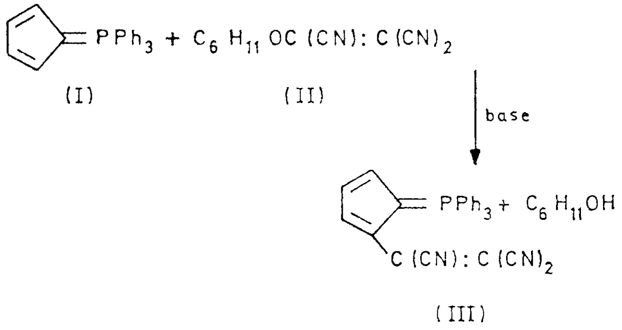
The Kinetics and Mechanism of the Reaction of Cyclopentadienylidenetriarylphosphoranes with Cyano-olefins. Part V.[1-4] Tricyanovinylation with Cyclohexyl 1,2,2-Tricyanovinyl Ether

By **M. P. Naan, A. P. Bell,** and **C. D. Hall,*** Department of Chemistry, King's College Strand, London WC2 2LS

The reaction of cyclohexyl tricyanovinyl ether (II) with cyclopentadienylidenetriphenylphosphorane (I) in benzene is catalysed by tertiary amine bases and affords triphenyl-2-(1,2,2-tricyanovinyl)cyclopentadienylidenephosphorane (III). Detailed kinetic studies of this reaction reveal a reversible nucleophilic addition of (I) to (II) as the initial step followed by an *E*1cB elimination of cyclohexanol *via* an ion-pair which involves hydrogen bonding between the conjugate acid of the base and the departing cyclohexyloxy-group.

A CONSIDERABLE volume of information now exists to support the concept of *E*1cB eliminations in aprotic media *via* ion-pair intermediates when the substrate contains an acidic hydrogen atom and a poor leaving group.[1,4-7] The use of tricyanovinyl ethers for the tricyanovinylation of a phosphorus ylide has already been reported[1] and offered an obvious choice for a mechanistic study to substantiate the previous findings. The substrate selected was cyclohexyl tricyanovinyl ether (II) since the base-catalysed reaction occurred at a convenient rate for a spectrophotometric study. Benzene was the solvent of choice and the products of reaction with (I) in the presence of a tertiary base were triphenyl-2-(1,2,2-tricyanovinyl)cyclopentadienylidenephosphorane (III)[1] and cyclohexanol. Despite the anticipated superior leaving group ability of cyanide ion *vs.* cyclohexyloxy-anion, no evidence was found for the formation of 2-(1-cyclohexyloxy-2,2-dicyanovinyl)cyclopentadienylidenetriphenylphosphorane. The reason for the latter observation is discussed below.



RESULTS

The rate of the base-catalysed reaction of (I) with (II) in benzene was followed by observing the appearance of product, $\lambda_{max.}$ 465 nm, spectrophotometrically. Plots of log $(A_\infty - A_t)$ *vs.* time (A = absorbance) were generally linear up to at least 85% reaction and pseudo-first-order rate coefficients (k_{obs}) were calculated from the slopes of these lines. With the weaker bases (*e.g.* pyridine) the absorbance ($\propto$[III]) *vs.* time (t) curves showed a definite inflection and were ' S shaped.' As a result, the logarithmic plots *vs.* t were initially curved and only became linear when $t > t_i$ the time at which the point of inflection occurred. With a 100 mole excess of pyridine (the weakest base used) over (II), t_i corresponded to *ca.* 50% product formation. This percentage reaction decreased as increasingly stronger bases were used (t_i occurred at <3% reaction with 20 mole excess of triethylamine) and also decreased as the concentration of each base was increased. All the kinetic results for this system relate to the portions of the [III] *vs.* t curves which gave linear logarithmic plots and the results are discussed on this basis.

Tables 1a and b show the reaction is first order in base (Et_3N) and in (Ia) and give the appropriate third-order rate constants. Table 2 shows the variation of rate ($k_3 = k_{obs}/[(I)]$ [base]) with base *strength* and suggests that the reaction is first order in base for all the bases used. The rates of reaction using tetradeuterio-(I) were also measured and the values of k_H/k_D for each base are shown in Table 3; in contrast to the results obtained with tetracyanoethylene,[1] all the isotope effects were positive and in the range 1·4—3·2. The activation parameters with triethylamine as the base catalyst were derived from the data in Table 4. Finally, the variation of rate with the structure of the ylide is revealed by the results of Table 5 which also establishes first-order behaviour in base and ylide for each ylide used.

TABLE 1

First-order (k_{obs}) and third-order ($k_3 = k_{obs}/[(I)][Et_3N]$) rate coefficients for the reaction of (I) with (II) in the presence of triethylamine in benzene

(a) $[(II)] = 3{\cdot}30 \times 10^{-5}$M; $[(I)] = 1{\cdot}65 \times 10^{-3}$M; temp. = 20·5 °C

$10^3[Et_3N]$/M	3·30	2·98	2·65	2·33	2·00	1·67	1·34	1·00	0·67
$10^4k_{obs}/s^{-1}$	22·2	19·5	16·5	15·0	12·9	10·7	8·33	6·46	4·18
$10^{-2}k_3$/ l^2 mol^{-2} s^{-1}	4·10	4·00	3·78	3·90	3·91	3·88	3·77	3·89	3·76

Average $k_3 = 3{\cdot}89 \pm 0{\cdot}12 \times 10^2$ l^2 mol^{-2} s^{-1}

(b) $[(II)] = 3{\cdot}28 \times 10^{-5}$M; $[Et_3N] = 1{\cdot}65 \times 10^{-3}$M; temp. = 30·0 °C

$10^4[(I)]$/M	16·4	13·1	9·84	6·56	3·28
$10^4k_{obs}/s^{-1}$	5·69	4·49	3·29	2·22	1·12
$10^{-2}k_3$/ l^2 mol^{-2} s^{-1}	2·11	2·08	2·03	2·06	2·08

Average $k_3 = 2{\cdot}07 \pm 0{\cdot}04 \times 10^2$ l^2 mol^{-2} s^{-1}

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[1] Part IV, C. W. Rigby, E. Lord, M. P. Naan, and C. D. Hall, *J. Chem. Soc.* (*B*), 1971, 1192.

[2] Part I, E. Lord, M. P. Naan, and C. D. Hall, *J. Chem. Soc.* (*B*), 1970, 1401.

[3] Part II, E. Lord, M. P. Naan, and C. D. Hall, *J. Chem. Soc.* (*B*), 1971, 213.

[4] Part III, E. Lord, M. P. Naan, and C. D. Hall, *J. Chem. Soc.* (*B*), 1971, 220.

[5] Z. Rappoport, *Adv. Phys. Org. Chem.*, 1969, **7**, 1.

[6] W. K. Kwok, W. G. Lee, and S. I. Miller, *J. Amer. Chem. Soc.*, 1969, **91**, 468.

[7] Z. Rappoport and E. Shohamy, *J. Chem. Soc.* (*B*), 1971, 2060.

TABLE 2

First-order (k_{obs}) and third-order ($k_3 = k_{obs}/[(I)]\ [base]$) rate coefficients for the reaction of (I) with (II) in the presence of various bases, in benzene

$[(II)] = 3.33 \times 10^{-5}$M; temp. = 25.0 °C

Base	pK_a[8]	10^3 [base]/M	10^4 [(I)]/M	$10^3 k_{obs}$/s^{-1}	k_3/l^2 mol^{-2} s^{-1}
Triethylamine	10·67	0·650	33·4	0·617	$2{\cdot}84 \times 10^2$
N-Methylpyrrolidine	10·46	3·98	3·35	15·1	$1{\cdot}13 \times 10^4$
		1·99	3·35	7·40	$1{\cdot}11 \times 10^4$
N-Methylpiperidine	10·19	8·25	6·67	9·35	$1{\cdot}70 \times 10^3$
		0·660	33·4	3·92	$1{\cdot}78 \times 10^3$
N-Methylmorpholine	7·38	0·667	33·4	1·15	$5{\cdot}09 \times 10^2$
		16·9	6·72	5·84	$5{\cdot}15 \times 10^2$
γ-Picoline	6·03	33·4	6·67	1·72	$7{\cdot}71 \times 10$ *
		8·39	66·7	4·24	$7{\cdot}59 \times 10$ *
Pyridine	5·21	16·4	66·7	3·38	$3{\cdot}09 \times 10$ *

* Runs carried out in 2 mm cells with $[(II)] = 1{\cdot}66 \times 10^{-4}$M.

TABLE 3

Deuterium isotope effects $[k_3(H)/k_3(D)]$ for the base-catalysed reaction of (I) and $^2H_4$-(I) with (II) in benzene at 25·0 °C

Base	10^5[(II)]/M	10^3 [base]/M	10^3[(I)]/M	10^3[$^2H_4$-(I)]/M	$10^3 k_{obs}$/s^{-1}	$k_3(H)/k_3(D)$ *
Triethylamine	3·35	3·25	1·67		1·22	3·2 ± 0·2
	3·35	3·25		1·67	0·377	
N-Methylpyrrolidine	3·33	1·64	0·333		5·86	2·5 ± 0·2
	3·33	1·64		0·333	2·33	
N-Methylpiperidine	3·35	3·28	1·67		9·32	2·2 ± 0·2
	3·35	3·28		1·67	4·28	
N-Methylmorpholine	3·35	1·67	1·67		1·57	1·4 ± 0·2
	3·35	1·67		1·67	1·16	
γ-Picoline	16·6	8·39	6·67		4·24	2·5 ± 0·2
	16·6	8·39		6·67	1·69	
Pyridine	16·6	16·4	6·67		3·38	2·5 ± 0·2
	16·6	16·4		6·67	1·36	

* Uncorrected; % deuteriation was 80 (± 5%) by n.m.r. spectroscopy.

DISCUSSION

Elemental analysis, m.p., mixed m.p., u.v., i.r., and ^{1}H n.m.r. spectra, showed (III) to be identical with the product of the reaction of (Ia) with tetracyanoethylene,[1] *i.e.* triphenyl-2-tricyanovinylcyclopentadienylidenephosphorane. No intermediate was isolated but the formation of (III) must occur through nucleophilic addition of (I) to (II) to form the equivalent of a σ complex (IVa or b) followed by elimination of cyclohexanol from either or both these intermediates. The tertiary protons in (IV) would be at least as acidic as those in 1-phenyl-1,2,2-tricyanoethylcyclopentadienylidenetriphenylphosphorane (V) [2] and alkoxy-groups are poor leaving groups. Thus by analogy with the elimination of HCN from (V),[4] the elimination of cyclohexanol from (IV) was expected, *a priori*, to proceed by an *E*1cB mechanism of the pre-equilibrium type.

TABLE 4

Variation of rate with temperature for the reaction of (I) with (II) in benzene in the presence of triethylamine

$[(II)] = 3{\cdot}33 \times 10^{-5}$M; $[(I)] = 1{\cdot}67 \times 10^{-3}$M;
$[Et_3N] = 1{\cdot}64 \times 10^{-3}$M

Temp. (°C)	39·2	34·8	29·8	24·5	20·5	15·9
$10^{-2}k_3$/l^2 mol^{-2} s^{-1}	1·81	1·92	2·30	2·62	3·49	4·00

$E_a = -$ 6·3 kcal mol^{-1}; $\Delta G^{\ddagger} =$ 14·1 kcal mol^{-1} and
$\Delta S^{\ddagger} = -$ 70 cal K^{-1} mol^{-1} at 25 °C.

TABLE 5

First-order (k_{obs}) and third-order (k_3) rate coefficients for the reactions of ylides (Ia—d) with (II) in the presence of triethylamine in benzene *

Ylide †	10^3[(I)]/M	10^3[Et$_3$N]/M	$10^4 k_{obs}$/s^{-1}	$10^{-2}k_3$/l^2 mol^{-2} s^{-1}
(Ia)	1·67	1·00	4·40	2·64
	1·67	3·33	14·57	2·62
	0·67	3·33	5·78	2·61
	Average $k_3 = 2{\cdot}62 \pm 0{\cdot}1 \times 10^2$ l^2 mol^{-2} s^{-1}			
(Ib)	1·33	1·67	22·37	10·08
	1·33	3·33	42·22	9·54
	1·67	3·33	55·75	10·02
	0·67	3·33	20·12	9·00
	Average $k_3 = 9{\cdot}66 \pm 0{\cdot}7 \times 10^2$ l^2 mol^{-2} s^{-1}			
(Ic)	1·67	1·67	12·67	4·54
	1·67	3·33	24·45	4·35
	0·67	3·33	9·72	4·38
	Average $k_3 = 4{\cdot}42 \pm 0{\cdot}2 \times 10^2$ l^2 mol^{-2} s^{-1}			
(Id)	3·33	1·67	5·85	1·05
	3·33	3·33	11·25	1·02
	1·67	3·33	5·50	0·99
	Average $k_3 = 1{\cdot}02 \pm 0{\cdot}1 \times 10^2$ l^2 mol^{-2} s^{-1}			

* Results are representative samples of at least seven runs for each ylide at different concentrations of ylide and base.
† Key (Ia) = $C_5H_4Ph_3$; (Ib) = $C_5H_4P(C_6H_4Me\text{-}p)_3$; (Ic) = $C_5H_4PPh_2C_6H_4Me\text{-}p$; (Id) = $C_5H_4PPh_2C_6H_4Cl\text{-}p$. A Hammett plot of log k_3 *vs.* σ gave a straight line with slope (ρ) − 1·3 and correlation coefficient, *r* 0·98.

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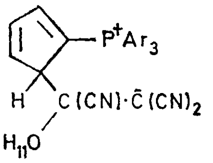
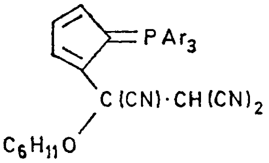
[8] D. D. Perrin, 'Dissociation Constants of Organic Bases in Aqueous Solution,' Butterworths, London, 1965.

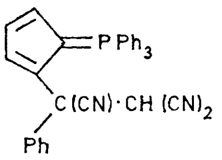
There are, however, distinct differences between the kinetic parameters obtained with (II) as substrate *vs.* those observed for tetracyanoethylene[1] and for the elimination of HCN from (V).[4] The former displays first-order dependence on (I) and positive deuterium isotope effects for each base (Tables **1**—**3** and **5**) whereas the latter two reactions are zero order in (I) and have k_H/k_D values of *ca.* 1 for all the bases used. Furthermore, the inflection observed in the product *vs.* time curves with the weaker bases and (II) is not apparent with either tetracyanoethylene or (V).



(IVa)



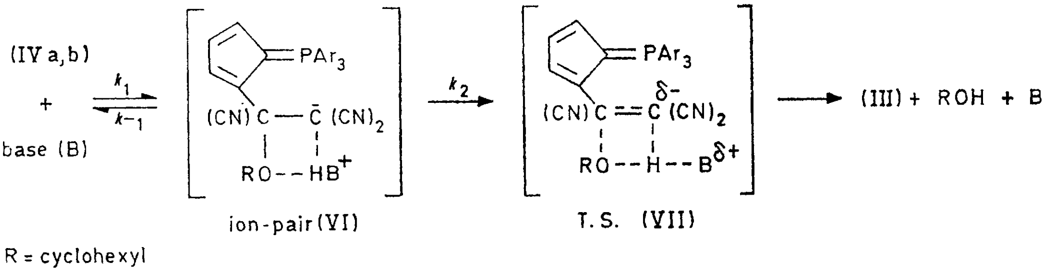
(IVb)



(V)

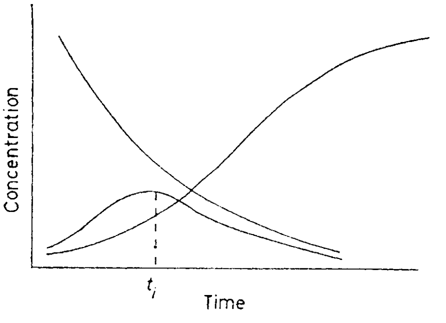
An explanation of the inflection in terms of a build-up of the intermediate σ complex (IVa or b) is unsatisfactory on three counts. First, from a knowledge of the nucleophilic addition reactions of (Ia—d) with other cyano-olefins,[2,3] the reaction to produce (IV) is expected to be much faster than the elimination step and secondly, the observed orders in base and the values of k_H/k_D are consistent with the elimination step [for (II)] being the slow step. Finally, if the reaction to (IVa or b) is comparable in rate to the elimination step, t_i would decrease, not increase, as weaker bases were used since the difference in rates of the two steps (addition *vs.* elimination) would become greater with decreasing base strength.

Thus in order to explain the variation of t_i with base strength it is necessary to propose the build-up of an intermediate *after* (IVa or b) is formed. Bearing in mind the *a priori* case for ion-pair intermediates, the proposed mechanism for the conversion of (IVa or b) to products is shown in the Scheme. The k_1 step is the removal of the tertiary proton of (IV) to give the ion-pair (VI) which is probably stabilised to some extent by hydrogen bonding with the cyclohexyloxy-group. With benzene as solvent, separation of the ion-pair is unlikely and the k_2 step proceeds *via* a transition state (VII) where there is more hydrogen bonding with the alkoxy-group, the proton of BH^+ ultimately being transferred to the alkoxy-group. Thus the leaving group is properly regarded as ROH and not RO^- and this explains why this group is lost in preference to CN^- when the reverse might have been expected.



SCHEME

When k_1 and $k_{-1} \gg k_2$ (strong base), a pre-equilibrium situation exists, the k_2 step is rate-limiting and no inflection is observed. As the base strength decreases however, k_1 decreases and k_{-1} and k_2 may be expected to increase. Although k_2 probably remains the slowest step, these changes cause k_1 and k_2 to become more nearly equal, a pre-equilibrium is no longer established immediately, and there will be some build-up of (VI) during the initial stages of product formation which results in an apparent ' induction period ' in the absorbance *vs.* t curve. Obviously, the ' induction period ' will decrease with increasing base strength and increasing base concentration.



Concentration *vs.* time curves for an A ⟶ C ⟶ D system

It is not possible to solve completely the differential rate equation for an $A + B \rightleftharpoons C \longrightarrow D$ system but with the use of analogue computers the concentration *vs.* t curves for A (B), C, and D for chosen $k_1 : k_2$ ratios may be drawn.[9] The general shape of these curves (Figure) is the same as that for an $A \longrightarrow C \longrightarrow D$

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[9] T. R. Crossley and M. A. Slifkin, *Progr. Reaction Kinetics*, 1970, **5**, 409.

system for which it may be shown that for $t > t_i$, d[D]/dt approximates to the value given by equation (1)[10]

$$\mathrm{d}[\mathrm{D}]/\mathrm{d}t = \mathrm{f}(k_1,k_2)[\mathrm{A}] \qquad (1)$$

Similarly for an $\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} \longrightarrow \mathrm{D}$ system, with an excess of B over A, for $t > t_i$, d[D]/dt is given by equation (2). Thus when $t > t_i$, a plot of log $(A_\infty - A_t)$

$$\mathrm{d}[\mathrm{D}]/\mathrm{d}t = \mathrm{f}(k_1,k_{-1},k_2)[\mathrm{A}][\mathrm{B}] \qquad (2)$$

vs. t will be linear. The complexity of $\mathrm{f}(k_1,k_{-1},k_2)$ depends on the relative magnitudes of k_1, k_{-1}, and k_2 but when k_1 and $k_{-1} \gg k_2$ $(1 \gg K_1[\mathrm{B}])$ equation (2) simplifies to (3).

$$\mathrm{d}[\mathrm{D}]/\mathrm{d}t = K_1k_2[\mathrm{A}][\mathrm{B}] \qquad (3)$$

For strong bases where k_1 and $k_{-1} \gg k_2$ this may be extended to the Scheme and when $t > t_i$, d[(III)]/dt is given by equation (4).

$$\mathrm{d}[(\mathrm{III})]/\mathrm{d}t = K_1k_2[(\mathrm{IV})]\ [\mathrm{base}] \qquad (4)$$

It is now necessary to consider the reaction to produce (IV) where there is an excess of (I) over (II). If the reaction is irreversible, d[(III)]/dt is given by equation (5); if there is an equilibrium to (IV) however (equilibrium constant, K_σ), the rate of formation of product is described by equation (6). Since the reactions are first

$$\mathrm{d}[(\mathrm{III})]/\mathrm{d}t = K_1k_2[(\mathrm{II})]\ [\mathrm{base}] \qquad (5)$$

$$\mathrm{d}[(\mathrm{III})]/\mathrm{d}t = K_\sigma K_1k_2[(\mathrm{II})]\ [\mathrm{base}]\ [(\mathrm{I})] \qquad (6)$$

order in ylide (Tables 1, 2, and 5) equation (6) must apply and hence it is proposed that the formation of (IV) is reversible. To provide a test of this hypothesis, a variety of substituted cyclopentadienylidene ylides (Ia—d) were prepared and the rates of their reactions with (II) were monitored. As required by reversible σ complex formation, the rates were enhanced by electron-donating groups, X (Table 5). A Hammett plot for the σ values of X gave ρ — 1·3, in fair agreement with the value of ρ (—1·8) for the addition of the same series of ylides to tricyanovinylbenzene.[2] It would appear, therefore, that the rate differences recorded in Table 5 reflect a change in K_σ in the differential rate equation (6). Reversible σ complex formation was also found for the reaction of *NN*-dialkylanilines with tricyanovinyl chloride in chloroform,[11] in contrast to the tricyanovinylation of aromatic amines[12] and (I)[1] by tetracyanoethylene.

The only conceivable alternative mechanism involves base catalysis by the ylides (Ia—d). This requires a rate expression of the form (7) which gives, from a plot of

$$\mathrm{d}[(\mathrm{III})]/\mathrm{d}t = k_{\mathrm{base}}[(\mathrm{II})]\ [\mathrm{base}] + k_{\mathrm{ylide}}[(\mathrm{II})]\ [\mathrm{ylide}] \qquad (7)$$

k_{obs} *vs.* [ylide] at constant [base] (Table 1b), $k_{\mathrm{ylide}} = 3{\cdot}45 \times 10^{-1}\ \mathrm{l\ mol^{-1}\ s^{-1}}$ and from a plot of k_{obs} *vs.* $[\mathrm{Et_3N}]$ at constant [ylide] (Table 1a), $k_{\mathrm{base}} = 6{\cdot}35 \times 10^{-1}$. The implication, that base catalysis by triethylamine has a rate of the same order of magnitude as base catalysis by (I) is certainly not valid. Although a spontaneous reaction (in the absence of tertiary amine) does occur, the rate is at least four times *slower* than the pyridine catalysed reaction and *ca.* 40 times slower than the triethylamine catalysed reaction. Furthermore, the spontaneous reaction is approximately second order in (I)[13] which is not consistent with equation (7), but fits equation (6). Plots of k_{obs} *vs.* $[\mathrm{Et_3N}]$ for each of the ylides in Table 5 reveal slight, positive intercepts on the ordinate which probably represent the ylide-catalysed reactions. The effect is most noticeable for (Ib) (presumably the most basic ylide) but even in this case, the intercept represents no more than a 5% contribution to the overall rate.

For the strong bases the proposed mechanism leads to equation (8) but for the weaker bases no exact equation

$$k_{\mathrm{obs}} = K_\sigma K_1k_2[(\mathrm{I})]\ [\mathrm{base}] \qquad (8)$$

may be derived without a much more detailed analysis of the [(III)] *vs.* t curves. Table 3 shows the reaction exhibits a normal primary isotope effect and for the strong bases this may be discussed in terms of the effects of deuteriation of (I) on K_σ, K_1, and k_2. Previous evidence suggests that the addition step (K_σ) would show a slight inverse deuterium isotope effect[1,2,14] and a slight inverse isotope effect is also observed in the elimination of HCN from (V)[4] and the reaction of tetracyanoethylene with (I).[1] Thus the normal isotope effect (Table 3) must arise from the k_2 step of the Scheme where there is a proton transfer from the conjugate acid of the base ($\mathrm{R_3N^+H}$) to the cyclohexyloxy-group of (VI). Such a step should show a normal deuterium isotope effect but its value cannot be compared with values obtained in other elimination reactions,[15] where proton transfer usually takes place from carbon to a base. In the case under study, the value will depend upon how much $\mathrm{B} \cdots \mathrm{H}$ bonding there is in the ion-pair (VI) as well as how much $\mathrm{O} \cdots \mathrm{H}$ bonding occurs in the transition state (VII). For the weaker bases there is still a normal isotope effect but here, where k_1 and k_2 are more nearly equal, there could be a contribution to the overall effect from the k_1 step. With the three strongest bases (*N*-methylpyrrolidine, *N*-methylpiperidine, and triethylamine) there is an almost negligible ' induction period ' and k_{obs} is given by equation (8). The isotope effects are of a similar magnitude but although the bases have very similar pK_a values in water, the k_3 values range over two orders of magnitude (Table 2). This points to the importance of something other than basicity in the slow step of the reaction, probably a steric factor arising from the involvement of the conjugate acid of the base in (VI).

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[10] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' Wiley, London and New York, 2nd edn., 1961.

[11] Z. Rappoport, P. Greenzaid, and A. Horowitz, *J. Chem. Soc.*, 1964, 1334.

[12] Z. Rappoport and A. Horowitz, *J. Chem. Soc.*, 1964, **1348**.

[13] M. P. Naan, Ph.D. Thesis, University of London, 1971.

[14] D. B. Denney and M. Tunkel, *Chem. and Ind.*, 1959, 1383.

[15] C. L. Dickinson, D. W. Wiley, and B. C. McKusick, *J. Amer. Chem. Soc.*, 1960, **82**, 6132.

The activation parameters (Table 4) are interesting since the $\Delta S^{\ddagger}$ value is more negative than those observed for the reaction of (I) with tetracyanoethylene[1] or the elimination of HCN from (V). This is consistent with the proposed mechanism which involves a high degree of orientation in the equilibrium to σ complex and another large degree of order in the transition state (VII) in which B^+H is oriented with respect to both the cyclohexyloxy-group and the developing carbanion.

The reaction has only been discussed in terms of the base reacting with (IV) to give the ion-pair (VI). The available evidence does not allow a distinction between mechanisms involving (IVa—b) or indeed a mechanism involving equilibrium of (IVa—b) with either or both reacting with base.

Finally, it is pertinent to note that the overall reaction to (III) is also subject to catalysis by carboxylic acids. Competing side reactions make a quantitative study of the acid-catalysed process very difficult but with proton transfer from B^+H to OR as the critical step in the base-catalysed mechanism, the observation of acid catalysis was predictable and affords ancillary evidence in favour of the mechanistic proposals.

EXPERIMENTAL

Materials.— Cyclopentadienylidenetriphenylphosphorane (Ia) and its tetradeuterio-analogue were prepared as described previously.[2] Derivatives of (Ia) with substituents in the phenyl rings (Ib—d) were prepared by the same method from the appropriate phosphine. Cyclohexyl tricyanovinyl ether (II) was prepared by the method of Dickinson *et al.*[15] and was recrystallised from cyclohexane (× 3) to give a crystalline solid, m.p. 67—68°. The tertiary amines (AnalaR where available) were dried (KOH) and distilled prior to use. Benzene (AnalaR) was purified and dried as described previously.[2]

Instruments and Kinetic Procedure.—These have been adequately described elsewhere.[1-4] For ylides (Ib—d) no attempt was made to isolate the reaction products; the u.v. spectra were entirely consistent with the product obtained from the parent ylide (Ia) and each showed $\lambda_{max.}$ 465 nm.

Triphenyl-2-tricyanovinylcyclopentadienylidenephosphorane (III).—A solution of (II) (0·1 g, 5×10^{-4} mol) in benzene (100 ml) was added with stirring to a solution of (Ia) (0·16 g, 5×10^{-4} mol) and triethylamine (2·6 g, $2\cdot6 \times 10^{-2}$ mol) in benzene (120 ml). After 1 h at room temperature when the absorbance at 465 nm had reached a maximum, benzene was evaporated off and the residue was chromatographed on neutral alumina (20 g; Woelm; grade III) using dichloromethane as eluant. The yellow fraction was collected and the solvent evaporated off to leave a glass-like froth. Anhydrous ether (25 ml) was added and the resultant solution was filtered quickly. The filtrate deposited orange-red crystals of (III) (0·2 g, 95%), with the m.p. 222—224°, mixed m.p. 222—224°; i.r., u.v., and ^1H and ^{31}P n.m.r. data agreeing precisely with those for authentic (III).[1]

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