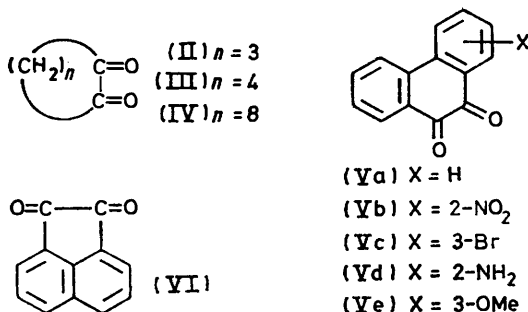
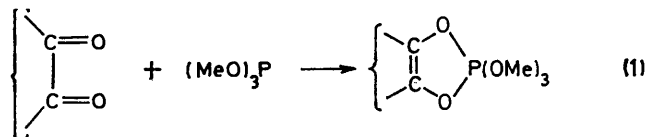


Kinetics of the Reaction of Trimethyl Phosphite with Cyclic α -Diketones

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The kinetics of the reaction of trimethyl phosphite with aliphatic α -diketones, 9,10-phenanthrenequinones, and acenaphthenequinone to form a cyclic adduct has been studied in anhydrous dioxan. The rates are expressed as $v = k[(\text{MeO})_3\text{P}][\alpha\text{-diketone}]$. The rate constant k decreases with an increase in the size of the α -diketone ring in the order 5 (cyclopentane-1,2-dione) \gg 6 (cyclohexane-1,2-dione) $>$ 10 (cyclodecane-1,2-dione), while acenaphthenequinone reacts more quickly than 9,10-phenanthrenequinone which has a condensed ring system. This suggests that the reaction proceeds with releasing strain by changing a carbonyl C atom of cyclopentane-1,2-dione from sp^2 to sp^3 , and that a β -ketophosphonium intermediate, *i.e.*, an attack of carbonyl carbon atom by the phosphorus atom, is involved. The Hammett equation for the phenanthrenequinones gives a ρ value of +1.5 for the reaction.

PHOSPHITES or phosphines react with cyclic α -diketones, *e.g.*, cyclohexane-1,2-dione (III)¹ and 9,10-phenanthrenequinone (Va).² Our previous papers reported that the reaction of phosphites with acyclic α -diketones may involve a rate-determining nucleophilic attack of the phosphorus atom on the carbonyl carbon atom, as shown by the acid catalysis³ and the substituent effect of α -diketones^{4,5} and phosphites.⁶



The reactions of cyclic compounds are accelerated by an increase of ring strain in the reactants, if such strain is released during the reaction.⁷ In the Arbuzov reaction, the cyclic five-membered ring shows reduced reactivity.⁸ The reaction of a phosphite of rigid structure, *e.g.*, 2,8,9-trioxa-1-phospha-adamantane, with biacetyl is slow.⁹ These ring-size effects suggest that the formation of a phosphonium intermediate is rate-determining in these reactions.

The present paper reports our kinetic study on the reaction of trimethyl phosphite with cyclic α -diketones to see the effect of ring strain on the nucleophilic attack

of phosphorus atom on the carbonyl carbon atom. The effect of substituents on compound (Va) will be discussed in connection with the mechanism.

RESULTS

Trimethyl phosphite (I) reacts with cyclic α -diketones to yield 1 : 1 adducts at room temperature. The reaction in anhydrous dioxan was followed by u.v. spectrophotometry of α -diketones or products. The rate law obtained is expressed by equation (2) to high conversion.

$$v = k[(\text{MeO})_3\text{P}][\alpha\text{-diketone}] \quad (2)$$

Reaction with Alicyclic Diketones.—The reaction of trimethyl phosphite (I) with alicyclic α -diketones was followed

TABLE I

The observed second-order dependence of rate for the reaction of (I) with alicyclic α -diketones in dioxan at 35 °C

α -Diketone	Initial concn./M		$10^4 k_{\text{obs}}$ l mol ⁻¹ s ⁻¹
	[(I)]	[Diketone]	
	0.0954	0.0441	11
(II)	0.225	0.0441	12
	0.450	0.0139	9
	0.533	0.628	2.5
(III)	0.585	0.196	2.3
	0.763	0.246	2.8
	0.745	0.258	2.41
(IV)	0.321	0.208	2.35

by measuring the decreasing absorption of the α -diketones in the visible region. The observed second-order dependence of rate, and rate constant k at various temperatures are listed in Tables 1 and 2, respectively. The value of k for compound (II) was much higher than that for (III) or (IV).

A slow keto-enol equilibrium with (II) and (III) is known.¹⁰ The approximate enol content (%) for these two ketones in dioxan were measured by bromination and n.m.r. spectra and is shown in Table 3 together with the second-order rate constants (k') corrected by taking

¹ V. A. Kukhtin, T. N. Voskoboeva, and K. M. Kirillova, *Zhur. obshchei Khim.*, 1962, **32**, 2333 (*Chem. Abs.*, 1963, **58**, 9127g).

² (a) F. Ramirez and N. B. Desai, *J. Amer. Chem. Soc.*, 1960, **82**, 2652; (b) F. Ramirez, R. B. Mitra, and N. B. Desai, *ibid.*, 1961, **83**, 492; (c) F. Ramirez and N. B. Desai, *ibid.*, 1963, **85**, 3252.

³ Y. Ogata and M. Yamashita, *J. Amer. Chem. Soc.*, 1970, **92**, 4670.

⁴ Y. Ogata and M. Yamashita, *Tetrahedron*, 1971, **27**, 2725.

⁵ Y. Ogata and M. Yamashita, *Tetrahedron*, 1971, **27**, 3395.

⁶ Y. Ogata and M. Yamashita, *J. Org. Chem.*, 1971, **36**, 2584.

⁷ L. N. Ferguson, *J. Chem. Educ.*, 1970, **47**, 46.

⁸ G. Aksnes and P. Eriksen, *Acta Chem. Scand.*, 1966, **20**, 2463.

⁹ A. D. Litt, Ph.D. Thesis, Rutgers University, 1968.

¹⁰ (a) G. Schwarzenbach and Ch. Wittwer, *Helv. Chim. Acta*, 1947, **30**, 663; (b) G. Hesse and G. Krehbiel, *Annalen*, 1955, **593**, 35.

TABLE 2

The observed second-order rate constants in dioxan at various temperatures

α -Diketone (IV) Bu ⁿ CO·COBu ⁿ ^b	Initial concn./M		10 ³ k/l mol ⁻¹ s ⁻¹			E_a kcal mol ⁻¹	ΔS^\ddagger ^a cal mol ⁻¹ K ⁻¹	ln A l mol ⁻¹ s ⁻¹
	[(I)]	[Diketone]	30.0 °C	35.0 °C	40.0 °C			
	0.745	0.258	1.67	2.41	3.30	13.1	-32.0	13.0
	0.803	0.302	3.01	4.07	5.33	11.0	-37.7	10.1

^a Values at 35.0 °C. ^b Ref. 5.

TABLE 3

Relative second-order rate for the reaction of trimethyl phosphite (I) with alicyclic α -diketones in dioxan at 35.0 °C

No. of C atoms in ring	Initial concn./M		10 ³ k _{obs} l mol ⁻¹ s ⁻¹	Approximate enol content of diketone in dioxan (%)		10 ³ k' l mol ⁻¹ s ⁻¹	Relative rate
	[(I)]	[Diketone]		25 °C	35 °C		
5 (II)	0.0954	0.0441	11	94—97 ^{a,c}	84—96 ^{a,c}	69—275	23—91
6 (III)	0.533	0.628	2.5	2 ^{a,d}	15—17 ^{a,d} 16 ^{b,e}	3.0	1
10 (IV)	0.745	0.258	2.41			2.41	0.8
Bu ⁿ CO·COBu ⁿ ^f	0.803	0.302	4.07			4.07	1.4

^a Estimated by bromination method.^{10a} ^b Based on n.m.r. spectra. ^c Concn. 0.881M. ^d Concn. 1.26M. ^e Concn. ca. 9.1% (w/w). ^f Ref. 5.

the content of keto-tautomer into account (see Discussion section).

TABLE 4

The observed second-order dependence of rate for the reaction of (I) with phenanthrenequinone (Va) and acenaphthenequinone (VI) in dioxan

α -Diketone	t/°C	Initial concn./M		10 ³ k l mol ⁻¹ s ⁻¹
		[(I)]	[Diketone]	
(Va)	22	0.734	0.000870	2.40
		0.248	0.000870	2.53
(VI)	33	0.329	0.0170	19.9
		0.165	0.0170	19.6
		0.329	0.00850	19.3

Reaction with Aromatic Diketones.—The reaction of (I) with 9,10-phenanthrenequinones (Va—e) and acenaph-thenequinone (VI) were followed spectrophotometrically by measuring the increasing absorption of 1:1 adducts and decreasing absorption of α -diketone. The second-order dependence of rate and rate constants (*k*) for (Va) and (VI) are listed in Tables 4 and 5, respectively. The rate of consumption of starting material agrees with the rate of formation of product for (Va), indicating that the consumption of (Va) is rate-determining, but not for (VI) at a lower temperature (ca. 20 °C). But at higher temperature (ca. 30 °C) both rates agreed within experimental error and showed a second-order rate dependence (Table 4).The substituent effect of (V) on *k* was measured at 21.5 °C and is shown in Table 6. The Hammett plot with ordinary σ gives a straight line, which is in contrast to that for mono-substituted benzil.⁴ The ρ value was calculated by the least-squares method to be +1.5 (σ) with a correlation

TABLE 5

The second-order rate constants for the reaction of trimethyl phosphite (I) with phenanthrenequinone (Va) and acenaphthenequinone (VI) in dioxan

α -Diketone	Initial concn./M		10 ³ k/l mol ⁻¹ s ⁻¹			E_a kcal mol ⁻¹	ΔS^\ddagger ^b cal mol ⁻¹ K ⁻¹	ln A l mol ⁻¹ s ⁻¹
	[(I)]	[Diketone]	20.0 °C	25.0 °C	30.0 °C			
(Va)	0.210	0.0115	2.10	2.96	4.12	6.29	-30.2	15.3
(VI) ^a	0.0230	0.0108	7.84	10.8	14.8	5.94	-29.9	15.4

^a The kinetics were followed by measuring the u.v. spectra of the product. ^b The values at 25.0 °C.

TABLE 6

The substituent effect on the rate of the reaction of trimethyl phosphite (I) with phenanthrenequinones (Va—e) in dioxan at 21.5 ± 0.5 °C

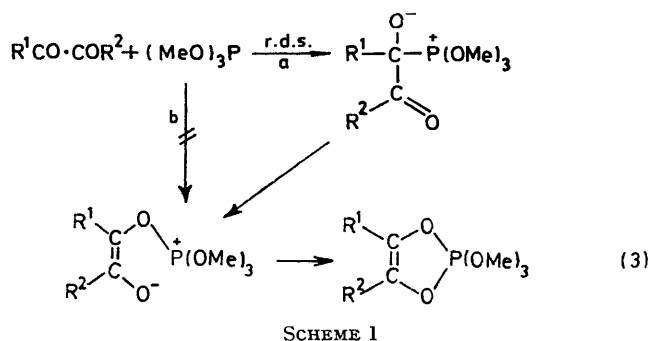
	Initial concn./M		10 ³ k l mol ⁻¹ s ⁻¹	log (Rel. rate)	Hammett σ value ^b	Reduction potential ^c E ₀ /mV
	[(I)]	[(V)]				
(Va)	0.248	0.000870	2.4	0.00	0.00	458
(Vb)	0.248	0.000818	25	1.01	0.71	540
(Vc)	0.248	0.000477	3.5	0.17	0.23	499
(Vd)	0.248	0.000583	1.5	-0.21	-0.16	443
(Ve)	0.497	0.000819	0.71	-0.53	-0.27	419

^a 2- And 3-positions correspond to *meta*- and *para*-positions, respectively. ^b Ref. 11. ^c Ref. 12.

coefficient (ρ) of 0.99.¹¹ This indicates a nucleophilic attack of phosphorus atom on the carbonyl group of the α -diketone. The reduction potentials of these diketones¹² correlate with the logarithm of relative rates.

DISCUSSION

The probable mechanism of the reaction of trialkyl phosphite with α -diketones involves a rate-determining attack by phosphorus either on a carbonyl carbon or an oxygen atom of the α -diketone. As reported previously, addition of acids accelerated the reaction of trimethyl phosphite with benzil.³ The substituent effect in benzil gave a Hammett correlation with σ better than with σ^- , and it afforded a large positive ρ value for symmetrically disubstituted benzils, while that for monosubstituted benzils gave two different positive values (one is for electron-attractive groups and the other is for electron-releasing groups).⁴ The substituent effect in phosphites fits Taft's equation: $\log(k/k_0) = -3.28\sigma^* + 0.40E_s$.⁶ Further, Taft's steric substituent constant E_s alone controls the rate of the reaction of trimethyl phosphite with aliphatic α -diketones.⁵ This evidence suggests that the reaction may involve a rate-determining nucleophilic attack of phosphorus atom on the carbonyl carbon atom (path a), but not on the carbonyl oxygen atom (path b) (see Scheme 1). Here, R^1 and R^2 may be either an alkyl

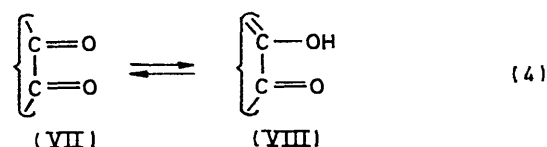


or an aryl group. The hybridisation of the carbonyl carbon atom changes from sp^2 to sp^3 in the rate-determining step, so the effect of ring strain of alicyclic α -diketones is expected.

The kinetic study on the reaction of biacetyl with a cyclic phosphite⁹ shows that the phosphorus atom has the sp^3 hybridisation in the transition state, because a cyclic phosphite with rigid structure retards the rate, but this result cannot distinguish whether the attack of phosphorus atom occurs on a carbonyl carbon or oxygen atom.

The keto-enol equilibria for (II) and (III) are slow,¹⁰

so it may be assumed that the concentration of enol tautomer is constant during the kinetic study. There-



fore, the rate is given by equation (5). The observed k' values are shown in Table 3. Cyclopentane-1,2-

$$v = k'[(I)][(VII)] \quad (5)$$

dione (II) reacts 20–90 times as fast as cyclohexane-1,2-dione (III). The observed rate enhancement for (II) is attributable to the ring-strain effect, but not to the acid catalysis of the enol tautomer, because the concentrations of (II) and (III) differ by a factor of 14 (Table 3). The di-imide reduction of cyclopentene is 16 times as fast as that of cyclohexene.¹³ The analogous effect of ring size suggests that both the reaction have an analogous transition state, *i.e.*, an sp^3 hybridised carbon atom. The change from sp^2 to sp^3 hybridisation releases the strain for (II) but not so much for (III), because the angle of $109^\circ 28'$ (sp^3) is closer to the internal angle of a pentagon than of a hexagon. This higher reactivity of cyclopentanedione is also observed with (Va) and (VI), *i.e.*, the order of the reactivity for (I) is (VI) > (Va). These facts suggest a nucleophilic attack of the phosphorus atom on the carbonyl carbon atom (path a), but not on the carbonyl oxygen atom (paths b and c), since there is no change of hybridisation on the carbon atom in paths b and c (Scheme 2). The one-electron transfer mechanism (path d) is also eliminated.⁵

On the basis of the concept of hard and soft acids and bases,¹⁴ $(RO)_3P$ and $>CO$ are a soft base and a hard acid, respectively.¹⁵ Since the bonding between soft base and hard acid is weak, the rearrangement of phosphorus from the carbon to the oxygen atom should easily occur [equation (8)].

The Hammett equation is applicable with phenanthrenequinones (Va–e). The obtained positive ρ value coincides with the suggested mechanism above. The order of reactivity of compounds (Va–e) agrees with the ease of reduction, which is estimated by the reduction potential¹² as a measure of the electrophilicity of the carbonyl group.

The Hammett plot was curved at the origin with benzils,⁴ but not with (Va–e). The configuration of the two carbonyl groups of 9,10-phenanthrenequinone is reported to be completely *cis*, but that of benzil is skew on the basis of the dipole moment.¹⁶ Therefore, the substituent effect transmitted through the carbonyl

¹¹ H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191.

¹² L. F. Fieser, *J. Amer. Chem. Soc.*, 1929, **51**, 3101.

¹³ (a) E. W. Garbisch, jun., *J. Amer. Chem. Soc.*, 1965, **87**, 505; (b) E. W. Garbisch, jun., S. M. Schilderout, D. B. Patterson, and C. M. Sprecker, *J. Amer. Chem. Soc.*, 1965, **87**, 2932.

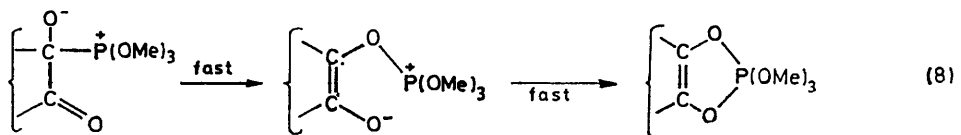
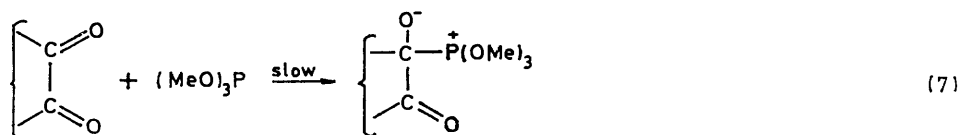
¹⁴ R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533.

¹⁵ (a) R. G. Pearson and J. Songstand, *J. Amer. Chem. Soc.*, 1967, **89**, 1827; (b) B. Saville, *Angew. Chem.*, 1967, **79**, 966.

¹⁶ C. C. Caldwell and R. J. W. Le Fèvre, *Nature*, 1939, **143**, 803.

group may be more effective with (V) than benzil because of more effective conjugation, and hence gives rise to the difference between the two plots, *i.e.*, mono-substituted benzil gave a curved Hammett plot, while (V) gives a straight line.

The twist angle (θ) of two carbonyl groups in alicyclic α -diketones increases with increasing size of ring ($0 \lesssim \theta \lesssim 180^\circ$),¹⁷ *i.e.*, the values of θ are reported to be 0–10, 0–60, 90–110, 100–140, and 100–180° for five-, six-, seven-, eight-, and 18-membered cyclic α -diketones, respectively, and 90–180° for open-chain aliphatic α -diketones. In view of the kinetic data for



SCHEME 2

The probable reaction mechanism of cyclic α -diketones with trimethyl phosphite (I). [9,10-Phenanthrenequinone (Va) and acenaphthenequinone (VI) do not require the equilibrium (6)].

cyclic and acyclic aliphatic α -diketones with $(\text{MeO})_3\text{P}$, the relative rate for (III), (IV) and $\text{Bu}^n\text{CO}\cdot\text{COBu}^n$ is almost the same. Therefore, the steric effect⁵ seems to have much more influence than the twist-angle effect. This is also evidence against the synchronous attack of phosphite on carbonyl oxygen atoms.

Provided that no ring strain is involved during the reaction, aromatic α -diketones such as benzil, (Va), and (VI) are more reactive toward (I) than aliphatic α -diketones. This may be explicable by Taft's σ^* value, *i.e.*, the polar substituent constant for aromatic groups has a positive value (electron-attracting), while that for alkyl groups has a negative value (electron-releasing), thus the electrophilicity of aromatic α -diketones becomes to be larger than that of aliphatic ones.

The reaction with (VI) is curious; at lower temperature (below 20 °C) the consumption of diketone is much faster than the appearance of 1 : 1 adduct on the basis of spectral changes at least. This is still under study.

¹⁷ (a) S. F. Mason, *Quart. Rev.*, 1961, **15**, 287; (b) T. R. Evans and P. A. Leermakers, *J. Amer. Chem. Soc.*, 1967, **89**, 4380; (c) N. J. Leonard and P. M. Mader, *ibid.*, 1950, **72**, 5388.

¹⁸ J. F. Thorpe and G. A. R. Kon, *Org. Synth.*, 1941, Coll. Vol. I, 192.

¹⁹ R. M. Acheson, *J. Chem. Soc.*, 1956, 4232.

²⁰ C. C. Hach, C. V. Banks, and H. Diehl, *Org. Synth.*, 1963, Coll. Vol. IV, 229.

²¹ N. L. Allinger, *Org. Synth.*, 1963, Coll. Vol. IV, 840.

²² A. T. Blomquist, R. E. Burge, jun., and A. C. Suesy, *J. Amer. Chem. Soc.*, 1952, **74**, 3636.

EXPERIMENTAL

Materials.—Cyclopentane-1,2-dione (II), prepared by decarboxylation of adipic acid¹⁸ followed by bromination and treatment with FeCl_3 ,¹⁹ had b.p. 60–62°/4 mm (lit.,¹⁹ b.p. 78–86°/8 mm), m.p. 54–55° (lit.,¹⁹ m.p. 55–56°), overall yield 4%. Cyclohexane-1,2-dione (III), prepared by oxidation of cyclohexanone with SeO_2 ,²⁰ had b.p. 81–82°/19 mm (lit.,²⁰ b.p. 75–79°/16 mm), m.p. 38° (lit.,¹⁰ m.p. 38°), yield 45% (based on SeO_2). Cyclo-decane-1,2-dione (IV) was prepared by intramolecular acyloin reductive condensation of diethyl sebacate²¹ followed by oxidation of sebacoïn with CrO_3 ²² and had b.p. 81–84°/4 mm (lit.,²² b.p. 104–105°/10 mm), overall

yield 9%. 9,10-Phenanthrenequinone (Va), prepared by CrO_3 oxidation of phenanthrene,²³ had m.p. 210° (lit.,²³ m.p. 208.5–210°), yield 51%. 2-Nitro-9,10-phenanthrenequinone (Vb), prepared by nitration of (Va) with excess of 63% nitric acid,²⁴ had m.p. 261–262° (from chlorobenzene) (lit.,²⁴ m.p. 264.8–265.3°), yield 23%. 3-Bromo-9,10-phenanthrenequinone (Vc), prepared by photobromination of (Va) in the presence of BPO [(Va) : Br_2 = 1 : 1.2],²⁵ had m.p. 254–255° (from acetic acid) (lit.,²⁵ m.p. 264–266°), yield 86%. 2-Amino-9,10-phenanthrenequinone (Vd), prepared by reduction of (Vb) with $\text{Sn}\cdot\text{HCl}$,²⁶ had m.p. 190–195° (decomp.) [lit.,²⁶ m.p. 213° (decomp.)], yield 60%. 3-Methoxy-9,10-phenanthrenequinone (Ve), prepared by the reaction of sodium methoxide with (Vc) in methanol, had m.p. 200–205° (lit.,²⁷ m.p. 209–209.5°), yield 30%. Acenaphthenequinone (VI), prepared by $\text{Na}_2\text{Cr}_2\text{O}_7$ oxidation of acenaphthene,²⁸ and purified by sublimation and then by recrystallisation from *o*-dichlorobenzene, had m.p. 261° (lit.,²⁸ m.p. 259–260°), yield 52%. Trimethyl phosphite (I) was purified by distillation with metallic

²³ R. Wendland and J. LaLonde, *Org. Synth.*, 1963, Coll. Vol. IV, 757.

²⁴ S. Kato, M. Maezawa, S. Hirano, and S. Ishigaki, *Yuki Gosei Kagaku Kyokai Shi*, 1957, **15**, 29.

²⁵ M. V. Bhatt, *Tetrahedron*, 1964, **20**, 803.

²⁶ S. Kato, H. Hashimoto, J. Hashimoto, B. Arikawa, and Y. Maeda, *Yuki Gosei Kagaku Kyokai Shi*, 1957, **15**, 32.

²⁷ C. S. Wood and F. B. Mallory, *J. Org. Chem.*, 1964, **29**, 3373.

²⁸ C. F. H. Allen and J. A. VanAllan, *Org. Synth.*, 1955, Coll. Vol. III, 1.

Na under N_2 , and had b.p. $58^\circ/116$ mm (lit.,²⁹ 111—112°). Trimethyl phosphite (I)–(Va) (1 : 1) adduct was prepared by the reaction of (Va) with excess of (I) at room temperature under N_2 without solvent or in dioxan for *ca.* 10 h. The other cyclic α -diketone (1 : 1) adducts were prepared by the same method.

Solvents were dried and purified before use.

Ultraviolet Spectra.—U.v. spectra of α -diketones and (I)–cyclic α -diketone 1 : 1 adducts were measured in dioxan or in n-hexane on a Hitachi double-beam 124 type spectrophotometer and/or a Hitachi EPU-2A type photoelectric spectrophotometer. The data used for kinetic studies were as follows: (II), $\lambda_{\max}^{\text{dioxan}}$ 247 nm ($\log \epsilon$ 3.55), $\lambda_{\text{infl.}}^{\text{dioxan}}$ 400 nm ($\log \epsilon$ 1.48); (III), $\lambda_{\max}^{\text{dioxan}}$ 264 nm ($\log \epsilon$ 3.64), $\lambda_{\text{infl.}}^{\text{dioxan}}$ 400 nm ($\log \epsilon$ -0.46); (IV), $\lambda_{\max}^{\text{dioxan}}$ 392 nm ($\log \epsilon$ 1.00); (Va), $\lambda_{\max}^{\text{n-hexane}}$ 243 ($\log \epsilon$ 4.41), 250 (4.45), and 313 nm (3.42), $\lambda_{\max}^{\text{dioxan}}$ 393 nm ($\log \epsilon$ 2.98); (Vb), $\lambda_{\max}^{\text{dioxan}}$ 378 nm ($\log \epsilon$ 3.52); (Vc), $\lambda_{\max}^{\text{dioxan}}$ 381 nm ($\log \epsilon$ 3.04); (Vd), $\lambda_{\max}^{\text{dioxan}}$ 390 nm ($\log \epsilon$ 3.11); (Ve), $\lambda_{\max}^{\text{dioxan}}$ 380 nm ($\log \epsilon$ 3.09); (VI), $\lambda_{\max}^{\text{n-hexane}}$ 298 ($\log \epsilon$ 3.83), 311 (ϵ 3.86), and 336 nm (3.77), $\lambda_{\max}^{\text{dioxan}}$ 473 nm ($\log \epsilon$ 1.24); (I)–(Va) 1 : 1 adduct, $\lambda_{\max}^{\text{n-hexane}}$ 306 ($\log \epsilon$ 4.04) and 319 nm (4.09) and (I)–(VI) 1 : 1 adduct, $\lambda_{\max}^{\text{n-hexane}}$ 317 ($\log \epsilon$ 3.77) and 337 nm (3.73). All adducts had no $\lambda_{\max}^{\text{vis}}$ in the visible region.

Products.—The structure of the products was confirmed by means of u.v. and i.r. spectra.

²⁹ Wm. W. Marshall, U.S.P. 2,848,474 (*Chem. Abs.*, 1959, **53**, 1144c).

Kinetic Procedure.—The kinetic experiments for the reaction of (I) with (II)–(VI) were carried out in a glass-stoppered flask or in a u.v. cell. The rate in dioxan was followed by estimating the remaining α -diketone or increasing product by means of u.v. spectrophotometry at appropriate intervals. A solution which had reached the keto–enol equilibrium was used with (II) and (III) alone. The other kinetic procedure was the same as reported before.³

Kinetic Analysis.—Assuming the constancy of enol content during the kinetic experiments, and assuming the completion of reaction at the time when the change of u.v. or visible absorption becomes unappreciable, we obtained the second-order rate constant (k) as shown in Tables 1 and 4. The k value for compounds (II) and (III) were corrected for the keto-content to give rate constants for keto-form alone (k') in Table 3. For the other α -diketones the k values were used for discussion.

Enol Content of Compounds (II) and (III).—The enol content (%) of (II) and (III) in dioxan was measured by means of Br_2 titration of enol^{10b} and/or n.m.r. spectra at 25 and 35 °C after attainment of the equilibrium (after more than one day). The n.m.r. spectra were as follows (δ /p.p.m. from dioxan): (II), 3.06 (s, enol OH), 2.84 (t, $-CH=C-OH$) and *ca.* -1.2 (m, other protons); (III), 3.54 (s, enol OH), 2.43 (t, $-CH=C-OH$), and -0.75 to -2.35 (m, other protons).

[1/977 Received, 14th June, 1971]