

Electrochemical Reductive Cleavage of Biaryls. The Formation of Anthracene and 9,10-Dihydroanthracene from 9,9'-Bianthryl

By OLE HAMMERICH†* and JEAN-MICHEL SAVÉANT

(Laboratoire d'Electrochimie, Université de Paris-VII, 2, place Jussieu, F-75221 Paris Cédex 05, France)

Summary 9,9'-Bianthryl is cleaved into anthracene and 9,10-dihydroanthracene by electrochemical injection of two, three or four electrons.

REDUCTIVE cleavage of carbon-carbon bonds in unfunctionalized aromatic systems has only received little

attention and the examples reported so far have been limited to the scission of aliphatic bonds in diarylalkanes¹⁻³ and related polymeric materials.^{4,5} For the 1,2-di-(1-naphthyl)ethane anion radical kinetic studies revealed the cleavage to follow a second order expression indicating a rate determining step involving the dianion, which is

† Permanent Address: Department of General and Organic Chemistry, The H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen, Denmark.

initially formed by disproportionation.³ We now report the reductive cleavage of a simple biaryl, 9,9'-bianthryl, in which the two aromatic ring systems are attached directly to each other.

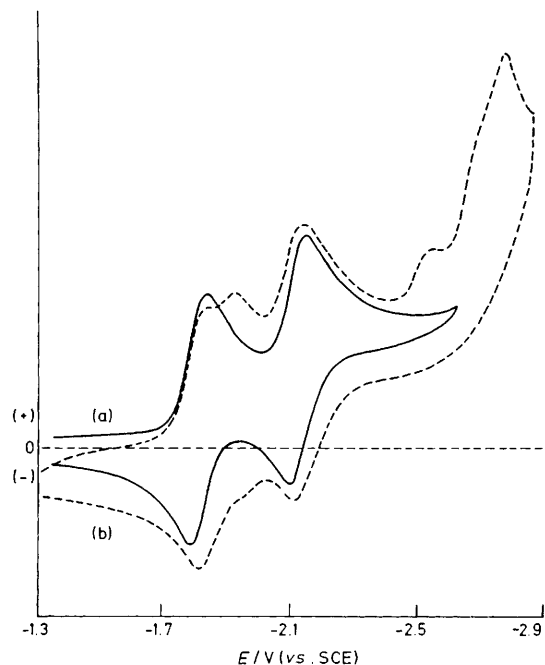
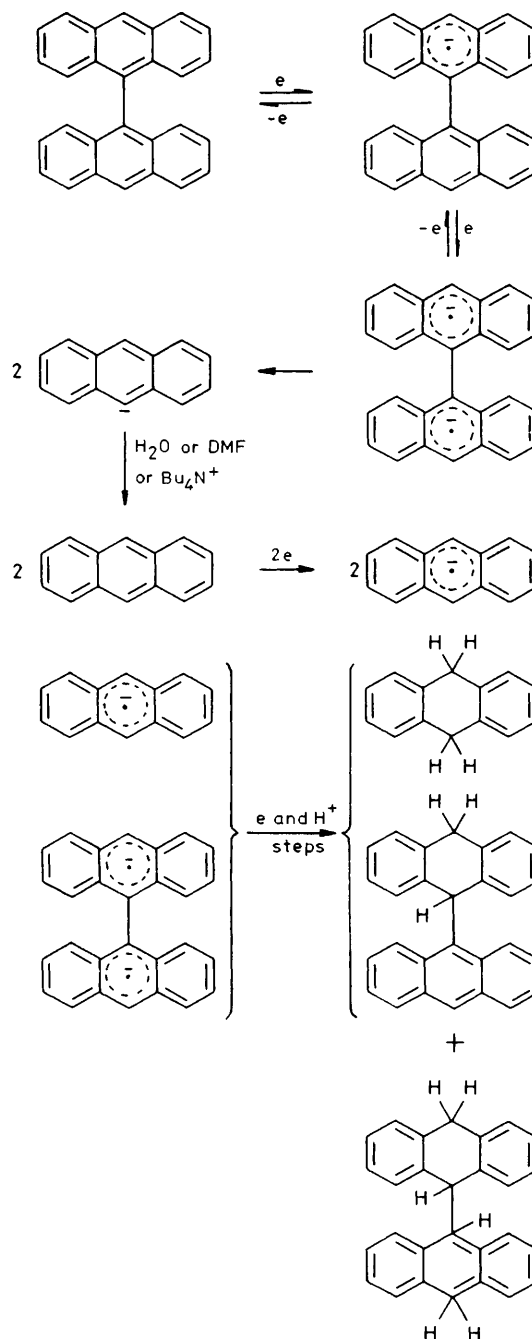


FIGURE. (a) Cyclic voltammogram of 9,9'-bianthryl at a glassy carbon electrode in DMF containing Bu_4NI . Scan rate: 200 mV/s. (b) Repetitive scan voltammogram obtained after 10 cycles. Scan rate: 1 V/s. The current amplification of curve (b) has been adjusted in order to facilitate comparison of the two voltammograms.

Two reversible waves for the successive formation of the anion radical and dianion were observed by cyclic voltammetry of the title compound in dry *NN*-dimethylformamide (DMF) containing Bu_4NI (Figure a). The associated cathodic peak potentials are -1.83 and -2.15 V *vs.* the saturated calomel electrode (SCE) to be compared with the corresponding values of -1.94 and -2.56 V, respectively, for anthracene under the same conditions. In the latter case the second wave is nearly irreversible. The earlier polarographic result⁶ that the second reduction wave of the dimer in aqueous dioxan is close to that for anthracene probably reflects the aqueous conditions employed and is more likely to be interpreted as further reduction of 9,10-dihydro-9,9'-bianthryl formed at the potential of the first wave. When the potential range was extended almost to the background two more reduction waves, both irreversible, appeared at -2.74 and -2.85 V corresponding to formation of the trianion radical and presumably the tetra-anion, the wave of the latter being shifted significantly anodic owing to fast follow-up reactions. A repetitive scan voltammogram including these waves showed the rapid formation of anthracene as revealed by the presence of voltammetric peaks at -1.94 and -2.56 V (Figure b).

Preparative reduction at -2.15 V demonstrated that the dianion undergoes cleavage although the rate is too low for the reaction to be observed by cyclic voltammetry. Exhaustive electrolysis at a mercury pool cathode resulted in

formation of anthracene and 9,10-dihydroanthracene in 7 and 30% yield, respectively. The remaining 60% could be accounted for by the amounts of 9,10-dihydro-9,9'-bianthryl and 9,9',10,10'-tetrahydro-9,9'-bianthryl formed by protonation of the dianion eventually followed by further reduction. This allows us to propose the reactions in the Scheme.



SCHEME

The voltammetric experiment indicated that cleavage *via* the trianion radical and tetra-anion is considerably faster and competes more favourably with protonation than cleavage *via* the dianion. This was indeed observed when

electrolysis was carried out at a potential, -2.80 V, corresponding to formation of these species; analysis of the resulting solution demonstrated the presence of monomers in a total yield of 80% (5% anthracene and 75% 9,10-dihydroanthracene).

Although a small gain in resonance energy is to be expected for a planar conformation of the neutral dimer, steric strain due to interaction between the hydrogen atoms in positions 1,8' and 1',8 causes the molecule to be twisted considerably around the 9,9'-linkage. This has been confirmed by results obtained by absorption and fluorescence spectroscopy⁷⁻⁹ as well as dipole moment and polarizability measurements,¹⁰ and is further substantiated by the present observation that the first reduction potential of the dimer is shifted only 110 mV anodic relative to that of anthracene. Furthermore, the small difference of 320 mV between the first and second redox couple and the comparatively low reactivity of the dianion towards protons supports the

conclusion, also based on spectral data, that only a small change in conformation takes place in passing from the neutral molecule to the anion radical and dianion.⁸ Thus a resonance structure possessing a formal double bond between the two ring systems can only be of minor importance for the description of the electronic distribution in these ions, which, in part, explains the observation of a cleavage reaction for the dianion.

To our knowledge this is the first example of the direct electrochemical cleavage of a biaryl to the corresponding monomer and/or dihydrogenated monomer. Other aromatic systems are now being investigated in order to evaluate the scope and limitations of this reaction.

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