Tetrahedron. Vol. 27. pp. 3395 to 3404. Pergamon Press 1971. Printed in Great Britain

KINETICS OF THE REACTION OF TRIMETHYL PHOSPHITE WITH ALIPHATIC α-DIKETONES[1]

Y. Ogata and M. Yamashita

Department of Applied Chemistry, Faculty of Engineering, Nagoya University,
Chikusa-ku, Nagoya, Japan

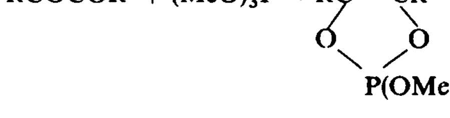
(*Received in Japan* 15 *February* 1971; *Received in the UK for publication* 4 *May* 1971)

Abstract—The substituent effect on the rate of reaction of trimethyl phosphite with aliphatic α-diketones has been studied in anhydrous dioxan by UV spectrophotometry. The rate constant (k) in the rate equation, $v = k[(MeO)_3P][RCOCR']$, decreases with change of R and R′ in the order methyl, ethyl, n-propyl, n-butyl, iso-propyl, iso-butyl and sec-butyl. Practically no reaction was observed with t-BuCOCOBu-t at room temperature. The reaction of $(MeO)_3P$ with RCOCOR fits the Taft equation, $\log(k/k_o) = +1{\cdot}08E_s + 0{\cdot}012$, which shows the predominance of steric effect, while the reaction of $(MeO)_3P$ with MeCOCOR′ fits the equation, $\log(k/k_o) = +1{\cdot}17\sigma^* + 0{\cdot}001$, which shows the superiority of polar effect. These results are discussed in terms of previous mechanism involving a nucleophilic attack of phosphorus on a carbonyl carbon of an α-diketone, and may exclude an one-electron transfer mechanism.

The reaction of trialkyl phosphites with α-diketones has been known,[2–5] but few studies on the mechanism have been reported.[6,7] In our kinetic studies, we postulated for the reaction of trialkyl phosphite with benzils a mechanism involving nucleophilic attack of phosphorus on a carbonyl carbon atom in view of the acid-base catalysis,[8a] and substituent effects of benzils[8b] and phosphites.[8c]

Another mechanism which involves radical ions *via* one-electron transfer is considered in view of the reactions of aromatic amines and chloranil[9] and the easiness of reduction of quinones.

The present paper deals with the kinetic study on the reaction of trimethyl phosphite (II) with aliphatic α-diketones (I) (Eq. 1) to obtain further support to the mechanism of the nucleophilic attack of the phosphorus atom on carbonyl carbon.



(1)

I II III

The rate was measured by UV spectrophotometry. The substituent effect will be discussed in connection with the Taft's E_s and σ^* constants and the attacked site.

RESULTS

The reaction of trimethyl phosphite (II) with aliphatic α-diketones (I) (except for R = R′ = t-Bu) proceeds quantitatively at room temp. to yield 2,2,2-trimethoxy-4,5-dialkyl-1,3,2-dioxaphospholes (III).

Rate law. The reaction was conducted in anhyd. dioxan at 30·0°, 35·0° and 40·0°, and the rate measured by means of UV spectrophotometry of the $n\pi^*$ transition of the carbonyl group of the disappearing α-diketones (Table 7). The rate law is expressed as Eq. 2 up to high conversion (over 80%).

$$v = k[(\mathrm{MeO})_3\mathrm{P}][\mathrm{RCOCOR'}] \qquad (2)$$

Substituent effect of symmetrical aliphatic α-diketones. The rates for the reaction of excess trimethyl phosphite with symmetrical aliphatic α-diketones were measured in dry dioxan at 35·0°. The second-order rate constants (k) are listed in Table 1.

TABLE 1. SECOND-ORDER RATE CONSTANTS, k, FOR THE REACTION OF TRIMETHYL PHOSPHITE WITH SYMMETRICAL ALIPHATIC α-DIKETONES IN DIOXAN AT 35·0°

RCOCOR R	Initial concn. (M) [I]	[II]	$10^4 k$ (M^{-1} sec^{-1})	Relative rate (k/k_0)	log (k/k_0)	E_s in Taft eq.
Me	0·3	0·5	8·52	1·000	0·000	0·00
Et	0·3	0·6	6·86	0·805	−0·094	−0·07
n-Pr	0·3	0·8	4·27	0·501	−0·300	−0·36
iso-Pr	0·3	0·8	1·88	0·221	−0·656	−0·47
n-Bu	0·3	0·8	4·07	0·353	−0·452	−0·39
iso-Bu	0·3	0·9	0·990	0·116	−0·936	−0·93
sec-Bu	0·3	1·1	0·449	0·0527	−1·29	−1·13
t-Bu	0·5	1·3	too slow to be measured			
Ph	0·05	0·1	82·5	9·68		

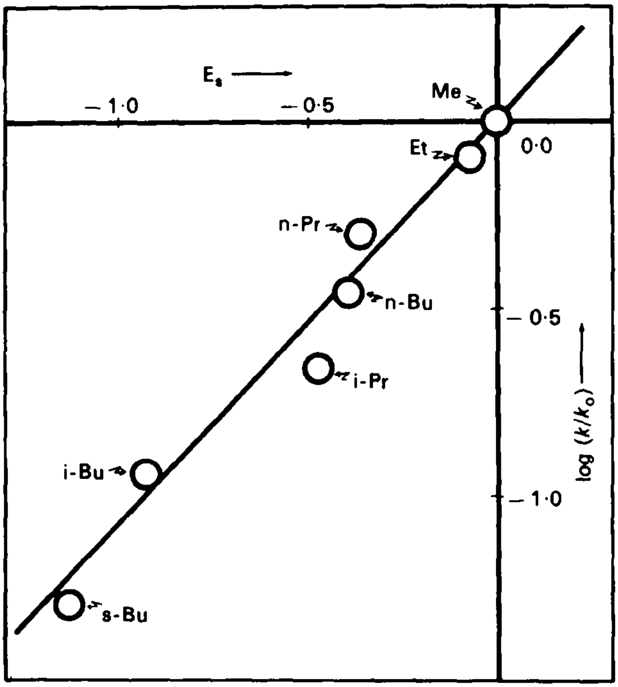


FIG 1. Taft plot for the reaction of trimethyl phosphite with symmetrical aliphatic α-diketones in dioxan at 35·0°

The plot of $\log(k/k_0)$ *vs* Taft's steric substituent constants, E_s, gives a straight line, whose reaction constant, δ, is +1·08 (correlation coefficient, r, is 0·985) as shown in Eq. 3 (Fig 1). Taft's polar term, $\rho^*\sigma^*$, has substantially no effect.

$$\log(k/k_0) = +1{\cdot}08E_s + 0{\cdot}012 \tag{3}$$

The rates at 30·0°, 35·0° and 40·0° afford energies of activation (E_a), entropies of activation ($\Delta S^\ddagger$) and frequency factors (A) as shown in Table 2. It seems that alkyl groups on α-diketones diminish both E_a and $\Delta S^\ddagger$ values.

TABLE 2. TEMPERATURE EFFECT AND THE ACTIVATION PARAMETERS FOR THE REACTION OF TRIMETHYL PHOSPHITE WITH SYMMETRICAL ALIPHATIC α-DIKETONES IN DIOXAN

RCOCOR R	Temp.	$10^4 k$ ($M^{-1}sec^{-1}$)	E_a (kcal/mol)	$\Delta S^{\ddagger a}$ (e.u.)	$\ln A^a$ ($M^{-1}sec^{-1}$)
Me	30·0	6·19	13·3	−28·6	14·7
	35·0	8·52			
	40·0	12·0			
Et	30·0	4·74	13·4	−29·4	14·8
	35·0	6·86			
	40·0	9·57			
n-Pr	30·0	3·01	13·2	−30·6	13·7
	35·0	4·27			
	40·0	5·96			
iso-Pr	30·0	1·41	10·5	−40·4	8·72
	35·0	1·88			
	40·0	2·45			
n-Bu	30·0	3·01	11·0	−37·7	10·1
	35·0	4·07			
	40·0	5·33			
iso-Bu	30·0	0·718	12·1	−36·5	10·7
	35·0	0·990			
	40·0	1·36			
sec-Bu	30·0	0·334	12·1	−38·4	9·76
	35·0	0·449			
	40·0	0·628			
Ph	30·0	66·4	10·1	−34·8	11·6
	35·0	82·5			
	40·0	113			

[a] Calculated by the least square method. The values at 35·0° were used

The rate of benzil (I, R = R′ = Ph) is *ca.* ten times as fast as that of butane-2,3-dione (I, R = R′ = Me). Virtually no reaction of trimethyl phosphite with 2,2,5,5-tetramethylhexane-3,4-dione (I, R = R′ = t-Bu) was observed at room temp. within two weeks.

Substituent effect of unsymmetrical aliphatic α-diketones. The observed second-order rate constants for the reaction of trimethyl phosphite with unsymmetrical aliphatic α-diketones in dioxan at 30·0° are listed in Table 3.

TABLE 3. SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF TRIMETHYL PHOSPHITE WITH UNSYMMETRICAL ALIPHATIC α-DIKETONES IN DIOXAN AT 30·0°

MeCOCOR′ R′	Initial concn. (M) [I]	 [II]	$10^4 k$ ($M^{-1} sec^{-1}$)	Relative rate (k/k_0)	log (k/k_0)	σ* in Taft eq.
Me	0·3	0·5	6·19	1·000	0·000	0·000
Et	0·3	0·7	5·18	0·837	−0·0776	−0·100
iso-Pr	0·3	0·7	3·70	0·598	−0·224	−0·200
iso-Bu	0·3	0·5	3·91	0·632	−0·199	−0·125
PhCOCOPh	0·05	0·1	66·4	10·7	+1·03	+0·600

The plot of log (k/k_0) *vs* Taft's σ^* affords a straight line, which gives ρ^* of +1·17 (r is 0·925). The Taft equation can be written as Eq. 4 (Fig 2).

$$\log (k/k_0) = +1{\cdot}17\sigma^* + 0{\cdot}001 \qquad (4)$$

The values of E_a, $\Delta S^{\ddagger}$ and A are listed in Table 4. The correlation coefficient for log (k/k_0) *vs* σ^* seems to decrease with rising temp. Also an alkyl group tends to decrease both E_a and $\Delta S^{\ddagger}$ values.

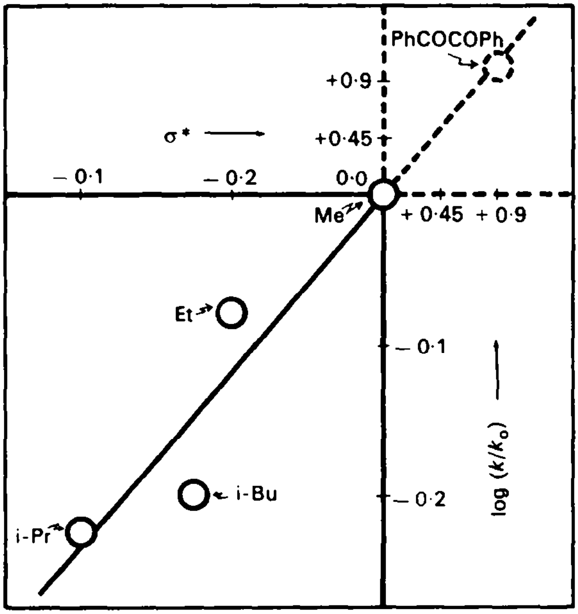


FIG 2. Taft plot for the reaction of trimethyl phosphite with unsymmetrical aliphatic α-diketones in dioxan at 30·0°

Effect of hydrogen chloride. Addition of a small amount of dry HCl to the reaction results in a sharp increase of rate constant as shown in Table 5. Acid catalysis has been observed in the reaction of trimethyl phosphite with benzil.[8a]

TABLE 4. TEMPERATURE EFFECT AND ACTIVATION PARAMETERS FOR THE REACTION OF TRIMETHYL PHOSPHITE WITH UNSYMMETRICAL ALIPHATIC α-DIKETONES IN DIOXAN

MeCOCOR′ R′	Temp.	$10^4 k$ ($M^{-1} sec^{-1}$)	E_a (kcal/mol)	$\Delta S^{\ddagger a}$ (e.u.)	ln A^a ($M^{-1} sec^{-1}$)
Et	30·0	5·18	13·0	−30·0	14·0
	35·0	7·02			
	40·0	10·2			
iso-Pr	30·0	3·70	13·1	−30·2	13·9
	35·0	5·28			
	40·0	7·36			
iso-Bu	30·0	3·91	11·0	−36·7	10·6
	35·0	5·26			
	40·0	7·01			

[a] Calculated by the least square method. The values at 35·0° were used.

TABLE 5. EFFECT OF A SMALL AMOUNT OF HCl ON THE SECOND-ORDER RATE CONSTANTS IN DIOXAN

MeCOCOR′ R′	Initial concn. (M) [I]	Initial concn. (M) [II]	Temp.	$10^3 k$ ($M^{-1} sec^{-1}$)
Et	0·3	0·6	30·0	1·22
			35·0	1·77
			40·0	2·44
iso-Pr	0·3	0·6	30·0	0·711
			35·0	0·965
			40·0	1·31
iso-Bu	0·3	0·6	30·0	0·412
			35·0	0·558
			40·0	0·773

DISCUSSION

We reported previously that in the reaction of trialkyl phosphites with benzil, addition of acids accelerated the reaction, while bases retarded it,[8a] which may be due to the change of electrophilicity of carbonyl by the interaction with acids or bases. The substituent effect in benzil gave Hammett's ρ value of $+1{\cdot}86$. The correlation with σ was better than that with σ^-.[8b] This suggests that the resonance of negative charge with substituent is forbidden in the transition state. The substituent effect in phosphite fits the Taft equation, $\log (k/k_0) = -3{\cdot}28\sigma^* + 0{\cdot}40E_s + 0{\cdot}03$.[8c] These facts suggest a mechanism which involves a rate-determining nucleophilic attack of phosphorus on a carbonyl carbon atom of benzil.

The substituent effect in trialkyl phosphites implies that the steric factor will be dominant in the substituent effect in aliphatic α-diketones, since even the substituent being situated in β-position of the phosphorus partially participated in the reaction rate. Table 1 and Fig 1 show that the rate is decreased with increasing bulkiness of alkyl groups, i.e., the E_s value controls the rate for symmetrical aliphatic α-diketones. The positive δ value implies that the steric hindrance is operating in the rate-determining step. Two bulky t-Bu groups in t-BuCOCOBu-t inhibit the reaction.

The E_s value is known to control the rate of the acid-catalysed alcoholysis of β-naphtyl carboxylate[10] and ethylation of 2-alkyl pyridine,[11] whose mechanisms are known to involve an attack on the next site of an alkyl group.

On the other hand, Table 3 and Fig 2 show that the rate decreases with an increase of electron-releasing power of alkyl group, i.e., the σ^* value controls the rate for unsymmetrical aliphatic α-diketones. Since the alkyl group nearer to the primarily attacked carbonyl group retards the reaction by steric hindrance, the attack may occur on the farther carbonyl group from R′ of MeCOCOR′, i.e., carbonyl of acetyl group. Thus the steric effect does not influence the farther carbonyl group. The positive ρ^* value indicates a nucleophilic attack on carbonyl. With an increase of reaction temp. the correlation coefficient r decreases (temp., r: 30·0°, 0·925: 35·0°, 0·898; 40·0°, 0·850). This means that the selectivity of carbonyl group attacked by phosphorus decreases with an increase of temp., since an alkyl group which lies nearer to the carbonyl initially attacked exerts a steric effect, whereas a farther one influences a polar effect alone. The temp. dependent stereoselectivity was also reported for the asymmetric synthesis.[12]

The reaction of benzil is *ca* ten times as fast as that of biacetyl. The neighbouring phenyl and carbonyl groups in benzil are known to be almost coplanar, while two carbonyl groups twist *ca.* 70° from each other.[8b, 13] In contrast, two carbonyls in aliphatic α-diketones such as glyoxal, biacetyl and dipivaloyl have a coplanar and *trans* configuration.[14] If a benzoyl group of benzil is coplanar and a phosphorus atom attacks vertically into the plane, there is no steric effect of phenyl group. Since the transmitted polar effect of phenyl group *via* a carbonyl group is reduced by a factor of *ca.* 0·5,[8b, 15] the total σ^* value in benzil may be $+0{\cdot}9$, i.e., $\sigma^*_{\mathrm{Ph}} + 0{\cdot}5\sigma^*_{\mathrm{Ph}} = +0{\cdot}6 + 0{\cdot}3 = +0{\cdot}9$. The ρ^* value in Fig 2 is $+1{\cdot}17$, then the expected logarithm of relative rate for benzil to biacetyl, $\log(k/k_0) = \rho^*(\sigma^*_{\mathrm{Ph}} + 0{\cdot}5\sigma^*_{\mathrm{Ph}})$, may be 1·05, *i.e.*, $0{\cdot}9 \times 1{\cdot}17 = 1{\cdot}05$, which is close to the observed value of $\log(k/k_0) = +1{\cdot}03$. The increase of rate for benzil may be explained by Taft's σ^* value (Fig 2).

Tables 2 and 3 show the small energies and entropies of activation. These values are characteristic for this reaction. The variation of E_a and $\Delta S^\ddagger$ is somewhat irregular. The more powerful electron-releasing group decreases the values of E_a and $\Delta S^\ddagger$. Since they stabilise the intermediate (IV in Scheme 1) by slightly neutralising the formed positive charge on phosphorus, and bring about a highly oriented and charge-separated intermediate.

HCl accelerates the reaction. This may be explained by increased electrophilicity of carbonyl carbon by interaction of acid.[8a]

If one-electron transfer from phosphorus to carbonyl is involved in the rate-determining step, the polar effect would be a dominant factor and the steric effect would be unimportant. The close approach of reactants is unnecessary for the one-electron transfer and hence there is little steric effect. It was reported that an electron transfer occurred at 7 Å, and that no *ortho* effect was observed for reduction potential of phenanthrenequinones.[17] Therefore, the one-electron transfer mechanism may be excluded.

If a carbonyl oxygen atom of α-diketone is attacked by a phosphorus atom, the steric effect would be negligible. Eq. 3 rules out this mechanism.

The control of rate by E_s value indicates the attack of phosphorus atom on the carbonyl carbon in the rate-determining step. It is reported by other workers that the E_s value controls the rate for the reaction of tervalent phosphorus compounds with Ac_2O, and that the mechanism involves a nucleophilic attack of phosphorus on the carbonyl carbon atom.[18, 19]

For unsymmetrical aliphatic α-diketones, MeCOCOR′, the σ^* value of R′ controls the rate. The phosphorus atom should attack selectively the less crowded carbonyl carbon, *i.e.*, acetyl carbon. The bulky alkyl group, R′, seems to have little steric influence on the farther carbonyl group, hence the polar effect transmitted by one carbonyl group controls the reaction rate.

The reaction of substituted benzils with trimethyl phosphite has large ρ values (*i.e.*, +2·75 for symmetrically disubstituted benzils and +1·86 for monosubstituted

TABLE 6. OVERALL YIELDS AND BOILING POINTS OF ALIPHATIC α-DIKETONES PRODUCED FROM CARBOXYLIC ACID[a] OR ALIPHATIC KETONE[b]

RCOCOR′		Overall yield (%)	b.p. [°(mm)]
R	R′		
Me	Me	—	87–88
Et	Et	16[a]	58 (51)
n-Pr	n-Pr	47[a]	72–73 (25)
iso-Pr	iso-Pr	39[a]	63–64 (34)
n-Bu	n-Bu	41[a]	100–101 (21)
iso-Bu	iso-Bu	57[a]	85–86 (21)
sec-Bu	sec-Bu	69[a]	81–82 (21)
t-Bu	t-Bu	70[a]	65–66 (20)
Me	Et	40[b]	65–65·5 (137)
Me	iso-Pr	26[b]	62–63 (111)
Me	iso-Bu	49[b]	79–81 (110)

TABLE 7. UV SPECTRA OF ALIPHATIC α-DIKETONES ($n\pi^*$ TRANSITION OF CARBONYL GROUPS) IN n-HEXANE

RCOCOR′		λ_{max} used for kinetic study (nm)	ε_{max} used for kinetic study
R	R′		
Me	Me	421	22·2
Et	Et	435	13·7
n-Pr	n-Pr	435	19·4
iso-Pr	iso-Pr	436	22·6
n-Bu	n-Bu	435	19·2
iso-Bu	iso-Bu	439	22·1
sec-Bu	sec-Bu	442	30·7
t-Bu	t-Bu	373	13·8
Me	Et	419	15·6
Me	iso-Pr	429	21·2
Me	iso-Bu	432	17·8

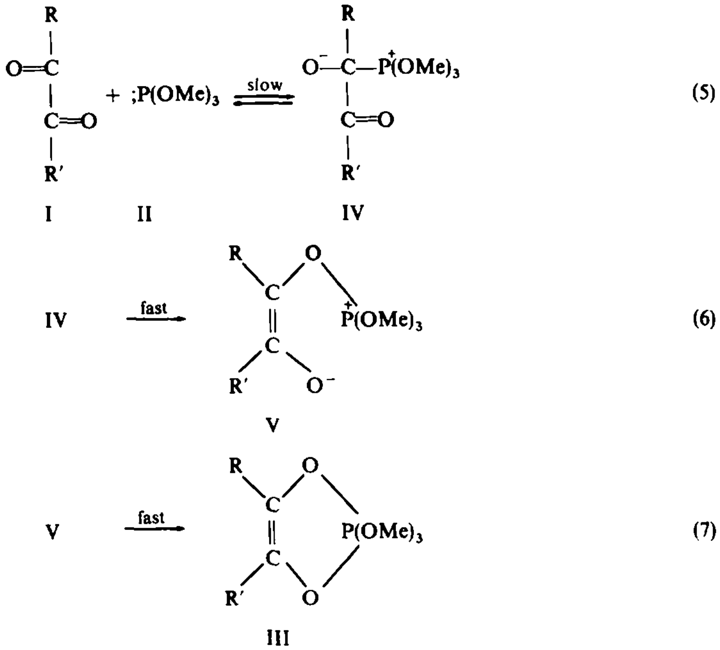
[a] The number of peaks in visible region was small for symmetrical aliphatic α-diketones, whereas it was many for unsymmetrical α-diketones. The highest peak was used for kinetics

benzils) and the control of rate by E_s for symmetrical aliphatic α-diketones suggest that the reverse of the first addition step is less important.

In conclusion, the mechanism of the reaction of trialkyl phosphite with α-diketones may be written as Scheme 1.

Here, Eq. 5 is a rate-determining nucleophilic attack of phosphite, and Eqs 6 and 7 are fast. R is a less bulky alkyl group than R .

SCHEME 1. THE MECHANISM OF THE REACTION OF TRIMETHYL PHOSPHITE WITH ALIPHATIC α-DIKETONES.



EXPERIMENTAL

Benzil was prepared as mentioned in our previous paper.[8a]

Hexane-3,4-dione was prepared by H_2SO_4-catalysed Et esterification of propionic acid (71%), followed by acyloin reductive condensation of ethyl propionate to give hexane-4-ol-3-one (49%),[20] and then oxidation of the acyloin with $Cu(OAc)_2 \cdot H_2O$ in AcOH aq.[21] The crude material was washed with 5% $NaHCO_3$ aq, dried and distilled repeatedly to yield pure hexane-3,4-dione, b.p. 58°/51 mm, overall yield 16%.

2,2,5,5-*Tetramethylhexane-3,4-dione* was prepared by CrO_3 oxidation of 2,2,5,5-tetramethyl-4-ol-3-one prepared by the similar procedure,[14a] b.p. 65–66°/20 mm, overall yield 70%.

Butane-2,3-dione (commercial G. R. grade) purified by distillation, b.p. 87–88°. The other symmetrical aliphatic α-diketones were prepared by the procedure similar to hexane-3,4-dione and listed in Table 6.

Pentane-2,3-dione was prepared by oximation of pentane-2-one with MeONO and HCl to give pentane-3-oxime-2-one,[22] followed by steam distillation with 10% H_2SO_4.[23] The crude material was purified by the procedure similar to hexane-3,4-dione, b.p. 65–65·5°/137 mm, overall yield 40%. Other unsymmetrical aliphatic α-diketones were prepared similarly. The purity of aliphatic α-diketones was checked by GLC using Apiezon grease L 3% on celite 545.

Trimethyl phosphite was purified by repeated distillation with metallic Na under N_2, b.p. 52°/86 mm (lit.[24] 111–112°).

2,2,2-*Trimethoxy-4,5-dialkyl-1,3,2-dioxaphospholes* (III) were prepared by the reaction of aliphatic α-diketones with excess trimethyl phosphite under N_2 at room temp. These reactions were complete within 3–24 hr. Virtually no reaction of 2,2,5,5-tetramethylhexane-3,4-dione with trimethyl phosphite was observed at room temp within 2 weeks (the decrease of UV absorption at 373 nm was *ca* 2%).

Solvents used were dried and purified before use.

UV spectra. The UV spectra of aliphatic α-diketones and III were measured in anhyd n-hexane. Aliphatic α-diketones had absorption in visible region (λ_{max}, 370–440 nm), while III did not in the above region (Table 7).

Kinetic procedure. The kinetic experiments for the reaction of trimethyl phosphite with aliphatic α-diketones were carried out in dioxan. The rate was followed by measuring the remaining α-diketone by means of UV spectrophotometry (Table 7) at appropriate time intervals. Effect of HCl was measured by introducing a small amount of dry HCl into the dioxan solution of aliphatic α-diketone. The other kinetic procedure was the same as the previous paper.[8a]

REFERENCES

[1] Contribution No. 166

[2] [a] F. Ramirez and N. B. Desai, *J. Am. Chem. Soc.* **82**, 2652 (1960)
[b] F. Ramirez, R. B. Mitra and N. B. Desai, *Ibid.* **83**, 492 (1961)
[c] F. Ramirez, N. Ramanathan and N. B. Desai, *Ibid.* **84**, 1317 (1962)
[d] F. Ramirez and N. B. Desai, *Ibid.* **85**, 3252 (1963)
[e] F. Ramirez, N. Ramanathan and N. B. Desai. *Ibid.* **85**, 3465 (1963)

[3] [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); *Ibid.* **56**, 10191a (1962)

[4] [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**, 358i (1961)
[c] V. A. Kukhtin, K. M. Kirillova and R. R. Shagidullin, *Ibid.* **32**, 649 (1962); *Chem. Abstr.* **58**, 546h (1963)
[d] V. A. Kukhtin and K. M. Kirillova, *Ibid.* **32**, 2797 (1962); *Chem. Abstr.* **58**, 8489d (1963)
[e] V. A. Kukhtin, K. M. Kirillova, R. R. Shagidullin, Yu. Yu. Samitov, N. A. Lyazina and N. F. Rakova, *Ibid.* **32**, 2039 (1962); *Chem. Abstr.* **59**, 4542h (1963)
[f] K. M. Kirillova and V. A. Kukhtin, *Ibid.* **35**, 544 (1965); *Chem. Abstr.* **63**, 523c (1965)
[g] V. A. Kukhtin, T. N. Voskoboeva and K. M. Kirillova, *Ibid.* **32**, 2333 (1962); *Chem. Abstr.* **58**, 9127g (1963)

[5] D. B. Denney and D. H. Jones, *J. Am. Chem. Soc.* **91**, 5821 (1969)

[6] A. D. Litt, Ph.D. Thesis (1968) at Rutgers University

[7] A. J. Kirby and S. G. Warren in *The Organic Chemistry of Phosphorus* Chapt. 3, Elsevier Co., Amsterdam (1967)

[8] [a] Y. Ogata and M. Yamashita, *J. Am. Chem. Soc.* **92**, 4670 (1970)
[b] Y. Ogata and M. Yamashita, *Tetrahedron* **27**, 2725 (1971)
[c] Y. Ogata and M. Yamashita, *J. Org. Chem.* in press

[9] [a] T. Nogami, K. Yoshihara, H. Hosoya and S. Nagakura, *J. Phys. Chem.* **73**, 2670 (1969)
[b] T. Yamaoka and S. Nagakura, *Bull. Chem. Soc. Japan* **43**, 355 (1970)

[10] M. Harfenist and R. Baltzly, *J. Am. Chem. Soc.* **69**, 362 (1947)

[11] H. C. Brown and A. Cahn, *Ibid.* **77**, 1715 (1955)

[12] D. R. Boyd and M. A. McKervey, *Quart. Rev.* **22**, 95 (1968)

[13] [a] C. J. Brown and R. Sadanaga, *Acta Cryst.* **18**, 158 (1965)
[b] N. K. Chaudhuri and M. A. El-Sayed, *J. Chem. Phys.* **47**, 1133 (1967)
[c] E. A. Braude, F. Sondheimer, *J. Chem. Soc.* 3754 (1955)

[14] [a] N. J. Leonard, R. T. Rapara, H. L. Herzog and E. R. Blout, *J. Am. Chem. Soc.* **71**, 2997 (1949)
[b] N. J. Leonard and P. M. Mader, *Ibid.* **72**, 5388 (1950)
[c] S. F. Mason, *Quart. Rev.* **15**, 287 (1961)

[15] K. Bowden, *Canad. J. Chem.* **41**, 2781 (1963)

[16] H. Knibbe, D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.* **72**, 257 (1968); *Chem. Abstr.* **68**, 100359w (1968)

[17] L. F. Fieser, *J. Am. Chem. Soc.* **51**, 3101 (1929)

[18] J. Koketsu, S. Kojima, S. Sakai and Y. Ishii, *Kogyo Kagaku Zasshi* **73**, 1004 (1970)

[19] G. Kamai and V. A. Kukhtin, *Khim. i Primenenie Fasfororgan. Soedinenii, Akad. Nauk SSSR Trudy 1-Oi Konferents* 1955, p. 91; *Chem. Abstr.* **52**, 2416 (1958)

[20] J. M. Snell and S. M. McElvain, *Org. Syntheses Coll. Vol.* **2**, 114 (1943)

[21] A. T. Blomquist and A. Goldstein, *Ibid. Coll. Vol.* **4**. 838 (1963)

[22] [a] W. L. Semon and V. R. Damerell, *Ibid. Coll. Vol.* **2**. 204 (1943)
[b] W. H. Hartung and F. Crossley, *Ibid. Coll. Vol.* **2**, 363 (1943)

[23] W. W. Hartman and L. J. Roll, *Ibid. Coll. Vol.* **3**. 20 (1955)

[24] Wm. W. Marshall, U.S. Patent 2,848,474 (1958); *Chem. Abstr.* **53**. 1144c (1959)