

Oxidative Cyclization of the Dianion of 1,3-Diphenylpropan-2-one

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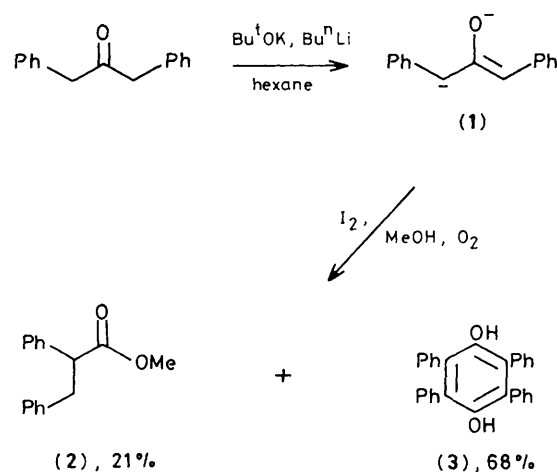
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Oxidation of the dianion of 1,3-diphenylpropan-2-one with iodine or ethylene dibromide gives methyl 2,3-diphenylpropionate (2) and tetraphenylhydroquinone (3).

Although the chemical consequences of oxidation of mono-anions have been peripherally studied,¹ little is known about dianion oxidations. We report here a new cyclization from a ketone dianion which, depending on conditions, leads either to functionalized six-membered rings or to rearrangement products derived from a cyclopropanone.

When 1,3-diphenylpropan-2-one is treated sequentially with potassium *t*-butoxide and *n*-butyl-lithium (2 equiv. each) in hexane, an orange-red solution of the dianion (1) is formed. Upon treatment with a chemical oxidant (*e.g.* I₂ or ethylene dibromide) followed by quenching with methanol, the dianion is converted into two products, Scheme 1.[†] The first, methyl-2,3-diphenylpropionate (2)[‡] is a known product of methanolysis² of 2,3-diphenylcyclopropanone, formed *via* a Favorski-like oxidative cyclization.³ The second product, tetraphenylhydroquinone (3)[‡] results from dimerization and

subsequent oxidative aromatization. The latter compound is obtained in yields sufficiently good to make this route potentially attractive for the synthesis of six-membered rings. Unfortunately, high yields are obtained only from stabilized



Scheme 1

[†] The reaction was conducted by adding sequentially at room temperature 2 equiv. of each base as a dilute solution in hexane. After stirring for 1 h, I₂ (2 equiv.) was added. After 20 min, the mixture was poured into excess of methanol and extracted with ether. The organic layer was washed with dilute aqueous sodium thiosulphate and saturated sodium chloride before being dried over MgSO₄.

[‡] Structures (2) and (3) were assigned on the basis of spectral comparison with authentic samples.

dianions; the dianions of 1-phenylpropan-2-one⁴ and 2,6-dimethylheptan-4-one, for example, give only poor yields of cyclization under similar conditions.

If the dianion is generated with lithium di-isopropylamide in tetrahydrofuran, and the mixture worked up with water after iodine oxidation, no monomeric products [*e.g.* (2) or isomers] can be detected. The product (3) and a presently unidentified isomeric dimer of (1) are formed in near quantitative yield.

Investigations are continuing to examine the role of the associated cation and ion pairing on the preferred route of oxidative cyclization.

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