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KINETICS OF THE REACTION OF TRIMETHYL PHOSPHITE WITH SUBSTITUTED BENZILS[1]

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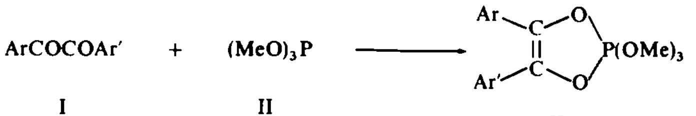
Abstract—The substituent effect on the rate of the reaction of trimethyl phosphite with substituted benzils has been studied in dioxan or acetonitrile by means of UV spectrophotometry. The rates are expressed as: $v = k\,[(MeO)_3P]\,[Ar\text{-}COCO\text{-}Ar']$. The Hammett plot in dioxan for Ar = Ar' gives a straight line with a ρ value of +2·75 (represented as ρ_X), while the plot for Ar ≠ Ar' and Ar = C_6H_5 gives a line bent at the origin, i.e., two ρ values of +1·86 ($\sigma > 0$, $\equiv \rho_Y$) and +1·24 ($\sigma < 0$, $\equiv \rho_Z$). In acetonitrile, the ρ_X and ρ_Y values are +2·22 ($\equiv \rho'_X$) and +1·63 ($\equiv \rho'_Y$), respectively. Hence $(\rho_X - \rho_Y)/\rho_Y = 0{\cdot}48$, $\rho_Z/\rho_Y = 0{\cdot}67$ and $(\rho'_X - \rho'_Y)/\rho'_Y = 0{\cdot}36$. The ratio of effects of two substituents which are separated differently from the reaction site changes with the solvent polarity. This seems to be caused by the change of configuration of benzils by solvents. A mechanism which involves a nucleophilic attack of P atom on the carbonyl C atom of benzil is postulated.

THE reaction of trialkyl phosphite with α-diketone was first reported in 1958[2] and it was not decided until recently whether the initial attack of P atom occurs on carbonyl C or O atom of α-diketone.[2–4] In our previous kinetic study,[5] we postulated, on the basis of its substituent effect in phosphite and its acid-base catalysis, a mechanism involving a nucleophilic attack of the P atom on the carbonyl C atom which is analogous to Litt's mechanism.[6]

The present paper deals with the kinetic study on the reaction of trimethyl phosphite with substituted benzils. The rate was measured UV spectrophotometrically. The effects of substituent and solvent on the rate and the transmission of polar effect will be discussed in connection with the configuration of benzil.



I II III (1)

RESULTS

The reaction of trimethyl phosphite (II) with substituted benzils (I) proceeds quantitatively at room temperature to yield 2,2,2-trimethoxy-4,5-diaryl-1,3,2-dioxaphosphole (III). The rate was measured by UV spectrophotometry of produced III or remaining benzil (I).

Rate law. The rate of the reaction was measured in dioxan or acetronitrile at various temperatures. The rate law fits Eq. 2 with all substituted benzils used.

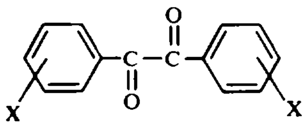
$$v = k\,[(MeO)_3P]\,[Ar\text{-}COCO\text{-}Ar'] \qquad (2)$$

Substituent effect of symmetrically disubstituted benzils in dioxan. The rates of the reaction of trimethyl phosphite with symmetrically disubstituted benzils (Ia) were measured in dioxan at 25·0°. The second-order rate constants (k) were listed in Table 1.

TABLE 1. RATE CONSTANTS FOR THE REACTION OF TRIMETHYL PHOSPHITE WITH SYMMETRICALLY DISUBSTITUTED BENZILES IN DIOXAN AT 25·0°

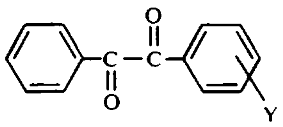
Benzil	Initial concn. (M) [I]	[II]	10^3k (M^{-1} sec^{-1})	Relative rate (k/k_0)	log (k/k_0)	σ^a
Unsubstituted	0·0500	0·0500	4·83	1·00	0·000	0·000
p,p'-Dinitro-	0·00100	0·00200	432	89·4	1·951	0·778
m,m'-Dinitro-	0·00500	0·00500	297	62·0	1·792	0·710
p,p'-Dichloro-	0·0200	0·0200	19·0	3·94	0·595	0·227
p,p'-Dimethyl-	0·0500	0·100	1·68	0·349	−0·458	−0·170
p,p'-Dimethoxy-	0·0200	1·00	0·387	0·0801	−1·096	−0·268

[a] H. H. Jaffé, *Chem. Rev.* **53**, 191 (1953)



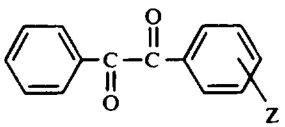
Ia

X: electron-withdrawing or -releasing group



Ib

Y: electron-withdrawing group



Ic

Z: electron-releasing group

TABLE 2. TEMPERATURE EFFECT AND ACTIVATION PARAMETERS FOR THE REACTION OF TRIMETHYL PHOSPHITE WITH SYMMETRICALLY DISUBSTITUTED BENZILS IN DIOXAN

Benzil	Temperature (°)	10^3k (M^{-1} sec^{-1})	E_a^a (kcal/mol)	$\Delta S^{\ddagger a}$ (e.u.)	$\ln A^a$ (M^{-1} sec^{-1})
Unsubstituted	20·0	3·76	9·90	−35·5	12·4
	25·0	4·83			
	30·0	6·64			
p,p'-Dinitro-	20·0	361	16·0	−41·1	10·3
	25·0	432			
	30·0	514			
m,m'-Dinitro-	20·0	224	10·3	−28·3	16·2
	25·0	299			
	30·0	390			
p,p'-Dichloro-	20·0	14·1	10·1	−34·5	13·1
	25·0	19·0			
	30·0	24·3			
p,p'-Dimethyl-	20·0	1·17	11·3	−31·5	14·5
	25·0	1·68			
	30·0	2·29			
p,p'-Dimethoxy-	20·0	0·272	13·6	−30·5	15·1
	25·0	0·387			
	30·0	0·567			

[a] Calculated by the least square method.

TABLE 3. RATE CONSTANTS FOR THE REACTION OF TRIMETHYL PHOSPHITE WITH MONOSUBSTITUTED BENZILS IN DIOXAN

Benzil	Initial concn. (M) [I]	[III]	10^3k (M^{-1} sec^{-1})	Relative rate (k/k_0)	log (k/k_0)	σ^a
Unsubstituted	0·0500	0·0500	4·83	1·00	0·000	0·000
p-Nitro-	0·0100	0·0100	134	27·7	1·442	0·778
m-Chloro-	0·0100	0·0300	18·1	3·75	0·575	0·373
p-Chloro-	0·0100	0·0400	11·3	2·33	0·368	0·227
p-Methoxy-	0·0100	0·250	1·82	0·377	−0·424	−0·268
p-Dimethylamino-	0·0100	1·00	0·862	0·178	−0·749	−0·600

[a] H. H. Jaffé, *Chem Rev.* **53**, 191 (1953).

TABLE 4. TEMPERATURE EFFECT AND ACTIVATION PARAMETERS FOR THE REACTION OF TRIMETHYL PHOSPHITE WITH MONOSUBSTITUTED BENZILS IN DIOXAN

Benzil	Temperature (°)	10^3k (M^{-1} sec^{-1})	$E_a{}^a$ (kcal/mole)	$\Delta S^{\ddagger a}$ (e.u.)	ln A^a (M^{-1} sec^{-1})
p-Nitro-	20·0	98·3	13·4	−27·9	16·4
	25·0	134			
	30·0	177			
m-Chloro-	20·0	12·9	10·8	−32·5	14·1
	25·0	18·1			
	30·0	23·1			
p-Chloro-	20·0	8·23	11·1	−31·7	14·5
	25·0	11·3			
	30·0	15·1			
p-Methoxy-	20·0	1·40	8·73	−43·8	8·41
	25·0	1·82			
	30·0	2·25			
p-Dimethylamino-	20·0	0·630	10·4	−44·4	8·11
	25·0	0·862			
	30·0	1·12			

[a] Calculated by the least square method.

TABLE 5. THE UV SPECTRA OF BENZIL (K-BAND) IN SOME SOLVENTS

Solvent	Dielectric constant	λ_{max} (mμ)	$10^{-4}\varepsilon_{max}$
n-Hexane	1·89	257	1·99
Dioxan	2·21	259	1·97
Methanol	32·6	259	2·13
Acetonitrile	37·5	260	2·16

The Hammett plot with σ gives a ρ value of $+2{\cdot}75$ ($\equiv \rho_X$) with a correlation coefficient (r) of 0·996 (Fig 1), whereas the plot with σ^+ and σ^{-7} the correlation coefficient is smaller (r = 0·989, and 0·960 respectively).

The rate measurements at 20·0°, 25·0° and 30·0° afford data of energies of activation (E_a), entropies of activation ($\Delta S^{\ddagger}$) and frequency factors (A) as shown in Table 2. It is of interest to note that the value of $\Delta S^{\ddagger}$ affects more than E_a on the rate of benzils

TABLE 6. RATE CONSTANTS FOR THE REACTION OF TRIMETHYL PHOSPHITE WITH BENZILS IN ACETONITRILE AT 25·0°

Benzil	10^2k (M^{-1} sec^{-1})	Relative rate (k/k_0)	log (k/k_0)	σ[a]
Unsubstituted	1·34	1·00	0·000	0·000
m,*m*′-Dinitro-	46·8	34·9	1·543	0·710
p,*p*′-Dichloro-	3·05	2·28	0·358	0·227
p-Nitro-	23·5	17·5	1·243	0·778
p-Chloro-	2·36	1·76	0·246	0·227

[a] H. H. Jaffé, *Chem. Rev.* **53**, 191 (1953).

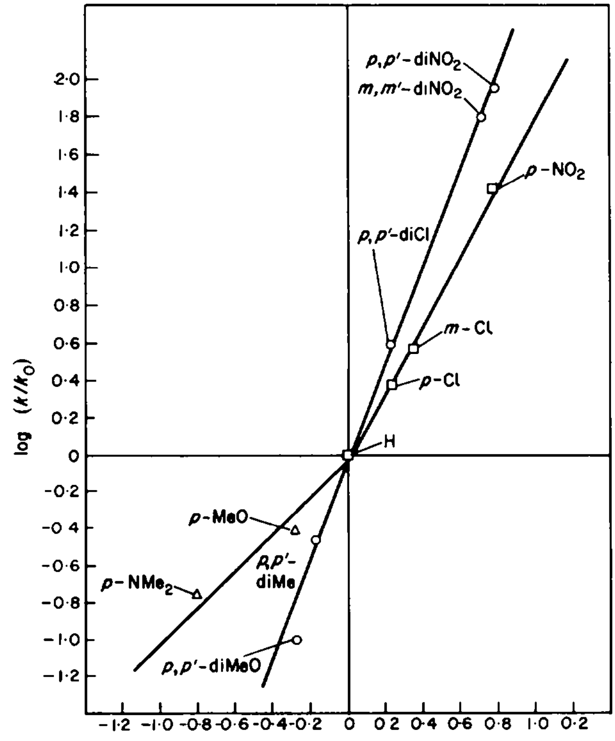


FIG 1. Hammett plot for the reaction of trimethyl phosphite with substituted benzils in dioxan at 25·0°.

with electron-withdrawing groups, whereas E_a is more important for those with electron-releasing groups.

Substituent effect of monosubstituted benzils in dioxan. The rates of trimethyl phosphite with monosubstituted benzils (Ib and Ic) were measured at 25·0°. The rate constants were summarised in Table 3.

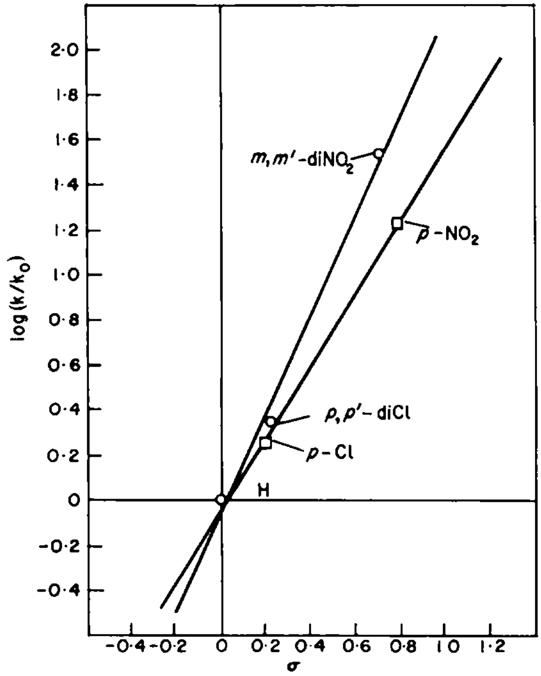


FIG 2. Hammett plot for the reaction of trimethyl phosphite with substituted benzils in acetonitrile at 25·0°.

TABLE 7. THE UV DATA OF BENZILS (I) AND 1,3,2-DIOXAPHOSPHOLES (III) IN *n*-HEXANE

Substituent on Ar	Substituent on Ar'	I		III	
		λ_{max}(mμ)	$10^{-4}\varepsilon_{max}$	λ_{max}(mμ)	$10^{-4}\varepsilon_{max}$
H	H	257	1·99	319	1·14
p-NO$_2$	p-NO$_2$	272	3·19	349	1·33
m-NO$_2$	m-NO$_2$	240	2·12	325	1·12
p-Cl	p-Cl	272	2·06	322	1·44
p-CH$_3$	p-CH$_3$	265	2·25	316	1·36
p-CH$_3$O	p-CH$_3$O	287	2·44	312	1·52
H	p-NO$_2$	269	2·40	382	1·16
H	m-Cl	258	2·05	322	1·12
H	p-Cl	269	2·04	322	1·20
p-CH$_3$O	H	286	1·54	316	1·20
p-N(CH$_3$)$_2$	H	341	2·09	330	1·63

The Hammett plot with σ gives a line bent at the origin. At $\sigma > 0$, the ρ value is $+1{\cdot}86$ ($\equiv \rho_Y$) with $r = 0{\cdot}996$, whereas at $\sigma < 0$, the value is $+1{\cdot}24$ ($\equiv \rho_Z$) with $r = 0{\cdot}991$ (Fig 1). The ratio of ($\rho_X - \rho_Y$) *vs* ρ_Y is 0·48, and that of ρ_Z *vs* ρ_Y is 0·67. The values of E_a, $\Delta S^\ddagger$ and A were also listed in Table 4.

Here also the value of $\Delta S^\ddagger$ affects more on the rate for substituted benzils with electron-withdrawing groups, whereas E_a is more important for those with electron-releasing groups.

Effect of solvent. The UV spectra of benzil was measured in some solvents. A slight change of the spectra was observed as shown in Table 5.

The rate data in acetonitrile at 25·0° are shown in Table 6. The Hammett plot with σ gives a ρ value of $+2{\cdot}22$ ($\equiv \rho'_X$) ($r = 0{\cdot}996$) for symmetrically disubstituted benzils, and a ρ value of $+1{\cdot}63$ ($\equiv \rho'_Y$) ($r = 0{\cdot}993$) for monosubstituted benzils (Fig 2). The ratio of ($\rho'_X - \rho'_Y$) *vs* ρ'_Y is 0·36.

DISCUSSION

In general, the mechanism for the reaction of trivalent phosphorus compounds with carbonyl compounds was obscure in that it was not decided whether the C or O atom of the carbonyl group is attacked by the P atom.[8] In our studies on the kinetics of the reaction of benzil with trialkyl phosphite, we suggested a mechanism involving a rate-determining nucleophilic attack of the P atom on a C atom.[5]

In the present study, a positive ρ value was observed for the reaction of substituted benzils, which supported the mechanism involving the nucleophilic attack of phosphite. The ρ value for benzils with electron-withdrawing group (Ib) ($\equiv \rho_Y$) is $+1{\cdot}86$. This value corresponds to the polar effect of substituent located in a benzene ring nearer from the reaction site (carbonyl C), since an electron-withdrawing group facilitates the nucleophilic attack of a P atom on the position nearer to the group. In general, the ρ value may depend on the distance between the attacked site and substituent on aromatic ring. In most cases, the absolute value of ρ may be more than unity for the reaction which has the site at α-position to the aromatic ring, while the value may be less than unity for the reaction in which the substituent and the site are separated farther, although the ρ value cannot be a measure of the α-carbon attack.[9] The ρ value observed in this reaction is a rather large positive value and it would suggest that the mechanism involves a rate-determining nucleophilic attack of a P atom on carbonyl C atom of benzil. The ρ value of the reaction of trimethyl phosphite with Ia ($\equiv \rho_X$) is $+2{\cdot}75$, and that of the reaction with Ic ($\equiv \rho_Z$) is $+1{\cdot}24$.

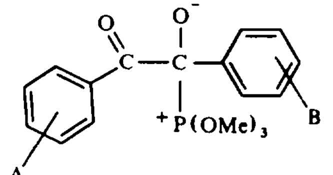
The Hammett plot for monosubstituted benzils (Ib and Ic) gives a line bent at the origin. This phenomenon implies that the attacked site (CO) is convertible depending on the substituent, i.e., the P atom tends to attack on the more electrophilic carbonyl C atom among two CO groups.

The net sensitivity to the transmitted effect of farther substituent X or Z at attacked CO may be expressed as ($\rho_X - \rho_Y$) or ρ_Z. If these values are divided by ρ_Y, the division indicates the extent of the sensitivity to the substituent X or Z relative to that of nearer substituent Y. The observed ratio of ($\rho_X - \rho_Y$) *vs* ρ_Y is 0·48, and that of ρ_Z *vs* ρ_Y is 0·67, which represent the decrease of relative sensitivity of polar effect by insertion of CO group between substituent and attacked CO group. It has been reported that the

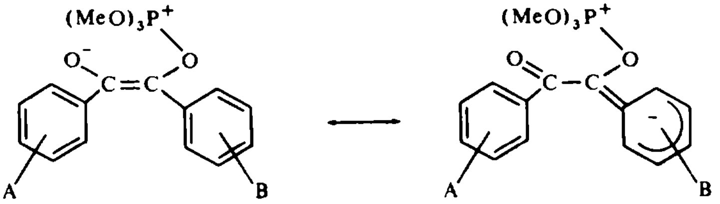
ρ value should decrease by insertion of any group between aryl group and attacked site,[9b, 10] e.g., the insertion of CH_2 group reduces it by a factor of 0·410 and even the insertion of conjugated —CH=CH— decreases it by a factor of 0·508 (observed) or 0·683 (calculated).[9b]

The crystal structure of benzil is known to be classified into two types by means of X-ray diffraction, UV spectra and dipole moment.[11–13] In one configuration the planes of two CO twists *ca* 90° each other around its CO—CO bond,[11, 12] and in the other the twist angle is smaller (68°24′ or so).[13] If the twist angle is *ca* 90°, the resonance of both benzoyl group is inhibited, so that the effect of a substituent located farther from the reaction site should be smaller (0·410). The ratio of $(\rho_X - \rho_Y)$ *vs* ρ_Y obtained in this reaction is close to that observed for the group —CH=CH— (0·508) in the dissociation of acids and the hydrolysis of esters, and the ratio of ρ_Z *vs* ρ_Y is nearly equal to that calculated by the molecular orbital method for —CH=CH— (0·683).[9b] This fact suggests that the CO—CO group of benzil is probably conjugated each other to some extent and the smaller twist angle of *ca* 70° is a more favourable one than *ca* 90° in view of the possibility of resonance.

In the reaction of trimethyl phosphite with symmetrically disubstituted benzils, the correlation coefficient (r) of the Hammett plot is 0·996 with σ, but 0·989 with σ^+ and 0·960 with σ^-. This indicates that σ is more adequate than σ^+ and σ^- for this nucleophilic attack, and that the delocalisation of positive charge on P atom or negative charge on carbonyl O atom due to resonance interaction with electron-releasing substituents or electron-withdrawing substituents contributes little to the stabilisation of its transition state.



IV



Va Vb

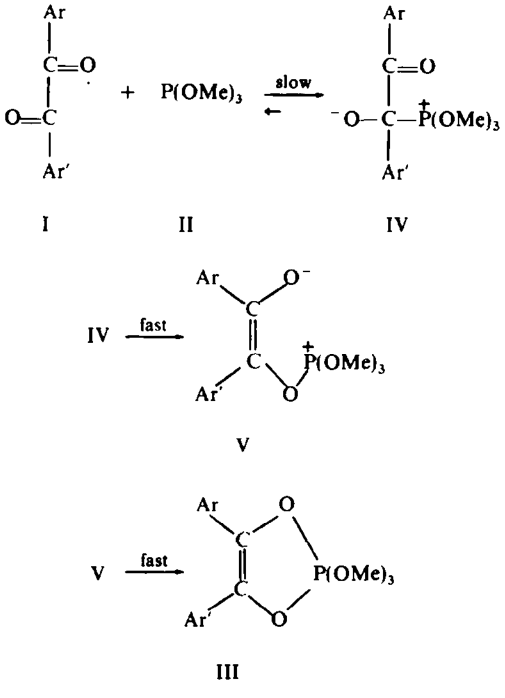
Assuming that the intermediate is V, in which B is a more powerful electron-withdrawing group than A, some canonical structures such as Va, Vb etc may be written, then the r value with σ^- would be larger than that with σ, but this is not the case. On the other hand, assuming the intermediate IV, canonical structures such as

Vb is impossible because of the insulation of charges from benzene system, so that the r value with σ should be larger than that with σ^+ or σ^- as is observed. Hence. the intermediate is probably IV, but not V.

The small activation energy (E_a) and large negative activation entropy ($\Delta S^\ddagger$) are to be noted.[5] $\Delta S^\ddagger$ depends on the nature of substituents and it ranges between $-27{\cdot}8$ and $-35{\cdot}5$ e.u. For the monosubstituted benzil, $\Delta S^\ddagger$ is influenced strongly by such a substituent as located at a position closer to the reaction site. This fact implies that the induced negative charge in the activated complex is localised on one CO group, but little delocalised to the other CO. The hybrid orbital of attacked C atom may be converted from sp^2 to sp^3. hence the delocalisation of charge to the farther benzoyl group is inhibited, i.e. the substituent effect of farther benzoyl group on $\Delta S^\ddagger$ is small. The increase of negative value of $\Delta S^\ddagger$ with decreasing electron-withdrawing power for symmetrically disubstituted benzils may be explained similarly.

For the reaction of trimethyl phosphite with benzils substituted by the electron-releasing group, E_a is more important than $\Delta S^\ddagger$ which differs little with the change of substituent, i.e., $\Delta S^\ddagger \cong -44$ e.u. for monosubstituted benzils and $\Delta S^\ddagger = -31 - -32$ e.u. for symmetrically disubstituted benzils. For mono- or disubstituted benzils, the E_a value increases with increasing electron-releasing power of group. In contrast with the little effect of farther substituent on $\Delta S^\ddagger$, the E_a value increases with increasing

SCHEME 1. The mechanism of the reaction of trimethyl phosphite with benzil.



(3)

(4)

(5)

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[a] Ar′ has an electron-withdrawing substituent more powerful than Ar.

electron-releasing power of the substituents on both rings. But E_a value tends to vary irregularly with increasing electron-withdrawing power of the substituent.

These results suggest a mechanism as shown in Scheme 1.

Here, the first step is a rate-determining nucleophilic attack of a P atom on a carbonyl C atom of benzil. The reverse step of Eq. 3 is very slow. The steps 4 and 5 are too fast to affect the rate constant.

The UV spectra of benzil vary with solvent polarity (Table 5). The value of λ_{max} of benzil shifts to longer wave length and the value of ε_{max} increases with increasing polarity of solvent. Probably, the configuration of benzil changes with the polarity of solvent, the twist angle around CO—CO changes and sometimes it may occur that the coplanarity of phenyl and carbonyl groups is recovered,[14] which means an increase of twist angle around CO—CO.[11b]

The observed ρ values in acetonitrile are $+2{\cdot}22$ ($\equiv \rho'_X$) for symmetrically disubstituted benzils and $+1{\cdot}63$ ($\equiv \rho'_Y$) for monosubstituted benzils ($\sigma > 0$). The ratio of $(\rho'_X - \rho'_Y)$ *vs* ρ'_Y is 0·36. This indicates that the twist angle around CO—CO bond increases in acetonitrile, which is supported by the UV spectra as mentioned above, but this is inconsistent with the result of Chaudhuri *et al.*, who reported that the molecular structure changes little by changing the phase of the molecule from solid to liquid.[13c]

The reaction of trimethyl phosphite with *m,m'*-dinitrobenzil in acetonitrile is somewhat different. The amount of product III (A = B = *m*-NO_2) reached rapidly to a maximum value, and then gradually decreased, although the consumption of starting material, *m,m'*-dinitrobenzil, was continuing. The further reaction of III is still under study.

EXPERIMENTAL

Materials. Benzil[15] was prepared from benzaldehyde,[16] and recrystallised from CCl_4 to give overall yield of 77%, m.p. 95·5–96° (lit.[15] 95°). (Found C, 79·75: H, 4.98. $C_{14}H_{10}O_2$ requires: C, 79·98; H, 4·80%). *m.m'*-Dinitrobenzil was prepared by nitration of benzil with HNO_3 (d = 1·5) at 0°. Recrystallisation from acetone, separation with liquid chromatography, silica gel from Mallinckrodt Chemical Works was used as a packing, (eluent: benzene) and then recrystallisation from CCl_4 gave overall yield of 35%. m.p. 128–129° (lit.[17] 132°). (Found: C, 58·61; H, 2.69; N, 9.34. $C_{14}H_8N_2O_6$ requires: C, 56·01; H, 2·69; N, 9·33%). *p,p'*-Dichlorobenzil was prepared by the benzoin condensation of *p*-chlorobenzaldehyde followed by oxidation with HNO_3. The crude material was recrystallised from CCl_4 in a overall yield of 27%, m.p. 195–196° (lit.[18] 195–196°). (Found: C, 60·87; H, 2·69. $C_{14}H_8Cl_2O_2$ requires: C, 60·24; H, 2·89%). *p,p'*-Dimethylbenzil was prepared by the benzoin condensation of *p*-methylbenzaldehyde followed by HNO_3 oxidation. The product, after being extracted with ether from 10% Na_2CO_3, recrystallised from EtOH, giving overall yield of 20%, m.p. 103° (lit.[19] 104–105°). (Found: C, 79·76; H, 5·54. $C_{16}H_{14}O_2$ requires: C, 80·64; H, 5·92%). *p,p'*-Dimethoxybenzil was prepared from *p*-methoxybenzaldehyde similarly as *p,p'*-dimethylbenzil; overall yield 25%, m.p. 133° (lit.[20] 133°). (Found: C, 71·25; H, 5·16. $C_{16}H_{14}O_4$ requires: C, 71·10; H, 5·22%). *p*-Nitrobenzil was prepared by nitration of benzoin with mixed acid at 0°, followed by HNO_3 oxidation. Recrystallisation from CCl_4. purification by liquid chromatography (eluent; light petroleum: EtOAc = 7:3) and then recrystallisation from CCl_4 gave overall yield of 22%, m.p. 142° (lit.[21] 142°). (Found: C, 67·12; H, 3·54; N, 5·55. $C_{14}H_9NO_4$ requires C, 65·88; H, 3·55; N, 5·49%). *m*-Chlorobenzil was prepared by the Grignard reaction of *m*-chlorobenzyl magnesium bromide with benzamide followed by oxidation with selenium dioxide in Ac_2O. After being extracted with ether, the product was purified by liquid chromatography (eluent: light petroleum: benzene = 4:1) and recrystallised from MeOH to give overall yield of 15%, m.p. 87–88° (lit.[22] 86°). *p*-Chlorobenzil was prepared similarly as *m*-chlorobenzil in a overall yield of 15%, m.p. 75° (lit.[22] 75·0°). (Found C, 69·18; H, 3·45. $C_{14}H_9ClO_2$ requires: C, 68·72; H, 3·71%). *p*-Methoxybenzil was prepared by the mixed benzoin condensation of benzaldehyde followed by air oxidation in the presence of pyridine-cupric sulphate complex. The purification by liquid chromatography and repeated recrystallisation from ligroin gave overall yield of 10%, m.p. 59° (lit.[23] 61–62°). (Found: C, 75·91; H, 4·57. $C_{15}H_{12}O_3$ requires: C, 74·99; H, 5·03%). *p*-Dimethylaminobenzil was prepared by the reaction of benzoin with *p*-dimethylaminobenzaldehyde[24] followed by oxidation with Fehling's soln. Recrystallisation from 60% aqueous EtOH gave overall yield of 60%, m.p. 116–116·5° (lit.[25] 116–117°). *p,p'*-Dinitrobenzil was prepared through 4,5-diphenylglyoxalone by the method of Chattaway *et al.*[26] Recrystallisation from AcOH gave overall yield of 8% (based on benzaldehyde), m.p. 213° (lit.[26] 213°). Trimethyl phosphite was purified by repeated distillation with metallic Na under N_2, b.p. 56°/101 mm (lit.[27]–112°). 2,2,2-Trimethoxy-4,5-diaryl-1,3,2-dioxaphospholes (III) were prepared by the reaction of substituted benzils with excess trimethyl phosphite under N_2 at 25·0° for 3-20 hr. The reaction proceeded quantitatively and there was no influence of the initial amount of trimethyl phosphite and longer reaction time on the yield. The further reaction of III was not observed in this system. The identification and estimation of III was done by UV spectroscopy without isolating it. The UV spectra were measured in *n*-hexane and listed in Table 7 together with those of substituted benzils. Solvents used were purified by ordinary methods.[28]

Kinetic procedure. The kinetic experiments for the reaction of trimethyl phosphite with substituted benzils were carried out in dioxan or acetonitrile. The rate was followed by measuring the produced III or remaining I by means of UV spectrophotometry. The kinetics for the reaction with *m,m'*-dinitrobenzil in acetonitrile was limited to the initial stage because of the further reaction of product. The other kinetic procedure was the same as the previous paper.[5]

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