

## Electro-organic Reactions. Part 20. Electrogenerated Bases, Ylide Formation, and Wittig Alkene Synthesis

Raj R. Mehta, Vera L. Pardini, and James H. P. Utley \*

Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS

Dicyano(fluoren-9-ylidene)methane (1a), dicyano(2,7-dibromofluoren-9-ylidene)methane (1b), and ethyl 2-cyano-2-fluoren-9-ylideneacetate (1c) may be cathodically reduced in *N,N*-dimethylformamide to give dianions which efficiently convert phosphonium salts into ylides. The potentials required are sufficiently modest to allow the electrogeneration of the bases in the presence of several phosphonium salts and of several aldehydes to give a convenient method of carrying out the Wittig alkene synthesis. This method has been explored for the synthesis of stilbene, 1,4-diphenylbutadiene, and vitamin A acetate. The basicity of the dianions varies according to the choice of electrolyte cation ( $\text{Bu}_4\text{N}^+$  or  $\text{Li}^+$ ). The cations also have a marked effect on the stereochemical course of the reaction and, in particular, mixtures of alkenes are obtained in which the *cis*-isomer predominates in the presence of lithium ion; in the vitamin A acetate synthesis, the 11-*cis*-isomer constitutes 76% of the product. The results are consistent with recent hypotheses concerning the mechanism of the Wittig reaction.

The dianion of azobenzene, generated cathodically in an aprotic solvent, has been used in the efficient preparation of stilbene from benzaldehyde and benzyltriphenylphosphonium salts.<sup>1</sup> Subsequently, alkyl-substituted azobenzenes have been used as precursors (probases) for cathodically generated bases which have been used to promote acetoacetic ester condensations<sup>2</sup> and the alkylation of nitriles.<sup>3</sup>

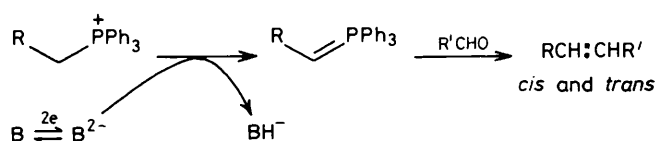
Saveant and Binh<sup>4</sup> have demonstrated that ylides are one of the products of the electroreduction of phosphonium salts under aprotic conditions, and it has further been shown<sup>5</sup> that ylides formed from benzyl-, allyl-, cinnamyl-, and polyenyl-phosphonium salts may conventionally be detected by cyclic voltammetry. In this paper we explore the practical possibilities for the synthetic route outlined in Scheme 1. Preliminary experiments have been described<sup>5</sup> which show that the ylide from benzyltriphenylphosphonium nitrate is formed in *N,N*-dimethylformamide (DMF) at the potential of an added probase and that it undergoes an *in situ* reaction with benzaldehyde to give stilbene in high yield.

Advantages which might be expected to accrue from the use of cathodically generated bases include the convenience of using stable and easily stored probases, control (through the current density) of the rate of generation of base, reproducibility of reaction conditions, and the possibility of influencing the stereochemical course of Wittig-type reactions by variation of the electrolyte cations. In principle it is possible also to devise, for one solvent system, a series of probases which would give rise to bases of a range of  $\text{p}K_a$  values.

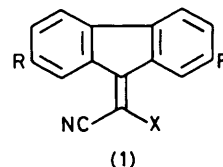
### Results and Discussion

**The Probases and Ylide Formation.**—The requirements for a useful probase are as follows: (i) reduction should take place at a low cathodic potential to give a relatively strong base; (ii) reduction should be reversible according to cyclic voltammetry so that the reactions of the base (radical-anion or dianion) may be monitored and ylide formation confirmed; (iii) the probase should be capable of being modified by substitution so that a range of reduction potentials and base strengths are available; and (iv) it should be possible ideally to regenerate the probase. This last aspect has not been examined in this study.

The probases examined here are derivatives of fluoren-9-ylidenemethane (1). In each case, cyclic voltammetric experiments showed that in DMF, at low cathodic potentials,



Scheme 1. *In situ* Wittig synthesis using electrogenerated base



- (1)  
 a; R = H, X = CN  
 b; R = Br, X = CN  
 c; R = H, X = CO<sub>2</sub>Et

radical-anions and dianions were formed reversibly. Reduction potentials and conditions for the voltammetric experiments are summarised in Table 1; a typical cyclic voltammogram is displayed in Figure 1. The reversible formation in DMF solution of the dianions is noteworthy; in acetonitrile solution the second peak is irreversible. In an earlier investigation<sup>6,7</sup> of the preparative electrochemistry of compounds of the type  $\text{Ph}(\text{R})\text{C}:\text{C}(\text{CN})_2$  it was found that unless the radical anion was hindered it underwent rapid dimerisation; if it were hindered, as for  $\text{R} = \text{Me}_3\text{C}$  and  $\text{Ph}$ , radical-anion formation was reversible but formation of the dianion was irreversible even in nominally dry DMF. In the presence of a proton donor, reduction at the first reduction potential gave the product of cathodic hydrogenation of the carbon-carbon double bond in high yield.<sup>7</sup> For the fluoren-9-ylidene compounds (1) the radical-anions and dianions are presumably less reactive because they are sterically inhibited from dimerisation and, through extensive charge delocalisation, of lower basicity than the derivatives used in the earlier study.

The dianions of the fluoren-9-ylidene compounds are nevertheless sufficiently basic to remove a proton from added phosphonium salts. This is demonstrated qualitatively, for one case, in Figure 2 which displays the effect upon the cyclic voltammogram of the reaction between base and the phosphonium salt. In Figure 2a, the protonation of the dianion is

**Table 1.** Cyclic voltammetric data <sup>a</sup> for probases

Probase	$E_p^{red}$ for (1) (V vs. Ag/AgI)	$E_p^{red}$ for (2) (V vs. Ag/AgI)
(1a)	-0.11	-0.88
(1b)	+0.13	-0.59
(1c)	-0.21	-0.75

<sup>a</sup> Hg-bead cathode; DMF-Bu<sub>4</sub>Ni (0.1M); 0.3 V s<sup>-1</sup>; in each case reversible or quasireversible behaviour was observed for both reduction steps.

**Table 2.** Cyclic voltammetric data <sup>a</sup> for phosphonium salts and corresponding ylides

Phosphonium salt	$-E_p^{red}$ for salt (V vs. Ag/AgI)	$-E_p^{red}$ for ylide (V vs. Ag/AgI)
PhCH <sub>2</sub> PPh <sub>3</sub> NO <sub>3</sub> <sup>-</sup>	1.39	2.02
PhCH:CHCH <sub>2</sub> PPh <sub>3</sub> NO <sub>3</sub> <sup>-</sup>	1.26	1.89
Me <sub>2</sub> C:CHCH <sub>2</sub> CH <sub>2</sub> (Me):CHCH:	1.45	2.02
CHC(Me):CHCH <sub>2</sub> PPh <sub>3</sub> Br <sup>-</sup>		
(2) Cl <sup>-</sup>	1.39	1.93

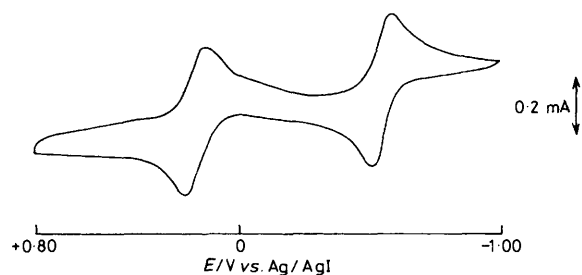
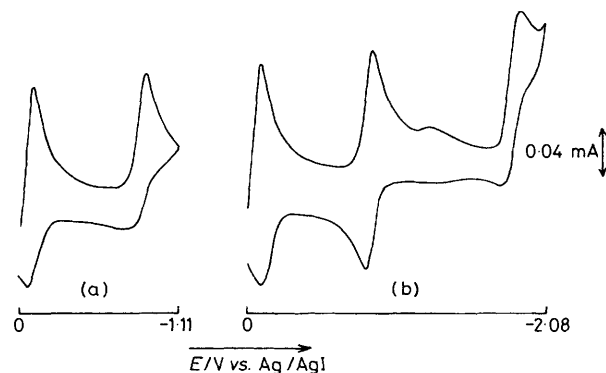
<sup>a</sup> Conditions as for Table 1.

the cause of irreversibility which accompanies addition of the phosphonium salt; the concomitant formation of ylide is shown in Figure 2b, in which the ylide is seen to reduce at  $E_p$  -1.93 V(vs. Ag/AgI).

The reduction potentials for several ylides have been measured either by direct reduction of the corresponding phosphonium salt<sup>5</sup> or by experiments involving electro-generated base such as that described in Figure 2. Peak potentials for reduction of the phosphonium salts and ylides are collected in Table 2. Not surprisingly, the more conjugated the ylide the more easily is it reduced.

A comparison of the reduction peak potentials listed in Tables 1 and 2 leads to the conclusion that the fluoren-9-ylidene probases might well be practically useful; the potential required for dianion formation is below that at which many phosphonium groups are reduced. It is also important, of course, that the carbonyl compounds intended for reaction with the ylides should not reduce at the potentials used for base generation and also that the olefinic products should similarly be electrochemically inert.

It is difficult to estimate the basicity of the fluoren-9-ylidene dianions although they will certainly be more basic than the fluorenyl monoanion ( $pK_a$  ca. 21). The potential for the second electron transfer should be related to the ease of accommodation of the second charge which in turn must be roughly related to the basicity. This criterion can only be used to make relative judgements and on this basis the order of basicity is (1a)  $\approx$  (1c) > (1e). The base-weakening effect of 2,7-dibromo-substitution would be expected from the inductive electron-withdrawing effect of the bromine atoms. These bases should be capable of converting all but simple alkyl-phosphonium salts into ylides. There is little data on the acidity of phosphonium salts; it has been estimated<sup>8</sup> that the  $pK_a$  of Ph<sub>3</sub>P<sup>+</sup>CH<sub>3</sub> is in the range 22–26 and it is known<sup>9</sup> that for PhCOCH<sub>2</sub>PPh<sub>3</sub> the  $pK_a$  is 6.2. Using this information and the  $pK_a$  values for PhCOCH<sub>3</sub> (19), PhCH<sub>3</sub> (ca. 35) and CH<sub>4</sub> (ca. 48), simple arithmetic based on the assumption of additivity of substituent effects suggests that for PhCH<sub>2</sub>PPh<sub>3</sub>

**Figure 1.** Cyclic voltammogram of probase (1b); see Table 1 for details**Figure 2.** Cyclic voltammograms of probase (1a) in the presence of an equivalent of PhCH:CHCH<sub>2</sub>PPh<sub>3</sub>NO<sub>3</sub><sup>-</sup> [vitreous carbon cathode; DMF-Bu<sub>4</sub>Ni (0.1M); 0.3 V s<sup>-1</sup>]: (a) sweep reversal at -1.11 V; (b) sweep reversal at -2.08 V

the  $pK_a$  is probably  $\leq 13$ . This is at least consistent with the experimental observation that ethoxide ion ( $pK_a$  16.0) is a convenient base for the formation of benzyl ylides.

The dicyano-substituted probases (1a) and (1b) are only sparingly soluble in DMF and, for reactions at high concentration, the more soluble probase (1c) is recommended.

**Wittig Reaction Induced by Electrogenerated Base.**—Preparative-scale electrolyses of mixtures of probase, phosphonium salt, and carbonyl compound were typically carried out in a divided cell, at a mercury-pool cathode, and under nitrogen. The cathode potential was controlled at or near the reduction-potential of the probase under study, and electrolysis was continued to 2 F mol<sup>-1</sup> with respect to the probase. It is convenient and instructive to consider the results according to the alkene produced.

**Stilbene.**—Table 3 summarises the conditions which were explored for the electro-synthesis of stilbene from benzaldehyde ( $E_p$  -1.34 V), benzyltriphenylphosphonium salts ( $E_p$  -1.39 V), and the fluoren-9-ylidene probases in the presence of various electrolytes. The products, *cis*- and *trans*-stilbene, are reduced, respectively, at  $E_p$ , -1.70 and -1.82 V.

The yields and isomer distribution depend on the base, electrolyte, and concentration of reactants; the yields of stilbene can be near quantitative. The best conditions for alkene formation involve the use of lithium perchlorate as electrolyte and, where the probase (1a) is used, this produces an excess (6 : 4) of *cis*-stilbene, the product of kinetic rather than thermodynamic control. In an attempt to relate these observations with the ion-pairing ability of lithium cation *vis à vis* tetrabutylammonium cation, magnesium perchlorate

Table 3. Preparation of stilbene using electrogenerated bases <sup>a</sup>

Probase	Cathode potential	Electrolyte cation <sup>b</sup>	% <i>cis</i>	% <i>trans</i>	Total yield (%) <sup>c</sup>
(1a)	-0.9	Bu <sub>4</sub> N <sup>+</sup>	39	61	46
(1a)	-0.9	Li <sup>+</sup>	59	41	74
(1b)	-0.6	Bu <sub>4</sub> N <sup>+</sup>	52	48	38
(1b)	-0.6	Li <sup>+</sup>	50	50	21
(1c)	-0.8	Bu <sub>4</sub> N <sup>+</sup>	50	50	68
(1c)	-0.8	Li <sup>+</sup>	46	54	94
(1c)	-0.7 <sup>d</sup>	Mg <sup>2+</sup>			Trace

<sup>a</sup> Divided cell, mercury-pool cathode, potential controlled *vs.* Ag/AgI reference, electrolysis in DMF-electrolyte (0.1M) to 2 F mol<sup>-1</sup>; probase concentration *ca.* 10<sup>-2</sup> mol dm<sup>-3</sup>, phosphonium salt (PhCH<sub>2</sub>PPH<sub>3</sub>NO<sub>3</sub><sup>-</sup>) at equivalent concentration. <sup>b</sup> As Bu<sub>4</sub>NBF<sub>4</sub>, LiClO<sub>4</sub> or Mg(ClO<sub>4</sub>)<sub>2</sub>. <sup>c</sup> By g.l.c. analysis with internal standard; related to amount of probase. <sup>d</sup> Electrolysis to 3 F mol<sup>-1</sup>.

was employed in the expectation that with its high charge : ionic radius ratio it would be more effective than lithium ion.

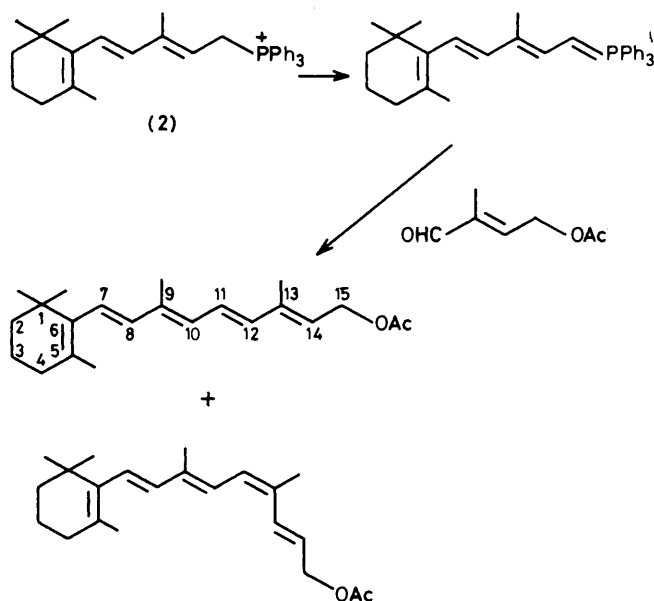
Cyclic voltammetry showed, however, that in the presence of anhydrous magnesium perchlorate formation of the dianion was irreversible. In a preparative scale experiment, in the presence of 0.1M-magnesium perchlorate, only traces of stilbene were produced even after the passage of 3 F mol<sup>-1</sup>. Explanations of this must include the possibilities that the effective bases are ion pairs between the dianions and electrolyte cations and that the ion pair with magnesium is so basic that it protonates indiscriminately from adventitious proton sources in the solvent. No extraordinary purification or drying procedures were used for the DMF. Alternatively it may be that the magnesium cation is so strongly solvated that it may scavenge adventitious water from the solvent and carry it to the electrode interface, thereby providing a hydrophilic environment which protonates the dianion. There is precedent for this effect in the protonation of azobenzene dianion in the presence of various cations.<sup>10</sup> Either explanation accounts for the irreversible formation of dianion in the presence of magnesium cation; the latter is the more attractive explanation, however, because the evidence from homogeneous systems is that tight ion-pairing, as envisaged in the first explanation, is base weakening by virtue of the high degree of charge dispersal involved.<sup>11</sup>

**1,4-Diphenylbutadiene.**—This system provides an interesting test of the selective use of probases and of the influence of added cations. For preparation of this alkene by *in situ* generation of ylides, combinations of cinnamaldehyde (*E<sub>p</sub>* -1.11 V) and benzyltriphenylphosphonium salts (*E<sub>p</sub>* -1.39 V) or cinnamyltriphenylphosphonium salts (*E<sub>p</sub>* -1.26 V) and benzaldehyde (*E<sub>p</sub>* -1.34 V) may be used. Generation of the base in the presence of cinnamaldehyde must, however, be at less than -1.11 V, a condition seemingly fulfilled by each of the probases. The results of preparative experiments are given in Table 4. The low reduction potential of cinnamaldehyde in practice allows only the use of the 2,7-dibromo-substituted probase (*E<sub>p</sub>* -0.59 V); when the unsubstituted probase (1a) was used, at -0.9 V, there was competing electrolysis of the aldehyde. With the dibromo-substituted probase (1b) the overall yield of 1,4-diphenylbutadiene is modest, possibly because this route involves the least basic dianion and the least acidic phosphonium salt. Ylide formation would therefore be expected to be less efficient than for the other combinations. For the combination involving the more acidic cinnamyl-phosphonium salt better results are obtained. The best conditions, giving a 67% yield of the diene, are with the

Table 4. Preparation of 1,4-diphenylbutadiene *via* electrogenerated base

Probase <sup>a</sup>	Electrolyte cation	<i>cis,trans</i> : <i>trans,trans</i>	Yield (%)
(1a) <sup>b</sup>	Bu <sub>4</sub> N <sup>+</sup>	7 : 93	7
(1a) <sup>b</sup>	Li <sup>+</sup>	52 : 48	54
(1b) <sup>b</sup>	Bu <sub>4</sub> N <sup>+</sup>	4 : 96	67
(1b) <sup>b</sup>	Li <sup>+</sup>	15 : 85	35
(1b) <sup>c</sup>	Bu <sub>4</sub> N <sup>+</sup>	2 : 98	34
(1b) <sup>c</sup>	Li <sup>+</sup>	7 : 93	26

<sup>a</sup> Cathode potentials as in Table 3. <sup>b</sup> Other reactants, benzaldehyde and cinnamyltriphenylphosphonium nitrate. <sup>c</sup> Other reactants, cinnamaldehyde and benzyltriphenylphosphonium nitrate.



Scheme 2. Wittig synthesis of vitamin A acetate

dibromo-substituted probase (1b) in the presence of tetrabutylammonium cation. A change to lithium cation is associated with a drop in yield, although lithium cation in combination with the stronger probase (1a) gives a respectable yield (54%). These observations are consistent with the concept of selecting the optimum base strength; if, as expected,<sup>10,11</sup> the presence of lithium ion is base weakening, then it would seem that the intrinsically more weakly basic dianion (1b) in the presence of tetrabutylammonium cation is of similar base strength to a combination of an intrinsically more basic dianion (1a) in the presence of lithium ion. The most basic conditions [(1a) plus tetrabutylammonium cation] give the lowest yield of diene (7%).

Apart from influencing yields the cation has a marked effect on stereochemistry, the *trans,trans* : *cis,trans* ratio varying from 96 : 4 to 48 : 52. As with stilbene formation, it is the presence of lithium which is associated with preferential formation of the product of kinetic control.

**Vitamin A Acetate.**—The preparation of vitamin A acetate, by the Wittig route according to Scheme 2, is well established<sup>12</sup> and this example provides a good test of the possibilities for production of the product of kinetic control (the 11-*cis*-isomer) under conditions which minimise the facile isomerisation to the all *trans*-isomer. The component aldehyde (*E<sub>p</sub>* -1.36 V) and phosphonium salt (2) (*E<sub>p</sub>* -1.39 V) are less

**Table 5.** Preparation of vitamin A acetate *via* electrogenerated base

Probase <sup>a</sup>	Electrolyte cation	11- <i>cis</i> : all- <i>trans</i> <sup>b</sup>	Yield (%) <sup>c</sup>
(1c)	Li <sup>+</sup>	76 : 24	40
(1a)	Li <sup>+</sup>	64 : 36	30
(1a)	Bu <sub>4</sub> N <sup>+</sup>		0

<sup>a</sup> Cathode potentials as in Table 3. <sup>b</sup> Analysis of isolated product by h.p.l.c. <sup>c</sup> Isolated by preparative t.l.c.

**Table 6.** Stereoselectivity in the Wittig reaction <sup>a</sup>

Alkene	Solvent/base	<i>cis</i> : <i>trans</i>	Yield (%)
PhCH:CHPh	EtOH/NaOEt	45 : 55	76
PhCH:CHPh	DMF/NaOEt	53 : 47	
PhCH:CHPh	H <sub>2</sub> O/CH <sub>2</sub> Cl <sub>2</sub> /NaOH	50 : 50	88
PhCH:CHPh	Et <sub>2</sub> O/PhLi	30 : 70	82
PhCH:CHCH:CHPh	H <sub>2</sub> O/CH <sub>2</sub> Cl <sub>2</sub> /NaOH	36 : 64 <sup>b</sup>	87

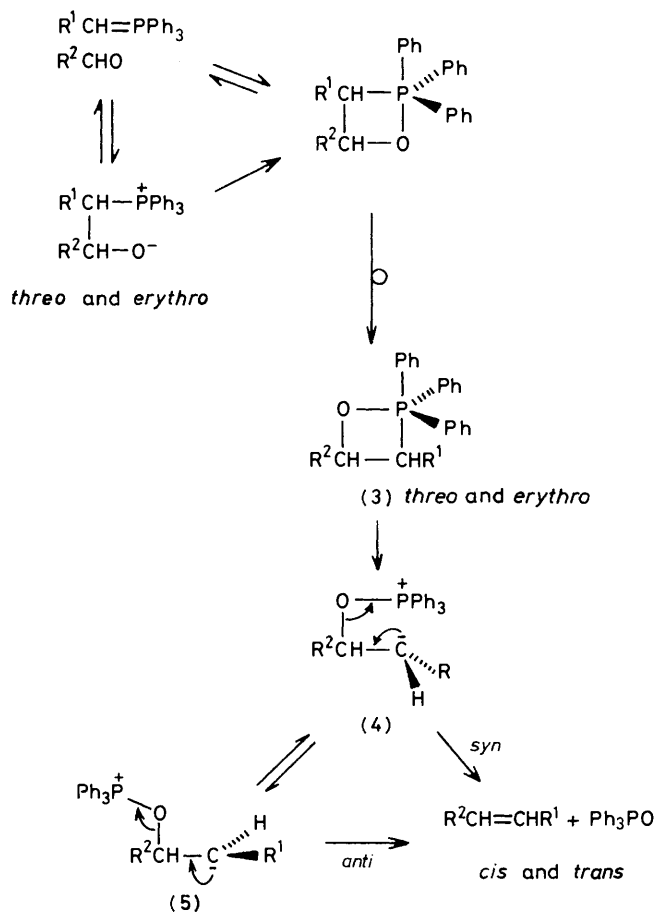
<sup>a</sup> Culled from ref. 13. <sup>b</sup> Refers to *cis,trans* and *trans,trans*.

easily reduced than any of the probases, and vitamin A acetate itself has  $E_p - 1.35$  V.

The overall yields in this reaction are modest (Table 5); indeed, under the most basic conditions [probase (1a) plus tetrabutyl ammonium ion], no vitamin A acetate was formed. The stereochemical results are, however, highly encouraging and under the best conditions the product contains 76% of the 11-*cis*-isomer.

**Stereoselectivity and the Electrolyte Cation.**—Factors known to influence the stereochemical course of Wittig reactions include the reactivity of the ylide and the reaction conditions, with the polarity of the solvent and the nature of cations present being particularly important. The relative importance of these factors have been well summarised <sup>13</sup> in terms of classification of the ylide as stabilised, non-stabilised, or of 'moderate reactivity'. The ylides which feature in this paper fall into the last category. A further relevant generalisation is that 'stabilised' ylides tend to give predominantly the *trans*-alkenes, with an increase in the proportions of the *cis*-isomer when protic solvents are used or when lithium salts are added. Reactive ylides give rise to *cis*-rich mixtures and, in polar aprotic solvents, the addition of lithium salts has little effect. Ylides of moderate reactivity give rise to mixtures of *cis*- and *trans*-isomers and the most powerful influence on the *cis* : *trans* ratio is believed to be the nature of substituents in the ylide. Results for benzyl and cinnamyl ylides, useful for comparison with the results from this investigation, are collected in Table 6. It is worth noting at this point that for DMF solutions, sodium alkoxides are commonly used as the base; alkyl-lithium compounds cannot be used because they react <sup>14</sup> with the solvent. Consequently it has previously been difficult to assess the effect of lithium cation on the stereochemistry of Wittig reactions in this solvent because other cations are also usually present. With electrogenerated bases it is possible to compare the results of experiments in which the main variable is the electrolyte cation.

The detailed mechanism of the Wittig reaction is not known with certainty; there is substantial agreement that oxaphosphetans are key intermediates, but these may arise either by nucleophilic addition of the ylide to the carbonyl compound or by ( $\pi 2a + \pi 2s$ ) cycloaddition of ylide with carbonyl compound.<sup>15</sup> It is further supposed<sup>16</sup> that pseudorotation must occur to place the breaking carbon-phosphorus bond of the phosphetane in an apical position; there is some doubt

**Scheme 3.** A summary scheme of mechanisms for the Wittig reaction

about whether oxaphosphetane formation is reversible.<sup>17</sup> The mechanistic possibilities are summarised in Scheme 3 which will form the basis for discussion of results presented here.

The overall stereochemical consequences of such a scheme are bound to be a complicated function of the relative rates of the separate steps, and the reversibility of formation of intermediates which determines the *erythro* : *threo* ratios in the oxaphosphetane and carbanion intermediates. It is not possible to draw firm conclusions from the literature concerning the likely stereochemistry of the oxaphosphetanes; although they are believed<sup>15</sup> to be formed preferentially in the less stable configuration (*erythro*) the more stable (*threo*) form would predominate if their formation were reversible.<sup>17</sup> For the mechanism given in Scheme 3, yet another factor affecting the stereochemical outcome of the reaction may be identified. Rotation about the carbon-carbon bond in the carbanion (4) is likely<sup>18</sup> to be faster than inversion at the carbanion centre. The operation of this factor will be most important when the lifetime of carbanion (4) is prolonged and our rationalisation of the results of the present investigation rest on this.

We propose that the lifetime of the carbanion (4) is: (a) greater for a *trans* configuration of  $R^1$  and  $R^2$  than for a *cis* configuration because there will be less steric interference with conjugative delocalisation of the negative charge;<sup>19</sup> and (b) greater when the negative charge is dispersed by association with cations. This latter effect will clearly be more important for lithium cations *vis à vis* tetra-alkylammonium ions. These considerations lead to the prediction that the interconversion of carbanions is likely to be in the direction *trans* to *cis* because the initially *cisoid* carbanions will react

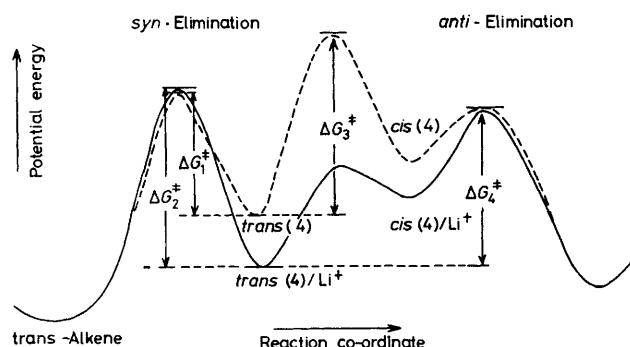


Figure 3. Potential energy–reaction co-ordinate diagram for elimination from carbanions (4) with and without lithium cation present

via *syn*-elimination to give *cis*-alkenes before rotation occurs; where *syn*-elimination is slower [*i.e.* carbanion (4) is stabilised] the preferred *anti*-elimination can take place from carbanion (5) made accessible by bond rotation. This will result in an overall increase in the proportion of *cis*-alkenes because it is mainly the initially *transoid* carbanions (4) which will be stabilised and in which rotation of the carbon–carbon bond will compete with *syn*-elimination.

The major feature of the results given in Tables 3–5 which gives support to the above hypothesis is that the addition of lithium cation causes an increase in the proportion of *cis*-alkene in those cases where conjugative stabilisation of the negative charge in carbanion (4) is especially important, *i.e.* for the reaction involving the cinnamyl and the C<sub>15</sub> (2) ylides to give, respectively, 1,4-diphenylbutadiene and vitamin A acetate. In contrast the proportion of *cis,trans*-1,4-diphenylbutadiene formed by reaction between cinnamaldehyde and the benzyl ylide is not significantly altered in the presence of lithium cation. In this case, R<sup>1</sup> is phenyl which does not stabilise the negative charge in carbanion (4) as effectively as when R<sup>1</sup> is PhCH:CH. For stilbene formation the stereochemical result in the absence of lithium salt is similar to that for use of sodium methoxide in DMF (Table 6). According to the hypothesis set out above the oxaphosphetan (3) is a *ca.* 1 : 1 mixture of *threo* and *erythro* isomers and, in the absence of lithium cation, *syn*-elimination takes place via the carbanion (4) to give a mixture of *cis*- and *trans*-stilbene which reflects the isomeric composition of the oxaphosphetan (3). The carbanions (4) would initially be formed with a similar isomeric ratio, but delocalisation of the charge would be more efficient in the *transoid* isomer; a consequence of this is that the benzylic carbon would have more sp<sup>2</sup> character which, in turn, would allow complexation of that isomer with lithium cation approaching from the side opposite to the phosphorus atom. Such preferential stabilisation of the *transoid* carbanion would permit rotation and *anti*-elimination to the *cis*-alkene. An attempt to portray these concepts qualitatively is made in terms of the potential energy–reaction co-ordinate diagram in Figure 3. It will be seen that a simplifying assumption built into this description is that the transition states for *syn*- and *anti*-elimination are similar whether or not the initial carbanion is stabilised by complexation with metal cation. Furthermore, the lowering of the energy of activation for formation of the *cis*-alkene relative to that for formation of the *trans*-alkene depends on the substantial lowering of the barrier to rotation of the carbon–carbon bond in the anion. This does not seem an unreasonable hypothesis; dispersal of charge onto a metal cation would clearly diminish greatly

the attractive coulombic interaction between the positive phosphorus atom and the carbanionic centre in (4).

## Experimental

The electrochemical apparatus, cells, and the methods used for the preparation of phosphonium salts and the purification of solvents have been described in earlier papers in this series.<sup>5,20</sup> Potentials for cyclic voltammetric and preparative experiments were measured against an Ag/AgI<sub>(s)</sub> electrode. Ether refers to diethyl ether.

**Preparation of the Probases (1).**—The dicyano-substituted probases (1a) and (1b) were prepared from the appropriate fluorenone and malononitrile by standard literature methods.<sup>21</sup> The 2,7-dibromofluorenone required for the preparation of (1b) was prepared by bromination of fluorenone using *N*-bromosuccinimide.<sup>22</sup> The probase (1c) was obtained from the reaction between ethylcyanoacetate and fluorenone using the procedure of Cragoe *et al.*<sup>23</sup>

**Preparative Electrolyses.**—The procedure used for the preparation of stilbene and 1,4-diphenylbutadiene via ylide formation by electrogenerated base has been described.<sup>5</sup> G.l.c. analysis (Hewlett-Packard 5830A, column 5% OV-17) was carried out on the crude product mixtures to which a known weight of biphenyl had been added as an internal standard; the detector response factor for each of the products was determined with respect to biphenyl.

For the preparation of *Vitamin A acetate* a different work-up and analytical procedure was used. To the catholyte, immediately after work-up, an equivalent volume of glacial acetic acid was added and the solution changed colour from red to yellow. It was then poured into water and shaken with ether. The ether extract was washed (H<sub>2</sub>O) and dried (MgSO<sub>4</sub>). The crude product was partly separated by t.l.c. [silica Me<sub>2</sub>CO–light petroleum (b.p. 40–60 °C) (1 : 4)]. The band of second highest R<sub>F</sub> value was shown by u.v. spectroscopy to be a mixture of isomers of vitamin A acetate; consequently that mixture was isolated from the plate and its yield recorded. The mixture was then analysed quantitatively by h.p.l.c. [microporosil column, (light petroleum–ether)–diisopropyl ether (2.5% v/v)] with the detector set at 320 nm. These conditions had been established<sup>24</sup> for providing efficient separation of the various isomers in the order of increasing retention time: hydrocarbon, 11-*cis*, di-*cis*, 9-*cis*- and all-*trans*. The major products were the 11-*cis* and all-*trans* isomers together with small amounts of the hydrocarbon and 9-*cis*-isomer. For vitamin A acetate the ratio of extinction coefficients<sup>25</sup> at 320 nm for all-*trans* : 11-*cis* is 1.6 and this was used in the calculation of the relative yields.

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