Figure 10. Colligative property data for 0.0250 m $(C_2H_5Li)_6$ with added diethyl ether in: O, cyclohexane; ▽, benzene.

data for a limited number of other systems indicate the same general trend shown in Figure 9. In the case of trimethylsilylmethyllithium, the results suggest that formation of an adduct with the first molecule of base must proceed quite readily, but that steric factors come into play with addition of further base molecules. Assuming conversion to solvated tetramer, the value of N at $R = 1.0$ corresponds to an average of only 1.3 bases per tetramer. Although there are significant differences in concentrations and temperature, the present studies are in very satisfactory general agreement with the results reported by Bartlett and

coworkers[18] for alkyllithium–dimethyl ether interactions.

The effect on the alkyllithium–base interaction of changing solvent from a saturated to an aromatic hydrocarbon is shown in Figure 10, in which N vs. R is shown for ethyllithium with added diethyl ether in cyclohexane and benzene. The equilibria appear to proceed to a smaller extent in benzene. This may be a reflection of the competition between added base and aromatic solvent for coordination to alkyllithium. Interaction of benzene or other aromatic hydrocarbons with alkyllithium compounds is suggested by the observation that certain of the alkyllithium compounds are hexameric in cyclohexane and tetrameric in benzene. In addition rates of intermolecular exchanges between alkyllithium oligomers appear to be faster in toluene than in cyclopentane.[22]

In summary, the present work provides new colligative property data of greater extent and precision than heretofore available regarding the associations of alkyllithium compounds in hydrocarbon solvents. Colligative property and nmr data indicate that bases interact with alkyllithium compounds in hydrocarbon solution to produce solvated tetrameric species at base concentrations corresponding to one base per lithium, or less. The number of solvating bases per tetramer is related to the steric requirements of the alkyl group in the $(RLi)_4$ species, to the steric requirements of the base, and to inherent donor ability of the base.

Acknowledgments. The authors are indebted to Dr. R. W. Lauver and Dr. D. L. Tibbetts for helpful discussions, and to Mr. Robert Thrift for assistance in obtaining nmr spectra.

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Kinetics of the Reaction of Trialkyl Phosphites with Benzil

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Abstract: The reaction of trialkyl phosphites with benzil to form a cyclic adduct (1) has been studied kinetically in anhydrous dioxane and benzene. The rate is expressed as $v = k[(RO)_3P][PhCOCOPh]$. An Arrhenius plot gives the values of 8.41 kcal mol^{-1} and -47.5 eu for the activation energy and entropy, respectively. The rate constant increases with increasing dielectric constant of the solvent. In a benzene solution the rate constant increases with an increasing amount of added organic acid (*e.g.*, acetic acid) and decreases with an increasing amount of added triethylamine. The plot of k vs. [acid] or [base] gives a straight line at low concentrations. The reactivity of trialkyl phosphites is affected by alkyl groups in the order of Me < *sec*-Bu < Et < *i*-Pr. A mechanism involving a nucleophilic attack of the phosphorus atom on the carbonyl carbon is postulated and discussed.

The reaction of trialkyl phosphites with α-diketones such as biacetyl and benzil was first reported by Kukhtin, *et al.*[1] Ramirez, *et al.*,[2,3] have postulated a

cyclic structure (1) for the 1:1 addition product (2,2,2-trialkoxy-1,3,2-dioxaphosphole) of trialkyl phosphite

(1) (a) V. A. Kukhtin, *Dokl. Akad. Nauk SSSR*, **121**, 466 (1958); *Chem. Abstr.*, **53**, 1105a (1959); (b) V. A. Kukhtin and K. M. Cerakhova, *Zh. Obshch. Khim.*, **30**, 1208 (1960); *Chem. Abstr.*, **55**, 358h (1961); (c) V. A. Kukhtin, T. N. Voskoboeva, and K. M. Kirillova, *ibid.*, **32**, 2333 (1962); *Chem. Abstr.*, **58**, 9127g (1963); (d) K. M. Kiril-

lova and V. A. Kukhtin, *ibid.*, **32**, 2338 (1962); *Chem. Abstr.*, **58**, 9128c (1963).

(2) (a) F. Ramirez, R. B. Mitra, and N. B. Desai, *J. Amer. Chem. Soc.*, **82**, 2651 (1960); (b) F. Ramirez and N. B. Desai, *ibid.*, **82**, 2652 (1960); (c) F. Ramirez and N. Ramanathan, *J. Org. Chem.*, **26**, 3046 (1961); (d) F. Ramirez and N. B. Desai, *J. Amer. Chem. Soc.*, **85**,

with an α-diketone, which was found to be an effective insecticide.[4]

$$(RO)_3P \ + \ R'COCOR' \ \longrightarrow \ \begin{array}{c} RO \\ RO \end{array} \!\! P \!\!\! \begin{array}{c} O \\ \diagdown \end{array} \!\!\! \begin{array}{c} C \\ \diagdown \end{array} \!\!\! R' \qquad (1)$$

1

However, no report is available on the mechanism of this reaction. The present paper deals with a kinetic study of the reaction of trialkyl phosphite with benzil (R' = phenyl). The rate was measured spectrophotometrically to clarify the effects of acid, base, and solvent and also structural effects on the rate. The mechanism for the reaction will be discussed on the basis of these findings.

Results

Rate Law. The reaction of trialkyl phosphite with benzil (neat) is irreversible and proceeds almost to completion within 15 min. The reaction rate in dioxane and benzene was measured by means of ultraviolet spectrophotometry of produced 2,2,2-trialkoxy-4,5-diphenyl-1,3,2-dioxaphosphole (1, R' = Ph). The ultraviolet spectra of 1 is shown in Figure 1. The structure was confirmed by ir and nmr spectra[2b,d,5] as described in the Experimental Section.

The rate of reaction 1 was measured in dioxane; the kinetic data obtained are listed in Table I. The rate

Table I. Typical Second-Order Rate Constants for the Reaction of Trimethyl Phosphite with Benzil in Dioxane at 25.0°

PhCOCOPh, M	$(MeO)_3P$, M	10^3k, M^{-1} sec^{-1}
0.0250	0.0250	4.70
0.0500	0.0500	4.83
0.100	0.100	4.85

law is expressed as eq 2. The k value is fairly constant up to 70–80% conversion.

$$v \ = \ k[\text{trialkyl phosphite}][\text{benzil}] \qquad (2)$$

Temperature Effect. The rate was measured in dioxane at various temperatures. The second-order rate constants (10^3k, M^{-1} sec^{-1}) were 2.95 at 15.0°, 3.76 at 20.0°, 4.83 at 25.0°, and 6.64 at 30.0°. The plot of log k *vs.* $1/T$ afforded a good straight line, which gave the values of 8.41 kcal mol^{-1} and -47.5 eu for the energy and entropy of activation, respectively.

Solvent Effect. The rate was measured at 25.0° in various solvents, and is shown in Table II. In acetone and cyclohexanone, the rate constant is small in spite of relatively high dielectric constant. In the other solvents, the rate constant increases with increas-

3252 (1963); (e) F. Ramirez, S. B. Bhatia, R. B. Mitra, Z. Hamlet, and N. B. Desai, *J. Amer. Chem. Soc.*, **86**, 4394 (1964).

(3) (a) W. C. Hamilton, S. J. LaPlaca, and F. Ramirez, *ibid.*, **87**, 127 (1965); (b) F. Ramirez, *Trans. N. Y. Acad. Sci.*, **30**, 410 (1968); *Chem. Abstr.*, **69**, 105720 (1968).

(4) (a) G. H. Birum and J. L. Dever, U. S. Patent 2,961,455 (1960); *Chem. Abstr.*, **55**, 8292g (1961); (b) G. H. Birum and J. L. Dever, U. S. Patent 3,014,949 (1961); *Chem. Abstr.*, **56**, 10191a (1962).

(5) (a) F. Ramirez, N. B. Desai, and N. Ramanthan, *Tetrahedron Lett.*, 323 (1963); (b) F. Ramirez, A. V. Patwardhan, and C. P. Smith, *J. Org. Chem.*, **30**, 2575 (1965); (c) F. Ramirez, A. V. Patwardhan, H. J. Kugler, and C. P. Smith, *Tetrahedron Lett.*, 3053 (1966).

Figure 1. The ultraviolet spectra of **1** from $(RO)_3P$ and PhCOCOPh in *n*-hexane: —, R = Me; - - -, R = Et; ····, R = *i*-Pr; — · —, R = *sec*-Bu.

ing dielectric constant, but in protic solvents, such as methanol, it is abnormally large.

Effect of Added Acid. When organic acids are added in a benzene solution of the reaction mixture at 25.0°, the rate constant increases as shown in Table III. The

Table II. Solvent Effect on the Reaction of Trimethyl Phosphite with Benzil at 25.0° (Initial Concentration $[(MeO)_3P] = [\text{PhCOCOPh}] = 0.0500$ M)

Solvent	Dielectric constant	10^3k, M^{-1} sec^{-1}
n-Hexane[a]	1.89	4.90
Dioxane	2.21	4.83
Benzene	2.28	6.83
Anisole	4.33	6.48
Chlorobenzene	4.65	7.67
Cyclohexanone	18.3	7.22
Acetone	20.7	3.27
Methanol[b]	32.6	158
Acetonitrile	37.5	13.4

[a] Initial concentration $[(MeO)_3P] = [\text{PhCOCOPh}] = 0.0400$ M. [b] Initial concentration $[(MeO)_3P] = [\text{PhCOCOPh}] = 0.00250$ M.

plot of k *vs.* [acetic acid] afforded a good straight line with a slope of +0.306 at low acetic acid concentration (0–5.80 × 10^{-3} M) as expressed in eq 3. Hammett's

$$k \ = \ 6.83 \ \times \ 10^{-3} \ + \ 0.306[\text{AcOH}] \qquad (3)$$

acidity function (H_0) cannot be measured because of the low acidity of this system. An increase of the acidity of acetic acid by the substitution of chlorine atoms results in an increase of rate constant (Table III).

Effect of Added Base. The addition of some tertiary amines to a benzene solution of the reaction mixture results in a decrease of the rate constant as shown in Table IV. The plot of k *vs.* [triethylamine] afforded a straight line with a slope of -1.16 at low concentration

Table III. Effect of Organic Acid on the Reaction of Trimethyl Phosphite with Benzil in Benzene at 25.0° (Initial Concentration $[(MeO)_3P]$ = [PhCOCOPh] = 0.0500 M)

Acid (pKa)	Acid concentration, 10^{-3} M	$10^3 k$, M^{-1} sec^{-1}
CH₃COOH (4.76)	0	6.83
	1.45	7.22
	2.90	7.59
	4.35	8.16
	5.80	8.59
	14.5	9.57
	29.0	9.88
	54.0	12.7
CH₂ClCOOH (2.87)	0.255	6.94
	0.510	7.88
	1.02	9.91
CCl₃COOH (0.635)	0.207	6.84
	0.414	7.85

Table IV. Effect of Base on the Reaction of Trimethyl Phosphite wit Benzil in Benzene at 25.0° (Initial Concentration $[(MeO)_3P]$ = [PhCOCOPh] = 0.0500 M)

Base (pKa)	Base concentration, 10^{-3} M	$10^3 k$, M^{-1} sec^{-1}
Et₃N (10.9)	0	6.83
	0.597	5.77
	1.19	5.35
	1.79	4.89
	2.39	4.08
	11.9	2.16
	23.9	1.52
PhNMe₂ (4.64)	1.32	6.90
	2.64	6.81
	26.4	6.84

of triethylamine, and fits eq 4, whereas the addition

$$k = 6.83 \times 10^{-3} - 1.16[\text{Et}_3\text{N}] \qquad (4)$$

of dimethylaniline has virtually no effect on k.

Effect of Substituents. The effect of changing alkyl group of trialkyl phosphite was studied for the reaction with benzil in dioxane, and is shown in Table V. In

Table V. Substituent Effect on the Reaction of Trialkyl Phosphite with Benzil in Dioxane at 25.0°

R of 1	$10^3 k$, M^{-1} sec^{-1}
Me	4.83
Et	11.3
i-Pr	18.5
sec-Bu	9.19

general, the rate increases in the order of Me < sec-Bu < Et < i-Pr, which corresponds to an increase of nucleophilicity of phosphites. But steric effect is also operating with bulky alkyl phosphite, e.g., tri-sec-butyl phosphite, its rate constant being smaller than expected.

Discussion

A mechanism postulated by Ramirez, et al., involves a nucleophilic attack of phosphorus atom on carbonyl

oxygen[6,7] followed by cyclization of the formed zwitterion as shown in mechanism A.

Mechanism A
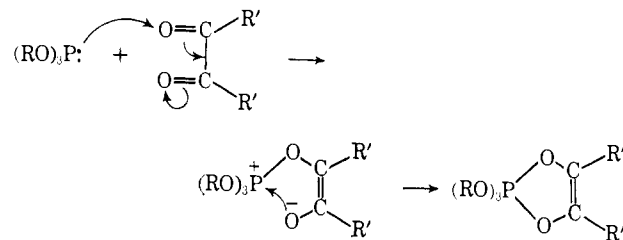
Another mechanism involves a nucleophilic attack of phosphorus atom on carbonyl carbon[1a,8] followed by rearrangement[9] and then cyclization as formulated in mechanism B.

Mechanism B
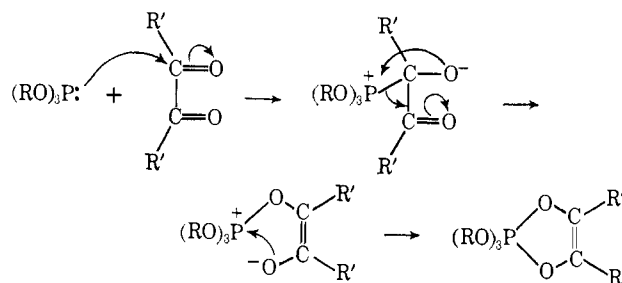
In view of rate eq 2, each molecule of trialkyl phosphite and benzil should participate in the rate-determining step. The value of 8.41 kcal mol^{-1} for activation energy and the value of -47.5 eu for activation entropy are usual for the addition reaction of carbonyl compounds.[10] The low value of activation energy shows that in the rate-determining step no large energy is needed and hence it involves probably no C–P bond fission.[11] The large negative entropy of activation reflects a high degree of orientation and/or a rigid structure in the transition state, and this negative value is consistent with a reaction of neutral molecules via polarized transition states to yield ions.[12] Diels–Alder reactions in general exhibit entropies of activation not more than -30 eu;[13] hence the Diels–Alder-type mechanism is unlikely for this reaction.

The solvent effect shows that the rate constant increases with increasing dielectric constant except in

(6) (a) F. Ramirez, N. Ramanathan, and N. B. Desai, *J. Amer. Chem. Soc.*, **85**, 3465 (1963); (b) F. Ramirez, S. B. Bhatia, and C. P. Smith, *Tetrahedron*, **23**, 2067 (1967).

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(10) (a) Y. Ogata, Y. Sawaki, and S. Gotoh, *J. Amer. Chem. Soc.*, **90**, 3469 (1968); (b) W. T. Brady and H. R. O'Neal, *J. Org. Chem.*, **32**, 612 (1967).

(11) S. B. Hartley, W. S. Holmes, J. K. Jacques, M. F. Mole, and J. C. McCoubrey, *Quart. Rev.* (London), **17**, 204 (1963).

(12) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1960, p 182.

(13) (a) R. Huisgen, R. Grashey, and J. Sauer, "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1964; (b) A. Wassermann, *J. Chem. Soc.*, 612 (1942).

some solvents (Table II). As the solvent is changed from n-hexane (ϵ 1.89) to acetonitrile (ϵ 37.5) the rate increases by a factor of 2.8. The reaction *via* a charge-separated complex should be facilitated by an increase of the solvent polarity[14] (*e.g.*, the quaternization of pyridine with ethyl iodide shows a solvent dependence in a factor of *ca.* 10³).[15] The poor dependence of this rate on the solvent polarity may be explained as follows: 2p–3d π bonding of oxygen and phosphorus atoms[16] may lead to some dispersal of the positive charge on a phosphorus atom, and the transition state is most likely in the form of an intimate ion pair in which there is a minimal separation of charge.[17] The small rate constant observed in the reaction in acetone or cyclohexanone may be explained by the solvation effect involving a polarizable carbonyl group which retards the reaction. A marked increase of rate in protic solvents such as methanol is probably due to its action an acid having $pK_a = 16.7$. The catalysis of methanol for the reaction of α-halo ketones with trivalent phosphorus compounds is known.[18]

No appropriate data are available on the basicity of trialkyl phosphites. Taft's σ^* value[19] predicts that the nucleophilicity of phosphite seems to be in the order of $(MeO)_3P < (EtO)_3P < (i\text{-}PrO)_3P < (sec\text{-}BuO)_3P$. This ρ^*–σ^* correlation is successful for pK_a of aliphatic phosphine,[20] and with aromatic phosphonic[21] and phosphinic acids,[22] the correlation between pK_a of acids and Hammett's σ parameter is very good. The observed reactivity order of the present reaction, *i.e.*, $(MeO)_3P < (EtO)_3P < (i\text{-}PrO)_3P$, is in agreement with the nucleophilicity of phosphite. Thus it is probable that the reaction involves a nucleophilic attack of phosphorus atom on carbonyl group in the rate-determining step.[17] The k value for $(sec\text{-}BuO)_3P$ is smaller than expected.

Mark, *et al.*, have explained the reactivity of $(t\text{-}BuO)_3P$ by the inductive and steric effects of alkyl groups.[23] When Taft's equation is applied to this reaction, the k value for $(i\text{-}PrO)_3P$ is also somewhat smaller than calculated. These facts imply that the steric hindrance is operating with $(i\text{-}PrO)_3P$ and $(sec\text{-}BuO)_3P$.

Acids catalyze this reaction. At low concentration of added acetic acid, the plot of k *vs.* [acetic acid] gives a straight line, while at higher concentration of added acetic acid (above 0.0145 M) it approaches a limiting value, and at the same time the rate law begins to deviate from the second-order plot. As reported by Ramirez,[24] the deviation may be due to the acid-

catalyzed hydrolysis followed by further reactions of the 1:1 adduct (see Experimental Section).
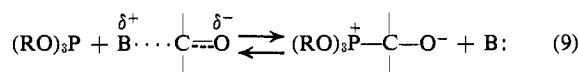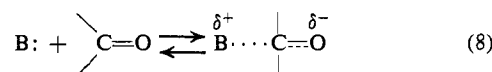
Acetic acid at such a low concentration in benzene solution cannot change the color of an indicator,[25] but ultraviolet spectra afforded evidence for the presence of hydrogen bonding to benzil (see Experimental Section). Because of the first-order dependence on [AcOH], benzil may be hydrogen bonded with one molecule of acetic acid, which activates the carbonyl group for the nucleophilic attack of trialkyl phosphite as follows.

$$\text{C=O} + \text{H—A} \rightleftarrows \overset{\delta^+}{\text{C}}\text{=O}\cdots\text{H}\cdots\overset{\delta^-}{\text{A}} \qquad (5)$$

$$(RO)_3P + \overset{\delta^+}{\text{C}}\text{=O}\cdots\text{H}\cdots\overset{\delta^-}{\text{A}} \rightleftarrows (RO)_3\overset{+}{P}\text{—}\overset{|}{\underset{|}{C}}\text{—O}^- + HA \qquad (6)$$

$$(RO)_3P + \overset{\delta^+}{\text{C}}\text{=O}\cdots\text{H}\cdots\overset{\delta^-}{\text{A}} \rightleftarrows (RO)_3\overset{+}{P}\text{—O—}\overset{|}{\underset{|}{C}}^- + HA \qquad (7)$$
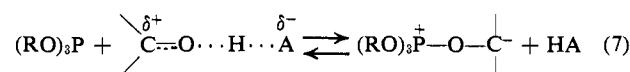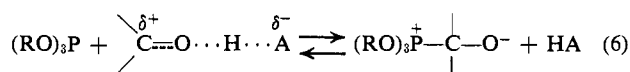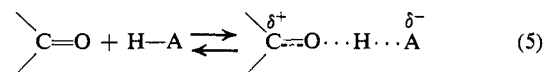
Since the nucleophilic attack of phosphorus atom on carbonyl carbon in the reaction of α-halo ketone with trialkyl phosphite is catalyzed by acetic acid,[18a,26] eq 7 is less probable. Chloroacetic and trichloroacetic acids are more effective catalysts in this reaction, because they are more acidic and thus more effective in forming a hydrogen bond to the carbonyl group.

On the other hand, bases retard the reaction; at lower concentrations of added triethylamine (below 0.0119 M), the plot of k *vs.* [Et₃N] gives a straight line, whereas at higher concentrations (above 0.0119 M) of triethylamine the plot approaches a horizontal line. The second-order rate law is not applicable at this high concentration of triethylamine, and in this case, the base-catalyzed hydrolysis of the product[24] occurs, the hydrolysis products acting as acid.

The fact that dimethylaniline has virtually no effect on k suggests that a fairly strong base is required to retard the reaction in this system. Therefore, the retarding effect of base cannot be explained as its neutralization of mineral acid which might be present in this system. This fact together with the first-order dependence of rate on 1/[Et₃N] suggests that the retardation may be due to the addition of the base to the carbonyl carbon atom to weaken its electrophilicity.

$$\text{B:} + \text{C=O} \rightleftarrows \overset{\delta^+}{\text{B}}\cdots\overset{\delta^-}{\text{C}}\text{=O} \qquad (8)$$

$$(RO)_3P + \overset{\delta^+}{\text{B}}\cdots\overset{\delta^-}{\text{C}}\text{=O} \rightleftarrows (RO)_3\overset{+}{P}\text{—}\overset{|}{\underset{|}{C}}\text{—O}^- + \text{B:} \qquad (9)$$

This behavior is in contrast to the analogous Diels–Alder reaction, where both trimethylamine and trichloroacetic acid have the accelerating effect;[27] the following mechanism may operate in the present reaction, which involves a nucleophilic attack of a phosphorus atom of trialkyl phosphite on the carbonyl carbon atom of benzil (mechanism B).

The reaction of α-halo ketone with trialkyl phosphite may involve the rearrangement of phosphorus atom

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(19) See, for example, (a) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1960, p 230; (b) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, 75, 4231 (1953).
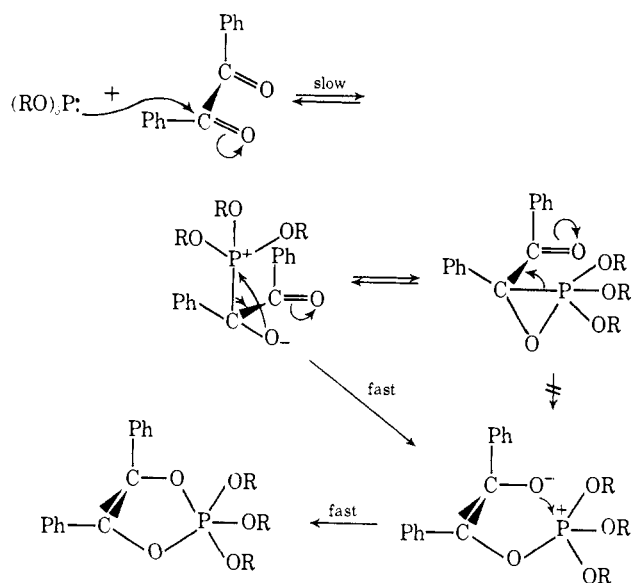
(20) W. A. Henderson, Jr., and C. A. Streuli, *ibid.*, 82, 5791 (1960).

(21) (a) H. H. Jaffé, L. D. Freedman, and G. O. Doak, *ibid.*, 75, 2209 (1953); (b) C. V. Banks and R. J. Davis, *Anal. Chim. Acta*, 12, 418 (1955).

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(23) V. Mark and J. R. Van Wazer, *ibid.*, 29, 1006 (1964).

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(25) See, for example, M. A. Paul, *Chem. Rev.*, 57, 1 (1957).

(26) I. J. Borowitz, M. Auschel, and S. Firstenberg, *J. Org. Chem.*, 32, 1723 (1967).

(27) (a) A. Wassermann, *J. Chem. Soc.*, 618 (1942); (b) A. Wassermann, *ibid.*, 623 (1942).

from carbonyl carbon to oxygen *via* either a concerted or a three-membered cyclic mechanism.[26] The present reaction may proceed *via* a concerted three-center rearrangement of the phosphorus atom initiated by nucleophilic attack of the negatively charged oxygen atom[9,28] because of the higher energy barrier for the complete fission of the C–P bond.[11,29] In analogy to the addition of nucleophile to carbonyl which is generally a reversible process,[30] the first step of the phosphorus–carbonyl addition is probably reversible.[30b,31] The reversibility of the first step is uncertain in view of the rate law alone, but the low energy of activation implies the step to be reversible.[32] Hence, the overall mechanism is shown as follows.

Experimental Section

Materials. Benzil was prepared from benzaldehyde,[33] and recrystallized several times from CCl₄. Trialkyl phosphites were

synthesized by the reaction of PCl₃ with alcohols in the presence of base,[34] and rectified several times with metallic sodium under reduced nitrogen pressure. Solvents used were purified by ordinary methods.[35]

Reaction Product Criterion. The authentic samples of 2,2,2-trialkoxy-4,5-diphenyl-1,3,2-dioxaphosphole (**1**)[2,5,36] was prepared by the reaction of benzil with excess phosphite in the absence of solvent under nitrogen atmosphere. The products were very hygroscopic crystals. The yields were almost quantitative. **1** (R = Me) was recrystallized from anhydrous *n*-hexane, mp 49–50°. Infrared spectrum (Nujol) showed peaks at 3045, 2980, 2940, 2830, 2000∼1700, 1665, 1595, 1490, 1450, 1315, 1273, 1173, 1135, 1097, 1039, 951, 847, 750, 690, and 650 cm⁻¹, which were characteristic of the monosubstituted benzene ring, C=C, and P–O–C. Nmr (CDCl₃, internal standard TMS) showed peaks at τ 2–3 (multiplet, 10 H) and 6.31 (doublet, 12 H, J_{HP} = 12.6 cps). **1** (R = Et) was recrystallized from anhydrous *n*-hexane, mp 45–46°. The infrared spectrum (Nujol) was analogous to that of **1** (R = Me). **1** (R = *i*-Pr and *sec*-Bu) was not isolated. The uv spectra of **1** (R = Me, Et, *i*-Pr, and *sec*-Bu) in *n*-hexane (Figure 1) were as follows [R, λ_{max} (mμ), ε]: Me, 321, 11,800; Et, 323, 11,800; *i*-Pr, 325, 11,200; *sec*-Bu, 319, 12,100.

The products of 0.2 *M* trimethyl phosphite with 0.2 *M* benzil in benzene at 25° containing an equivalent amount of acetic acid were examined by tlc (silica gel; eluent, ethyl acetate–petroleum ether 1:1), ir, uv (*n*-hexane), and nmr (CDCl₃). Besides the 1:1 adduct, small amounts of hydrolysis product of the adduct[24] and an unknown product (tlc, R_f 0.40) having P=O and C=O groups were observed.

Kinetics. The reaction was started by the rapid addition of a solution of trialkyl phosphite to an equimolar solution of benzil, both of which had reached the temperature equilibrium in a thermostat. The reaction was carried out as a homogeneous system with stirring in a glass-stoppered flask. No difference in rate was observed between reactions under nitrogen and air. Aliquots were taken out at appropriate intervals of time. The reaction was stopped by diluting it with *n*-hexane. Products were estimated by means of ultraviolet spectrophotometry at the wavelength stated above.

In the study of the effect of acid or base catalysis addition order of three components afforded no effect on the rate constant. Initial rate constants were considered at high catalyst concentrations. No reaction of trimethyl phosphite with acetic acid or triethylamine occurs under these conditions. Interaction between benzil and acid or base was studied by uv spectrum as a slight change of molar extinction coefficient (ε) at 259 and 265 mμ in *n*-hexane. No appreciable shift of C=O absorption (1670 and 1650 cm⁻¹) was observed.

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