to the general procedure, 1.14 g (2.89 mmol) of phosphonium alkoxide **10** was allowed to react under the above conditions. Silica gel chromatography eluting with 40:1 methylene chloride/methanol afforded 604 mg (66%) of phosphine oxide **23** as a colorless oil.

Diphenyl((2′,3′-dimethyl-3′-hydroxybut-2′-oxy)methyl)phosphine Oxide (23): R_f 0.24 (40:1 methylene chloride/methanol); IR (CCl_4) 3580, 3360, 3080, 2960, 1470, 1445, 1390, 1375, 1200, 1170, 1085 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.04 (s, 6H, CH_3), 1.09 (s, 6H, CH_3), 4.16 (d, 2H, $^2J_{PH}$ = 8.1 Hz), 7.4–7.6 and 7.7–7.9 (m, 10H, arom H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 19.3 (q, CH_3), 24.5 (q, CH_3), 60.3 (td, $^1J_{PC}$ = 90.5 Hz, C-1), 74.8 (s, C-3′), 82.4 (sd, $^2J_{PC}$ = 9.7 Hz, C-2′), 128.5 (dd, $^3J_{PC}$ = 11.6 Hz, *m*-C), 130.9 (ds, $^1J_{PC}$ = 99.4 Hz, *ipso*-C), 131.3 (dd, $^2J_{PC}$ = 9.1 Hz, *o*-C), 132.2 (dd, $^4J_{PC}$ = 2.8 Hz, *p*-C); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 30.4. Anal. Calcd for $C_{19}H_{25}O_3P$ (332.4): C, 68.65; H, 7.60. Found: C, 68.67; H, 7.76.

Hydrolysis of Phosphonium Alkoxide 11. According to the general procedure, 109 mg (0.288 mmol) of phosphonium alkoxide **11** was allowed to react under the above conditions. Silica gel chromatography eluting with 20:1 methylene chloride/methanol gave 65.1 mg (71%) of the phosphine oxide **24** as a colorless oil.

Diphenyl(1-(2′-hydroxy-2′-methylpropoxy)ethyl)phosphine Oxide (24): R_f 0.43 (20:1 methylene chloride/methanol); IR (CCl_4) 3580, 3080, 2990, 2970, 2940, 1610, 1440, 1270, 1190, 1130, 1105, 1045 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.03 (s, 3H, CH_3), 1.07 (s, 3H, CH_3), 1.43 (dd, 3H, $^2J_{HH}$ = 6.9 Hz, $^2J_{PH}$ = 15.1 Hz, CH_3), 2.27 (br s, 1H, OH), AB system (δ_A = 3.05; δ_B = 3.50, d, $^2J_{HH}$ = 8.9 Hz, 2H, CH_2), 4.27 (m, 1H, CH), 7.3–7.6 and 7.7–8.0 (m, 10H, arom H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 13.5 (qd, $^2J_{PC}$ = 2.5 Hz, CH_3), 25.8 and 26.0 (q, CH_3), 70.0 (s, C-2′), 75.5 (dd, $^1J_{PC}$ = 88.3 Hz, C-1), 79.4 (td, $^3J_{PC}$ = 9.3 Hz, C-1′), 128.4 (dd, J_{PC} = 8.4 Hz), 128.6 (dd, J_{PC} = 8.4 Hz), 131.1 (sd, $^1J_{PC}$ = 131.5Hz), 132.2 (d, *p*-C); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 32.0. Anal. Calcd for $C_{18}H_{23}O_3P$ (318.4): C, 67.90; H, 7.30. Found: C, 67.94; H, 7.53.

Hydrolysis of Phosphonium Alkoxide 12. According to the general procedure, 841 mg (2.14 mmol) of phosphonium alkoxide **12** was allowed to react under the above conditions. Silica gel chromatography eluting with 40:1 methylene chloride/methanol afforded 622 mg (87%) of phosphine oxide **25** as a colorless oil.

Diphenyl(1-(2′-hydroxy-2′-methylpropoxy)-1-methylethyl)phosphine Oxide (25): R_f 0.42 (20:1 methylene chloride/methanol); IR (CCl_4) 3050, 3000, 1440, 1370, 1190, 1170, 1120, 1070, 920 cm^{-1}, ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.18 (s, 6H, CH_3), 1.47 (d, 6H, $^3J_{PH}$ = 13.9 Hz), 3.29 (s, 2H), 7.3–7.6 and 7.9–8.1 (m, 10H, arom H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 20.2 (qd, $^2J_{PC}$ = 4.0 Hz, CH_3), 26.3 (q, CH_3), 69.7 (td, $^3J_{PC}$ = 8.1 Hz), 69.9 (s, C-2), 77.2 (sd, $^1J_{PC}$ = 96.0 Hz, C-1), 128.3 (dd, $^3J_{PC}$ = 11.2 Hz, *m*-C), 130.0 (sd, $^1J_{PC}$ = 136.9 Hz, *ipso*-C), 131.8 (dd, $^4J_{PC}$ = 2.8 Hz, *p*-C), 132.3 (dd, $^2J_{PC}$ = 8.4 Hz, *o*-C); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 33.6. Anal. Calcd for $C_{19}H_{25}O_3P$ (332.4): C, 68.65; H, 7.60. Found: C, 68.83; H, 7.84.

Hydrolysis of Phosphonium Alkoxide 13. A sample of 675 mg (1.53 mmol) of a 30:70 mixture of phosphonium alkoxide **13** and phosphorinane **19** was dissolved in a mixture of 5 mL of methanol and 10 mL of water and stirred at ca. 20 °C for 2 h. The workup was performed as described in the general procedure for the other phosphonium alkoxides. Silica gel chromatography eluting with 20:1 methylene chloride/methanol afforded as first fraction 230 mg (80%) of a 51:49 mixture of 1-(benzyloxy)-2-methylpropan-2-ol (**26**) and 2-hydroxy-2-methylpropyl benzoate (**27**). As a second fraction, 361 mg (85%) of triphenylphosphine oxide was obtained as a colorless solid. Finally, 31.0 mg (17%) of 2-methylpropane-1,2-diol was isolated as a colorless oil. Products **26** and **27** are literature known; **27** was identified by comparison of its ^{1}H NMR spectrum with reported values.[24] Triphenylphosphine oxide and the diol were identified by comparison of their ^{1}H and ^{13}C NMR data with those of authentic samples.

1-(Benzyloxy)-2-methylpropan-2-ol (26): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.22 (s, 6H, CH_3), 3.30 (s, 2H, CH_2), 4.57 (s, 2H, CH_2), 7.2–7.3 (m, 5H, arom H).

(24) Trathnigg, B.; Gödl, S.; Junek, H. *Monatsh. Chem.* **1984**, *115*, 1185–1197.

Reaction of Phosphonium Alkoxide 8 with Benzaldehyde. A solution of 160 mg (0.439 mmol) of phosphonium alkoxide **8** and 47.0 mg (0.439 mmol) of benzaldehyde was prepared in 30 mL of dry tetrahydrofuran under a nitrogen gas atmosphere and allowed to reflux for 7 h. The ^1H NMR spectrum of the crude product mixture showed traces of a compound with olefinic protons (δ 6.25, J = 7.0 Hz) as the only definitive product.

Reaction of Phosphonium Alkoxide 8 with Sodium Hydride and Benzaldehyde. A solution of 910 mg (3.29 mmol) of triphenylmethylene phosphorane (**4**) in 25 mL of dry tetrahydrofuran under a nitrogen gas atmosphere was cooled to –20 °C, and 290 mg (3.29 mmol) of dimethyldioxetane (**1**) was added. The mixture was stirred for 20 min and allowed to warm up to ambient temperature (ca. 20 °C). To the solution was added 96.0 mg (4.00 mmol) of sodium hydride, and the mixture was kept under gentle reflux for 1.5 h. Next, 349 mg (3.29 mmol) of benzaldehyde was added, and stirring was continued for 1 h. The reaction mixture was hydrolyzed with water (20 mL) and extracted with ether (3 × 50 mL). Drying over $MgSO_4$ was followed by evaporation of the solvent (20 °C/15 Torr) and silica gel chromatography eluting with methylene chloride to afford 306 mg (47%) of β-hydroxy enol ether **28** as a pale yellow oil.

2-Methyl-1-((2-phenylethenyl)oxy)propan-2-ol (28): R_f 0.53 (methylene chloride); IR (CCl_4) 3560, 3000, 2950, 2900, 2840, 1630, 1480, 1430, 1370, 1300, 1250, 1120, 1090, 900 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.31 (s, 6H, CH_3), 3.79 (s, 2H, CH_2), 5.26 (d, 1H, J = 7.0 Hz), 6.25 (d, ^1H, J = 7.0 Hz), 7.2–7.5 (m, 3H, arom H), 7.59 (d, 2H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 26.0 (q), 70.5 (s), 82.0 (t), 105.8 (d), 125.8 (d), 128.1 (d), 128.2 (d), 135.7 (s), 147.1 (d). Anal. Calcd for $C_{12}H_{16}O_2$ (192.3): C, 74.95; H, 8.40. Found: C, 74.56; H, 8.46.

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