Intramolecular Radical Cyclization Reactions — Scope and Limitations for Electrochemical Processes

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Auteur	Grimshaw, James [1], Grimshaw, Jadwiga T [2], Gibson, Mandy [3], Dias, Marylène [4]
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Résumé en anglais	Radical-anions formed by one electron attachment to aryl halides undergo cleavage of the carbon-halogen bond in a unimolecular process to give an aryl σ-radical and halide ion. Aryl σ-radicals are highly reactive intermediates and the objective of our work is to find conditions under which they can be trapped in an intramolecular reaction by an adjacent phenyl or alkene substituent. Further steps lead to a stable cyclised product and the process is of interest in synthesis. The corresponding intermolecular reactions between phenyl radicals and either benzene or an alkene have been shown to have bimolecular rate constants1 in the range 105 to 108 M−1s−1 so that the related intramolecular and unimolecular processes are expected to be very fast. Alternative reactions for the aryl σ-radical intermediates include abstraction of a hydrogen atom from the solvent and further electron transfer at the electrode surface to form a carbanion which undergoes protonation.
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