Electro-organic Reactions. Part 17.† The Competition between Cleavage and Ylid Formation in the Cathodic Reduction of Benzyl-, Allyl-, Cinnamyl-, and Polyenyl-phosphonium Salts

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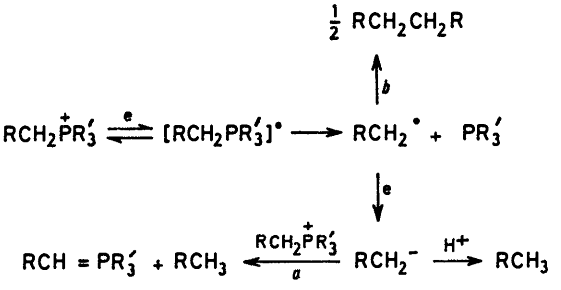
In aprotic solvents benzyl-, allyl-, cinnamyl-, and polyenyl-phosphonium salts undergo overall one-electron reduction with the formation of up to 50% of the corresponding ylid. In cyclic voltammetric experiments peaks for the reduction of ylids have been clearly identified and the mechanism of formation is found to involve initial two-electron cleavage to a benzylic or allylic carbanion which abstracts proton from a second molecule of phosphonium salt. Benzyltriphenylphosphonium nitrate, in *NN*-dimethylformamide, is converted into the ylid by the dianion generated cathodically at −1.50 V *versus* saturated calomel electrode) from dicyano(fluoren-9-ylidene)methane and *in situ* reaction with benzaldehyde gives stilbene in 74% yield. Competitive electrolyses in acidic solution of *p*-methoxycarbonylbenzyltriphenylphosphonium and triethylammonium salts, and *p*-methoxycarbonylbenzyl naphthalene-1-carboxylate give for these two-electron cleavages a qualitative order of leaving group ability of $Et_3N > Ph_3P \gg RCO_2^-$.

In a series of papers[1-3] on the mechanism of cathodic reduction of phosphonium salts in aprotic solvents Saveant and Binh produced convincing evidence that in many cases the starting material is sufficiently acidic to react with basic intermediates formed during reduction. In particular the second reduction peak in voltammetric experiments has been ascribed to reduction of ylids in those cases where the phosphonium salt contains α-hydrogen atoms. For two examples[1] in which the ylid is especially well stabilised, *i.e.* the phenacyl and diphenylmethyl derivatives, direct evidence has been obtained by voltammetric experiments on the preformed ylid or by isolation of the ylid following electrolysis. Route *a* of Scheme 1 has therefore been established under voltammetric conditions.

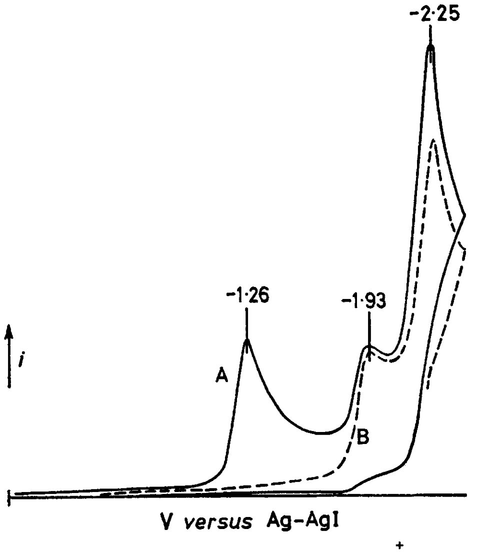


SCHEME 1

On the longer time scale of preparative electrolysis, however, phosphonium salts may cleave to radical intermediates[4] which may combine or be further reduced (Scheme 1, route *b*). We report herein on experiments which (a) confirm the formation in reduction of ylids from benzyl-, allyl-, cinnamyl-, and polyenyl-phosphonium salts and (b) establishes conditions in which, even on the voltammetric time scale, cleavage is predominant. Under these latter conditions it has proved possible to employ competitive electrolysis[5] to estimate the relative rate of loss of Ph_3P and NEt_3 from respectively phosphonium and ammonium salts following controlled potential reduction.

RESULTS AND DISCUSSION

Voltammetry and Coulometry.—The cyclic voltammetric behaviour of the phosphonium salts followed a pattern similar to that displayed in the Figure for cinnamyltriphenylphosphonium nitrate. For the *p*-methoxycarbonylbenzyltriphenylphosphonium salt the voltammetric behaviour was somewhat different and this is discussed separately. The other phosphonium salts showed, on the first scan, three reduction peaks;



Cyclic voltammogram of $PhCH{:}CHCH_2\overset{+}{P}Ph_3\ NO_3^-$ (see Table 1 for details): A, first scan; B, second scan

the first peak was diffusion controlled as shown by linear plots of i_p *versus* $v^{\frac{1}{2}}$ and i_p was also found to be directly proportional to the concentration of phosphonium salt. Peak widths ($E_p/2 - E_p$) were of the order of 75 mV and independent of scan rate. No oxidation peaks were observed on the reverse scan, even at 150 V s^{-1}. Addi-

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tion of quinol generally caused the disappearance of the second peak and a doubling of peak height for the first peak. In a separate experiment at higher concentrations (10^{-3}M) an additional reduction peak, at —2.50 V, was observed; this observation was not made in earlier work.[1] The peak is due to formation of triphenylphosphine oxide (see below) which suggests that the solvent was not completely dry.

TABLE 1

Cyclic voltammetric [a] and coulometric data

Compound	Peak potentials [b] $-E_1$; $-E_2$; $-E_3$	n
$PhCH_2\overset{+}{P}Ph_3Cl^-$	1.91; 2.66; 2.82	1.00 [c]
	(1.91; 2.82) [d]	2.00
	(1.91; 2.50; 2.66; 2.82) [e]	
$PhCH_2\overset{+}{P}Ph_3NO_3^-$		1.02 [f]
$PhCH{:}CHCH_2\overset{+}{P}Ph_3NO_3^-$	1.77; 2.41; 2.75	1.03,[c] 1.01,[f]
	(1.26; 1.93; 2.25) [h]	1.86 [g]
[3-Methyl-5-(2,6,6-trimethylcyclohex-1-enyl)penta-2,4-dienyl]triphenylphosphonium iodide	(1.74; 2.33; 2.74) [i]	0.9 [f]

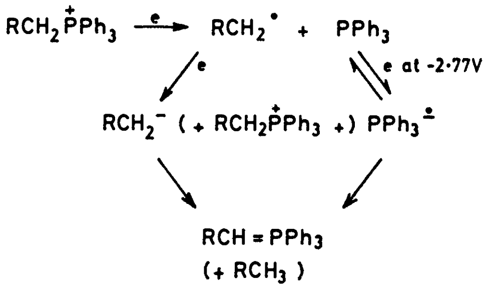
[a] Concentration of substrate *ca.* 5 × 10^{-4}M in DMF–Bu_4NClO_4 (0.1M) [or Bu_4NI (0.1M)]; vitreous carbon or Hg coated Pt bead microelectrode; sweep rate 0.3 V s^{-1}. [b] Volts *vs*, s.c.e. [c] Controlled potential coulometry at first reduction potential, Hg pool cathode. [d] Quinol added, doubling of i_p at —1.91 V observed. [e] At 10^{-3}M. [f] As *c* but Al foil cathode. [g] In presence of quinol. [h] Volts *versus* Ag–AgI. [i] At 1.3 × 10^{-3}M and 0.15 V s^{-1}.

With consecutive cycling a significant change is observed on the second and subsequent scans. When the potential sweep is reversed at —3.0 V the subsequent cathodic sweep gave only the second and third reduction peaks. Reversal of the scan between the first and second reduction potentials did not result in loss of the first peak and gave only the normal decrease in peak current on the second sweep. The voltammetric data, together with the results of controlled potential coulometric experiments, are summarised in Table 1.

The reduction potentials of triphenylphosphine and triphenylphosphine oxide are —2.77 and —2.47 V respectively (*cf.* literature values [6] of —2.75 and —2.54 V). Reduction peaks at *ca.* —2.75 to —2.80 V [—2.24 to —2.29 V (*versus* Ag–AgI)] are common to the voltammograms of each of the phosphonium salts studied and it must be concluded that in each case cleavage to triphenylphosphine occurs. The other product of cleavage, the hydrocarbon, is less easily reduced except in the case of methyl *p*-toluate (see below). It is noteworthy that triphenylphosphine oxide is not formed under normal voltammetric conditions; at high concentration or during the longer time required for controlled potential coulometry the reduction peak of triphenylphosphine oxide is observed. The *NN*-dimethylformamide used in these experiments was not rigorously dried and consequently it is likely that triphenylphosphine oxide is produced by slow hydrolysis of the ylid.

Assignment of the second reduction peak representing reduction of an ylid is supported by the variation of that peak's potential as a function of structure. The highly conjugated systems of the cinnamyl and the C_{15}-polyenyl-ylids are reduced at —2.41 and —2.33 V respectively compared with —2.66 V for the benzyl ylid.

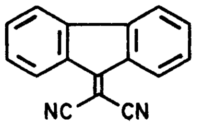
The coulometric experiments show that the first reduction peak is associated with a 1 F mol^{-1} process; addition of proton donor results in a change to a 2 F mol^{-1} process. The simplest rationalisation of these results is that one molecular equivalent of phosphonium salt is cleaved at the first reduction potential, in a 2 F mol^{-1} process, to a carbanion and triphenylphosphine. The carbanion is protonated by another molecular equivalent of the phosphonium salt which is thereby converted into the ylid. As two molecular equivalents of phosphonium salt are consumed in a two-electron process the coulometry works out at 1 F mol^{-1}. The disappearance of the first reduction peak following scans to > —2.8 V is completely consistent with the depletion of phosphonium salt at the cathode by reaction with the strongly basic triphenylphosphine anion-radical. The detailed mechanism of reduction of phosphonium salts is displayed in Scheme 2.



SCHEME 2

Ylid Formation by Electrogenerated Base.—Benzyltriphenylphosphonium salts have been converted [7] into the ylid in the presence of a cathodically generated base (the azobenzene anion-radical) and in this case efficient reaction between the ylid and added carbonyl compounds was observed. This provides the basis of further proof of the assignment of reduction peaks in the voltammetric experiments.

The compound (pro-base) chosen for conversion into base was dicyano(fluoren-9-ylidene)methane (1). The



(1)

cyclic voltammogram of (1) shows two consecutive and reversible reduction peaks at relatively low potentials [—0.71 V (—0.20 V *versus* Ag–AgI) and —1.46 V (—0.95 V *versus* Ag–AgI) in DMF–Bu_4NClO_4 (0.1M) at 0.3 V s^{-1}]. Addition of an equivalent amount of benzyltriphenylphosphonium nitrate [E_p — 1.91 V (—1.40 V *versus* Ag–AgI)] causes the second reduction peak of (1) to become irreversible without any significant change in peak current. In these systems the second reduction peak is associated with dianion formation[8] and it is reasonable to conclude therefore that the phosphonium salt is sufficiently acidic to protonate the dianion. Furthermore, extension of the scan reveals that in the presence of the pro-base (1) the height of the ylid reduction peak is enhanced; in this case dianion formation from (1) is not completely irreversible.

A direct demonstration of ylid formation in this system is the formation of *trans*-stilbene in 74% yield from an experiment in which a mixture of benzaldehyde, benzyltriphenylphosphonium nitrate and the pro-base (1) was reduced at −1.50 V (−1.0 V *versus* Ag–AgI), *i.e.* the potential required for formation of the dianion of (1). The preparative consequences of this and related experiments will be the subject of a subsequent publication.

The Reduction of 4-*Methoxycarbonylbenzyltriphenylphosphonium Nitrate*.—The mechanism in Scheme 2 requires that the maximum yield of ylid should be 50%; the earlier study[1] suggested that from phenacyl- and diphenylmethyl-phosphonium salts, ylids were formed nearly quantitatively. This raises the question of whether a previously unconsidered base is formed at the cathode or whether protons at the cathode can be removed directly from the acidic phosphonium salts. The fact that a less acidic phosphonium salt (the benzyl derivative) is efficiently converted into an ylid by base generated at a mere −1.50 V (see above) argues against the involvement of an unspecified base generated in the electrolyte. If that were the case there would not be such a marked difference in behaviour between the phenacyl and diphenylmethyl derivatives on the one hand and the benzyl derivative on the other; electrogenerated base would convert each of them rapidly into the ylid.

We have accordingly examined the reductive behaviour of 4-methoxycarbonylbenzyltriphenylphosphonium nitrate; the ylid formed from this salt is highly stabilised. The results of cyclic voltammetric and controlled potential coulometry experiments are given in Table 2, which also includes for comparison results relating to the reductive cleavage of 4-methoxycarbonylbenzyltriethylammonium bromide. The behaviour of the phosphonium salt is qualitatively similar to that of the other benzylic and allylic phosphonium salts except that the second reduction peak [at −2.39 V (−1.88 V *versus* Ag–AgI)] is quasi-reversible with i_p^c/i_p^a 2.5 at 0.2 V s^{-1}. Under the same conditions methyl *p*-toluate gives quasi-reversible reduction at E_p^c −2.38 V but in this case i_p^c/i_p^a is 1.1. The ylid is therefore formed but its irreversible reduction is masked by reduction of the cleavage product, methyl *p*-toluate. Another indication of ylid formation is the yellow colour which develops during reduction; this was observed also for the compounds given in Table 1. Under aprotic conditions preparative scale reduction, controlled at −1.7 V, of the 4-methoxycarbonylbenzylphosphonium salt gives[4] after aqueous work-up methyl *p*-toluate in 81% yield with no detectable quantity of the corresponding bibenzyl. This may be a result of cleavage and/or hydrolysis of the ylid during work-up. The bibenzyl is formed in 35% yield at an aluminium cathode with high current densities, *i.e.* conditions under which the parent benzylphosphonium salt is coupled[4] in high yield.

TABLE 2

Cyclic voltammetry[a] of 4-methoxycarbonylbenzylphosphonium and -ammonium salts

Compound	Peak potentials[b] $-E_1$; $-E_2$; $-E_3$	n[c]
$4\text{-MeO}_2CC_6H_4CH_2\overset{+}{P}Ph_3NO_3^-$	(1.70; 2.37;[e] 2.78)[d]	0.99, 1.20,[f]
	1.21; 1.88;[e] 2.26	1.80,[g] 2.0[h,i]
	1.17[h]	
$4\text{-MeO}_2CC_6H_4CH_2\overset{+}{N}Et_3Br^-$	1.12; 1.87[e]	1.10, 1.98,[f]
	1.15; 1.91[h]	1.06,[h] 2.0[i]

[a] As for Table 1; sweep rate 0.35 V s^{-1}. [b] Volts *versus* Ag–AgI. [c] As in Table 1. [d] Volts *versus* s.c.e. [e] Quasi-reversible. [f] Quinol added. [g] Guanidinium perchlorate added. [h] In MeCN–Bu$_4$NI (0.1M). [i] Acetic acid added.

The stability (and relatively low basicity) of the ylid is evident from the effect of added proton donor on the cyclic voltammetric behaviour. In controlled potential coulometry added quinol (13 mol. equiv.) causes a change from 0.99 to 1.20 F mol^{-1} and the electrolyte remains yellow. Addition of the much stronger proton donor, guanidinium perchlorate,[8] allows the observation of a 1.8 F mol^{-1} reduction at the first potential [−1.90 V (−1.40 V *versus* Ag–AgI)]. An excess of acetic acid brings about 2 F mol^{-1} reduction and in this case the i_p^c/i_p^a value at 350 mV s^{-1} for the second peak is decreased from 1.9 to 1.1, *i.e.* methyl *p*-toluate is the sole product of the two-electron reduction. The behaviour shown in this series of experiments contrasts with that of benzylphosphonium salts for which relatively small amounts of quinol cause a change from 1 to 2 F mol^{-1} reduction.

Compelling support for Scheme 2 comes finally from the establishment of the yield of ylid as 50%. This was shown by a controlled potential coulometric experiment at −2.00 V (−1.50 V *versus* Ag–AgI) at the conclusion of which (1 F mol^{-1}) an excess of acetic acid was added. The yellow colour of the electrolyte was discharged and the cyclic voltammogram of the solution showed that the starting material had reappeared (E_p −1.70 V) and that the associated peak current had the same value as before exhaustive electrolysis. In fact this means that 50% of the starting material is regenerated because in acidic solution the peak current corresponds to a two-electron process compared with the one-electron process in aprotic conditions.

Relative Rates of Loss of PPh_3 *and* NEt_3.—Benzylic quaternary ammonium salts are reduced by a mechanism[9] analogous to route *b* of Scheme 1; in aprotic solvents 1 F mol^{-1} reduction to benzyl radicals occurs whereas in the presence of proton donors 2 F mol^{-1} hydrogenolysis is observed. In acidic solution therefore ammonium and phosphonium salts will give 2 F mol^{-1} cleavage by the same mechanism and, providing their reductions potential are similar, the relative rates of cleavage are amenable to study by competitive electrolysis. This method has been used[5] successfully to compare the relative leaving group abilities of carboxylate ions from the anion radicals of the corresponding *p*-methoxycarbonylbenzyl carboxylates. The solvent–electrolyte system used for these latter studies was acetonitrile–tetra-n-butylammonium iodide with acetic acid as proton donor. Proton donation is more efficient in acetonitrile than in the relatively basic solvent dimethylformamide.[8]

In the above, context, cyclic voltammetry of *p*-methoxycarbonylbenzyltriphenylphosphonium nitrate and of *p*-methoxycarbonylbenzyltriethylammonium bromide (Table 2) shows that in acetonitrile solution the parameters for reduction are closely similar. Controlled potential electrolysis at −1.9 V (1.40 V *versus* Ag–AgI) of an equimolar mixture (total 2×10^{-4} mol) of the two salts, in acetonitrile–tetra-n-butylammonium iodide containing an excess of acetic acid, was run to 1 F mol^{-1} (based on the combined amounts of the 'onium salts); complete electrolysis would require 2 F mol^{-1} under these conditions. The crude product obtained after aqueous work-up and ether extraction was analysed by ^1H n.m.r. spectroscopy. The benzylic proton signals of the 'onium salts are characteristic and well separated in $CDCl_3$ solution [$CH_2\overset{+}{P}Ph_3$, δ 5.19, 5.43 ($J_{P\text{-}CH_2}$ 15 Hz); $CH_2\overset{+}{N}Et_3$, δ 4.85]. It is therefore possible by comparison of integration of the relevant signals in the spectra of the starting mixture and of the crude electrolysis product to estimate which 'onium salt is consumed more quickly and by how much. In the experiment described above the ammonium salt was cleaved more quickly by a factor of 1.5. In an attempt to relate these rates of cleavage to the series of carboxylates studied previously[5] it was found by similar competitive electrolysis that the NEt_3 group was lost immeasurably faster than the best of the carboxylate leaving groups (naphthalene-1-carboxylate). Examination of the products of competitive electrolysis to 1 F mol^{-1} revealed that the ammonium salt had been completely electrolysed. At this stage therefore leaving group abilities from the benzylic position of anion-radicals may be put in the qualitative order $Et_3N > Ph_3P \gg RCO_2^-$.

EXPERIMENTAL

Methods used for the purification of solvents, for the preparation of materials, and for competitive electrolysis have been described previously[4,5] as has the electrochemical apparatus used. Potentials were measured against a commercial saturated calomel electrode (s.c.e.) or against an Ag–AgI(s) electrode; in several cases both references have been employed and the potentials with respect to Ag–AgI were consistently 0.51 V anodic of those with respect to s.c.e.

Constant Potential Coulometry.—These experiments were carried out in a specially constructed H cell equipped so that the cathode compartment contained both a mercury pool cathode and a mercury coated platinum bead microelectrode; each cathode had a reference electrode nearby and the electrodes were connected *via* a junction box to a potentiostat, a current integrator, a sweep generator, and an *X–Y* recorder. The junction box allowed controlled potential electrolysis to be interrupted at intervals and concentration changes in 'onium salt monitored by cyclic voltammetry without disturbing the electrode configuration. Linear plots of i_p *versus* charge passed were obtained and extrapolation to i_p 0 allowed calculation of *n*.

Ylid Formation by Electrogenerated Base.—Benzyltriphenylphosphonium nitrate (0.129 g, 3.1×10^{-4} mol), benzaldehyde (0.041 g, 3.9×10^{-4} mol), and dicyano-(fluoren-9-ylidene)methane (1) (0.091 g, 4×10^{-4} mol) were dissolved in dimethylformamide containing 0.1M dry lithium perchlorate in the cathode compartment of a divided cell (catholyte volume *ca.* 25 cm^3). Electrolysis at the mercury pool cathode, at −0.9 V (*versus* Ag–AgI), was continued until the current had dropped to the background level; 2 F mol^{-1}, based on (1), were consumed. After aqueous work-up and ether extraction a known weight of an internal standard (biphenyl) was added to the crude product mixture which was then analysed by g.l.c. (Hewlett–Packard 5830A, column 5% OV-17). The detector response factor for stilbene with respect to diphenyl was previously determined to be 1.1. The averaged results from two injections gave the yield of stilbene as 74% (based on phosphonium salt) with a *trans* : *cis* ratio of 1.44 : 1.

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