was added and the solution was worked up as in the preparative runs. The crude product was separated on the Chromatotron using 2% MeOH in CH_2Cl_2 to give a leading band (0.067 g, yellow color, sulfur odor, unidentified), a second band identified as 6α-methyl-17α-hydroxy-21-acetoxy-4,9(11)-pregnadiene-3,20-dione (**35**,[16] 0.050 g, 0.12 mmol, 12%), and finally 6α-methylcortisone acetate (**34**, 0.230 g, 58%).

Addition of 9α-fluorohydrocortisone acetate (**36**,[17] 0.218 g, 0.516 mmol) in 45 mL of CH_2Cl_2 to 11 mmol of oxidant in 30 mL of CH_2Cl_2 was carried out as for **33**. After workup, separation of the crude product from a 15-min reaction at −60 °C on the Chromatotron using 2% MeOH in CH_2Cl_2 gave 0.010 g (0.024 mmol, 5%) of 9α-fluorocortisone acetate (**37**)[18] and 0.202 g (89%) of recovered **36**. When the reaction was repeated and continued for 120 h at −20 °C, the crude product showed at least nine major spots on TLC. Two of these corresponded in R_f value to **36** and **37**, but none appeared to comprise more than 25% of the mixture, which was not examined further.

Registry No. **4**, 23372-58-9; **10**, 497-37-0; **11**, 497-36-9; **12**, 124-76-5; **13**, 507-70-0; **14**, 7443-70-1; **15**, 7443-52-9; **16**, 937-05-3; **17**, 21862-63-5; **18**, 502-41-0; **19**, 589-98-0; **20**, 2890-98-4; **21**, 694-97-3; **22**, 536-50-5; **23**, 111-87-5; **24**, 98-85-1; **25**, 100-51-6; **26**, 75-84-3; **27**, 1737-26-4; **28**, 91-01-0; **29**, 340-04-5; **30**, 3319-15-1; **31**, 88288-58-8; **32**, 88288-59-9; **33**, 88288-60-2; **36**, 514-36-3; Me_2SO, 67-68-5; $(COCl)_2$, 79-37-8.

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Reaction of Tetramethyl-1,2-dioxetane with Phosphines: Deuterium Isotope Effects

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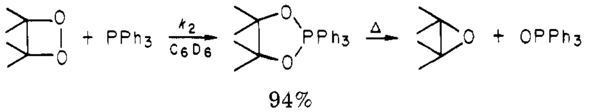
The reaction of tetramethyl-1,2-dioxetane (**1**) in C_6D_6 with methyldiphenylphosphine (**2a**), methyl-d_3-diphenylphosphine (**2d**), dimethylphenylphosphine (**2c**), and dimethyl-d_6-phenylphosphine (**2d**) produced the corresponding 2,2-dihydro-4,4,5,5-tetramethyl-2,2,2-trisubstituted-1,3,2-dioxaphospholanes **3a–d** in 90% yield or better. The phosphoranes were characterized by ^1H and ^{31}P NMR spectroscopy and by their thermal decomposition (60 °C) to tetramethyloxirane and the corresponding phosphine oxides. Kinetic studies of the rate of phosphorane formation in benzene were carried out by the chemiluminescence method. The reaction was found to be of the first order with respect to **1** and to the phosphines. Inverse deuterium isotope effects were observed for the reaction of **1** with phosphines **2a–d**. The value of k_{CH_3}/k_{CD_3} obtained with phosphines **2a,b** was found to be 0.94 ± 0.01 while that with phosphines **2c,d** was found to be 0.91 ± 0.01. The rates of phosphorane formation for the reaction of tetramethyl-d_{12}-1,2-dioxetane (**1d**) with **2a,c** and triphenylphosphine were also investigated and compared to those for reaction with **1**. For all three phosphines, the rate constants with **1d** were slower than those obtained with **1** ($k_H/k_D = 1.06 \pm 0.02$). This result is in marked contrast with the results obtained with the deuterated phosphines. The results are consistent with a concerted insertion of the phosphine into the peroxy bond of the dioxetane.

1,2-Dioxetanes have been studied extensively because of their unique chemiluminescent thermal decomposition to two carbonyl fragments (reaction 1).[2] Under controlled conditions, dioxetanes have been shown to undergo a number of interesting reactions (metal ion catalyzed decomposition,[3a] BF_3-catalyzed rearrangement,[3b] reduction to 1,2-glycols,[3c] insertion into the peroxy bond[4–6]) in which no excited products are formed.[2] The reaction of trivalent phosphorus compounds with dioxetanes is the most studied nonthermolytic reaction of dioxetanes. In 1973, the reaction of triphenylphosphine with tetramethyl-1,2-dioxetane was shown[4] to produce an isolable phosphorane, the thermal decomposition of which resulted in the formation of the expoxide and the phosphine oxide (Scheme I). Previously, Denney had shown[7] that the reaction of

(1)

CL = chemiluminescence

Scheme I



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0022-3263/84/1949-0793$01.50/0

Table I. Product Yields for the Reaction[a] of 1 and 2a-e in C_6D_6 at 34 °C and NMR Spectral Data for 3a-e

phosphorane	phosphorane yield,[b] %	pinacolone yield,[b,c] %	NMR chemical shifts	
			^{31}P[d]	^{1}H[e]
3a	92	8	43.5	1.02 (s, 12 H), 1.85 (d, 3 H, J = 11 Hz)
3b	93	7	43.7	1.02 (s, 12 H)
3c	90	10	47.2	1.02 (s, 12 H), 1.49 (d, 6 H, J = 9 Hz)
3d	91	9	48.0	1.01 (s, 12 H)
3e	94[f]	6	48.5	1.01 (s, 12 H)

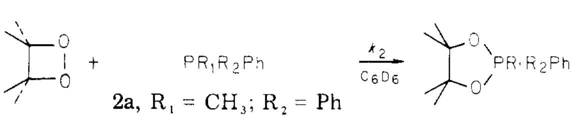
[a] Initial concentrations of 1 and the phosphines = 5×10^{-2} M. [b] Determined by integration of the ^1H NMR signals. [c] Side product, concomitant yield of phosphine oxide. [d] Trimethylphosphate (δ −3.1) used as an internal standard. [e] Aromatic signals (δ 7-8), complex. [f] Good agreement with previous values. See ref 4 and 8a.

diethyl peroxide with triethyl phosphite produced pentaethoxyphosphorane as a stable intermediate. Insertion into the peroxy bond of dioxetanes by trivalent phosphorus compounds has been shown[8] to be a synthetically useful procedure for the preparation of phosphoranes. In addition, this reaction (with triphenylphosphine) has been employed as an analytical method[9] to determine dioxetane concentrations and to characterize[3c,8c,10] dioxetanes.

Denney had shown[7] that the results for the reaction of diethyl peroxide with trivalent phosphorus compounds were consistent with a biphilic process. The experimental evidence for the reaction of trivalent phosphorus compounds with tetramethyl-1,2-dioxetane has also been interpreted[11] in favor of a concerted (biphilic) mechanism of phosphorane formation. In the concerted (biphilic) mechanism of insertion into a peroxy bond, the phosphorus atom is required[7,11] to bond with both oxygen atoms in the transition state. The specific interactions that lead to the biphilic contributions are not understood. In addition, little is known as to the effects of structure on the mechanism of insertion of the phosphorus atom into the peroxy bond. We report a study of deuterium isotope effects on the reaction of tetramethyl-1,2-dioxetane and a series of phosphines.

Results

The reaction of tetramethyl-1,2-dioxetane (1) in C_6D_6 with methyldiphenylphosphine (**2a**), methyl-d_3-diphenylphosphine (**2b**), dimethylphenylphosphine (**2c**), and dimethyl-d_6-phenylphosphine (**2d**) in C_6D_6 produced the corresponding 2,2-dihydro-4,4,5,5-tetramethyl-2,2,2-trisubstituted-1,3,2-dioxaphospholanes **3a–d** in 90% yield or better (reaction 2). As noted in the reaction of triarylphosphines with **1**, pinacolone and the concomitant amount of phosphine oxide were formed directly as side products in 10% yield or less. 2,3-Dimethyl-3-hydroxybut-1-ene (trace) was noted as a minor side product in several reactions. In solution, phosphoranes **3a–d** were stable for approximately 1 h at 25 °C (without detectable decomposition). Complete decomposition of the phosphoranes in solution occurred over the course of several days at room temperature. The phosphoranes were characterized by ^1H and ^{31}P NMR spectroscopy and by their thermal decomposition (at 60 °C) to tetramethyloxirane and the corresponding phosphine oxides **4a–d** (reaction 3). The results for the reaction of 1 with triphenylphosphine (**2e**) were in agreement with the published values and are included for comparison. Product yields for the reaction of 1 with phosphines **2a–e** and the NMR data for phosphoranes **3a–e** are summarized in Table I.

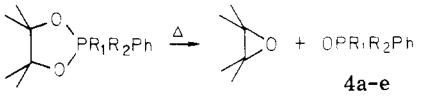


(2)

1

2a, $R_1 = CH_3$; R_2 = Ph
b, $R_1 = CD_3$; R_2 = Ph
c, $R_1 = R_2 = CH_3$
d, $R_1 = R_2 = CD_3$
e, $R_1 = R_2$ = Ph

3a-e



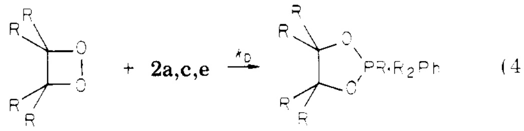
(3)

4a-e

3a-e

Kinetic studies of the rate of phosphorane formation in benzene were carried out by the chemiluminescence method. In agreement with earlier results, the reaction was found to be of the first order with respect to the phosphines and to 1. The second-order rate constants (k_2) were determined by dividing the pseudo-first-order rate constants by the initial phosphine concentrations. Inverse deuterium isotope effects were observed for reaction with phosphines **2a–d** over the entire temperature range employed. The value of k_{CH_3}/k_{CD_3} obtained for phosphines **2a,b** was found to be 0.94 ± 0.01 and the value with phosphines **2c,d** was found to be 0.91 ± 0.01. The observed deuterium isotope effect *per CD_3 group* with **2c,d** is of similar magnitude to that with phosphines **2a,b**. Thus, the isotope effect per CD_3 group appears to be additive. The kinetic data for phosphines **2a–d** are summarized in Tables II and III.

Tetramethyl-d_{12}-1,2-dioxetane (**1d**) was prepared by the standard procedure. The reaction of **1d** in C_6D_6 with phosphines **2a,c,e** produced 2,2-dihydro-4,4,5,5-tetramethyl-d_{12}-2,2,2-trisubstituted-1,3,2-dioxaphospholanes **3a′,c′,e′** in high yield (reaction 4). Kinetic studies were carried out as above. For the three phosphines investigated, the values of k_2 determined for reaction with **1d** were slower than those determined for 1. For all three cases, k_H/k_D was 1.06 ± 0.02. This is in the opposite direction to the deuterium isotope effects observed with



(4)

1d, R = CD_3

3a′,c′,e′

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Table II. Kinetic Data for the Reaction of 1 with Phosphines 2a-b in C_6D_6

T,[a] °C	$[Ph_2PMe] \times 10^3$, M	$\frac{[2a]}{[1]}$	k_2[b]	$[Ph_2PCD_3] \times 10^3$, M	$\frac{[2b]}{[1]}$	k_2[b]	k_{CH_3}/k_{CD_3}
19.5	10.99	14	5.70	6.53	11	6.04	
	11.29	15	5.73	6.39	14	6.11	
	6.68	11	5.76			6.08 ± 0.04	0.94
			5.73 ± 0.02				
21.0	5.43	12	6.70	9.83	14	7.16	
	7.15	16	6.74	9.62	11	7.20	
			6.72 ± 0.02			7.18 ± 0.02	0.94
25.0	5.28	12	7.79	6.33	14	8.16	
	7.31	17	7.74	10.44	23	8.42	
			7.77 ± 0.03			8.29 ± 0.23	0.94
30.4	5.24	12	10.4	8.27	21	10.9	
	3.95	18	10.6	8.27	21	10.7	
	4.36	10	10.3	8.39	11	10.8	
			10.4 ± 2			10.8 ± 0.1	0.97
39.7	5.75	13	16.1	4.18	9	17.0	
	6.00	14	16.1	4.27	19	17.1	
	6.26	14	16.1	7.46	34	17.3	
	5.24	24	16.2			17.1 ± 0.2	0.94
			16.1 ± 0.1				
49.5	3.52	16	22.3	3.19	14	23.5	
	4.80	22	22.4	4.87	22	24.0	
			22.3 ± 0.1	4.34	9	23.6	
						23.7 ± 0.2	0.94
						av	0.94 ± 0.01

[a] ±0.3 °C. [b] $M^{-1}\ s^{-1}$.

Table III. Kinetic Data for the Reaction of 1 with Phosphines 2c,d in C_6D_6

T,[a] °C	$[PhPMe_2] \times 10^3$, M	$\frac{[2c]}{[1]}$	k_2[b]	$[PhP(CD_3)_2] \times 10^3$, M	$\frac{[2d]}{[1]}$	k_2[b]	k_{CH_3}/k_{CD_3}
19.5	7.68	17	12.4	8.43	13	13.6	
	9.01	14	12.5	7.90	12	13.6	
			12.5 ± 0.1	7.00	10	13.6	
						13.6	0.92
25.0	6.68	15	16.3	4.17	9	17.4	
	4.82	11	15.7	4.13	14	17.9	
			16.0 ± 0.3			17.6 ± 0.2	0.91
30.4	7.68	17	19.4	7.32	19	21.8	
	5.50	12	19.3	5.42	13	21.7	
			19.3 ± 0.1			21.8 ± 0.1	0.89
34.4	6.68	17	24.7	6.13	16	26.1	
	4.82	13	24.4	5.07	11	26.4	
			24.5 ± 0.2			26.3 ± 0.2	0.93
39.7	3.28	17	31.7	4.17	21	34.1	
	5.50	35	30.7	2.55	13	34.6	
			31.2 ± 0.5			34.3 ± 0.3	0.91
						av	0.91 ± 0.01

[a] ±0.3 °C. [b] $M^{-1}\ s^{-1}$.

the deuterated phosphines. The data are summarized in Table IV.

Discussion

Historically, the reaction of peroxides with trivalent phosphorus compounds was regarded to proceed via nucleophilic attack on oxygen by phosphorus.[12] Denney showed[7] that the results for the reaction of trivalent phosphorus compounds with dialkyl peroxides were consistent with a biphilic mechanism in which the phosphorus atom was bonding to both oxygen atoms in the transition state. Denney suggested[7b] that the biphilic mechanism of insertion into the peroxy bond occurred in a manner similar to that proposed for insertion reactions of iridium complexes. The lone pair of the phosphorus compound (biphile) must interact with the peroxy σ^* orbital and the biphile must have an available orbital to accept a pair of electrons.

The mechanism of the reaction of tetramethyl-1,2-dioxetane with trivalent phosphorus compounds has been considered[8a] in terms of two extremes: (a) concerted (biphilic) and (b) ionic (S_N2 displacement) (Scheme II). Studies on the reaction of dioxetanes with trivalent phosphorus compounds have been interpreted[8a] to be consistent with a concerted (biphilic insertion into the

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[12] For example, see: Kirby, A. J.; Warren, C. "The Organic Chemistry of Phosphorus"; Elsevier: New York, 1967.

Table IV. Kinetic Data for the Reaction of 1 and 1d with Phosphines

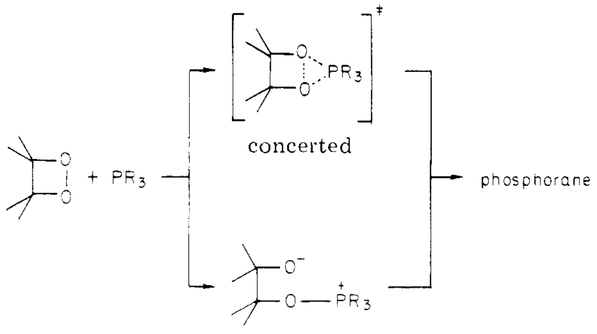
T,[a] °C	$[Ph_3P] \times 10^3$, M	$\frac{[2e]}{[1d]}$	k_2[b]	$[Ph_3P] \times 10^3$, M	$\frac{[2e]}{[1]}$	k_2[b]	k_H/k_D
23.9	7.46	17	1.59	7.19	16	1.66	
	10.98	25	1.61	10.17	23	1.74	
	14.19	33	1.63	13.93	32	1.74	
			1.61 ± 0.02			1.70 ± 0.04	1.06
29.4	6.47	30	2.16	6.47	15	2.29	
	8.92	40	2.20	8.42	19	2.24	
	11.57	52	2.16	10.85	25	2.25	
			2.17 ± 0.03			2.26 ± 0.03	1.04
35.0	5.04	11	2.61	3.89	13	2.82	
	6.57	15	2.61	7.71	18	2.78	
	9.02	21	2.58	9.59	22	2.82	
			2.60 ± 0.02			2.80 ± 0.02	1.08
40.1	6.96	31	3.50	8.91	40	3.78	
	6.96	31	3.51	10.12	46	3.78	
	9.15	42	3.52	12.53	56	3.77	
			3.51 ± 0.01			3.78 ± 0.01	1.08
						av	1.06 ± 0.02

T,[a] °C	$[Ph_2PMe] \times 10^{-3}$ M	$\frac{[2a]}{[1d]}$	k_2[b]	$[Ph_2PMe] \times 10^{-3}$ M	$\frac{[2a]}{[1]}$	k_2[b]	k_H/k_D
25.5	8.56	18	7.72	7.31	8	8.15	
	7.39	15	7.68	6.38	14	8.11	
	6.65	14	7.84	6.25	7	8.26	
			7.75 ± 0.09			8.17 ± 0.09	1.05

T,[a] °C	$[PhPMe_2] \times 10^{-3}$ M	$\frac{[2c]}{[1d]}$	k_2[b]	$[PhPMe_2] \times 10^{-3}$ M	$\frac{[2c]}{[1]}$	k_2[b]	k_H/k_D
27.6	6.97	16	18.4	6.83	16	19.4	
	4.13	9	17.9	5.04	11	19.4	
	5.33	12	18.2	3.98	9	19.7	
			18.2 ± 0.3			19.5 ± 0.2	1.07

[a] ±0.3 °C. [b] $M^{-1} s^{-1}$.

Scheme II



Scheme III

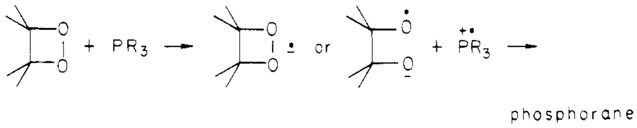


Table V. Activation Parameters for the Reaction of 1 and 2a-e in C_6D_6

phosphorane	E_a, kcal/mol	$\Delta S^{\ddagger}$, eu	k_2, $M^{-1} s^{-1}$ (30 °C)	r[a]
3a	8.8 ± 0.5	-27	10.4 ± 0.2	0.998
3b	8.8 ± 0.5	27	10.8 ± 0.1	0.998
3c	8.2 ± 0.4	-27.6	19.3 ± 0.1	0.996
3d	8.2 ± 0.4	-27.4	21.7 ± 0.1	0.996
3e	9.6 ± 0.8[b]	27	2.34 ± 0.05	0.999

[a] Correlation coefficient. [b] Good agreement with literature values; ref 17.

peroxy bond on the basis of relative reactivity studies and the lack of a polar solvent effect. The results for the reaction of tetramethyl-1,2-dioxetane with triphenylarsine and triphenylantimony were found[5] to be in agreement with a concerted (biphilic) insertion mechanism for group 5A compounds. Recently, a Hammett-type study of the reaction of triarylphosphines with tetramethyl-1,2-dioxetane concluded[11] that the observed ρ^+ value of −0.8 was consistent with a concerted process. Thus, the evidence (lack of polar solvent effect, relative rate studies, Hammett-type study) clearly rules out an ionic (S_N2 type) mechanism for the reaction of trivalent phosphorus compounds with dioxetanes in favor of a biphilic or concerted process.

The relative reactivity series for the reaction of 1 with the nondeuterated phosphines was found to be dimethylphenylphosphine (~10) > methyldiphenylphosphine (~5) > triphenylphosphine (≡1). This result is in accord with the conclusions of the Hammett-type study.[11] In a series of structurally similar phosphorus compounds, the nucleophilic characteristics of a compound appear to be more important than the electrophilic characteristics in determining reactivity. However, methyl diphenylphosphinite[8a] has roughly the same relative reactivity as dimethylphenylphosphine. Thus, the less nucleophilic phosphinite is more reactive than the more nucleophilic phosphines. These data support the concept of a concerted or biphilic mechanism in which nucleophilic and electrophilic characteristics (phosphorane stability) are involved.

Table VI. Physical Data for Phosphine Oxides **4a-d**

phosphine oxide	mp, °C	δ ^{31}P[a]	δ ^{1}H[b]	IR (KBr)
4a	111-112[c]	−30.4	1.87 (d, 3 H, J = 13 Hz)	3050 w, 2975 w, 2910 w, 1435 s, 1170 s
4b	108-109	−24.8		3050 w, 2150 w, 2230 w, 1440 m, 1175 s
4c	102-103[d]	−28.3	1.60 (d, 6 H, J = 12 Hz)	3050 w, 3000 w, 2920 w, 1440 m, 1290 m, 1180 s
4d	115-117	−27.9		3050 w, 2240 w, 2150 w, 1430 m, 1170 s

[a] Trimethyl phosphate (δ −3.1) used as an internal standard. [b] In CCl_4, aromatic region δ 7-8. [c] Literature value 109-111 °C; Beilstein, *16*, II, 378. [d] Literature value 100 °C, Beilstein, *16*, II, 378.

The concept of a concerted insertion of the phosphorus atom into the peroxy bond via a three-centered transition state has considerable appeal and experimental support. However, another mechanistic possibility, electron transfer (Scheme III), must also be considered since electron-transfer-type mechanisms have been shown[13a] to be important for the chemiluminescent decompositions of peroxides in the presence of suitable donors. The thermal decomposition of dioxetanes with readily oxidizable groups is postulated[2c,13] to occur via an intramolecular electron-transfer process. The catalytic decomposition of *cis*-diethoxy-1,2-dioxetane by amines was found[14] to correlate with the ionization potential of the amines, suggesting a mechanism involving a charge-transfer complex. However, intermolecular-type electron-transfer processes (CIEEL[13a]) have not been observed for tetraalkyl-1,2-dioxetanes. Although remote, the possibility of an electron-type mechanism of phosphorane formation cannot be evaluated on the basis of previous studies.

Pryor has proposed[15] an isotope effect test that can be applied to the present case. Pryor has shown[15] that the magnitude of a β-deuterium isotope effect can be used to distinguish S_N2 reactions from electron-transfer reactions. Most S_N2 reactions are predicted[15] to show inverse β-deuterium isotope effects ($k_H/k_D < 1$) with the deuterated nucleophile while electron-transfer reactions would be expected to show normal isotope effects ($k_H/k_D > 1$). Application of this test to the reaction of dioxetanes with phosphorus compounds should allow evaluation of the electron-transfer-type mechanism. Clearly, the large inverse deuterium isotope effects noted for reaction of **1** with **2a-b** and **2c,d** are in the opposite direction from that predicted[15] for an electron-transfer process. Thus, the electron-transfer mechanism as depicted in Scheme III can be ruled out. Interestingly, the deuterium isotope effect of 0.91 for **2c,d** is greater than that reported[16] for the S_N2 reaction of these phosphines with methyl tosylate ($k_{CH_3}/k_{CD_3} = 0.95$). However, the observed deuterium isotope effects do not rule out the concerted (biphilic) process in favor of the S_N2 process as both would be expected to show similar inverse isotope effects.

A study of the activation parameters for the reaction of tetramethyl-1,2-dioxetane with triarylphosphines showed[17] that the reaction is enthalpy controlled with large negative $\Delta S^‡$ terms. Similar behavior has been noted[18] for the reaction of 2,3-dioxabicyclo[2.2.1]heptane and other cyclic peroxides with triphenylphosphine. The activation parameter data (Table V) for the reaction of **1** with phoshines **2a-e** are in agreement with the previous conclusions. The values of $\Delta S^‡$ obtained for the reaction of the series of phosphines with dioxetane **1** were found to be essentially invarient (~−27 eu), indication of a highly organized transition state for the insertion reaction. The isotope effect test data (with the deuterated phosphines) and the activation parameter data could be interpreted to be indicative of a S_N2 process. However, a three-centered concerted mechanism and a S_N2-type mechanism could be expected to show similar deuterium isotope effects and activation parameters.

The results obtained with the deuterated dioxetane provide additional evidence to evaluate the insertion process. The reaction of the phosphines with **1d** produced a normal[19] deuterium isotope effects (1.06 ± 0.02) that is surprisingly large considering the distance from the site of insertion (γ-deuteration). The origin of secondary deuterium isotope effects can be difficult to evaluate.[20] The present results may be discussed in terms of steric effects. Such an explanation of the isotope effect observed with the deuterated dioxetane would invoke a lessening of steric interactions on the methyl group(s) of the dioxetane in the transition state as compared to that in the ground state. Another, similar argument would be based on relief of strain. Calculations have shown[21] that the steric energy of **1d** is ~1 kcal less than that of **1**. If there is a partial relief of strain[22] in the transition state, **1** would be expected to undergo the insertion reaction faster than **1d**. While a S_N2-type process cannot be ruled out on the basis of the isotope effect data, a concerted or biphilic process can account for the observed deuterium isotope effects as well as the relative reactivity data.

Experimental Section

All solvents were of reagent grade. Tetramethyl-1,2-dioxetane and tetramethyl-d_{12}-1,2-dioxetane[19] were prepared according to published procedures[3c] and recrystallized from *n*-pentane at −78 °C. The resulting pale yellow needles were stored as the solid at −30 °C until use. Dimethyl-d_6-phenylphosphine and methyl-d_3-diphenylphosphine, prepared according to the procedure of Kaplan and Thornton,[16] were vacuum distilled at 48 °C (2 mmHg, 48% yield) and at 120 °C (2 mmHg, 35% yield), re-

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(22) The enhanced reactivity[8a] of dioxetanes compared to that of dialkyl peroxides in insertion reactions has been attributed to partial relief of ring strain in the transition state.[5]

spectively, and stored under nitrogen. 9,10-Dibromoanthracene (Aldrich) was recrystallized from xylenes before use. 9,10-Diphenylanthracene (Aldrich), methyldiphenylphosphine (Alfa), dimethylphenylphosphine (Aldrich), and triphenylphosphine (Aldrich) were used without further purification. Melting points were determined in open capillary tubes and are uncorrected. ^{1}H NMR spectra were recorded on a Varian 360L spectrometer. ^{31}P NMR spectra were recorded on a JEOL FX-60Q NMR spectrometer. IR spectra were recorded on a Perkin-Elmer Model 700 spectrometer.

Kinetics of Phosphorane Formation. For all phosphines, the following procedure was employed. A 10-fold or greater excess of the phosphine in benzene solution (prepared and stored under nitrogen, using benzene that was distilled over triphenylphosphine and under nitrogen) was added in the dark, via microsyringe with an 8-in. needle, directly into the bottom of the jacketed cell of a chemiluminescence apparatus containing 2.000 mL of benzene with $[1]_0 = 10^{-3}$ to 10^{-4} M. All runs contained 8×10^{-3} M 9,10-dibromoanthracene (DBA) as added fluorescer. Use of 9,10-diphenylanthracene as added fluorescer did not effect the rates of reaction. The reagents were rapidly mixed via magnetic stirring. The chemiluminescence intensity served as a measure of the instantaneous concentration of 1. The rate of thermal decomposition of 1 was negligibly slow compared to the rate of phosphorane formation. The decay of luminescence was monitored vs. time on a strip-chart recorder. Plots of the natural logarithm of the intensity vs. time were linear for at least 3 half-lives. The values of the pseudo-first-order rate constants were not effected by variations of the initial dioxetane concentration and varied linearly with the initial phosphine concentrations. The second-order rate constants were obtained by dividing the pseudo-first-order rate constants by the initial phosphine concentration.

Formation and Thermal Decomposition of Phosphoranes in C_6D_6. To 0.5 mL of a 5×10^{-2} M C_6D_6 solution of 1 was added an equal molar amount of phosphine. After the yields of the phosphorane were determined by ^{1}H NMR, the phosphoranes were heated at 60 °C in tightly capped NMR tubes until the NMR spectra showed no remaining phosphoranes. The products were tetramethylethylene oxide and the corresponding phosphine oxide as determined by integration of the NMR spectrum in each case. Tetramethyloxirane was identified by GC analysis. After the solvent and volatile components were removed, the solid residues were recrystallized from CCl_4/petroleum ether and identified as the phosphine oxides, on the basis of melting points and spectral data (IR, ^{1}H NMR, ^{31}P NMR). The data are summarized in Table VI.

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Registry No. 1, 35856-82-7; **1d**, 88635-83-0; **2a**, 1486-28-8; **2b**, 3947-90-8; **2c**, 672-66-2; **2d**, 88635-84-1; **2e**, 603-35-0; **3a**, 88635-85-2; **3b**, 88635-86-3; **3c**, 88635-87-4; **3d**, 88635-88-5; **3e**, 49595-63-3; **4a**, 2129-89-7; **4b**, 3947-89-5; **4c**, 10311-08-7; **4d**, 88635-89-6; D_2, 7782-39-0.

α-Chloro Ketoximes as Precursors of Nitrosoalkenes: Preparation, Stereochemistry, and Conformation

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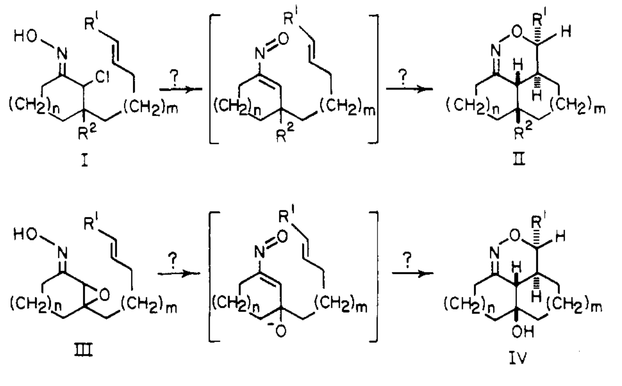
The ability of α-chloro and α,β-epoxy ketoximes and silyloximes of substituted cyclohexanones to serve as precursors for nitrosoalkenes has been investigated. α-Chloro ketoximes produced nitrosoalkenes efficiently with triethylamine regardless of oxime geometry or disposition of the chlorine atom. α-Chloro silyloximes were less efficient in production of nitrosoalkenes with tetrabutylammonium fluoride and led to a faster decay of reactive species. Nitrosoalkenes that cannot tautomerize are extremely stable and efficiently generated even from silyloximes. α,β-Epoxy ketoximes were shown to be incapable of generating nitrosoalkenes in detectable amounts under several conditions. A striking dependence of oxime geometry on oximation conditions was discovered. (*tert*-Butyldimethyl)silyloxime (*E*)-*trans*-**12** showed an unusual preference for the conformation in which both substituents assume axial orientations.

The transient existence of nitrosoalkenes has been known to organic chemists since the turn of the century. As early as 1898 nitrosoalkenes were postulated as intermediates in the reaction of α-halo oximes with nucleophilic bases.[1] Since then many groups have made good use of this method for the nucleophilic functionalization of carbons α to ketones with amines,[2] enamines,[3] alcoholates,[4] thiolates,[4] β-dicarbonyls,[2a,5] enolates,[6] phosphines,[7] sulfonium ylides,[8] and organomagnesium,[5a,9] -zinc,[9] and -lithium[10] reagents. Most of these nucleophiles are sufficiently

Scheme I



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