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INTRAMOLECULAR TRAPPING AND REDUCTION OF, AND HYDROGEN ABSTRACTION BY σ-RADICALS INTERMEDIATE IN THE ELECTROCHEMICAL REDUCTION OF SOME ARYL HALIDES

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σ-Radicals, generated by decomposition of the initially formed radical-anion, have been postulated as intermediates in the electrochemical reduction of some aryl halides.[1] Evidence for such intermediates can be obtained by intramolecular trapping experiments and we have used a second benzene ring as the radical trap.

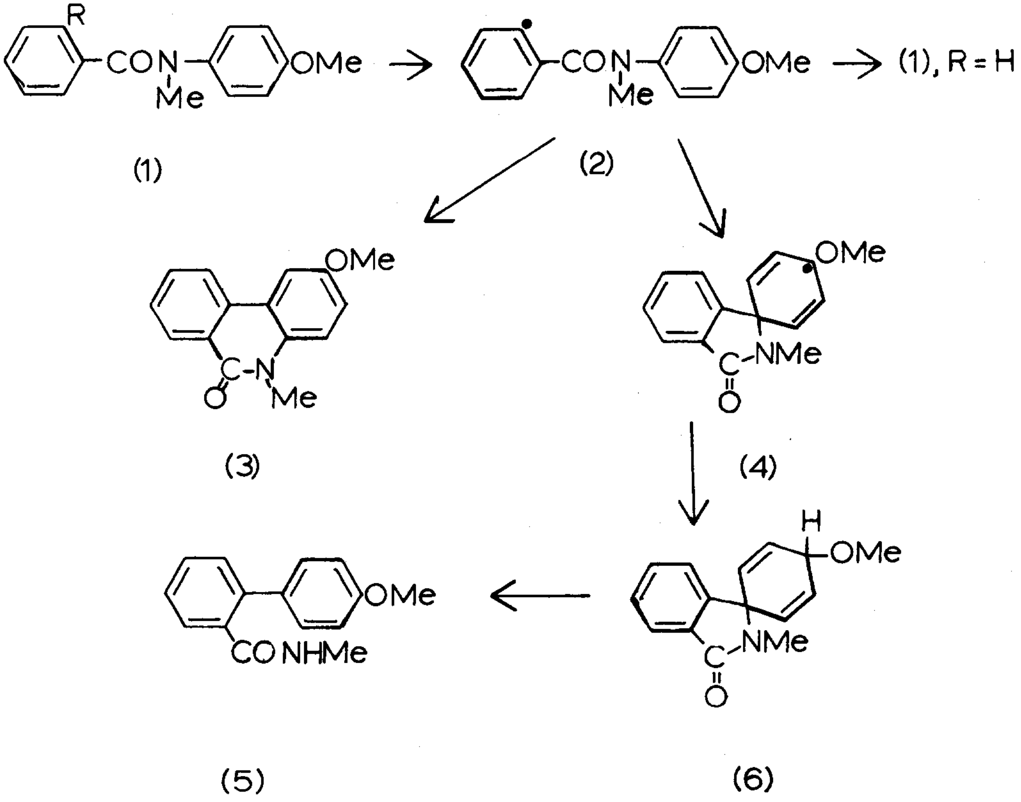
Electrochemical reduction of the amides (1, R = I) which has $E_{\frac{1}{2}}$ - 1.66 V *versus* s.c.e. and (1, R = Br) which has $E_{\frac{1}{2}}$ - 2.16 V *versus* s.c.e. in anhydrous dimethylformamide at a mercury cathode with 0.1 M tetra-n-propylammonium perchlorate as supporting electrolyte afforded (1, R = H) and two other products (3) and (5) in yields given in the table. The products were separated by column chromatography and identified by m.p., spectral data, and comparison with the literature. The same products along with dimeric compounds not encountered here have been obtained by photochemical decomposition of the amide (1, R = H) in benzene[2] and by thermal decomposition of a salt of the diazonium cation (1, R = N_2^+) in water.[3]

Table

Isolated % Yields from Electrochemical Reduction

Substrate	(1), R = H	(3)	(5)
(1), R = Br	35	9	46
(1), R = I	38	11	10

Compounds (3) and (5) are interpreted as being formed by attack of the σ-radical intermediate (2) on the methoxybenzene ring. Compound (5) may be formed from the cyclised radical (4) either <u>via</u> the spirodiene (6) which subsequently rearranges or by carbon-nitrogen bond cleavage to give a nitrogen radical which is later reduced to (5). Compound (5) crystallises directly from a solution of the reaction products in ether so that if (6) is an intermediate it is converted to (5) under very mild conditions.



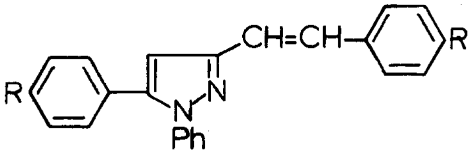
When these two reductions were repeated in dimethylformamide containing 1% deuterium oxide, deuterium was incorporated to give (1, R = D) but no deuterium was incorporated into (3) and (5). Any deuterium attached to nitrogen in compound (5) would be replaced by hydrogen during the isolation procedure. These observations are consistent with overall reduction of the radical (2) to give (1, R = H) by addition of one electron and one proton:

$$Ar^{\bullet} \xrightarrow{e\ +\ H^{+}} ArH$$

and this reaction may involve organomercury intermediates:

$$Ar^{\bullet} \xrightarrow{Hg} ArHg^{\bullet} \xrightarrow{e\ +\ H^{+}} ArH + Hg.$$

They are not consistent with the radical (2) exclusively abstracting a hydrogen atom from the solvent since this would lead to predominant hydrogen incorporation by attack on dimethylformamide. Previous workers[1] have proposed the latter route by which σ-radicals, such as (2), acquire a hydrogen atom.



(7)

Electrochemical reduction of (7, R = Cl) which has a first polarographic wave with $E_{\frac{1}{2}}$ - 2.02 V *versus* s.c.e. and (7, R = Br) which has the first $E_{\frac{1}{2}}$ - 2.92 V *versus* s.c.e. in dimethylformamide gave (7, R = H). In these reactions, removal of the halogen atoms is probably stepwise but the pure monohalogenointermediates cannot be isolated. Both halogenoderivatives show other polarographic waves at more negative potentials corresponding to the reduction of (7, R = H).[4] In the presence of 1% deuterium oxide, up to two deuterium atoms were incorporated during reduction of (7, R = Br) but no deuterium was incorporated during reduction of (7, R = Cl). We suggest that the σ-radicals generated during reduction of aryl halides are reduced further by either mechanism discussed in the previous paragraph. Which reaction predominates is dependent on the proximity of the newly generated radical to the electrode surface, and on the electrode potential which must be sufficiently negative to reduce the radical. In the case of chloroderivative (7, R = Cl) the first formed radical-anion has sufficient time to diffuse from the electrode surface before it decomposes to a σ-radical which decompos to a σ-radical which abstracts a hydrogen atom from the dimethylformamide. The radical-anion from the bromoderivative (7, R = Br) decomposes more rapidly and close to the electrode surface to a σ-radical which is then reduced with incorporation of deuterium.

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