

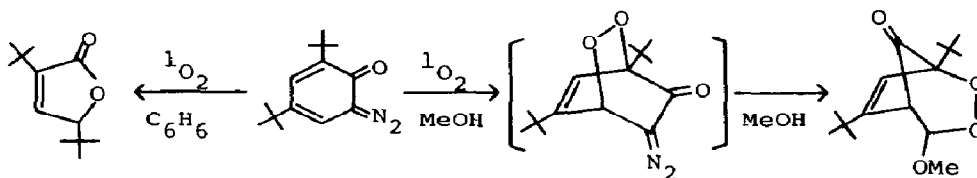
Photosensitized oxygenation of di-*tert*-butyl-2-diazo-1,2-benzoquinone

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Several reactions have been reported as non-enzymic models for the enzymatic hydroxylation and cleavage of aromatic compounds by singlet oxygen, superoxide, molecular oxygen activated by salts, and carbonyl carbonyl oxide. In the hope of generating carbonyl carbonyl oxide or the hydroperoxy hemiketal directly in the non-enzymatic oxidation of *o*-benzoquinone, the photosensitized oxygenation of 4,6-di-*tert*-butyl-2-diazo-1,2-benzoquinone was studied and the unusual bicyclic carbonyl peroxide was isolated with a high yield.

The bicyclic carbonyl peroxide decomposed at 80 °C in benzene to cyclopentadienone epoxide and 4,6-di-*tert*-butyl-2-pyrone together with methyl formate.



The importance of light intensity in photochemical reactions

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It has been known for many years that quantum yields of photochemical reactions can vary with light intensity, but the fact that products can also vary has only been reported in a few cases. We investigated the effect of light intensity in the classical photopinacolization of benzophenone (BP) in aliphatic alcohols. The classical mechanism is shown to be correct only for the special case of a high concentration of ketone and a low light intensity. At high intensities (using conventional light sources, not lasers) unsymmetrical pinacols (from one molecule of BP and one molecule of alcohol) and *p*-substituted benzophenones are formed; with primary alcohols these may constitute the major products. The effect of quenchers in reducing the effective light intensity also leads to changes in product composition paralleling those observed at reduced light intensity. The results obtained are not consistent with the proposal that the reaction of BP with isopropyl alcohol involves 90% of free radicals plus a 10% in-cage component; this