RING CLOSURES OF ARYL RADICALS

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SUMMARY

The ring closure of aryl radicals bearing suitable unsaturated ortho side chains is an efficient, regiospecific process which is of potential utility in organic synthesis.

A variety of reagents has been used to generate aryl radicals; this thesis examines methods of radical generation and develops convenient, new procedures for the preparation of cyclic compounds.

Procedures involving sodium iodide, tri-n-butyltin hydride, sodium methoxide, copper halides, nitroxides or thiolate ions have been demonstrated to be particularly effective for cyclizing appropriate diazonium salts. Methods involving the generation of the radicals from aryl halides are less efficient.

The scope of the reaction has also been examined. The reaction is effective for the synthesis of 5- or 6-membered rings by exo mode ring closure; cyclization in the exo mode to form 7-membered rings is, however, too slow to compete effectively with interception of the aryl radicals by intermolecular processes.

A number of mechanistic inferences evolve from this work.

In many cases, the electron spin resonance spectra of the cyclized radical intermediates have been observed, both directly and by spin trapping experiments.