

in ether, washed with 5% sodium hydroxide, and dried over anhydrous sodium sulfate. After evaporation of the ether, the triphenylmethane was recrystallized twice from ethanol. Two samples of the triphenylmethane were counted and found to have a specific activity of  $1.34 \times 10^7$  decompositions  $\text{min}^{-1} \text{mol}^{-1}$ . The melting point of the recrystallized triphenylmethane was 93–94°. <sup>16</sup>

**4-Triphenyl-1-diphenylmethylene-2,5-cyclohexadiene (I).**—Mercury (20 g, 0.1 mol) was added to a solution of 5.78 g (0.021 mol) of triphenylchloromethane in 250 ml of dry toluene in the first flask, following with minor modification the procedure of Gomberg.<sup>17</sup> The system was closed, degassed three times, and allowed to react at 20° for 12 hr with vigorous stirring.

**Reaction of Triphenylmethyl with Thiophenol.**—The yellow solution of I was filtered from the first flask through a glass wool plug and then through a fritted glass filter into the second flask. To the third flask, 16 g (0.15 mol) of tritium-labeled thiophenol was added to 235 ml of dried reagent-grade toluene. The thiophenol-toluene solution was degassed three times. The entire apparatus was then submerged in a bath controlled to within  $\pm 0.05^\circ$  and allowed to attain thermal equilibrium. Compound I was then added dropwise through the stopcock to the thiophenol-toluene solution, which was magnetically stirred.

**Isolation of Triphenylmethane, Trityl Phenyl Sulfide, and *p*-Benzhydryltetraphenylmethane (II).**—The reaction mixture was washed with 5% sodium hydroxide and dried over anhydrous sodium sulfate. Toluene was removed by distillation, counted,

(16) W. R. Orndorff, R. C. Gibbs, S. A. McNulty, and C. V. Shapiro, *J. Amer. Chem. Soc.*, **49**, 1543 (1927).

(17) M. Gomberg and C. S. Schoepfle, *ibid.*, **39**, 1659 (1917).

and found to have no tritium. A 3 ft  $\times$  1 in. chromatographic column packed with neutral aluminum oxide was used to separate the viscous oil. A 2:1 mixture of low-boiling petroleum ether-benzene was used to elute the mixture and obtain complete separation of the triphenylmethane. A 1:2 petroleum ether-benzene mixture was then used to elute the trityl phenyl sulfide. After all trityl phenyl sulfide was removed, methylene chloride was used to elute any remaining compounds. Only at  $-25^\circ$  and  $-15^\circ$  were any other compounds found. At these low temperatures compound II was found, as shown by its melting point, 226–227° (lit.<sup>18</sup> mp 227°), and mixture melting point and nmr (singlet,  $\tau$  4.45, 1 H; multiplet,  $\tau$  2.60–3.00, 29 H). The triphenylmethane had mp 93–94°, and the nmr showed a singlet at  $\tau$  4.66 (1 H) and another singlet at  $\tau$  3.02 (15 H). Trityl phenyl sulfide had mp 100–101° (lit.<sup>7</sup> mp 105–106°), and the nmr showed a singlet at  $\tau$  3.15 (5 H) and a multiplet between  $\tau$  2.50 and 3.10 (15 H). No attempt was made to determine the exact yields since purity of the products was our main goal. The isolated yields of purified triphenylmethane at  $-25.0$ ,  $-15.0$ ,  $0.0$ ,  $25.0$ ,  $40.0$ , and  $60.0^\circ$  were 14.0, 40.0, 58.0, 73.0, 82.0, and 90.0%, respectively. The isolated yields of recrystallized II at  $-25.0$  and  $-15.0^\circ$  were 24.0 and 22.0%, respectively. The low total yields at the lower temperatures do not represent incomplete reaction, for ditrityl peroxide would have been produced on work-up and is easily detected. We attribute the low yields merely to the difficulty of separating triphenylmethane and compound I.

**Registry No.**—II, 3416-63-5; triphenylmethane, 519-73-3; trityl phenyl sulfide, 16928-73-7.

(18) W. Schlenk, E. Marcus, *Ber.*, **47**, 1665 (1914).

## Kinetics of the Reaction of Some Trialkyl Phosphites with Benzil

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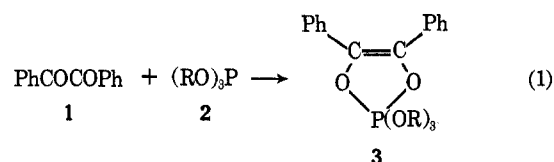
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The effect of substituents on the reaction rates of trialkyl phosphites [(RO)<sub>3</sub>P] with benzil has been studied. The rate constant,  $k$ , in the rate equation,  $v = k[(\text{RO})_3\text{P}][\text{PhCOCOPh}]$ , increases with the change of R in the order of methyl, ethyl, and isopropyl, while a little change of  $k$  is observed with R of *n*-propyl, *n*-butyl, *n*-amyl, *n*-octyl, and *sec*-butyl, and the  $k$  value decreases by substitution of 2-methoxyethyl for methyl. The relative rates fit the Taft equation,  $\log(k/k_0) = -3.28 \sigma^* + 0.40 E_s + 0.03$ . Both polar and steric effects affect the rate with R of C<sub>*n*</sub>H<sub>2*n*+1</sub> ( $n \geq 3$ ), while polar effect alone is dominant with R of methyl and ethyl. The correlation between the <sup>31</sup>P nmr chemical shift relative to (CH<sub>3</sub>O)<sub>3</sub>P,  $\Delta\delta^{31}\text{P}$ , and the relative reaction rate or Taft's  $\sigma^*$  value is discussed. These facts present an additional support for our previous mechanism involving a nucleophilic attack of the phosphorus atom on the carbonyl carbon.

In our previous papers,<sup>1–3</sup> kinetics of the reaction of trialkyl phosphite with benzil and substituted benzils favored a mechanism involving a nucleophilic attack of a phosphorus atom of phosphite on a carbonyl carbon atom of benzil, which is similar to a mechanism proposed by Litt for aliphatic  $\alpha$  diketones.<sup>4</sup>

The present paper deals with the kinetic study on the reaction of a number of trialkyl phosphites (2) with benzil (1) forming substituted 1,3,2-dioxaphospholes (3) (eq 1) to clarify the effect of substituents at phosphorus atom. The rate was measured by means of uv spectrophotometry.<sup>5–7</sup>



### Results

The reaction of a number of trialkyl phosphites (2) with benzil (1) proceeds quantitatively at room temperature to yield 2,2,2-trialkoxy-4,5-diphenyl-1,3,2-dioxaphospholes (3). The rate was measured by means of ultraviolet spectrophotometry of the product 3.

**Rate Law.**—The rate was measured in dioxane at 20.0, 25.0, 30.0, and 35.0°. The rate law is expressed

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 (2) Y. Ogata and M. Yamashita, *Tetrahedron*, in press.  
 (3) Y. Ogata and M. Yamashita, *ibid.*, in press.  
 (4) A. D. Litt, Ph.D. Thesis, Rutgers University, 1968.  
 (5) (a) V. A. Kukhtin, *Dokl. Akad. Nauk SSSR*, **121**, 466 (1958); *Chem. Abstr.*, **53**, 1105a (1959); (b) V. A. Kukhtin and K. M. Orekhova, *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. Kirillova and V. A. Kukhtin, *ibid.*, **32**, 2338 (1962); *Chem. Abstr.*, **58**, 9128c (1963).  
 (6) (a) F. Ramirez and N. B. Desai, *J. Amer. Chem. Soc.*, **82**, 2652 (1960); (b) F. Ramirez and N. B. Desai, *ibid.*, **85**, 3252 (1963); (c) F. Ramirez, N. Ramanathan, and N. B. Desai, *ibid.*, **84**, 1317 (1962); (d) F. Ramirez, N.

Ramanathan, and N. B. Desai, *ibid.*, **85**, 3465 (1963); (e) F. Ramirez, A. V. Patwardhan, N. Ramanathan, N. B. Desai, C. V. Greco, and S. R. Heller, *ibid.*, **87**, 543 (1965).

(7) (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).

TABLE I  
SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF TRIALKYL PHOSPHITES (2)  
WITH BENZIL (1) IN DIOXANE AT 25.0°

(RO) <sub>3</sub> P, R =	Registry no.	Concn, M		10 <sup>3</sup> k, M <sup>-1</sup> sec <sup>-1</sup>	Relative rate (k/k <sub>0</sub> )	Log (k/k <sub>0</sub> )	σ* <sup>a</sup>
		[1]	[2]				
CH <sub>3</sub>	121-45-9	0.05	0.05	4.83	1.00	0.000	0.000
C <sub>2</sub> H <sub>5</sub>	122-52-1	0.05	0.05	10.8	2.34	0.369	-0.100
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	116-17-6	0.02	0.1	13.5	2.80	0.447	-0.200
<i>sec</i> -C <sub>4</sub> H <sub>9</sub>	7504-61-2	0.02	0.1	9.19	1.90	0.279	-0.210
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	923-99-9	0.05	0.05	8.37	1.73	0.238	-0.115
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	102-85-2	0.05	0.05	9.64	2.00	0.301	-0.130
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	1990-22-3	0.05	0.05	10.4	2.15	0.332	
<i>n</i> -C <sub>8</sub> H <sub>17</sub>	3028-88-4	0.1	0.1	10.1	2.09	0.320	
CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub>	4156-80-3	0.01	0.1	2.94	0.609	-0.216	

<sup>a</sup> R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **75**, 4231 (1953).

TABLE II  
TEMPERATURE EFFECT AND ACTIVATION PARAMETERS FOR THE REACTION OF  
TRIALKYL PHOSPHITES WITH BENZIL IN DIOXANE<sup>a</sup>

(RO) <sub>3</sub> P, R =	10 <sup>3</sup> k, M <sup>-1</sup> sec <sup>-1</sup>			E <sub>a</sub> , kcal/mol	ΔS‡, <sup>b</sup> eu	Ln A, M <sup>-1</sup> sec <sup>-1</sup>	
	20.0°	25.0°	30.0°				
CH <sub>3</sub>	3.76	4.83	6.64	9.90	-35.5	12.4	
C <sub>2</sub> H <sub>5</sub>	8.08	10.8	12.8	8.32	-41.1	9.78	
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	10.3	13.5	16.8	9.12	-38.4	11.1	
<i>sec</i> -C <sub>4</sub> H <sub>9</sub>	7.29	9.19	11.1	7.85	-43.6	8.53	
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	6.10	8.37	11.4	11.2	-32.9	13.9	
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	7.64	9.64	13.8	10.9	-32.9	13.9	
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	7.68	10.4	13.1	9.78	-36.9	11.9	
<i>n</i> -C <sub>8</sub> H <sub>17</sub>		10.1	12.9	16.6	9.92	-36.5	12.1
CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub>	2.18	2.94	3.82	10.4	-37.3	11.7	

<sup>a</sup> Calculated by the least-squares method. <sup>b</sup> ΔS‡ was calculated at 25.0°.

as eq 2 up to high conversion for all phosphites used as has been reported with trimethyl phosphite.<sup>1-3</sup>

$$v = k[(RO)_3P][PhCOCOPh] \quad (2)$$

**Effect of Substituents at Phosphorus Atom.**—The rate in dioxane at 25.0° is summarized in Table I. The rate increases with an increase of the electron-releasing power of substituents of alkyl groups of the phosphites. Both polar and steric effects in the Taft equation are important, since the correlation between the logarithm of the relative rate constant and Taft's σ\* or E<sub>s</sub> alone is not so good.

The rate measurements at various temperatures afford energies of activation (E<sub>a</sub>), entropies of activation (ΔS‡), and frequency factors (A) as shown in Table II. As obvious from the table, both E<sub>a</sub> and ΔS‡ are low.

**<sup>31</sup>P Nmr Chemical Shift.**—The <sup>31</sup>P nmr chemical shift relative to (CH<sub>3</sub>O)<sub>3</sub>P, Δδ <sup>31</sup>P, was measured by a JNM-C60-HL high-resolution spectrometer at 24 MHz neat at room temperature. The values of Δδ <sup>31</sup>P are listed in Table III. A plot of Δδ <sup>31</sup>P vs. σ\* for R of CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, *n*-C<sub>3</sub>H<sub>7</sub>, *i*-C<sub>3</sub>H<sub>7</sub>, *n*-C<sub>4</sub>H<sub>9</sub>, and *sec*-C<sub>4</sub>H<sub>9</sub> gave a correlation coefficient (r) of -0.925 except for R of *sec*-C<sub>4</sub>H<sub>9</sub>. (*sec*-C<sub>4</sub>H<sub>9</sub>O)<sub>3</sub>P has a little different value.

A plot of Δδ <sup>31</sup>P vs. log (k/k<sub>0</sub>) for all phosphites, except R of *sec*-C<sub>4</sub>H<sub>9</sub> and CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>, seems to show a good correlation coefficient (r = 0.969). The substituents of *sec*-C<sub>4</sub>H<sub>9</sub> and CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub> seem to give a somewhat different effect on Δδ <sup>31</sup>P.

### Discussion

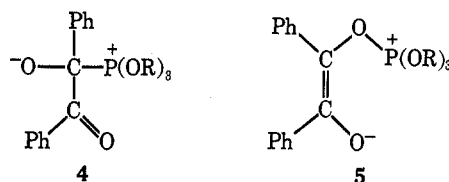
The mechanism of the reaction of trialkyl phosphites with benzil may involve a nucleophilic attack of a phos-

TABLE III

(RO) <sub>3</sub> P, R =	Δδ <sup>31</sup> P, <sup>a</sup> ppm
CH <sub>3</sub>	0.00
C <sub>2</sub> H <sub>5</sub>	+1.21
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	+1.16
<i>sec</i> -C <sub>4</sub> H <sub>9</sub>	+0.16
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	+1.01
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	+0.98
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	+1.08
<i>n</i> -C <sub>8</sub> H <sub>17</sub>	+1.06
CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub>	+0.75 <sup>b</sup>

<sup>a</sup> The + sign indicates the higher field shift. <sup>b</sup> In ca. 50% CCl<sub>4</sub> solution.

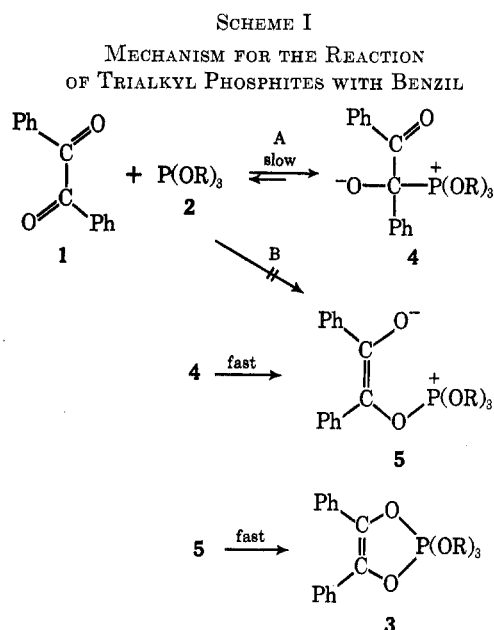
phorus atom of phosphite either on a carbonyl carbon atom or an oxygen atom of benzil,<sup>1-3</sup> thus, the corresponding intermediate may be 4 or 5, respectively. A probable mechanism involving path A or B may be written as Scheme I.



In view of the data of acid-base catalysis,<sup>1</sup> we observed that the acid accelerates the reaction, while the base retards it. The substituent effect in benzil gave a good Hammett's correlation with σ but not with σ<sup>-</sup>, and it afforded a large positive ρ value.<sup>2</sup> Moreover, the

(8) (a) L. D. Quin, "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York, N. Y., 1967, Chapter 3; (b) G. Pfundt and G. O. Schenck, ref 8a, Chapter 11; (c) A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier, Amsterdam, 1967, Chapter 3.

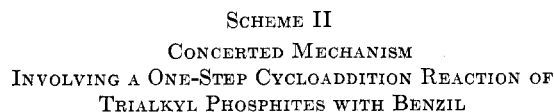
substituent effect in aliphatic  $\alpha$  diketones revealed that the steric substituent constant,  $E_s$ , controls the rate.<sup>3</sup> These results suggest that a more probable intermediate may be **4** and that the reaction involves a nucleophilic attack of the phosphorus atom of phosphite on a carbonyl carbon atom of the  $\alpha$  diketone in the rate-determining step.



With the change of an alkyl group R of the phosphite from  $\text{CH}_3$  to a more electron-releasing group, *e.g.*,  $\text{C}_2\text{H}_5$  and *i*- $\text{C}_3\text{H}_7$ , a modest increase of the rate was observed, while with the change to an electron-withdrawing group such as  $\text{CH}_3\text{OCH}_2\text{CH}_2$  the rate decreased (Table I).

As will be discussed later, the substituent effect in phosphites implies that a nucleophilic attack of phosphorus atom is involved in the rate-determining step, since an electron-releasing group on phosphite accelerates the reaction. Both rearrangement of **4** to **5** and the cyclization of **5** to **3** involve an electrophilic attack of a phosphorus atom, since the phosphorus atom has a positive charge. Hence, the observed substituent effect in phosphites suggests that these steps cannot be rate-determining.

Therefore, path A in Scheme I may be more probable than path B. The concerted one-step cycloaddition of  $\alpha$  diketone with phosphite (Scheme II) may be ex-



cluded, since the first step must involve an attack of phosphite on an oxygen atom of carbonyl, which is inadequate as stated above.

The observed small value of  $E_a$  and the large negative value of  $\Delta S^\ddagger$  are characteristic of this sort of reaction,<sup>1-3</sup> *e.g.*, the condensation reaction of carbonyl compounds with amines.<sup>9</sup> In general, a large negative value of  $\Delta S^\ddagger$  is observed in the reaction in which the total number of species decreases or a strongly polarized and/or crowded transition states are involved.<sup>10</sup> Hence, it is supported that the first step is rate determining. The values of  $E_a$  and  $\Delta S^\ddagger$  for  $(n\text{-C}_n\text{H}_{2n+1}\text{O})_3\text{P}$  ( $n \geq 3$ ) are nearly constant, but the alkyl substituents such as  $\text{C}_2\text{H}_5$ , *i*- $\text{C}_3\text{H}_7$ , and *sec*- $\text{C}_4\text{H}_9$  decrease the  $E_a$  value.

A plot of  $\log(k/k_0)$  vs.  $\sigma^*$  (Figure 1) gives a very poor correlation coefficient ( $r$ ) of  $-0.806$ ; this implies that not only a polar effect but also a steric effect of phosphite is a controlling factor in the rate-determining step. The negative value of  $r$  also supports the rate-determining nucleophilic attack of phosphite.

A plot of  $\log(k/k_0)$  vs.  $E_s$  (Figure 2) may be classified into three groups with the change of substituents, *i.e.*, (1)  $\text{CH}_3$  and  $\text{C}_2\text{H}_5$ , (2) *i*- $\text{C}_3\text{H}_7$ , *n*- $\text{C}_3\text{H}_7$ , *n*- $\text{C}_4\text{H}_9$ , *n*- $\text{C}_5\text{H}_{11}$ , and *n*- $\text{C}_8\text{H}_{17}$ , and (3) *sec*- $\text{C}_4\text{H}_9$ . For group 2 the plot gives a negative correlation coefficient, which indicates the acceleration of reaction by releasing the steric hindrance of phosphites by going to the transition state.<sup>11</sup> This may not be the case, since the negative Taft's  $\rho^*$  value and the large negative  $\Delta S^\ddagger$  value were observed in this reaction and positive Hammett's  $\rho$  value was observed in the substituent effect of benzil.<sup>2</sup>

Figure 1 shows that the steric effect operates little upon  $\text{C}_2\text{H}_5$  but much upon *sec*- $\text{C}_4\text{H}_9$ . A line passing through the points for  $\text{CH}_3$  and  $\text{C}_2\text{H}_5$  ( $\equiv 1_0$ , with slope of  $-3.69$ ) was drawn and the deviation from the line [ $\equiv \Delta \log(k/k_0)$ ] was calculated with various alkyl groups. The plot of  $\Delta \log(k/k_0)$  vs.  $E_s$  gave a straight line whose slope was  $+0.46$  ( $r = 0.977$ ). When the slope of  $1_0$  was changed little, the correlation between  $\Delta \log(k/k_0)$  and  $E_s$  becomes worse ( $r < 0.977$ ). A plot of  $\log(k/k_0)$  vs.  $(-3.69 \sigma^* + 0.46 E_s)$  gave a straight line with a slope of  $+0.888$  ( $r = 0.981$ ). In other words, the Taft equation may be applied, which is expressed in a form of eq 3 for this reaction (Figure 3).

$$\log(k/k_0) = -3.28\sigma^* + 0.40E_s + 0.03 \quad (3)$$

As apparent from the coefficients of the equation the polar effect is more important. In view of the reported values of  $E_s$  for *n*- $\text{C}_5\text{H}_{11}$  ( $-0.40$ ) and *n*- $\text{C}_8\text{H}_{17}$  ( $-0.33$ ),<sup>12</sup> a probable  $\sigma^*$  value for *n*- $\text{C}_5\text{H}_{11}$  and *n*- $\text{C}_8\text{H}_{17}$  may be  $-0.140$ .

Assuming the activated complex **4** (path A), in which a carbonyl carbon atom of benzil was attacked by a nucleophilic phosphorus atom of phosphite, the reaction site of benzil (carbonyl carbon) is shielded by two benzene rings, a carbonyl group, and an oxygen atom. Then a phosphorus atom carrying bulky alkyl groups is prevented from an attack of the carbonyl carbon atom. Figures 1-3 imply that for  $(\text{C}_n\text{H}_{2n+1}\text{O})_3\text{P}$ , the steric factor of  $(\text{C}_n\text{H}_{2n+1}\text{O})_3\text{P}$  is unimportant when  $n$  is 1 and 2, but it is important when  $n \geq 3$ .

(9) (a) G. M. Santerre, C. T. Hansrote, Jr., and T. I. Crowell, *J. Amer. Chem. Soc.*, **80**, 1254 (1958); (b) Y. Ogata, A. Kawasaki, and N. Okumura, *J. Org. Chem.*, **29**, 1985 (1964).

(10) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt, New York, N. Y., 1959, p 181.

(11) L. N. Ferguson, *J. Chem. Educ.*, **47**, 46 (1970).

(12) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **74**, 3120 (1952).

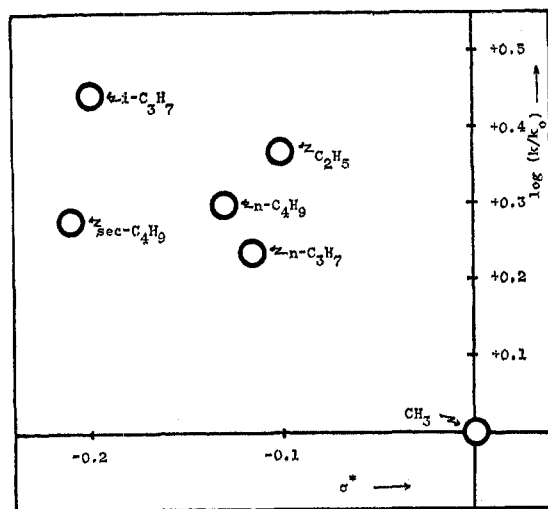
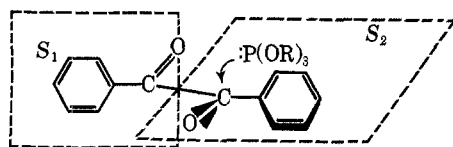


Figure 1.—Plot of  $\log(k/k_0)$  vs. Taft's  $\sigma^*$  for the reaction of  $(RO)_3P$  with  $PhCOCOPh$  in dioxane at  $25.0^\circ$ .

On the contrary, if the intermediate were **5** (path B) the steric factor would be less important, since the attacked carbonyl oxygen is out of the plane of the benzil molecule.

These data also show that the phosphorus atom attacks on the carbonyl carbon atom in the rate-determining step (path A).



The lower side of the carbonyl carbon atom on the  $S_2$  plane is hindered by the benzene ring on  $S_1$  plane, and *vice versa*.<sup>13</sup> The phosphorus atom may chiefly attack on the carbonyl carbon atom from one side, probably from an upper side of the  $S_2$  plane.

The  $^{31}P$  nmr chemical shifts relative to  $(CH_3O)_3P$  ( $\equiv \Delta\delta$   $^{31}P$ , ppm) were measured at room temperature. The shift may reflect the shielding efficiency of substituents on the phosphorus atom. The studies on  $\delta$   $^{31}P$  have been reported for many phosphorus compounds.<sup>14–18</sup> The linear correlation between  $\delta$   $^{31}P$  and the additive group contribution ( $\Sigma\sigma^P$ ) has been known with secondary and tertiary phosphines, phosphorus halides, phosphonium salts, etc.<sup>15,16</sup> The Taft equation is applicable to the  $\delta$   $^{31}P$  values of some alkyl or aryl phosphorus difluorides<sup>17</sup> but not to those for phosphine

(13) Two benzoyl groups of benzil seem to be almost in one plane (carbonyl group twists ca.  $7^\circ$  from benzene ring), and the dihedral angle of two carbonyl groups may be ca.  $70^\circ$  [N. K. Chaudhuri and M. A. El-Sayed, *J. Chem. Phys.* **47**, 1133 (1967); C. J. Brown and R. Sadanaga, *Acta Crystallogr.*, **18**, 158 (1965)].

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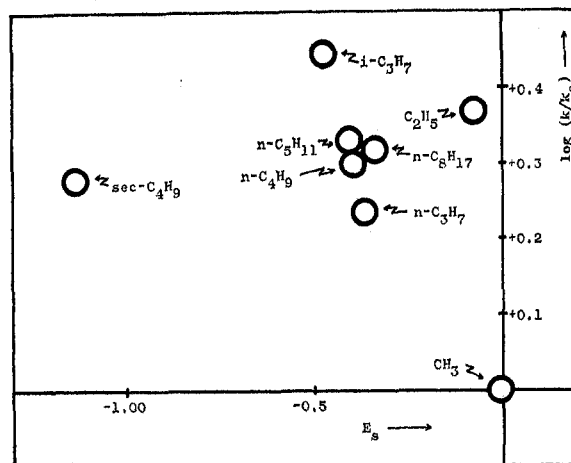


Figure 2.—Plot of  $\log(k/k_0)$  vs. Taft's  $E_s$  for the reaction of  $(RO)_3P$  with  $PhCOCOPh$  in dioxane at  $25.0^\circ$ .

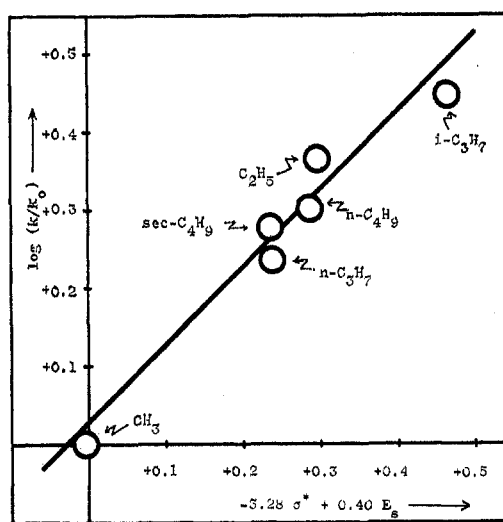


Figure 3.—Plot of  $\log(k/k_0)$  vs.  $(-3.28\sigma^* + 0.40E_s)$  for the reaction of  $(RO)_3P$  with  $PhCOCOPh$  in dioxane at  $25.0^\circ$ .

and some of other phosphorus compounds,<sup>15a,e,18</sup> since many factors, besides the inductive effect, may influence  $\delta$   $^{31}P$ .<sup>14b,19</sup>

The plot of  $\log(k/k_0)$  vs.  $\Delta\delta$   $^{31}P$  gives a correlation coefficient of 0.969 except for *sec-C*<sub>4</sub>H<sub>9</sub> and  $CH_3OCH_2CH_2$ . The good correlation with  $\Delta\delta$   $^{31}P$  seems to mean the control of rate by the electronic state of the phosphorus atom, while the poor correlation with  $E_s$  ( $r = -0.254$ ) seems to mean that the steric effect on  $\Delta\delta$   $^{31}P$  is unimportant.

Assuming the virtually constant bond angle of ca.  $100^\circ$  for O–P–O of the phosphite,<sup>19a,20</sup> the substituent effect may be parallel to the polar effect. The observed poor correlation in  $\sigma^*$  with *sec-C*<sub>4</sub>H<sub>9</sub> and  $CH_3OCH_2CH_2$  may reflect the deviation of the O–P–O angle and the other factors influencing  $\Delta\delta$   $^{31}P$ , e.g., the effect of oxygen atom.

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TABLE IV  
CHARACTERISTICS OF TRIALKYL PHOSPHITES PREPARED BY THE REACTION OF  
PHOSPHORUS TRICHLORIDE WITH CORRESPONDING ALCOHOLS

(RO) <sub>3</sub> P, R =	Base	Yield, %	Bp, °C (mm)	<i>n</i> <sub>D</sub> (deg)
C <sub>2</sub> H <sub>5</sub>	Diethylaniline	60	54 (17)	1.4104 (25)
<i>i</i> -C <sub>3</sub> H <sub>7</sub>		70	57 (9)	1.4049 (25)
<i>sec</i> -C <sub>4</sub> H <sub>9</sub>		70	77-78 (3.5-4)	1.4294 (25)
CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub>		80	99 (1.5)	1.4365 (25)
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	Pyridine	73	89 (10)	1.4239 (24)
<i>n</i> -C <sub>4</sub> H <sub>9</sub>		65	100-101 (4)	1.4307 (25)
<i>n</i> -C <sub>5</sub> H <sub>11</sub>		64	94-99 (1-1.5)	1.4369 (25)
<i>n</i> -C <sub>8</sub> H <sub>17</sub>		67	189-195 (1)	1.4468 (25)

TABLE V

UV SPECTRA OF DIOXAPHOSPHOLES (3) IN *n*-HEXANE

R =	Registry no.	$\lambda_{\max}$ , m $\mu$	$\epsilon_{\max}$ $\times 10^{-4}$
CH <sub>3</sub>	4850-55-9	319	1.14
C <sub>2</sub> H <sub>5</sub>	6509-75-7	323	1.18
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	4850-57-1	322	1.12
<i>sec</i> -C <sub>4</sub> H <sub>9</sub>	30415-15-7	319	1.23
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	30415-16-8	321	1.28
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	30415-17-9	321	1.21
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	30415-18-0	321	1.19
<i>n</i> -C <sub>8</sub> H <sub>17</sub>	30415-19-1	322	1.19
CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub>	30477-09-9	316	1.15

### Experimental Section

**Materials.**—Trialkyl phosphites were prepared by the reaction of phosphorus trichloride with corresponding alcohols in the presence of base below 15°<sup>21</sup> and purified by repeated distillations with metallic sodium under reduced pressure with nitrogen atmosphere. The characteristics of prepared trialkyl phosphites were listed in Table IV. Benzil was prepared as mentioned in our previous paper.<sup>1</sup>

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2,2,2-Trialkoxy-4,5-diphenyl-1,3,2-dioxaphospholes (3) were prepared by the reaction of benzil with excess trialkyl phosphite without solvent or in anhydrous dioxane under nitrogen atmosphere at 25.0° for 3-12 hr. The structure of 3 (R = Me) was confirmed by ir, nmr, and uv spectra.<sup>1</sup> The uv spectra of 3 were measured in anhydrous *n*-hexane and listed in Table V.

The hydrolysis product of 3 (R = Me) showed new peaks in ir and uv spectra: ir 3350 (OH, broad) and 1230 cm<sup>-1</sup> (P=O, broad); uv  $\lambda_{\max}$  285 m $\mu$  but not 313 m $\mu$  (in dioxane). Solvents were purified and dried before use.

**Kinetic Procedure.**—The kinetic experiments for the reaction of trialkyl phosphite with benzil were carried out in anhydrous dioxane. The rate measurements were done by means of the procedure as mentioned previously.<sup>1-3</sup> An isosbestic point was observed during the reaction of 1 (R = Me) at 287 m $\mu$  in dioxane.

The <sup>31</sup>P nmr chemical shifts were measured by a JNM-C60-HL model of Japan Electron Optics Laboratory Co., Ltd., at 24 MHz with proton decoupling at room temperature. The data were shown in Table III.<sup>19a,22-24</sup>

**Registry No.**—1, 134-81-6.

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## Lithium-Ammonia Reduction of Aromatic Ketones to Aromatic Hydrocarbons<sup>1</sup>

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Aromatic ketones are reduced, almost quantitatively, to aromatic hydrocarbons by lithium-ammonia solutions followed by an ammonium chloride quench. Lithium is more effective than sodium as the dissolving metal; in addition, the reduction is apparently catalyzed by trace amounts of metals such as cobalt or aluminum. The series of aromatic ketones which were reduced to aromatic hydrocarbons includes 1-tetralone to tetralin, 7-*tert*-butyl-1-tetralone to 6-*tert*-butyltetralin, 1-indanone to indan, 3,3-dimethyl-1-indanone to 1,1-dimethylindan, 2,2,3,3-tetramethyl-1-indanone to 1,1,2,2-tetramethylindan, 5-chloro-3,3-dimethyl-1-indanone to 1,1-dimethylindan, 3,3,4,5,6,7-hexamethyl-1-indanone to 1,1,4,5,6,7-hexamethylindan, benzophenone to diphenylmethane, xanthenone to xanthene, and dibenzoylmethane to 1,3-diphenylpropane. This study reveals various reduction rate relationships which are interpreted as due to steric effects, relief of strain, or stable ketyl radical formation. A mechanism is proposed for the catalyzed and uncatalyzed reduction.

Hitherto, it has been assumed that aromatic ketones are reduced, as are alkyl ketones, to alcohols in metal-ammonia reductions.<sup>3</sup> This presumption is apparently

based on work involving the reduction of benzophenone to diphenylmethanol with sodium in liquid ammonia.<sup>4</sup>

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