

Since neither the ylide nor aldehyde could be detected, we have used a steady-state approximation wherein their disappearance is rapid relative to their formation (i.e.,  $k_1$  and  $k_2$  are much greater than  $k_3$  and  $k_4$ ); so, the change in their concentration with time is zero (i.e.,  $d[Y]/dt = 0$ ). At  $-78$  °C, the low temperature of mixing, oxaphosphetanes are completely formed but they are not interconverting or decomposing to alkenes. Thus,  $k_3$ ,  $k_4$ ,  $k_5$ , and  $k_6$  are nearly equal to zero and analysis of eq 2 and 3 affords the ratio  $R = [C]/[T] = k_1/k_2$ . This ratio is assumed to be independent of temperature, within experimental error. Substitution of  $R$  and eq 1 into eq 2 and 3 provided the general eq 6 and 7, which were used along with eq 4 and 5 to calculate the rate constants ( $k_3$ ,  $k_4$ ,  $k_5$ , and  $k_6$ ) as well as  $[C]$  and  $[T]$  at  $t = 0$  (using the program NONLIN).<sup>26</sup>

$$d[C]/dt = \{R/(1 + R)\}k_4[T] - \{1/(1 + R)\}k_3[C] - k_5[C] \quad (6)$$

$$d[T]/dt = \{1/(1 + R)\}k_3[C] - \{R/(1 + R)\}k_4[C] - k_6[T] \quad (7)$$

The exact starting time ("real"  $t = 0$ ) was unknown because the first data points were collected after the sample was allowed to equilibrate in the NMR probe at the reaction temperature for ca. 20 min (the sample had to be warmed from  $-78$  to  $-30$  °C in the probe and then stabilized). Thus, an offset in the time scale was introduced such that the sum of weighted, squared deviations between fitted curve and observed data was minimized via iterative calculations.

**X-ray Crystallographic Analysis.** Data were collected on an Enraf-Nonius CAD4 diffractometer (Mo  $K_\alpha$  radiation,  $\lambda = 0.71073$  Å) and programs were part of the Enraf-Nonius Structure Determination package, as revised in 1982, and implemented on a PDP 11/34 computer. Crystals of **8a** ( $R = Ph$ ) were grown from methylene chloride/hexanes (3:1). The crystal used for the analysis, an irregular one cut from a larger crystal, measured  $0.3 \times 0.3 \times 0.25$  mm<sup>3</sup>.

*threo*-(1-Hydroxy-1-phenyl-2-pentyl)triphenylphosphonium bromide

(**8a**,  $R = Ph$ ):  $C_{29}H_{30}POBr$ , mol wt 505.43; orthorhombic,  $a = 10.108$  (3) Å,  $b = 15.004$  (4) Å,  $c = 16.912$  (4) Å,  $V = 2565$  (3) Å<sup>3</sup>,  $d_{\text{calcd}} = 1.308$  g/cm<sup>3</sup> for  $Z = 4$  molecules/unit cell, space group  $Pca2_1$ . Of 3301 unique reflections collected up to  $2\theta = 56.7^\circ$ , 1170 had  $I > 2\sigma(I)$  and were used for the subsequent structure analysis (data corrected for Lorentz and polarization factors, but not for absorption). The bromine position was determined by Patterson techniques; the other non-hydrogen atoms were determined from subsequent difference Fourier maps. Final anisotropic refinement of non-hydrogen atoms (benzene carbons were only refined isotropically, and hydrogens were not included) gave  $R = 0.061$  and  $R_w = 0.063$ , where  $R = (\sum||F_o| - |F_c||)/\sum|F_o|$ ,  $R_w = [\sum(|F_o| - |F_c|)^2/\sum F_o^2]^{1/2}$ , and the function minimized was  $(\sum|F_o| - |F_c|)^2$ . A figure showing the crystallographic numbering system and tables of atomic positional parameters, thermal parameters, bond distances, bond angles, and torsional angles are collected in the supplementary material.<sup>24</sup>

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**Supplementary Material Available:** Figure showing **8a** ( $R = Ph$ ) with the crystallographic numbering system; tables of bond distances, bond angles, torsional angles, and positional and thermal parameters, for **8a** ( $R = Ph$ ); complete rate data used in the kinetic analyses; experimental procedures for the preparation of some phosphonium salts (21 pages). Ordering information can be found on any current masthead page.

## Kinetics of Ozonation. 5. Reactions of Ozone with Carbon-Hydrogen Bonds

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**Abstract:** Rates of ozonation for 10 ethers, 2 aldehydes, and 2 saturated hydrocarbons are reported in carbon tetrachloride solvent, over a 36–60 °C temperature range. More limited data are reported in acetonitrile. The resulting activation parameters are inconsistent with a mechanism involving prior complexation of ozone with an  $\alpha$  oxygen atom or with hydrogen-atom abstraction. Of the mechanisms previously proposed in the literature, a hydride abstraction and the concerted insertion of ozone into a C–H bond are most consistent with our kinetic data. A comparison of rate constants in carbon tetrachloride to rate constants measured in acetonitrile indicates that the effect of solvent polarity is small, so either an ionic mechanism must involve a high degree of ion pairing or an insertion mechanism involves a dipolar contribution.

Ozone is a reactant of considerable interest in organic chemistry, largely due to its reactions with alkenes.<sup>1</sup> A growing body of work, however, has been reported on the reactions of ozone at carbon-hydrogen bonds.<sup>2–19</sup> Special attention has been given to

the reactions of ozone at activated C–H bonds, such as the  $\alpha$  hydrogens of alcohols, ethers, and aldehydes and at benzylic positions;<sup>2,3</sup> however, some saturated hydrocarbons also have been studied.<sup>2,3</sup> In a number of cases, the initial products have been

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**Table I.** Absolute Rate Constants and Activation Parameters of the Reactions of Ozone with Various Substrates in CCl<sub>4</sub>

substrate	$k$ , M <sup>-1</sup> s <sup>-1</sup> <sup>a</sup>	$T$ range, °C	$n^b$	$E_a$ , kcal/mol	log $A^c$
1,3-trioxolane	7.7	-19-40	9	7.6	6.7 <sup>d</sup>
tetrahydrofuran	4.1	-15-40	7	8.2	6.6
butyl ether	2.0	-20-40	8	9.7	7.4
isopropyl ether	1.5	-15-40	4	10.0	7.9
ethyl ether	0.9	-15-40	6	9.9	7.3
tetrahydropyran	0.4	-20-40	7	9.7	6.8
1,2-dimethoxyethane	0.09	-20-40	8	11.1	7.6
<i>tert</i> -butyl methyl ether	0.017	-20-40	6	10.6	6.3
1,4-dioxane	0.01	-15-40	7	12.6	7.3
2-chloroethyl ether	0.01	-11-40	5	10.1	5.5
2,3-dimethylbutane	0.035	-15-40	5	11.4	7.3
cyclohexane	0.001 <sup>e</sup>	+9-45	4	14.6	7.7
pivaldehyde	28.9	-15-45	7	8.6	8.3
2-phenylethanal	4.0	-15-45	6	10.3	8.9

<sup>a</sup>These are experimentally determined rate constants measured at 0 °C. <sup>b</sup>This is the number of temperatures at which measurements were made. <sup>c</sup>These values are corrected statistically for the number of hydrogens  $\alpha$  to oxygen for the ethers, for the number of tertiary hydrogens in 2,3-dimethylbutane, and for the total number of hydrogens in cyclohexane. <sup>d</sup>For 1,3-trioxolane a statistical factor of 2 was used, with the assumption that only the hydrogens at C-2 are ozonated. <sup>e</sup>This is an extrapolated value.

shown to be hydrotrioxides,<sup>3-5</sup> which are generally stable below about -40 °C. The reaction of ozone with C-H bonds has been shown to occur with net retention of configuration,<sup>5-8</sup> to have a pronounced kinetic isotope effect,<sup>5-7,9</sup> and to have a relative reactivity of 3° > 2° > 1° for both ethers<sup>7,9</sup> and saturated hydrocarbons.<sup>10</sup>

The mechanism for the ozonation of C-H bonds has not been clearly established. Proposals have included mechanisms involving initial attack at an oxygen atom,<sup>11</sup> abstraction of either hydride<sup>12</sup> or a hydrogen atom,<sup>6,7,13</sup> and a concerted cycloaddition.<sup>9,11,14-19</sup> Nangia and Benson have argued, based on thermochemical considerations, that only the reaction mechanism involving an initial hydride abstraction by ozone is energetically feasible.<sup>12</sup> In an attempt to evaluate the likelihood of the proposed mechanisms, we have measured the absolute rates of reaction, at several temperatures, of a series of ethers, aldehydes, and saturated hydrocarbons with ozone in CCl<sub>4</sub> and in acetonitrile.

### Experimental Section

All materials were of the highest purity commercially available. With the exceptions of the aldehydes, 2-chloroethyl ether, and 2-cyanoethyl ether, substrates were distilled prior to use. Solvents were pretreated with ozone before use to assure the absence of reactive impurities. Most of the absolute rate data were collected by stopped-flow spectroscopy.<sup>20</sup> A solution of ozone (<2 mM) was mixed in the cell with a solution of a substrate (>250 mM), and the decrease in the absorbance due to ozone was monitored with time at 280 nm. Second-order rate constants were calculated from the observed pseudo-first-order loss of ozone. Data in CCl<sub>4</sub> were collected at four to nine temperatures for each substrate ranging from -20 to 40 °C; when acetonitrile was used as the solvent, data were collected only at 20 ± 0.1 °C.

The rates of ozonation of chloroform and deuterated chloroform were too slow to measure by stopped-flow spectroscopy. These materials were initially distilled and then added to a solution of ozone in CCl<sub>4</sub> at 23 °C. The UV absorbance of ozone was measured periodically on a Varian Cary 219 spectrophotometer until no further change in absorbance was observed. Pretreatment of the substrate with ozone followed by redistillation resulted in no change in the measured rate constants, indicating that the observed reaction was not due to trace amounts of reactive impurities. Both this procedure and the stopped-flow technique were described in part I.<sup>20</sup>

### Results

The activation parameters determined in this study are collected in Table I, along with representative rate constants (measured at 0 °C). The preexponential terms are statistically corrected for the number of reactive hydrogens. Standard deviations were less than 0.5 kcal mol<sup>-1</sup> and 0.5 log  $A$  units.

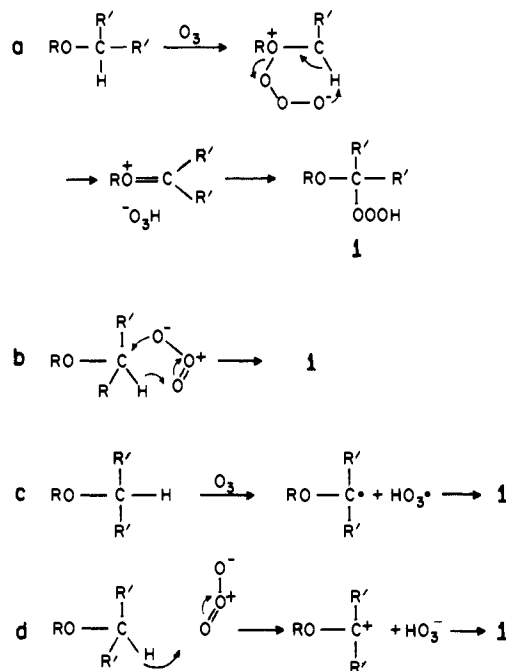
Table II compares rate constants (not statistically corrected) for the ozonation of some ethers in CCl<sub>4</sub> and in CH<sub>3</sub>CN at 20.0 °C.

**Table II.** A Comparison of Absolute Rate Constants for the Ozonation of Ethers in CCl<sub>4</sub> and in CH<sub>3</sub>CN

substrate	$k$ , M <sup>-1</sup> s <sup>-1</sup> <sup>a</sup>	
	CCl <sub>4</sub>	CH <sub>3</sub> CN
tetrahydrofuran	12.5 ± 0.5	31.9 ± 0.9
butyl ether	6.0 ± 0.3	14.8 ± 1.0
tetrahydropyran	1.3 ± 0.06	3.3 ± 0.1
1,2-dimethoxyethane	0.4 ± 0.01	0.86 ± 0.04
2-chloroethyl ether	0.04 ± 0.002	0.08 ± 0.01

<sup>a</sup>These data were collected at 20 °C.

### Scheme I



The rate constant for the reaction of ozone with chloroform at 23 °C is  $(7 \pm 1) \times 10^{-5}$  M<sup>-1</sup> s<sup>-1</sup>. This can be compared with the rate constant for deuterated chloroform, measured under the same conditions, of  $(0.95 \pm 0.20) \times 10^{-5}$  M<sup>-1</sup> s<sup>-1</sup>.

### Discussion

Four different mechanisms have been proposed for the reaction of ozone at C-H bonds to form hydrotrioxides; these possibilities are illustrated in Scheme I. Strong evidence for a mechanism involving initial attack at the heteroatom, similar to that shown in Scheme Ia, has been presented for the ozonation of amines and sulfides (with initial attack at, or association with, nitrogen or sulfur),<sup>21</sup> and it has also been proposed for the ozonation of

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ethers.<sup>11</sup> A mechanism involving a 1,3-dipolar insertion of ozone into a C–H bond (Scheme Ib) has been proposed for the reaction of ozone with ethers,<sup>9,11,15</sup> acetals,<sup>14</sup> aldehydes,<sup>16,17</sup> and saturated hydrocarbons.<sup>18,19</sup> A radical mechanism (hydrogen-atom abstraction; Scheme Ic) has been suggested for alcohols,<sup>13</sup> ethers,<sup>9</sup> and hydrocarbons.<sup>6,7</sup> A fourth mechanism, hydride abstraction by ozone (Scheme Id), has been suggested by Nangia and Benson<sup>12</sup> based on thermochemical considerations. Also, Hamilton has suggested that hydrogen-atom abstraction and hydride abstraction (Scheme Ic,d) might be considered as two extreme resonance forms of the intermediates of a single mechanism.<sup>6,7</sup>

The pathway presented in Scheme Ia is not possible for saturated hydrocarbons, which have no heteroatom  $\alpha$  to the C–H bond undergoing ozonation. If such a mechanism were the major pathway for oxygen-containing substrates, one would expect ozone to behave quite differently toward hydrocarbons than ethers. In fact the energies of activation for ozonation of isopropyl ether and 2,3-dimethylbutane differ by at most 2 kcal mol<sup>-1</sup>, and at 0 °C the ether reacts only 50-fold faster than does the hydrocarbon. These relatively small differences can be accounted for by resonance stabilization due to the ether oxygen of a cation or radical intermediate or by the weakening of the C–H bond  $\alpha$  to oxygen. In addition, our measured kinetic isotope effect, as well as others measured earlier,<sup>5-7,9</sup> is fairly large, consistent with a mechanism involving C–H bond breaking in the rate-determining step. In the ozonation of chloroform,  $k_H/k_D$  is about  $7 \pm 2$ . Other values, for toluene,<sup>6</sup> benzyl *tert*-butyl ether,<sup>9</sup> and saturated hydrocarbons,<sup>5,7</sup> are all near 4. This does not completely rule out an initial attack at oxygen in the latter two substrates, but it is more consistent with the mechanisms given in Scheme Ib–d. At present, and for reasons of economy, we favor a single mechanism common to the ozonation of ethers and saturated hydrocarbon C–H bonds; therefore, we conclude that the mechanism in Scheme Ia can be excluded.

The two aldehydes included in this study exhibit activation parameters that suggest that aldehydes may be reacting by a different mechanism than that of the other compounds. The preexponential terms for the aldehydes are significantly higher than those of the ethers or of the saturated hydrocarbons, although the energies of activation are comparable. Also the kinetic isotope effect (KIE) for the reaction of an aldehyde with ozone in the absence of oxygen was found to be about 1.2;<sup>17,22</sup> this is significantly less than the KIE's observed for the other substrates.<sup>5-7,9</sup> Again for reasons of economy, we will treat aldehydes as if they react by a common mechanism, along with ethers and saturated hydrocarbons, but recognize that this assumption is subject to revision should further data support a discrete mechanism for aldehydes.

We will now focus our attention on the remaining three proposed mechanisms. A comparison of entropies of activation for the ozonation of C–H bonds to those expected for the reactions presented in Scheme I is informative. From Table I it can be seen that  $\log A$  ranges from 5.5 to 7.9 for the ozonation of ethers, while the values of  $\log A$  for 2,3-dimethylbutane and cyclohexane are 7.3 and 7.7, respectively. Hendry et al. estimate that the hydrogen abstraction reactions of free radicals should have a  $\log A$  of about 9.4 for tertiary alkanes and about 8.7 for ethers and aldehydes.<sup>23</sup> Thus, our values of  $\log A$  for these ozonation reactions are lower than those expected for radical reactions (for all of the substrates except aldehydes, for which  $\log A = 8.3$ – $8.9$ ), implying that there is a greater degree of order in the transition states than would be the case of a hydrogen-atom abstraction. However, with the exceptions of 2-chloroethyl ether and *tert*-butyl methyl ether, our  $\log A$  values are somewhat higher than would be expected for a 1,3-dipolar insertion mechanism ( $\log A < 7$ ).<sup>24</sup> Thus, our

**Table III.** Relative Reactivities of Some Alkanes Toward Ozone and Some Radical Species

type of alkane	ozone <sup>a</sup>	radicals <sup>b</sup>		
		Br <sup>•</sup>	ROO <sup>•</sup>	RO <sup>•</sup>
primary	0.003	0.02	0.024	0.08
secondary	1.0 (1)	1.0	1.0	1.0
tertiary	87.0 (120)	40.0	10.0	3.7
Ar-CH <sub>3</sub> (p) <sup>c</sup>	-2.07	-1.88	-0.76	-0.34

<sup>a</sup> These data are taken from ref 10, collected at 25 °C in CCl<sub>4</sub>, and, except for the value for a primary C–H bond, averaged for several substrates. Parenthetical values were collected by us under the same conditions and are for cyclohexane and 2,3-dimethylbutane only. <sup>b</sup> R = *tert*-butyl. These data are taken from ref 25. <sup>c</sup> These Hammett  $\rho$  values are taken from ref 6 (ozone) and ref 26 (radicals).

**Table IV.** Relative Rates of Ether Ozonation in Comparison to Some Relative Rates of Hydrogen Abstraction<sup>a</sup>

substrate	ozone	RO <sup>•</sup> <sup>b</sup>	ROO <sup>•</sup> <sup>c</sup>
tetrahydrofuran	1.0	1.0	1.0
butyl ether	0.49		0.27
isopropyl ether	0.73	0.92	0.05
ethyl ether	0.22	0.71	
tetrahydropyran	0.10	0.47	0.13
<i>tert</i> -butyl methyl ether	0.0056	0.19	
1,4-dioxane	0.0012	0.14	0.11

<sup>a</sup> All rates presented are per hydrogen relative to tetrahydrofuran. The rates of ozonation were measured at 0 °C. <sup>b</sup> R = *tert*-butyl. These data are measured at 0 °C and are taken from ref 28. <sup>c</sup> R = *tert*-butyl. These data are measured at 30 °C and are taken from ref 27.

measured preexponential terms do not support a hydrogen-atom abstraction (Scheme Ic) and also are somewhat inconsistent with a concerted insertion (Scheme Ib). Nangia and Benson<sup>12</sup> have suggested that the  $\log A$  for hydride abstraction by ozone from a hydrocarbon should be about 7.5, which is in good agreement with our data.

Tables III and IV present relative rate data for the reactions of alkanes and ethers with ozone and a series of radicals. From Table III it can be seen that ozone reactions exhibit greater selectivity between primary, secondary, and tertiary alkanes than do the radicals.<sup>10,25</sup> Also, the Hammett  $\rho$  value for reaction with substituted toluenes is slightly more negative for ozonation than for any of the radicals shown.<sup>6,26</sup> The greater sensitivity of ozone reactions to changes in ring substituents suggests that the transition state for the ozonation of alkanes is more polar than that of a hydrogen-atom abstraction by a free radical.

For a series of ethers (Table IV) rates of ozonation parallel rates of free-radical hydrogen abstraction,<sup>27,28</sup> particularly those of alkoxy radicals.<sup>28</sup> However, note that the reactivity of 1,4-dioxane toward ozone is far less than would be anticipated by analogy to peroxy radicals. This suggests that while resonance interactions with the  $\alpha$  oxygen impart similar stabilizations to the transition states, the ozone reactions are more sensitive to the inductive effects of a  $\beta$  substituent. The large inductive effect on rates of ozonation of ethers is also seen in a comparison of butyl ether, ethyl ether, 1,2-dimethoxyethane (DME), and 2-chloroethyl ether. Correcting DME for reactivity at the methyl groups (by assuming that they react at the same rate as does *tert*-butyl methyl ether) yields relative rate constants for the series of 200:90:5.6:1 or a Hammett-Taft<sup>29</sup>  $\rho^*$  value of  $-1.98$  ( $r^2 = 0.983$ ). (For comparison,  $\rho^*$  values for solvolysis reactions in ethanol are  $-3.3$  for tertiary alkyl chlorides and  $-0.74$  for primary alkyl tosylates.)<sup>30</sup> Once

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again, this implies a substantial degree of polar character in the transition state of ozonation.

The above discussion rules out a mechanism involving hydrogen-atom abstraction (Scheme Ic). Therefore, we will discuss the data below in terms of the two remaining mechanisms we favor.

The electronic effects discussed above, as well as the thermochemical calculations of Nangia and Benson<sup>12</sup> support a hydride abstraction mechanism. Nangia and Benson also disfavor the insertion route both because of the entropy differences cited above and because of the high-energy requirements (20–26 kcal mol<sup>-1</sup>) that they estimate is required in achieving a pentavalent carbon transition state.<sup>12</sup> We observe energies of activation no greater than 14.6 kcal mol<sup>-1</sup>. Additionally, one might expect the preexponential term for the insertion of ozone into a C–H bond to be lower than those of 1,3-dipolar additions of ozone to a C=C double bond, typically 10<sup>6</sup>–10<sup>7</sup>.<sup>20</sup> In fact the values measured herein are higher by about one-half of a log *A* unit.

Other evidence, however, seems to favor an insertion mechanism over a hydride abstraction. First, reactions of ozone with hydrocarbons occur with net retention of configuration.<sup>5–8</sup> Second, the polarity of the solvent has less effect on the reaction rates than might be expected for a reaction producing ionic intermediates. Data presented in Table II illustrate this point: even for the least-reactive substrates, going from CCl<sub>4</sub> to CH<sub>3</sub>CN increases the rate constants by less than a factor of 3. Our value for the rate constant for ozonation of tetrahydrofuran in water<sup>31</sup> is roughly equal to our value measured in CCl<sub>4</sub>. Erickson et al.<sup>9</sup> have determined relative reactivities for the ozonation of several ethers

in acetone and propyl acetate; their values are similar to those we observe in acetonitrile. Taillefer et al.<sup>14</sup> have noted that the rate of ozonation of an acetal varies by less than a factor of 2 when hexane, Freon-11, ethyl acetate, or acetone is used as the solvent.

A possible rationalization for these data in terms of the hydride abstraction mechanism involves the observation of Hellmann and Hamilton<sup>6</sup> that the percent retention of configuration is higher in more viscous solvents. They suggest that the intermediate is a solvent-caged radical pair.<sup>6</sup> The intermediacy of a solvent-caged ion pair might also account for the small polar solvent effect, suggesting only minor solvation of reaction intermediates and rationalizing the observed retention of configuration. However, we do not favor this explanation without further experimental support.

In summary, of the two mechanisms we consider most likely, the retention of configuration<sup>5–8</sup> and the small solvent effects are most consistent with an insertion mechanism (Scheme Ib), while the relatively high log *A* values and the thermochemical calculations of Nangia and Benson<sup>12</sup> are more consistent with an initial hydride abstraction (Scheme Id). Neither mechanism can be ruled out with finality, and further experimental tests of these two mechanisms are needed.

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**Registry No.** 1,2,3-Trioxolane, 6669-36-9; tetrahydrofuran, 109-99-9; butyl ether, 142-96-1; isopropyl ether, 108-20-3; ethyl ether, 60-29-7; tetrahydropyran, 142-68-7; 1,2-dimethoxyethane, 110-71-4; *tert*-butyl methyl ether, 1634-04-4; 1,4-dioxane, 123-91-1; 2-chloroethyl ether, 111-44-4; 2,3-dimethylbutane, 79-29-8; cyclohexane, 110-82-7; pivaldehyde, 630-19-3; 2-phenylethanal, 122-78-1.

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## Regioselective Phosphorylation and Cyclodehydration of Triols with Diethoxytriphenylphosphorane

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**Abstract:** Diethoxytriphenylphosphorane (DTPP) selectively diphosphorylates the vicinal diol functional group in 1,2,4-triols affording thermodynamically stable 2,2,2-triphenyl-1,3,2-dioxaphospholanes. When subjected to thermolysis conditions, these dioxaphospholanes dissociate to form transient betaines which subsequently collapse, via 3-exo-tet extrusion of triphenylphosphine oxide, to epoxides. The structures of the 2,2,2-triphenyl-1,3,2-dioxaphospholanes are readily assessed from <sup>13</sup>C-<sup>31</sup>P coupling constants and <sup>31</sup>P chemical shifts. Alkyl and aryl substituents attached to the dioxaphospholane ring also induce pronounced substituent shielding effects on the <sup>31</sup>P resonance of the phospholanes. These effects are useful in corroborating the structural assignments of the dioxaphospholanes.

Recently, we demonstrated the versatility of diethoxytriphenylphosphorane (DTPP) for the mild, selective cyclodehydration of various diols to cyclic ethers.<sup>1</sup> Our findings stimulated intense interest in the origin and structural characteristics of the phosphorylated intermediates which apparently preceded the requisite, but transitory, betaines.<sup>1,2</sup>

"Phosphorylation" of a nucleoside hydroxyl group is generally viewed as a critical step in oligonucleotide synthesis.<sup>3</sup> This process is uniquely different from the "phosphorylation" methodology described here involving triols. Nevertheless, both processes involve

formation of a new phosphorus–oxygen bond by combining a hydroxyl group with an organophosphorus reagent, and it seems plausible that fundamental knowledge on "site selective" phosphorylation of polyols would be useful in predicting the preferred sites of phosphorylation within polyhydroxy substrates as well. Thus, it seemed reasonable, based on the conceptual similarity of the two processes, that results from phosphorylation chemistry could serve as stimuli for development of new regioselective phosphorylation reagents. In fact, phosphorylated intermediates have been shown to be essential in transphosphorylation of dinucleotides initiated by ribonucleases.<sup>4</sup>

Herein, we present pertinent details on the mechanism of phosphorylation and cyclodehydration of triols as well as im-

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