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References

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WITTIG TYPE REACTIONS INDUCED BY ELECTROGENERATED BASES

A.P. Bettencourt, A.P. Esteves, A.M. Freitas and M.I. Montenegro

*Centro de Química Pura e Aplicada da Universidade do Minho
Largo do Paço, 4719 Braga Codex, Portugal*

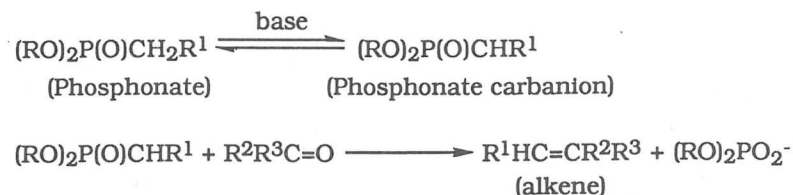
Recently, a great deal of progress has been made in understanding the mechanisms by which organic reactions may be carried out electrochemically and the advantages of these routes have been widely discussed. Therefore, organic chemists become increasingly interested in the possibility of using electrolyses as an alternative to the conventional chemical methods.

It has been shown for several years that the deliberate cathodic generation of anionic bases, in aprotic solvents, may be particularly convenient for preparative purposes since factors such as base strength and concentration can be easily controlled [1].

The synthesis of unsaturated compounds from organophosphorous reagents and carbonyl compounds has been largely explored and olefin formation by means of phosphonate carbanions has been referred as the Wittig-Horner reaction. Different techniques have been employed to generate the carbanion resulting from the phosphonate deprotonation. The technique described here is based on the deprotonation by electrogenerated bases. Compounds which form electrogenerated bases (EGB) by electroreduction, such as azobenzene, are called probases (PB). Lund [2] has shown that stilbene results from the electrolysis, at the azobenzene reduction potential, of a mixture of benzaldehyde, benzyltriphenylphosphonium bromide and azobenzene in *N,N*-dimethylformamide (DMF). The phosphonate carbanions, however, are generally more reactive than the corresponding phosphoranes, and therefore the phosphonates are less acidic. The possibility of generating the bases *in situ* is, therefore, highly desirable and the success of these reactions has already been preliminary observed [3].

We report here examples of Wittig-Horner reactions carried out electrochemically with different probases.

The reaction can be schematically represented by:



A convenient PB satisfies the following conditions: 1) It is reduced at less negative potentials than other species present in the reaction solution; 2) The corresponding EGB is sufficiently strong to deprotonate the weak acid and reacts preferentially as a base, e.g., it is a weak nucleophile and a weak reducing agent.

EGB's offer some advantages over conventional bases:

- The corresponding PB's are stable and therefore can be easily stored and can be regenerated in some cases.
- It is possible to control the rate of generation of base by means of the current density.
- The influence of metal cations, present in the reaction medium, on the yield and on the stereochemistry of the reaction can be studied.
- The experimental conditions can be easily reproduced since the base is formed *in situ*.
- It is possible to deprotonate some less acidic phosphonates which require quite drastic conditions when conventional bases are used.

Using cyclic voltammetry it is possible to detect the deprotonation reaction of the phosphonate, $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Et}$, by the anion radical of the azobenzene, obtained by cathodic reduction of this PB. It is also possible to observe the Wittig-Horner reaction between the carbanion and benzaldehyde:

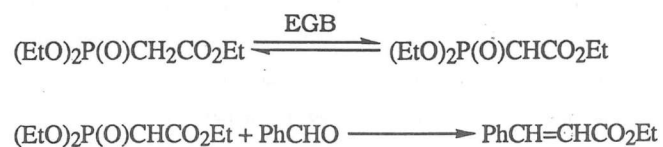


Fig. 1a) shows a cyclic voltammogram (CV) for a solution containing azobenzene and Bu_4NBF_4 (TBAB) in DMF. When phosphonate is added, the corresponding CV (**Fig. 1b**) shows an increase in the cathodic peak current together with loss of reversibility, indicating that reaction between phosphonate and azobenzene anion radical has occurred.

Addition of benzaldehyde (**Fig 2**) leads to a CV presenting further peaks: one corresponding to benzaldehyde reduction (1) and another corresponding to the alkene ($\text{PhCH}=\text{CHCO}_2\text{Et}$) reduction (2) (see **Fig. 3** for comparison).

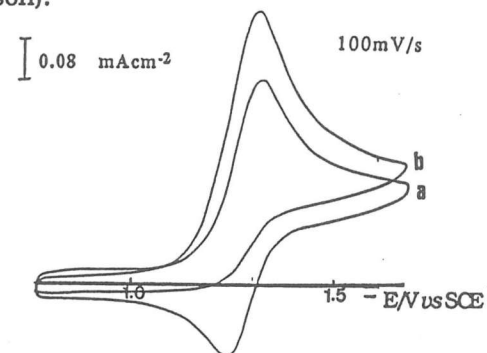


Figure 1 - Cyclic voltammograms, at a vitreous carbon electrode, of a solution 0.1 mol dm^{-3} TBAB, in DMF, containing:

- a) $10^{-3} \text{ mol dm}^{-3}$ $\text{PhN}=\text{NPh}$
- b) $10^{-3} \text{ mol dm}^{-3}$ $\text{PhN}=\text{NPh}$ + $10^{-3} \text{ mol dm}^{-3}$ $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Et}$

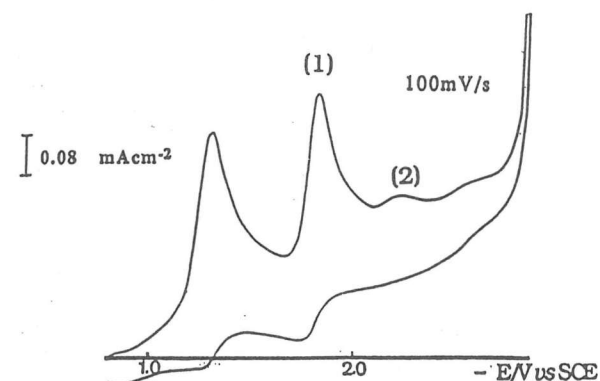


Figure 2 - Cyclic voltammograms, at a vitreous carbon electrode, of a solution $10^{-3} \text{ mol dm}^{-3}$ $\text{PhN}=\text{NPh}$, $10^{-3} \text{ mol dm}^{-3}$ $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Et}$ and 0.1 mol dm^{-3} TBAB, in DMF.

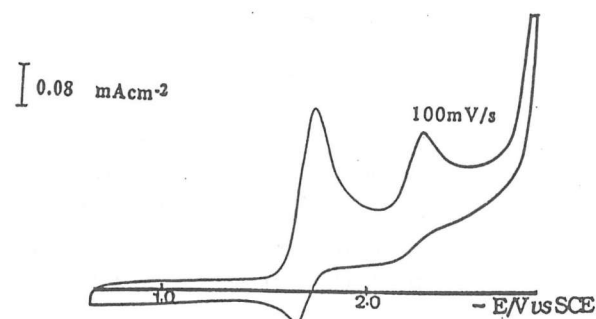
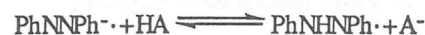


Figure 3 - Cyclic voltammograms, at a vitreous carbon electrode, of a solution 10^{-3} mol dm^{-3} $\text{PhCH=CHCO}_2\text{Et}$ and 0.1 mol dm^{-3} TBAB, in DMF.

Controlled potential electrolyses were carried out at potentials 50 mV after the first reduction process which corresponds to the formation of the azobenzene anion radical. The concentration ratios azobenzene : phosphonate : benzaldehyde was 1:2:2. The electrolysis product was identified by HPLC and the yield was determined to be 80%. Coulometry data suggest that the number of electrons consumed by molecule was 2.

The following mechanism is proposed for the reaction [3]:



It should be emphasized that, although azobenzene is a convenient PB [2,3], the work-up in acidic media of the electrolysis solution leads to the formation of benzidine which is a carcinogenic product. It is, therefore, desirable to search for other PB's and some attempts were made to use fluoren-9-ylidenemethane derivatives which present a reasonable reduction potential. It was observed by cyclic voltammetry, however that even the corresponding dianion is not a strong enough base to deprotonate the phosphonate. This fact was confirmed by controlled potential electrolyses since no alkene was obtained as a product.

Fuchsone was also used as a PB and Fig.4a) shows a CV of fuchsone and TBAB in DMF at a vitreous carbon cathode. When phosphonate, is added, only a small decrease in the anodic peak current intensity is observed (Fig. 4b)) indicating that the anion radical of fuchsone is a weaker base than the anion radical of azobenzene. Controlled potential electrolyses of fuchsone in the presence of phosphonate and aldehyde, however, yielded 60% of alkene suggesting that in an electrolysis time scale the phosphonate is deprotonated by the EGB.

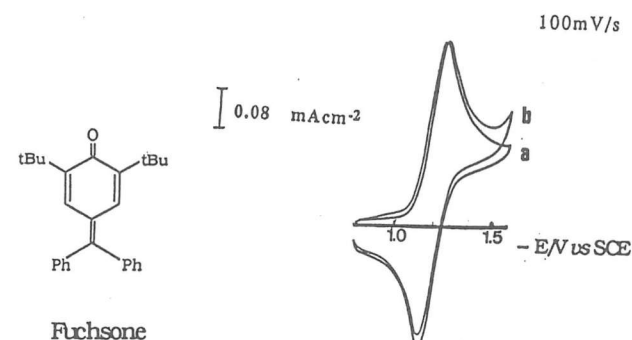


Figure 4 - Cyclic voltammograms, at a vitreous carbon electrode, of a solution 0.1 mol dm^{-3} TBAB, in DMF, containing:

a) $10^{-3} \text{ mol dm}^{-3}$ Fuchsone

b) $10^{-3} \text{ mol dm}^{-3}$ Fuchsone + $10^{-3} \text{ mol dm}^{-3}$ $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Et}$

In this programme of work it is intended to optimize the experimental conditions in order to increase the reaction yield. Therefore, the influence of solvent, electrolyte, temperature and the addition of small metal cations will be investigated.

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