Oxidation Reactions of Phosphaalkenes

Th. A. van der Knaap, Th. C. Klebach, R. Lourens, M. Vos, and F. Bickelhaupt*

Contribution from the Vakgroep Organische Chemie, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands. *Received October 4, 1982*

Abstract: Phosphaalkenes such as **1** and **2** [(2,6-dimethylphenyl)(diphenylmethylene)phosphine] are quite reactive in many respects but are rather sluggish in their reaction with oxygen and sulfur. Primary intermediates in the reactions of **2** are its oxide, the phosphene **6** (or the sulfur analogue **18**, respectively), and the phosphinidene oxide **10** (or its sulfur analogue **19**), which together with (thio)benzophenone is formed by oxidative cleavage of the P=C bond. The occurrence of these unstable intermediates is concluded from their interception by ethanol (yielding **3** and **10**) or water (yielding **23** and **26**) in the oxygen reactions and by ethanol (yielding **16** and **17**) in the sulfur reaction. With oxygen, **6** reacts in part further under cleavage of the P=C bond and formation of benzophenone and the phosphinidene dioxide **7** which is intercepted by ethanol (yielding **4**) or water (yielding **30**). These interception reactions are feasible because **1** and **2** are unreactive toward water and alcohol in the absence of acid or base catalysis. Treatment of **2** with H_2O_2 in ethanol proceeds also largely via **6**; it leads to **3**, **23**, and **25**; in this case, cleavage of the P=C bond is not observed. The mechanism of these reactions and the competition between various reactants (e.g., between O_2, H_2O, EtOH) are discussed. The structure of the reaction products is determined from their spectral properties and by alternative synthesis along unequivocal routes.

According to the "double bond rule",[1] phosphorus, as an element of the third period, does not in general yield stable compounds in which it forms double bonds in its 3p π hybridized, two-coordinate state; under normal circumstances, these compounds rapidly polymerize.[2] Stabilization can be achieved by incorporation into an aromatic system,[3] by neighboring heteroatoms,[4] or by bulky substituents.[5] In view of this inherent instability, we were surprised to find that mesityl(diphenylmethylene)phosphine (**1**) is rather sluggish in some of its reactions with small molecules. While the reactivity of **1** with HCl is high, **1** is quite inert toward H_2O and alcohols in the absence of catalysts.[5] Still more surprising was the slowness of the reaction of **1** with dry oxygen,[5b] as even the highly stabilized monocyclic phosphabenzenes are sensitive toward oxygen,[3b,6] while the similarly aromatic, though somewhat less stable, 2-phosphanaphthalenes[7] and 9-phosphaanthracenes[8] react instantaneously.

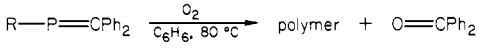
In this paper, we describe a more detailed investigation of the reactions of **1** and of its lower homologue (2,6-dimethylphenyl)(diphenylmethylene)phosphine (**2**) with oxygen, sulfur, and hydrogen peroxide.

Results and Discussion

Reaction with Oxygen. Both **1** and **2** are stable in benzene solution when dry oxygen is bubbled through for several hours at room temperature. Prolonged heating and reflux are required to effect reaction leading to a polymeric material (containing all the phosphorus) and benzophenone (30–50%; Scheme I). Apparently, oxygen attacked the P=C bond under complete cleavage, but only the carbon part survived as benzophenone; the phosphorus species formed from the other part of the molecule was unstable and polymerized.

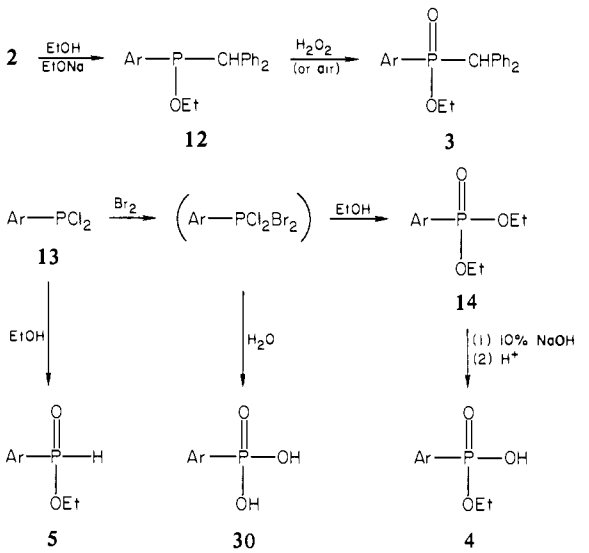
More insight into the primary steps of this reaction was obtained by making use of the fortunate circumstance that **1** and **2**, in the absence of base catalysis, are unreactive toward alcohols,[5] even toward boiling ethanol. Thus, the oxidation was performed with **2** by heating under reflux in ethanol under an atmosphere of oxygen. After 1.5 h, **2** was completely consumed and a mixture of benzophenone (40%), **3** (44%), **4** (40%), and **5** (16%) was formed (see Schemes II, V, and VI). According to the ^{31}P NMR spectrum, **3**, **4**, and **5** were the only phosphorus-containing products. Performing the reaction in the dark, or under irradiation with light of 350 nm, was of no influence on the reaction rate and product composition. When treated with oxygen under the conditions of the reaction of **2**, **5**, was recovered unchanged; thus, **4** cannot be derived from it.

Scheme I

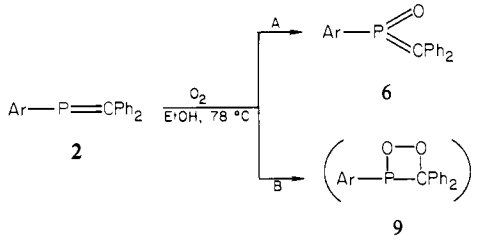


1, R = 2,4,6-trimethylphenyl (=Mes)
2, R = 2,6-dimethylphenyl (=Ar)

Scheme II



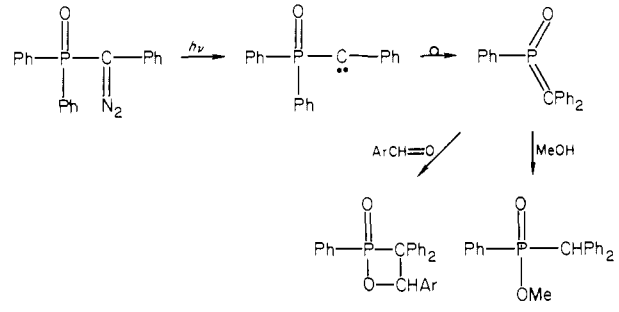
Scheme III



(1) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529.
(2) Hopkinson, M. J.; Kroto, H. W.; Nixon, J. F.; Simmons, N. P. C. *J. Chem. Soc., Chem. Commun.* **1976**, 513.
(3) (a) Märkl, G. *Angew Chem.* **1966**, *78*, 907. (b) Dimroth, K. *Top. Curr. Chem.* **1973**, *38*, 1. (c) Jongsma, C.; Bickelhaupt, F. "Topics in Nonbenzenoid Chemistry"; Nozoe, T.; Breslow, R.; Hafner, K.; Ito, S.; Murata, I., Eds.; Hirokawa Publishing Co.: Tokyo, 1977; Vol. II, p 139. (d) Ashe, A. J. *Acc. Chem. Res.* **1978**, *11*, 153.
(4) Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem.* **1981**, *93*, 771, and references cited therein. Fluck, E. *Top. Phosphorus Chem.* **1980**, *10*, 193.
(5) (a) Klebach, T. C.; Lourens, R.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1978**, *100*, 4886. (b) Van der Knaap, T. A.; Klebach, T. C.; Visser, F.; Lourens, R.; Bicklehaupt, F. *ACS Symp. Ser.* **1981**, *171*, 401.
(6) Ashe, A. J. *J. Am. Chem. Soc.* **1971**, *93*, 3293.
(7) De Graaf, H. G.; Bickelhaupt, F. *Tetrahedron* **1975**, *31*, 1097.
(8) (a) De Koe, P.; Bickelhaupt, F. *Angew. Chem.* **1967**, *79*, 533. (b) Ibid. **1968**, *80*, 912. (c) Jongsma, C.; Vermeer, H.; Bickelhaupt, F.; Schäfer, W.; Schweig, A. *Tetrahedron* **1975**, *31*, 2931.

0002-7863/83/1505-4026$01.50/0

Scheme IV[13]



The new compounds were characterized by their molecular ions in the field desorption mass spectrum and by comparison of their ^1H and ^{31}P NMR and mass spectra with those of authentic samples synthesized by unambiguous routes (Scheme II).

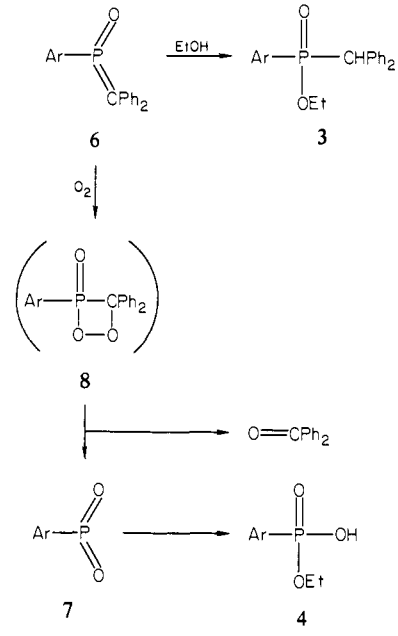
Ethoxide-catalyzed addition of ethanol[5b] to the P=C bond of **2** gave **12**, which was oxidized by H_2O_2 or by air to **3**. (2,6-Dimethylphenyl)dichlorophosphine (**13**) served as the starting material for **4** and **5**: treatment with bromine followed by ethanol[9] afforded **14**, which was partially hydrolyzed[10] to **4** by boiling in 10% aqueous NaOH; direct treatment of **13** with ethanol[11] gave **5**.

We propose that the oxidation products of **2** are formed by two different pathways A and B (Scheme III). The first one, A, starts with the transformation of **2** to the corresponding phosphene **6** in the same manner as tertiary phosphines are transformed to the corresponding phosphine oxides, a reaction that apparently proceeds by a complicated radical mechanism.[12] Phosphenes have been generated by a different route and extensively studied by Regitz and co-workers[13] (Scheme IV); they are highly reactive intermediates which may be trapped by alcohols to form phosphinic esters[13b] or with aldehydes to form 1,2-oxaphosphetanes.[13d]

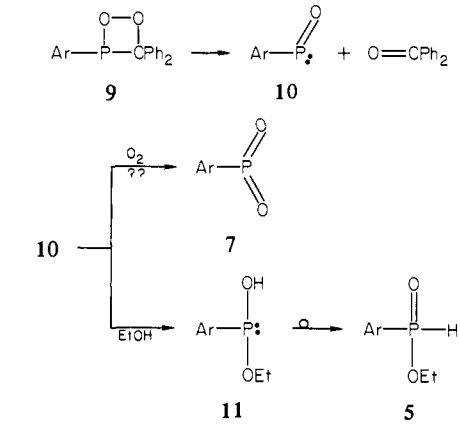
In our case, phosphene **6** is in part intercepted by ethanol to give **3**, but with an approximately equal rate it is oxidized to the phosphinidene dioxide **7** which adds ethanol to furnish the ethyl phosphonate **4**. Considering the presumably high reaction rate of **6** with ethanol and hence with oxygen, it is not surprising that the attempted alternative interception of **6** by *m*-chlorobenzaldehyde in THF was not successful. The mechanism of the oxidation of **6** to **7** and benzophenone is not known. Possibly, the addition of O_2 to **6** leads to the dioxaphosphetane oxide **8**. This reaction is apparently not sensitized ([$^1O_2$]; vide supra) but may be of radical nature; **8** then may fragment to **7** and benzophenone. Another pathway to **7** involving oxidation of **10** cannot be excluded but is considered less likely in analogy with the sulfur reaction (vide infra) (Scheme V).

While the pathway discussed so far can explain the formation of the products **3**, **4**, and benzophenone from the primary intermediate **6**, the formation of **5** must be due to a different pathway, B (Scheme VI). We propose the occurrence of **10** as a key intermediate. The phosphinidene oxide **10** may be formed from **2** by (radical?) addition of O_2 to the P=C bond under formation of the dioxaphosphetane **9**; the latter fragments to **10** and benzophenone in a fashion similar to that proposed for **8**. Phosphinidene oxides have repeatedly been invoked as reaction intermediates. In a recent investigation,[14] Quast and Henschmann have provided convincing evidence for the occurrence of *tert*-butylphosphinidene oxide (*t*-BuP=O; **15**). These authors have

Scheme V



Scheme VI



also investigated the chemical behavior of **15** in detail and proved the addition of alcohols to the P=O bond. In analogy, the reaction of **10** with ethanol is expected to give **11**, which rearranges to the more stable **5**. A substituted aminophosphinidene oxide has been studied by Niecke and co-workers; it trimerizes rapidly[15a] but can be stabilized as the pentacarbonylchromium(O) complex.[15b]

Reaction with Sulfur. The proposed scheme for the reaction between **2** and oxygen was corroborated by an investigation of the analogous reaction of **2** with sulfur (Scheme VII).

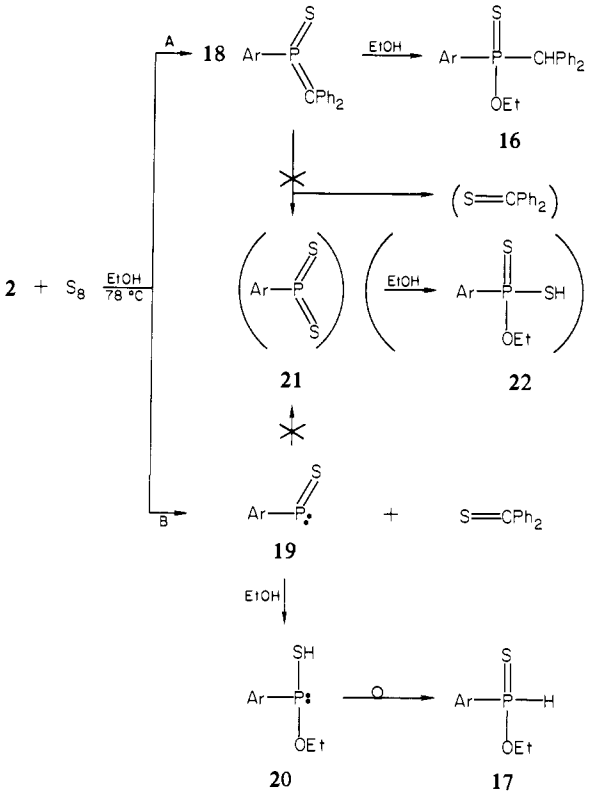
In general, the course of the two reactions is quite similar. No reaction was observed between **1** and sulfur in benzene at room temperature; when the mixture was heated to 80 °C for 3 h, **1** was consumed; a polymer and thiobenzophenone (50% after sublimation) were obtained. When the reaction was repeated with **2** in boiling ethanol, **16**, **17**, and thiobenzophenone were obtained in a ratio of 85:15:15, respectively. The new compounds were characterized by their spectra data and by independent syntheses (Scheme VIII).

Boiling **12** in benzene with sulfur furnished **16**. The Grignard reagent from 2,6-dimethylbromobenzene was, in four unequivocal steps, converted to **17** (see Scheme VIII and Experimental Section).

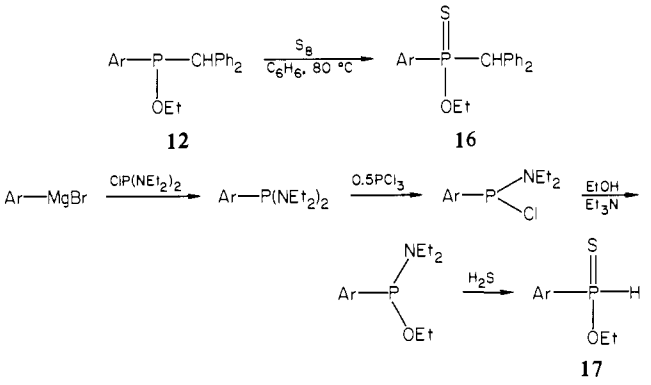
The products **16** and **17** are analogous to **3** and **5** in the oxygen reaction, and their formation can be explained similarly. Sulfur

(9) (a) Kosolapoff, G. M.; Huber, W. F. *J. Am. Chem. Soc.* **1947**, *69*, 2020. (b) Sasse, K. *Methoden Org. Chem.* (*Houben-Weyl*), *4th Ed.* **1963**, *12* (1), 430.
(10) Rabinowitz, R. *J. Am. Chem. Soc.* **1960**, *82*, 4564.
(11) Kosolapoff, G. M. *J. Am. Chem. Soc.* **1950**, *72*, 4292.
(12) Buckler, S. A. *J. Am. Chem. Soc.* **1962**, *84*, 3093.
(13) (a) Regitz, M.; Illger, W.; Maas, G. *Chem. Ber.* **1978**, *111*, 705, and references cited therein. (b) Regitz, M. *Angew. Chem.* **1975**, *87*, 259. (c) Regitz, M.; Eckes, H. *Tetrahedron Lett.* **1975**, 447. (d) Regitz, M.; Scherer, H.; Illger, W.; Eckes, H. *Angew. Chem.* **1973**, *85*, 1115.
(14) Quast, H.; Heuschmann, M. *Chem. Ber.* **1982**, *115*, 901, and references cited therein.
(15) (a) Niecke, E.; Zorn, H.; Krebs, B.; Henkel, G. *Angew. Chem.* **1980**, *92*, 737. (b) Niecke, E.; Engelmann, M.; Zorn, H.; Krebs, B.; Henkel, G. *Angew. Chem.* **1980**, *92*, 738.

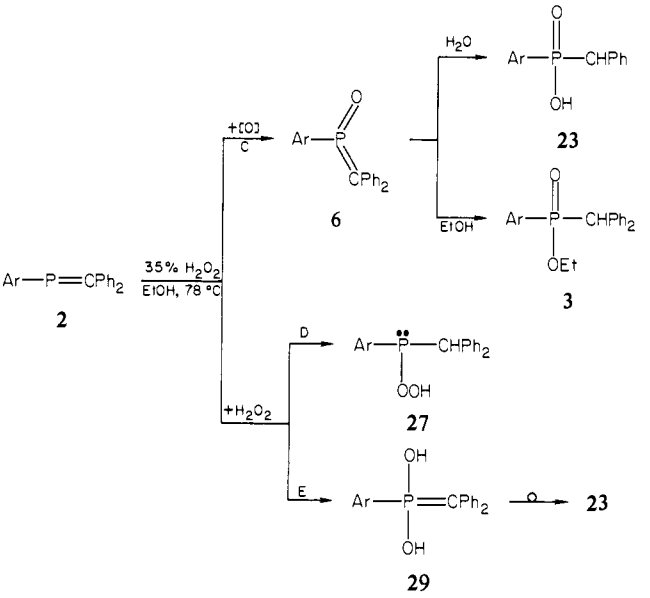
Scheme VII



Scheme VIII



Scheme IX



reacts with **2** by two independent pathways A and B to form either **18** or **19**; an analogy to the formation of **18** may be found in the addition of sulfur to aminoiminophosphines[16a] and to aminomethylenephosphines.[16b] Addition of ethanol to the P=C bond of the thiophosphene **18** leads directly to **16**; addition of ethanol to the P=S bond of the phosphinidine sulfide **19** leads via **20** to **17**. Remarkable is the absence of **22**, the sulfur analogue of **4**, among the reaction products; this means that its potential precursor **21**, the sulfur analogue of **7**, is not formed. Obviously, both potential precursors of **21**, i.e., **18** and **19**, react much faster with ethanol than with sulfur. Ony in the absence of ethanol the cleavage of **18** to **21** may occur as no other, faster reaction pathway is competing; the high yield of thiobenzophenone from **1** under these conditions (≥50%) points in this direction—although, alternatively, an influence of the solvent on the ratio of the mesityl analogues of **18** and **19** cannot be excluded as long as the identity and composition of the phosphorus-containing polymer is not known.

Returning to the reaction in ethanol, where **21** is not formed at all, the thiobenzophenone actually found must originate exclusively from the cleavage of **2** to **19**; in excellent agreement with this hypothesis, the yields of **17** (the product from **19**) and of thiobenzophenone are equal (15%). In comparison, the material balance for the products of cleavage of the P=C bond with oxygen [phosphorus derived: **4** + **5** (56%); carbon derived: benzophenone (40%)] is not perfect but still satisfactory in view of the presumably more aggressive circumstances in the oxygen reaction. For both the oxygen and the sulfur reaction, the yields of phosphorus-containing products arising from pathway A (i.e., **3** + **4** = 84% and **16** = 85%) and from pathway B (i.e., **5** = 16% and **17** = 15%) are in strikingly close agreement. We therefore feel strengthened in our previous conclusion that **7** is formed from **6** only (pathway A) and not from **10** (pathway B).

Like in the oxygen reaction, we were unable to detect any aldehyde-derived interception product (e.g., derived from **18**) when we performed the reaction of **2** with sulfur in boiling benzene in the presence of *m*-chlorobenzaldehyde.

Thus, the reactions of **2** with oxygen and with sulfur are closely parallel. The main difference resides in the behavior of the primary products of pathway A; while phosphene **6** reacts with oxygen and ethanol with about an equal rate, the corresponding thiophosphene **18** reacts much faster with ethanol and is not noticeably attacked by sulfur; this is not surprising in view of the expected difference in reactivity between oxygen and sulfur.

Reaction with Hydrogen Peroxide. Oxidation of phosphines with H_2O_2 to the corresponding phosphine oxides is a well-known reaction. In spite of the considerable differences in electronic structure and general chemical behavior between three-coordinate and two-coordinate phosphines, the H_2O_2 oxidation of **2** to its phosphine oxide, i.e., the phosphene **6**, also proceeds in a very efficient manner.

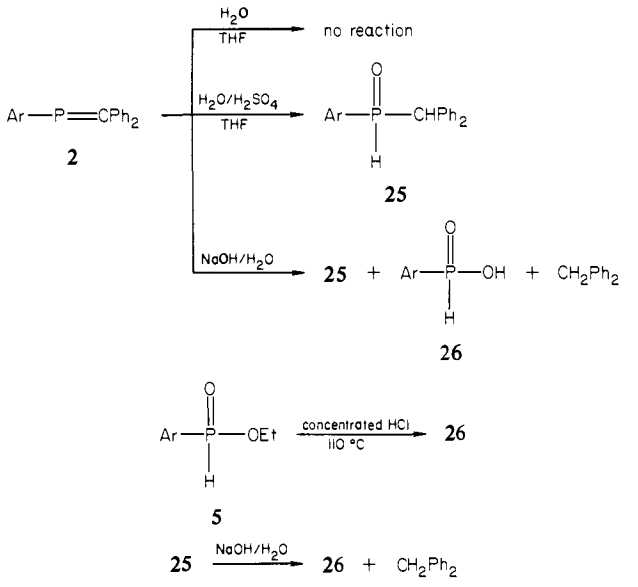
Treatment of **2** in boiling acetone with ca. 2 equiv of H_2O_2 (as 35% aqueous solution) afforded **23** (50%); **23** was identical with an authentic sample prepared by boiling **3** for 2 h with concentrated aqueous HCl (Scheme IX).

Although this reaction can be explained by invoking **6** as an intermediate, other pathways are conceivable. Therefore, we repeated the reaction using boiling ethanol as the solvent instead of acetone. The reaction was instantaneous, as judged from the disappearance of the yellow color of **2**, and yielded **3** (66%), **23** (18%), and **25** (16%); the yields were determined by ^1H and ^{31}P NMR spectroscopy of the crude mixture of reaction products (Schemes IX, XI, and XII).

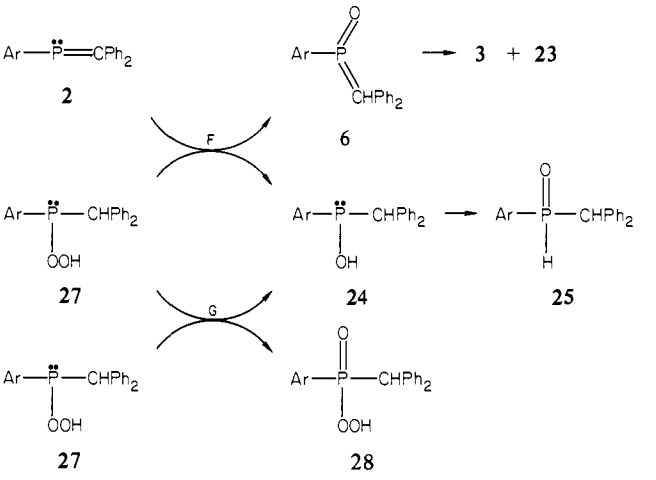
Although **12** is oxidized to **3** by H_2O_2 oxidation (cf. Scheme II), it cannot be the precursor of **3** in this reaction, because **2** does not react with ethanol under the reaction conditions (vide supra). The sequence **2** → **12** → **3** can thus be excluded; **3** must be the ethanol addition product of **6**. Phosphene **6** apparently is the

(16) (a) Scherer, O. J.; Kuhn, N. *Angew. Chem.* **1974**, *86*, 899. (b) Niecke, E.; Wildbredt, D. A. *J. Chem. Soc., Chem. Commun.* **1981**, 72.

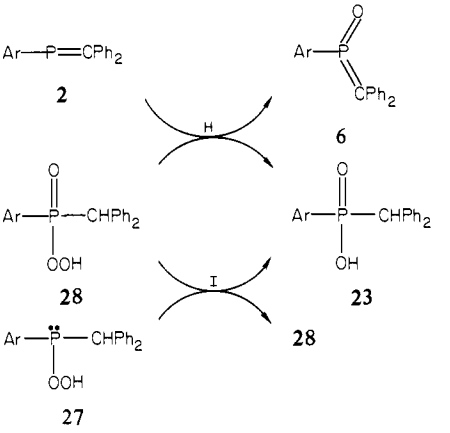
Scheme X



Scheme XI



Scheme XII



product of direct oxidation of **2** by H_2O_2 (Scheme IX, pathway C). For the possible alternative formation of **6** from **2** by oxidation with **27** or **28**, see Scheme XI (pathway F) and Scheme XII (pathway H), vide infra.

The second product whose formation has to be explained is **25**. It was conceivable that **25** was formed by addition of water to **2** and rapid rearrangement of the intermediate **24** for the following two reasons. In general, one may expect that water is more reactive toward **2** than ethanol (which does not add by itself, vide supra) because of its smaller size; an illustration of such a difference in reactivity (e.g., toward **6**) will be presented later. More in particular, we had previously observed the formation of the *P*-mesityl analogue of **25** from **1** on exposure of a solution of **1** in $CHCl_3$ to (moist) air.[5b] However, in this latter case, the reaction must have been inadvertently promoted by an unrecognized catalyst. When the reaction of **2** with H_2O in THF was conducted under carefully controlled conditions (see Experimental Section), **2** was recovered unchanged (Scheme X).

In contrast, addition of H_2O to **2** in THF solution occurred readily on acid or base catalysis. A trace of H_2SO_4 was sufficient to form **25** quantitatively, and a higher acid concentration increased the rate considerably; together with the spectral data, this synthesis of **25** confirms the structure assignment. With 0.1 N NaOH, **25** was rapidly formed from **2** but also in part cleaved to **26** and diphenylmethane. Compound **26** was independently prepared by hydrolysis of **5** with boiling concentrated hydrochloric acid. The base-catalyzed cleavage of **2** became more pronounced at higher NaOH concentrations; obviously, **25** is an intermediate in this reaction, as it gave **26** and diphenylmethane when treated separately with aqueous NaOH in THF solution. Thus H_2O, like methanol[5a] and ethanol,[5b] needs polar catalysis for addition to the P=C bond of phosphaalkenes such as **1** and **2**. The small amount of acid catalyst formed in this reaction (15% **23**) cannot explain the formation of **25** except for a negligeable fraction (see the following section).

The direct addition of water to **2** having been eliminated as a possible mode of formation for **25** under the reactions conditions, alternative pathways have to be considered. In the first place, it is conceivable that H_2O_2, being more nucleophilic than H_2O,[17] does add to the P=C bond of **2** to a certain extent to form **27** (Scheme IX, pathway D). The peroxy acid **27** may oxidize **2** to **6** (cf. the analogous reaction of H_2O_2); in this process, **27** is reduced to **24** which rearranges to **25** (Scheme XI, pathway F). Alternatively, **27** (or H_2O_2) may oxidize a second molecule of **27** to **28**. (Scheme XI, pathway G). The oxidant **27** is thereby reduced to **24**. This disproportionation is plausible because **27** is the only stable tricoordinate phosphorus(III) compound capable of undergoing oxidation in the reaction mixture; the only other candidate, **24**, probably rearranges to **25** too rapidly to be oxidized to **23**. Presumable, both pathways F and G contribute to the formation of **25**. In addition, pathway F opens a second route to **6** and pathway G via **28** to **6** and **23** (Scheme XII, vide infra).

Finally, the formation of **23** has to be discussed. Its structure was confirmed by independent synthesis from **3** with boiling concentrated hydrochloric acid. A plausible source of **23** is the oxidation of **25**. Normally, secondary phosphine oxides are quite suspectible to oxidation;[18] however, sterically hindered secondary phosphine oxides have been reported to be stable toward oxidation.[19] On treatment with H_2O_2 under the conditions of the reaction with **2**, **25** was recovered completely unchanged; obviously, the two bulky groups on phosphorus furnish sufficient steric protection against oxidation.

Thus, **23** cannot be derived from **25**, but there are three other plausible routes to **23**. The first one begins with the already mentioned pathway G (Scheme XI). Subsequently, peroxy acid **28** is reduced to **23**. As shown in Scheme XII both **2** (furnishing **6**, pathway H) and **27** (furnishing **28**, pathway I) may function as an acceptor of an oxygen atom from **28**.

The second route has **6** as the central intermediate; it is formed from **2** by the action of the peroxy compounds H_2O_2, **27**, or **28**. Ethanol and water—the latter is present in the 35% aqueous H_2O_2—are expected to compete for **6** (Scheme IX). Although the ratio of H_2O:EtOH = ca. 1:25, the higher reactivity of H_2O

(17) Liebmann, J. F.; Pollack, R. M. *J. Org. Chem.* **1973**, *38*, 3444, and references cited concerning the α effect.

(18) Hamilton, L. A.; Landis, P. S. In "Organic Phosphorus Compounds"; Kosolapoff, G. M.; Maier, L., Eds.; Wiley-Interscience: New York, 1972; Vol. 4, Chapter 1, p 486.

(19) Frank, A. W. *J. Org. Chem.* **1959**, *24*, 966.

Table I. Products from the Reaction of **2** with Oxygen in THF Containing H_2O-EtOH, 1:1[a]

intermediate	product[b] from reaction with H_2O	EtOH	H_2O + EtOH	ratio of products, H_2O:EtOH
6	**23** (53)	**3** (6)	(59)	8.8
7	**30** (15)	**4** (15)	(30)	1
10	26 (ca. 2)	**5** (ca. 2)	(ca. 4)	(ca. 1)

[a] Other products were **25** (4%), benzophenone (33%), and some minor, unidentified phosphorus-containing products. [b] Yields are in parentheses (%).

toward **6** will contribute to the observed higher ratio of the products **23**:**3** = 1:3.7. This hypothesis is strongly supported by results of the oxygen oxidation performed in the presence of both H_2O and EtOH (see the following section).

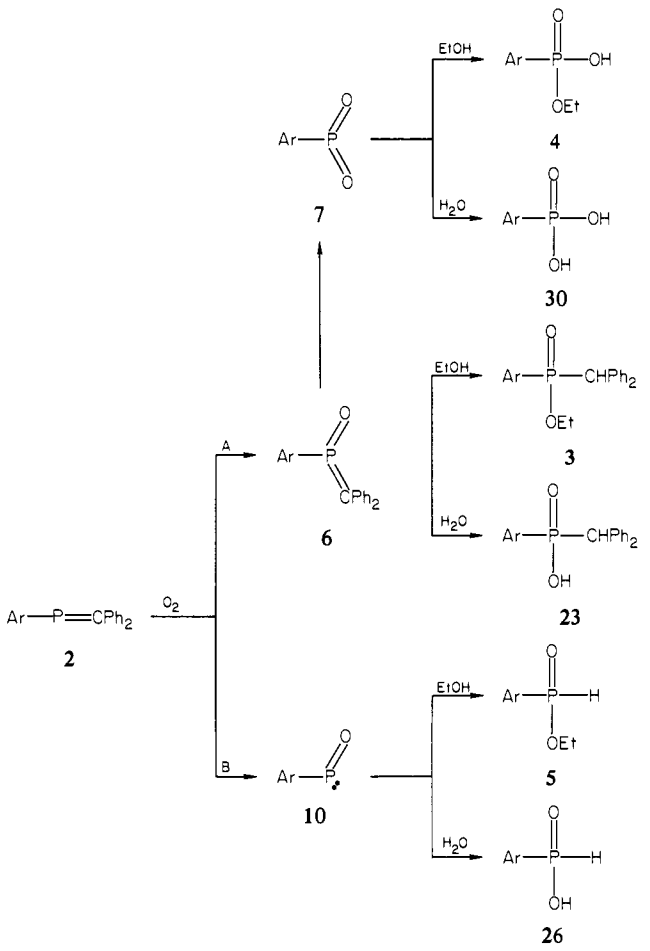
The third route to **23** involves the direct biphilic addition[20] of H_2O_2 to **2** (Scheme IX, pathway E). The primary product of this reaction is ylide **29** which rapidly rearranges to **23**. The postulated formation of an ylide finds a certain precedence in the reaction of **2** with methyl iodide[21] and of aminoiminophosphine with alkyl halides or halogen;[22] for the H_2O_2 oxidation of phosphabenzenes to the corresponding (dihydro)phosphinic acids, a similar mechanism has been proposed.[3b] We consider this route less likely; in any case it must be of minor importance, as it can explain the formation of only one product—i.e., **23**—and does not comprise the intermediacy of **6**.

A reliable distinction between these three modes of formation of **23** is not possible at this stage; in fact, two or more may actually be involved. Nevertheless, it appears that the H_2O_2 oxidation of a phosphaalkene to the corresponding oxide is a rather efficient reaction; for **2**, the yield of **6** is between a minimum of 66% (=the yield of **3**) and up to 84% [=the combined yield of **3** and **23**, if the latter is exclusively derived from **6** (Scheme IX, pathway C)].

Oxidation of 2 in the Presence of Water and Ethanol. As pointed out in the previous section, it was impossible to obtain clear-cut evidence from the H_2O_2 oxidation for the hypothesis that H_2O is more reactive toward **6** than EtOH, because **23** might also be formed from precursors other than **6**. A reaction where this ambiguity does not exist is the reaction with oxygen. In this reaction, **6** has been shown to be formed in high yield; furthermore, end products such as **3** or **23** can under these conditions only be derived from **6**. It will become evident that this latter assumption needs a minor correction only.

The reaction of **2** with oxygen was repeated under conditions closely analogous to those in ethanol with the exception that the solvent was THF containing ca. 10% by volume of a 1:1 molar mixture of H_2O and EtOH; after the mixture was heated to reflux for 3 h, **2** was completely consumed. The formation of products from intermediates **6**, **7**, and **10** is schematically presented in Scheme XIII (for mechanistic details see Schemes III, V, and VI); the yields are summarized in Table I. A product not previously encountered is **30**: its structure was assigned by independent synthesis from **13** (Scheme II). Considering the differences in reaction conditions (solvent, temperature), the yields agree reasonably well with those obtained in pure ethanol; also, the yield of benzophenone (33%) agrees quite well with the sum of the cleavage products **4** + **5** + **26** + **30** (36%). Another factor contributing to the slight differences is the presence of phosphorus-derived acids in the reaction mixture (**4**, **23**, **26**, **30**; total yield 93%), as strong acids have been demonstrated to catalyze the addition of H_2O and EtOH to **2** (preceding section). Undoubtedly, **25** originates by this route (cf. Scheme X); the low yield of **25** (4%) indicates that this pathway is of minor importance only.

Scheme XIII



The results of Table I confirm that H_2O and EtOH do indeed compete for **6**, **7**, and **10** and that H_2O is the more reactive nucleophile (cf. the considerations about the formation of **23** in the previous section). The difference in reactivity depends strongly on the nature of the substrate: H_2O is ca. 9 times as reactive as EtOH toward **6**, while toward **7** and **10**, both nucleophiles are about equally reactive. Undoubtedly, steric factors are important for the selectivity displayed by **6**; the smaller H_2O has considerable advantage over EtOH. For **7** and **10**, steric hindrance does not play an important role; moreover, the lack of selectivity may reflect the high reactivity of their P=O bonds.

Conclusion

The reactions of phosphaalkenes such as **1** or **2** with oxidizing reagents occur by two pathways. Predominantly, the reaction starts by oxidation at phosphorus (O_2, S_8, H_2O_2) leading to the corresponding oxide, i.e., the phosphene **6** (O_2, H_2O_2) or to its thio analogue **18** (S_8) as intermediates. Initiation of the reaction at phosphorus can be understood in terms of electrophilic or radical attack at the lone pair at phosphorus which is the HOMO.[23] Frontier orbital control has also been observed with soft electrophiles such as methyl iodide[21] or complexes of Cr(O)[24] and Pt(O);[25] in contrast, hard electrophiles such as HCl presumably

(20) Denney, D. B.; Denney, D. Z.; Hall, C. D.; Marsi, K. L. *J. Am. Chem. Soc.* **1972**, *94*, 245, and references cited therein. Emsley, J.; Hall, D. "The Chemistry of Phosphorus"; Harper and Row: London, 1976; p 152.

(21) Van der Knaap, T. A.; Bickelhaupt, F. *Tetrahedron Lett.* **1982**, *23*, 2037.

(22) Niecke, E.; Bitter, W. *Chem. Ber.* **1976**, *109*, 415.

(23) Ros, P.; Visser, F., personal communication. The calculations were performed on HP=CH_2, Ph—P=CH_2, and H—P=CHPh with the HFS program developed by E. J. Baerends and P. Ros (*Chem. Phys.* **1973**, *2*, 52), using double ζ basis sets (STO) according to E. Clementi and C. Roetti (*At. Data Nucl. Data Tables* **1974**, *14*, 177). W. W. Schoeller and E. Niecke (*J. Chem. Soc., Chem. Commun.* **1982**, 569) found a reverse order: HOMO = π and NHOMO = σ (lone pair); however, both calculations agree in predicting the two orbitals to be very close in energy. A full account of our calculations is in preparation.

(24) (a) Klebach, Th. C.; Lourens, R.; Bickelhaupt, F.; Stam, C. H.; Van Herk, A. *J. Organomet. Chem.* **1981**, *210*, 211. (b) Eshtiagh-Hosseini, H.; Kroto, H. W.; Nixon, F. J.; Maah, M. J.; Taylor, M. J. *J. Chem. Soc., Chem. Commun.* **1981**, 199.

start attacking the carbon atom of the P=C bond (electrostatic control).

The second, minor pathway (pathway B in Schemes III and VII) is only encountered with O_2 and S_8 and results in oxidative cleavage of the P=C bond under formation of a phosphinidene oxide (or sulfide) and a ketone (or thioketone), respectively. The mechanistic details of this interesting reaction deserve further investigation.

Experimental Section

NMR spectra were recorded on a Bruker WH-90 or a WM-250 spectrometer. Mass spectra were recorded on a Varian CH5DF (EI) or a Varian MAT 711 (field desorption). Reactions of **2** were performed under an argon or a nitrogen atmosphere. Melting points are uncorrected. Elemental analyses were performed by Organisch Chemisch Instituut TNO, Zeist, The Netherlands.

Reactions of 1. (1) With Oxygen in Benzene. Through a solution of 2.34 g (7.4 mmol) of **1**[5a] in 40 mL of benzene dry oxygen was bubbled for 3 h. No reaction had occurred, according to the ^1H NMR spectrum. The same solution was heated under reflux for 10 h, while dry oxygen was bubbled through. During that period the color of the solution changed from yellow to brown. After evaporation to dryness, the ^1H NMR spectrum of the dark brown residue indicated the presence of benzophenone and of polymeric material. Sublimation of the residue at 80–85 °C/10^{-1} torr yielded 0.4 g (2.2 mmol, 30%) of benzophenone, of which the ^1H NMR spectrum and mass spectrum were in agreement with those of an authentic sample.

(2) With Sulfur in Benzene. Compound **1** (618.2 mg, 1.96 mmol) was dissolved in 50 mL of benzene and sulfur (83.2 mg, 2.6 mmol) was suspended in this solution; for 2 h the mixture was stirred. The ^1H NMR spectrum of a sample indicated the presence of 90% **1**. To the yellow solution excess sulfur (120 mg, 3.7 mmol) was added and the resulting solution was heated under reflux for 3 h. The color of the solution had changed to blue. After evaporation to dryness, the residue was extracted with *n*-pentane. Filtration and evaporation of the pentane solution yielded a blue residue which, according to ^1H NMR spectroscopy, contained besides polymeric material (broad signals) thiobenzophenone as the only identifiable product. Sublimation of this residue at 50 °C/10^{-1} torr yielded thiobenzophenone (200 mg, 1 mmol, 50%) according to ^1H NMR and mass spectrum: *m/z* (rel intensity) 198 (88, M·), 165 (199, $C_{13}H_{10}^{+}$·), 121 (82, $C_7H_5S^{+}$·).

Reactions of 2. (1) With Ethanol and Sodium Ethoxide. Compound **2** (470 mg, 1.62 mmol) was dissolved in ethanol, and the yellow solution was boiled for 3 h. After evaporation to dryness **2** was not changed according to the ^1H NMR spectrum. The residue was dissolved in ethanol in which a trace of sodium had been dissolved; the color of the solution changed immediately from yellow (**2**) to colorless. The solution was evaporated to dryness and the residue was extracted with 15 mL of hot cyclohexane. After filtration and evaporation 480 mg (85%) of **12** remained as a viscous, colorless oil: ^1H NMR ($CDCl_3$) δ 0.94 (t, $^3J_{HH}$ = 7 Hz, 3 H, OCH_2–CH_3), 2.32 (s, 6 H, *o*-CH_3), 3.33–3.72 (m, 2 H, O–CH_2), 4.87 (d, $^2J_{PH}$ = 4 Hz, 1 H, P–CH), 6.52–7.90 (m, 13 H, aryl H); ^{31}P NMR ($CDCl_3$) δ 122.7; mass spectrum *m/z* (rel intensity) 348 (12, M^{+}·, 181 (48, M^{+}· – Ph_2CH), 167 (100, Ph_2CH^{+}·); exact mass *m/z* 348.1650 (calcd for $C_{23}H_{25}OP$ *m/z* 348.1643).

(2) With Oxygen in Ethanol. Compound **2** (130 mg, 0.43 mmol) was dissolved in boiling ethanol. A stream of oxygen (dried with phosphorus pentoxide) was conducted over the boiling solution for 2 h. Then the yellow color had disappeared; after evaporation a colorless viscous oil remained. This oil was a mixture of **3** (44%), **4** (40%), **5** (16%), and benzophenone (40%), according to the ^1H NMR and ^{31}P NMR spectra: FD mass spectrum *m/z* (rel intensity) 364 (100, $\mathbf{3}^{+}$·), 214 (15, $\mathbf{4}^{+}$·), 198 (3, $\mathbf{5}^{+}$·). **3** could be separated by crystallization from cyclohexane or TLC with chloroform.

(3) With Sulfur in Ethanol. Compound **2** (116 mg, 0.38 mmol) was dissolved in 10 mL of EtOH and sulfur (36 mg, 1.13 mmol) was added. The solution was heated under reflux for 2.5 h; during this period the solution turned blue. ^1H NMR and ^{31}P NMR spectra indicated the presence of 85% **16**, 15% **17**, and 15% thiobenzophenone: FD mass spectrum *m/z* (rel intensity) 198 (<1, Ph_2C=S), 214 (<1, $\mathbf{17}^{+}$·), 380 (100, $\mathbf{16}^{+}$·). The spectra were identical with those of **16**, **17**, and thiobenzophenone obtained by unambiguous syntheses (vide infra).

(4) With Hydrogen Peroxide in Acetone. Compound **2** (230 mg, 0.76 mmol) was dissolved in 10 mL of acetone and aqueous H_2O_2 (35%, 200 μL) was added dropwise under stirring. The yellow solution was partly decolorized. The solution was heated under reflux for 10 min. A ^1H NMR spectrum indicated the presence of about 50% **23**. The acetone was evaporated almost to dryness and the residue was extracted with chloroform–water. The organic layer was dried with $CaCl_2$ and evaporated. The residue was a yellowish oil which partly solidified on standing. After two extractions with 1 mL of chloroform colorless crystals of **23** (31 mg, 13%), mp 222–226 °C, remained. This product was, according to its NMR and mass spectra, identical with **23** prepared from **3** (vide infra).

(5) With Hydrogen Peroxide in Ethanol. Compound **2** (160 mg, 0.53 mmol) was dissolved in 5 mL (87 mmol) of ethanol; H_2O_2 (35%, 100 μL, containing 1 mmol of H_2O_2 and 3.6 mmol of H_2O) was added dropwise at 78 °C during 5 min; the solution was completely decolorized. After evaporation almost to dryness the residue was extracted with chloroform–water. The organic layer was dried with $CaCl_2$ and evaporated. ^1H NMR and ^{31}P NMR spectra indicated the presence of 66% **3**, 18% **23**, and 16% **25**. According to their NMR spectra **3**, **23**, and **25** were identical with authentic compounds obtained by unambiguous synthesis.

(6) With Water in Tetrahydrofuran. Compound **2** (169 mg, 0.55 mmol) was dissolved in 5 mL of THF (oxygen free) and water (25 mg, 1.38 mmol) was added. The yellow solution was heated under reflux for 4.5 h; the yellow color persisted. According to the ^1H NMR spectrum, **2** was unchanged. Then 5 mL of water was added (pH 5.5); after 24 h at room temperature again, the ^1H NMR spectrum indicated the presence of **2** only.

Finally **2** (183 mg, 0.6 mmol) was dissolved in 6 mL of THF and 0.6 mL of 2 N aqueous H_2SO_4 (1.2 mmol) was added. The solution was heated under reflux for 11 h and then neutralized with 2 N NaOH. The organic layer was dried with $CaCl_2$ and evaporated to dryness to give 160 mg of a yellowish white solid which consisted of almost pure **25** (88%), mp 130–137 °C. Two sublimations (10^{-4} torr, 120 °C) raised the melting point to 163–168 °C: ^1H NMR ($CDCl_3$) δ 2.22 (s, 6 H, *o*-CH_3), 4.57 (d of d, $^2J_{PH}$ = 14 Hz, $^3J_{HH}$ = 4 Hz, 1 H, P–CH), 6.87–7.04 (m, 2 H, aryl H), 7.13–7.89 (m, 11 H, aryl H), 8.20 (d of d, $^1J_{PH}$ = 476 Hz, $^3J_{HH}$ = 4 Hz, 1 H, P–H); ^{31}P NMR ($CDCl_3$) δ 23.4; mass spectrum *m/z* (rel intensity) 320 (13, M^{+}·), 167 (100, Ph_2CH^{+}·), 152 (12, Xy–P=O^{+}·). Exact mass: found *m/z* 320.1341 (calcd for $C_{21}H_{21}OP$ *m/z* 320.1330). Anal. Calcd for $C_{21}H_{21}OP$: C, 78.73; H, 6.61; P, 9.67. Found: C, 78.59; H, 6.79; P, 9.77.

(7) With Water and Ethanol under Acid Catalysis. Under argon, EtOH (0.43 mL, 7.2 mmol) was added to a solution of **2** (108.72 mg, 0.36 mmol) in THF (5 mL); afterward, 2 N H_2SO_4 (0.13 mL; 7.2 mmol of H_2O; 0.4 mmol of H_2SO_4) was added. The mixture was heated under reflux for 5 h. According to ^1H NMR spectroscopy, **25** was the only product. Addition of H_2O and $CHCl_3$, drying of the organic layer ($MgSO_4$), and evaporation gave **25** (70.4 mg, 90%), identified by its ^1H NMR spectrum.

(8) With Oxygen in the Presence of Water and Ethanol in Tetrahydrofuran. Compound **2** (112.8 mg, 0.37 mmol) was dissolved in 5 mL of THF; water (0.134 mL, 7.46 mmol) and ethanol (0.43 mL, 7.46 mmol) were added. The solution was heated under reflux for 5 h under a stream of dry oxygen and subsequently evaporated. White solid and colorless liquid remained (130.7 mg). A ^1H NMR and a ^{31}P NMR spectrum indicated the presence of **3**, **4**, **5**, **23**, **25**, **26**, **30**, and benzophenone (for yields, see Table I). A mass spectrum (GC–MS) indicated the presence of benzophenone and **3**.

Ethyl (2,6-Dimethylphenyl)(diphenylmethyl)phosphinate (3). Compound **12** (430 mg, 1.23 mmol) was dissolved in 10 mL of acetone. At room temperature 150 μL of 35% aqueous H_2O_2 was added, and the solution heated under reflux for 5 min. After evaporation the solid residue was extracted with water–chloroform. The chloroform layer was separated, dried with $CaCl_2$ and evaporated. **3** (430 mg, 96%) remained as a white solid: mp 119 °C after two crystallizations from cyclohexane: **1H** NMR ($CDCl_3$) δ 1.11 (t, $^3J_{HH}$ = 7 Hz, 3 H, OCH_2CH_3), 2.45 (d, $^4J_{PH}$ = 2 Hz, *o*-CH_3), 3.71–4.11 (m, 2 H, CH_2), 4.48 (d, $^2J_{PH}$ = 16 Hz, 1 H, P–CH), 6.77–7.77 (m, 13 H, aryl H); ^{31}P NMR ($CDCl_3$) δ 42.20; mass spectrum (rel intensity) *m/z* 364 (30, M^{+}·), 197 (55, M^{+}· – PhCH), 169 (100, $C_8H_{10}O_2P$), 152 (12, C_8H_9OP), 105 (25, C_8H_9). Anal. Calcd for $C_{23}H_{25}O_2P$: C, 75.80, H, 6.92; P, 8.49. Found: C, 75.71; H, 6.92; P, 8.46.

Ethyl (2,6-Dimethylphenyl)phosphonate (4). The diester **14** (87 mg, 0.35 mmol) was suspended in 0.6 mL of 10% NaOH and heated under reflux for 2 h; the solution was then acidified with concentrated hydrochloric acid. The solution and the white precipitate were extracted twice with chloroform. The combined chloroform layers were dried with $CaCl_2$. After evaporation a colorless oil of **4** (60 mg, 80%) remained: ^1H NMR ($CDCl_3$) δ 1.24 (t, $^3J_{HH}$ = 7 Hz, 3 H, CH_2CH_3), 2.59 (d, $^4J_{PH}$ = 2 Hz, 6 H, *o*-CH_3), 4.04 (d of q, $^3J_{PH}$ = $^3J_{HH}$ = 7 Hz, 2 H, CH_2), 6.83–7.41 (m, 3 H, aryl H), 12.10 (br s, s, 1 H, P–OH); ^{31}P NMR ($CDCl_3$) δ 22.7; mass spectrum *m/z* (rel intensity) 214 (80, M^{+}·), 199 (56), 186 (77, M^{+}· – C_2H_4), 168 (100, M^{+}· – C_2H_5OH), 105 (71,

(25) Van der Knaap, T. A.; Bickelhaupt, F.; Van der Poel, H.; Van Koten, G.; Stam, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 1756.

$C_8H_9^+$). Exact mass: found m/z 214.0761 (calcd for $C_{10}H_{14}O_3P$ m/z 214.0758).

Ethyl (2,6-Dimethylphenyl)phosphinate (5). **13**[26] (200 mg, 0.97 mmol) was dissolved in 5 mL of ethanol. After 30 min the ethanol was evaporated and pure **5** (120 mg, 72%) remained as a colorless oil (loss of material as **5** is volatile). After two sublimations (10^{-2} torr, 50 °C) **5** was obtained as a white solid; mp 26 °C: ^1H NMR ($CDCl_3$) δ 1.39 (t, $^3J_{HH}$ = 7 Hz, 3 H, CH_2CH_3), 2.60 (s, 6 H, o-CH_3), 3.96–4.40 (m, 2 H, CH_2), 6.87–7.42 (m, 3 H, aryl H), 7.98 (d, $^1J_{PH}$ = 556 Hz, 1 H); ^{31}P NMR ($CDCl_3$) δ 24.3; mass spectrum m/z (rel intensity) 198 (83, $M^{+\cdot}$), 169 (86, $M^{+\cdot} - C_2H_5$), 152 (38, Xy–P=O$^{+\cdot}$), 105 (100, Xy^+). Exact mass: found m/z 198.0811 (calcd for $C_{10}H_{15}O_2P$ m/z 198.0809). Attempted elementary analysis was thwarted due to the instability of **5** toward hydrolysis; instead, the analytical results for **26** were obtained. Anal. Calcd for $C_{10}H_{15}O_2P$ (**5**): C, 60.60; H, 7.63; P, 15.63. Calcd for $C_8H_{11}O_2P$ (**26**): C, 56.47; H, 6.47; P, 18.24. Found C, 56.29; H, 6.68; P, 16.61.

Attempted Reaction of 5 with Oxygen. Compound **5** (105 mg, 0.53 mmol) was dissolved in 5 mL of ethanol under an atmosphere of oxygen and the solution was heated under reflux for 2 h. A ^1H NMR spectrum of a sample indicated the presence of pure **5**: no trace of **4** was found.

Diethyl 2,6-Dimethylphenylphosphonate (14). To a solution of (2,6-diphenylphenyl)phosphinous dichloride (**13**)[26] (170 mg, 0.82 mmol) in anhydrous ether bromine was added until a brown color persisted. Subsequently, ethanol (2 mL) was added. The solution was washed with water and the ether layer was dried with $MgSO_4$. After evaporation, pure **14** remained (166.7 mg, 84%): ^1H NMR ($CDCl_3$) δ 1.33 (t, $^3J_{HH}$ = 7 Hz, 6 H, CH_2CH_3), 2.64 (d, $^4J_{PH}$ = 2 Hz, 6 H, o-CH_3), 3.87–4.40 (m, 4 H, CH_2), 6.94–7.42 (m, 3 H, aryl H); ^{31}P NMR ($CDCl_3$) δ 20.6; mass spectrum m/z (rel intensity) 242 (76, $M^{+\cdot}$), 228 (85), 199 (100), 186 (72, $M^{+\cdot} - 2C_2H_4$), 168 (75, $M^{+\cdot} - OEt - C_2H_5$), 105 (48, C_8H_9). Exact mass: found m/z 242.1057 (calcd for $C_{12}H_{19}O_3P$ m/z 242.1072).

Ethyl (2,6-Dimethylphenyl)(diphenylmethyl)thiophosphinate (16). Compound **2** (141 mg, 0.47 mmol) was dissolved in 4 mL of ethanol together with a trace of sodium; on solution, the yellow color of **2** disappeared immediately. Subsequently sulfur (20 mg, 0.62 mmol) was added and the solution was heated under reflux for 2 h. After filtration and evaporation of the solvent, a viscous oil (containing a small amount of sulfur) remained. Attempts to crystallize **16** failed. **16** was the only product of the reaction according to the ^1H and ^{31}P NMR spectra: ^1H NMR ($CDCl_3$) δ 1.08 (t, $^3J_{HH}$ = 7 Hz, 3 H, CH_2CH_3), 2.56 (d, $^4J_{PH}$ = 1 Hz, 6 H, o-CH_3), 3.67–4.11 (m, 2 H, CH_2) 4.92 (d, $^2J_{PH}$ = 13 Hz, 1 H, P–CH), 6.78–7.61 (m, 13 H, aryl H); ^{31}P NMR ($CDCl_3$) δ 92.5; mass spectrum m/z (rel intensity) 380 (100), 381 (31).

Ethyl (2,6-Dimethylphenyl)thiophosphinate (17). (2,6-Dimethylphenyl)phosphonous chloride diethylamide (prepared by standard procedures according to Scheme VI; 1.9 g, 7.8 mmol) was dissolved in 20 mL of benzene and cooled to 5 °C. Then ethanol (358 mg, 7.8 mmol) and triethylamine (788 mg, 7.8 mmol) in 5 mL of benzene were added dropwise. A white precipitate formed. After 24 h the solution was filtered and the solvent was removed from the filtrate. Ethyl (2,6-dimethylphenyl)phosphonous diethylamide remained as a light yellow oil (1.76 g, 89%): ^1H NMR ($CDCl_3$) δ 0.98 (t, $^3J_{HH}$ = 7 Hz, 6 H, NCH_2CH_3), 1.27 (t, $^3J_{HH}$ = 7 Hz, 3 H, OCH_2CH_3), 2.51 (d, $^4J_{PH}$ = 2 Hz, 6 H, o-CH_3), 3.06 (d of q, $^3J_{PH}$ = 9 Hz, $^3J_{HH}$ = 7 Hz, 4 H, NCH_2), 3.79 (d of q, $^3J_{PH}$ = 9 Hz, $^3J_{HH}$ = 7 Hz, 2 H, OCH_2), 6.86–7.39 (m, 3 H, aryl H); ^{31}P NMR ($CDCl_3$) δ 139.0. Through a solution of this ester–amide (1.63 g, 6.42 mmol) in 30 mL of benzene, H_2S was bubbled for 2.5 h, while heating under reflux. After 24 h at room temperature, crystals of $Et_2NH{\cdot}H_2S$ had appeared in the solution and in the reflux condenser. The crystals were dissolved in water; the benzene layer was dried with Na_2SO_4. After evaporation of the solvent, **17** was purified by sublimation (60 °C, 10^{-2} torr); **17** was obtained as white crystals (488 mg, 36%): mp 51.5–54 °C; ^1H NMR ($CDCl_3$) δ 1.37 (t, $^3J_{HH}$ = 7 Hz, 3 H, CH_2CH_3), 2.58 (s, 6 H, o-CH_3), 3.89–4.49 (m, 2 H, CH_2CH_3), 6.92–7.40 (m, 3 H, aryl H), 8.66 (d, J_{PH} = 520 Hz, 1 H, P–H); ^{31}P NMR ($CDCl_3$) δ 58.6 (d, $^1J_{PH}$ = 519 Hz). Anal. Calcd for $C_{10}H_{15}OPS$: C, 56.06; H, 7.06; P, 14.46; S, 14.96. Found: C, 56.42; H, 7.21; P, 14.16; S, 14.54. Mass spectrum m/z (rel intensity) 214 (100, $M^{+\cdot}$), 181 (43, $M^{+\cdot}$ – HS), 153 (68, XyP–OH$^{+\cdot}$), 105 (49, $Xy^{+\cdot}$). Exact mass: found m/z 214.0594 (calcd for $C_{10}H_5OPS$ m/z 214.0581).

(2,6-Dimethylphenyl)(diphenylmethyl)phosphinic Acid (23). Compound **3** (106 mg, 0.30 mmol) was suspended in 5 mL of concentrated HCl and boiled for 1.5 h. Chloroform and water were added, and the organic layer was dried with $CaCl_2$. After evaporation the residue was crystallized twice from ethanol; colorless crystals of **23** were obtained (28 mg, 27%): mp 227–229 °C; ^1H NMR ($CDCl_3$) δ 2.29 (s, 6 H, o-CH_3), 4.40 (d, $^2J_{PH}$ = 16 Hz, 1 H, P–CH), 6.73–7.40 (m, 13 H, aryl H), 11.02 (δ variable, br s, 1 H, OH); ^{31}P NMR ($CDCl_3$) δ 45.6; mass spectrum m/z (rel intenstiy) 336 (47, $M^{+\cdot}$), 167 (100, $Ph_2CH^{+\cdot}$), 152 (C_8H_9P=O$^{+\cdot}$). Exact mass: found m/z 336.1299 (calcd for $C_{21}H_{21}O_2P$ m/z 336.1279). Anal. Calcd for $C_{21}H_{21}O_2P$: C, 74.98; H, 6.29; P, 9.21. Found: C, 74.63; H, 6.37; P, 9.04.

(2,6-Dimethylphenyl)(diphenylmethyl)phosphine Oxide (25). To a solution of **12** (0.52 mmol; prepared from **2** and EtOH–EtONa, vide supra, containing a trace of **3** from oxidation of **12**) in THF (5 mL) 2 N H_2SO_4 (0.187 mL) was added; the solution was heated under reflux for 2 h. Addition of H_2O–$CHCl_3$, drying of the $CHCl_3$ layer, and evaporation yielded **25**, which, according to its ^1H NMR spectrum, was identical with the product from **2** plus H_2O (vide supra). It contained a trace of **3** but no **23**; obviously, **12** is hydrolyzed much easier than **3**.

Attempted Reaction of 25 with H_2O_2. Compound **25** (9.1 mg, 0.028 mmol) was dissolved in 2 mL of ethanol, and 5 μL of aqueous H_2O_2 (30%, 0.42 mmol) was added dropwise at room temperature. Then the solution was heated under reflux for 5 min. The solution was evaporated, the residue was dissolved in chloroform and the excess of H_2O_2 was extracted with water. The organic layer was dried with $CaCl_2$ and evaporated to dryness. Pure **25** (9.1 mg, 100%) remained. Its ^1H NMR spectrum was identical with that of the starting material.

Reaction of 25 with NaOH. A solution of **25** (13.7 mg, 0.043 mmol) in THF (2 mL) and 2 N NaOH (44 μL, 0.086 mmol of NaOH) was heated under reflux for 2 h. After the solution was cooled to room temperature, chloroform and water were added. The organic layer was dried with $CaCl_2$ and evaporated to dryness; diphenylmethane remained (3.6 mg, 50%); it was identified by its ^1H NMR spectrum. The basic water layer was acidified by HCl and extracted with chloroform. The organic layer was dried with $CaCl_2$ and evaporated to dryness. Almost pure **26** (7.1 mg, 97%) remained; it was identified by comparing ^1H and ^{31}P NMR spectra with those of an authentic sample.

(2,6-Dimethylphenyl)phosphinic Acid (26). Compound **5** (35.4 mg, 0.179 mmol) and 36% HCl (1 mL) were heated together under reflux for 45 min. After the mixture was cooled, H_2O (ca. 5 mL) was added and twice extracted with $CHCl_3$; the latter was washed with H_2O and dried ($CaCl_2$). Evaporation yielded a slightly yellowish oil of **26** (18.5 mg, 61%): ^1H NMR ($CDCl_3$) δ 2.57 (s, 6 H, o-CH_3), 6.80–7.40 (m, 3 H, aryl H), 8.03 (d, $^1J_{PH}$ = 562 Hz, 1 H, P–H), 9.91 (br s, 1 H, POH); ^{31}P NMR ($CDCl_3$) δ 23.47; mass spectrum (rel intenstiy) m/z 170 (100, $M^{+\cdot}$), 152 (34, $M^{+\cdot} - H_2O$). Exact mass: found m/z 170.0503 (calcd for $C_8H_{11}O_2P$ m/z 170.0496).

2,6-Dimethylphenylphosphonic Acid (3). Compound **13** (102 mg, 0.49 mmol) was dissolved in 2.5 mL of ether and bromine (35 μL, 0.65 mmol) was added. A yellow precipitate was formed which disappeared again when 1 mL of water was added. The solution was boiled for 15 min, and the reaction mixture was extracted twice with chloroform. After the organic layer was dried with $CaCl_2$ and evaporated, 50.4 mg of **30** (56%) remained as a white solid: mp 174–179 °C; ^1H NMR ($CDCl_3$ plus 3% trifluoroacetic acid-d) δ 2.62 (d, $^4J_{PH}$ = 2 Hz, 6 H, o-CH_3), 6.84–7.68 (m, 3 H, aryl H); ^{31}P NMR ($CDCl_3$ plus 3% trifluoroacetic acid-d) δ 29.31; mass spectrum m/z (rel intensity) 186 (96, $M^{+\cdot}$), 168 (100, $M^{+\cdot}$ – H_2O), 105 (55, $Xy^{+\cdot}$). Exact mass: found m/z 186.0440 (calcd for $C_8H_{11}O_3P$ m/z 186.0445).

Acknowledgment. We thank Drs. P. Ros, E. J. Baerends, F. Visser, M. Regitz, and H. Quast for stimulating discussions and R. Fokkens for measuring the field desorption mass spectra.

Registry No. 1, 67565-91-7; **2**, 85320-16-7; **3**, 85320-17-8; **4**, 85320-18-9; **5**, 6782-00-9; **12**, 85320-24-7; **13**, 85320-25-8; **14**, 54057-96-4; **16**, 85320-19-0; **17**, 85354-76-3; **23**, 85320-20-3; **25**, 85320-21-4; **26**, 85320-22-5; **30**, 85320-23-6; (2,6-dimethylphenyl)phosphonous chloride diethylamide, 85320-26-9; ethyl (2,6-dimethylphenyl)phosphonous diethylamide, 85320-27-0.

(26) Compound **13** was prepared by reacting (2,6-dimethylphenyl)magnesium bromide with bis(diethylamino)chlorophosphine, followed by treatment with HCl; cf.: Bickelhaupt, F.; Jongsma, C.; De Koe, P.; Lourens, R.; Mast, N. R.; Van Mourik, G. L.; Vermeer, H.; Weustink, R. J. M. *Tetrahedron* **1976**, *32*, 1921, and references cited therein.