

AN ELECTROCHEMICAL TEST OF A PHOTOCHEMICAL MECHANISM
ELECTROREDUCTION OF CROSS CONJUGATED DIENONES

A. Mazzenga, D. Lomnitz, J. Villegas and C. J. Polowczyk

Department of Chemistry
Bronx Community College
Bronx, New York 10468

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There has been considerable attention devoted to the photochemistry of cross conjugated 4, 4-disubstituted 2, 5-cyclohexadienones(I).⁽¹⁾ Molecular orbital calculations have been utilized to indicate the possibility of 3, 5 bond formation in the (n, π^*) state as a result of increased electron density at these positions.⁽²⁾ These calculations are based on a consideration of the development of a seven electron π system following an $n \rightarrow \pi^*$ transition. We now wish to report that generation of the seven π electron system by electrochemical means does not result in cross bond formation.

It has been previously noted that polarographic half wave potentials are linearly related to the calculated coefficient of the energy of the lowest vacant molecular orbital.⁽³⁾ This correlation should extend to the lowest excited state energy if there is a state relationship between the electrochemistry and photochemistry. A strict relationship in reactivity would be limited to those cases where the electron density change in the excited state resulted in an electronic reorganization to product ground state. These criteria would ensure the absence of a thermal rearrangement following the primary process. The state correlation is emphasized by a plot of half wave potentials vs. triplet energies for a series of hydrocarbons which is presented in Figure 1. Similar correlations with aldehydes and ketones can be demonstrated but the data is much more limited.

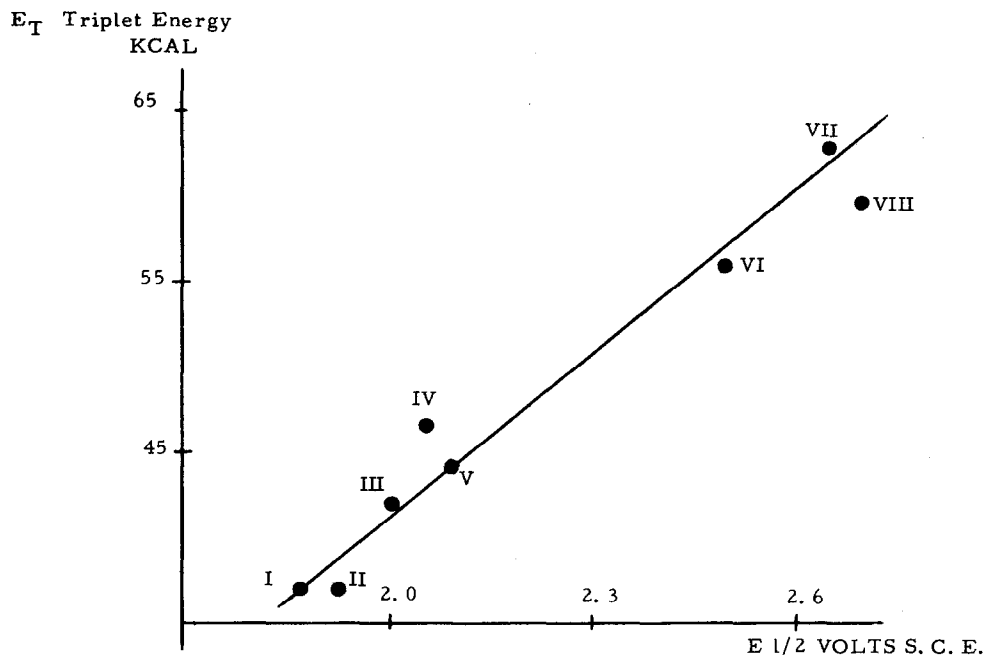
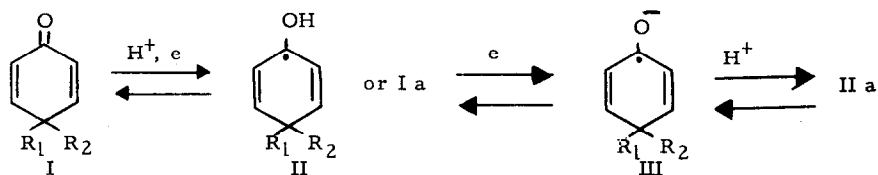


Fig. 1. Half-wave potentials⁽⁴⁾ versus triplet energies of organic compounds.⁽⁵⁾
 I, 3, 4 Benzpyrene; II, Anthracene; III, 1, 2 Benzanthracene; IV, 1, 2, 5, 6 Dibenzanthracene
 V, Pyrene; VI, Phenanthrene; VII, Napthalene; VIII, Fluorene.

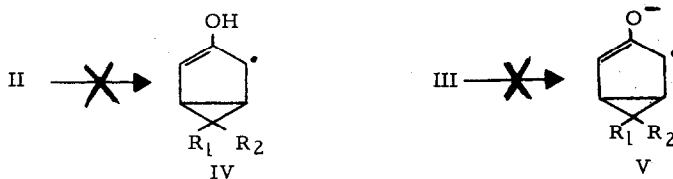
Graphs similar to Fig. 1 could be utilized to estimate the triplet energy of compounds of known electrochemistry.

A comparison of the molecular orbitals involved in the $n \rightarrow \pi^*$ transition of cross conjugated dienones with the seven electron π system of electroreduction indicates that if the only requirement for 3, 5 bond formation is an increase in electron density at the 3 and 5 position, then the electroreduction should benefit by virtue of charge and an unchanged oxygen core potential. The possibility of an interfering surface reaction is remote since little effect was noted on the more subtle stereochemical aspects of electro vs. photochemical pinacol formation for other ketones.⁽⁶⁾

It has been previously demonstrated for androsta-1, 4-diene-17 B-ol-3-one⁽⁷⁾ and confirmed by us for I a that a pH dependent reversible one electron polarographic wave⁽⁸⁾ is observed for dienones. This wave corresponds to either:

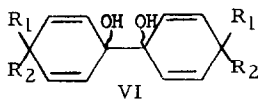


I a; $R_1 = R_2 = C_6H_5$; II a; $R_1 = R_2 = C_6H_5$; I b; $R_1 = CH_3, R_2 = CCl_3$; II b; $R_1 = CH_3, R_2 = CCl_3$



Large scale electrolysis of I a in acid or base gave a single product, (~ 96% isolated yield) the pinacol VI a. The structure of VI was confirmed by cleavage with periodic acid to I a and appropriate molecular weight, elemental analysis, infrared and nmr spectra. (9) In an attempt to demonstrate that the rapid conversion of III \rightarrow II a did not compete with the rearrangement of III, the electrolysis of I a was studied in nonaqueous media, (N, N-dimethyl formamide, 0.15 M KI). After addition of water only pinacol VI a was isolated. In addition electrolysis in DMF under carbon dioxide gave only pinacol. It has previously been noted that delocalization of electron density to carbon gave rise to carboxylic acids in the presence of carbon dioxide, while in the absence of carbon dioxide dimerization at carbon was encountered. (10)

In contrast I b gave identical electrochemical and photochemical results (11) in that generation of the intermediate II b by electrolysis in acid solution gave 76% yield of p cresol. The pinacol VI b accounts for 10% of the yield and an additional 5% was assigned to VII. The structure of VI b and VII were assigned on the basis of acceptable analysis and infrared and nmr spectral data. (9) In addition periodic acid cleavage of VI b gave II b.



VI a $R_1 = R_2 = C_6H_5$; VI b $R_1 = CH_3; R_2 = CCl_3$

Our interpretation of these results is that (1) Cross bond formation in the seven electron cross conjugated system is at the very least endothermic and therefore the seven electron π system of the $n \rightarrow \pi^*$ state does not rearrange to ground state of a cross bonded structure. (2) There is little evidence for extensive delocalization of the seven electron π system to positions 3 and 5. (3) A disrotary ring puckering relative to positions 3 and 5 may be necessary to complete cross bonding in the excited state of these dienones. It is interesting to note that photorearrangement of Ia was not observed in an EPA glass at 77°K⁽²⁾. This could be the result of freezing out of the required motion by the glassy matrix. (4) The description of the excited state in terms of a zwitterionic intermediate, while obviating the necessity of the seven π electron system is not a required alternative but should be reevaluated as a description of the excited state of dienones.

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