Electrochemical Carbon–Carbon Bond Formation: Synthesis of New Substituted Butadienes

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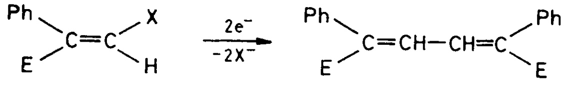
Summary Electrochemical coupling of vinylic compounds forms substituted butadienes which are reversibly reduced at the potential of their formation.

The electrochemical method is an efficient carbon–carbon bond-formation process as shown by well known anodic[1] and cathodic[2] reactions. At the cathode, coupling reactions of activated olefins may occur *via* several mechanisms, especially anion radical–anion radical, anion radical–substrate, and anion–substrate, which lead, in most cases, to the hydrodimer.

Obviously it is of interest electrochemically to couple two vinylic carbon compounds (**1**) with the simultaneous loss of the two groups X in order to obtain, *in one step*, a conjugated diene, according to equation (1). The preliminary work described herein refers to the activated olefins with E = CN or CO_2R' in which X may be either an ether group or an amino-group (similar studies are being undertaken with vinylic sulphides).



(1)

(a) E = CN, X = OMe
(b) E = CN, X = $OCH_2OCH{=}C(Ph)CN$
(c) E = CN, X = NPhMe
(d) E = CO_2Me, X = $OCH{=}C(Ph)CO_2Me$

(2)

(a) E = CN
(b) E = CO_2Me

In aprotic solvents the mechanism of the formation of compounds (**2**) is rather complex and will be discussed elsewhere.[3] However, the main features are that the initial chemical reaction is a nucleophilic addition of the anion radical to the substrate followed by the loss of X^-. Then, a fast second electron-transfer is followed by anionic elimination. Since compound (**2**) is readily reduced to a dianion at the potential of its formation, macroelectrolyses led to a polymerization process, probably *via* a Michael-type addition of the electrochemically generated nucleophile to the substrate.

In protic solvents, the anionic polymerization is inhibited and the dihydro- and tetrahydro-forms of compound (**2**) were isolated.[4]

TABLE. Preparative electrolyses using a double-electrode flow cell with DMF–Bu_4NBF_4 (0·1 M) as solvent.

Substrate	E/V[a]	ΔE[b]	i/mA	Flow (cm^3/min)	[(**1**)] (mol l^{-1} × 10^{-2})	Product[c]
(E)- or (Z)-(**1a**)	−1·55	4·55	255	4·3	3	(**2a**)[f] 37[d] 32[e]
(**1b**)	−1·41	5·05	225	3·2	1·25	(**2a**)[f] 36[d] 34[e]
(**1c**)	−1·68	4·60	240	3·8	3·2	(**2a**)[f] 38[d] 33[e]
(**1d**)	−1·40	4·75	180	3·9	1·8	(**2b**)[g] 37[d] 25[e]

[a] Peak potential of compounds (**1**) measured in aprotic medium (mercury microcathode; sweep rate, 100 mV/s; concentration, 10^{-3} mol l^{-1}). [b] Difference between potential applied to anode and cathode. [c] Starting material also obtained. [d] Yield obtained by polarographic means directly after one passage of solution through the cell. [e] Isolated yields of compounds (**2**). [f] M.p. 214 °C; M^+, 256·099; ^{1}H and ^{13}C n.m.r. in agreement with structure given; E_1° − 0·35 V (1F), E_2° − 0·94 V (1F). [g] M.p. 168 °C; M^+, 322·120; E_1° − 0·72 V (1F), E_2° − 1·03 V (1F).

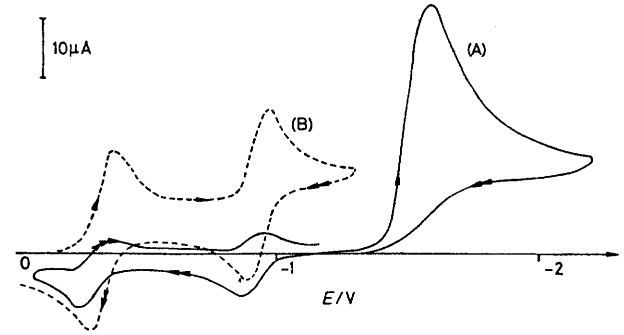


FIGURE 1. Cyclic voltammogram of compound (**1a**) (A) and compound (**2a**) (B) in dimethylformamide (DMF)–Bu_4NBF_4 (0·1 M); sweep rate 500 mV/s; mercury microcathode.

Rather fast (sweep rates > 500 mV/s), repetitive cyclic voltammetry [potential sweeps between 0 and −1·7 V *vs.* Ag–AgI–I$^-$ (0·1 M)] exhibits (Figure 1) two reversible steps at cathodic potentials less than the reduction potential of compound (**1**). They were attributed to the reduction of the butadienes (**2**). However, at present, confirmation of this is not possible since the butadienes (**2**) could not be directly synthesised, probably due to their high reactivity.

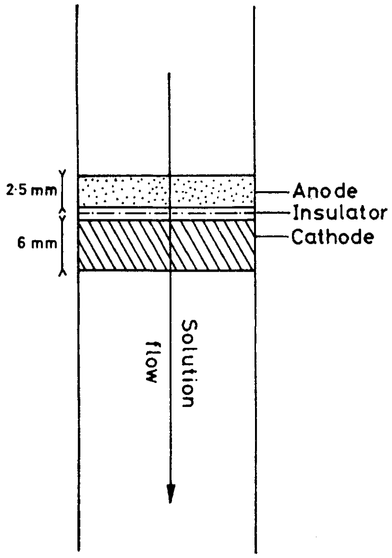
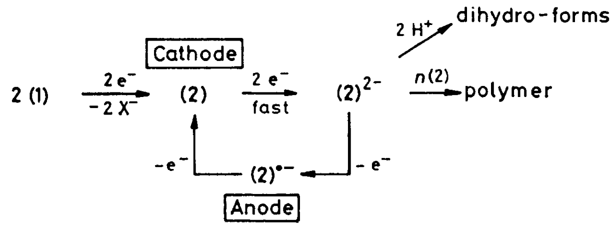


FIGURE 2. Cathode: porous disc of amalgamated copper. Anode carbon felt (Carbone Lorraine). A porous insulator (glass microfibres) is set between the two electrodes.

The use of a flow cell with porous working electrodes (Figure 2) may provide an elegant synthetic method for compounds (**2**) especially in the case of the formation of rather unstable intermediates, such as the dianion (**2**)$^{2-}$. The substrate is fully reduced at the cathode and then the primary reduction product is immediately partly reoxidized to the final product at an anode located next to the cathode. The solution flow through the two-electrode cell system is regulated in order to reduce compound (**1**) as much as possible before any side-reactions of compound (**2**) occur (protonation or polymerization). The minimal potential difference applied to the two-electrode system may be estimated from the cyclic voltammograms of compounds (**1**) and (**2**). It has to be large enough to oxidize totally the dianion according to a two-electron process and to account for the ohmic drop. As the number of electrons exchanged is higher at the cathode, a partial oxidation of dimethylformamide at the anode may occur. This anodic side-reaction does not influence the product distribution.



Preliminary data are given in the Table. They represent the first results in aprotic medium concerning a new cell which will be tested for aqueous systems and described elsewhere.[5]

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[1] See, for example, M. R. Rifi and F. H. Covitz, 'Introduction to organic electrochemistry,' Marcel Dekker, New York, 1974, p. 265.

[2] M. M. Baizer, 'Organic electrochemistry. An introduction and a guide,' Marcel Dekker, New York, 1973, p. 698.

[3] G. Mabon and J. Simonet, to be published.

[4] G. le Guillanton, M. Cariou, and A. Lebouc, *Bull. Soc. Chim. Fr.*, 1974, 2981.

[5] C. Moinet, unpublished results.