

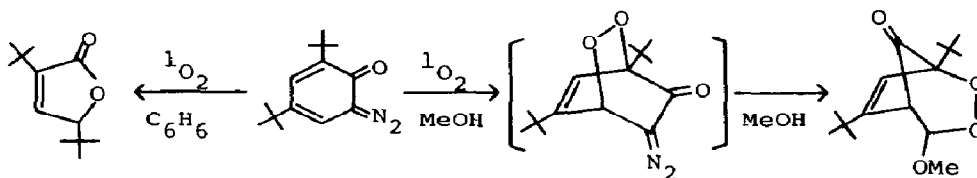
Photosensitized oxygenation of di-*tert*-butyl-2-diazo-1,2-benzoquinone

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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

is shown to be incorrect. A general mechanism for BP photopinacolization is proposed. It may also be noted that measurements at low light intensities (*e.g.* quantum yield determinations) and at high light intensities (*e.g.* flash photolysis) in a given system may be probing different mechanisms.

Time-resolved spectroscopy and chemical reactivity of energetic transient species of nitroaromatics

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Electronic excitation of trinitrobenzene (s-TNB) leads to a charge transfer complex between deprotonated s-TNB and molecular oxygen. Electronic excitation of trinitrotoluene (s-TNT) generates an *aci*-quinoid transient in non-polar solvents. In the gas phase, electronic excitation of s-TNT forms the 2,4,6-trinitrobenzyl radical. This species is also formed from electronically excited s-TNT, 2,4,6-trinitrobenzyl chloride and hexanitrobibenzyl in 1,4-dioxane at room temperature and in ether–isopentane–ethanol at 77 K. Nanosecond laser spectroscopy and kinetic studies of nitronaphthalenes indicate that the triplet states of these molecules behave like η, π^* states in non-polar solvents while in polar solvents the η, π^* character is reduced with a simultaneous increase in the charge transfer character of the states. Because of the symmetry of nitro substitution, the triplet state of 1,4-dinitronaphthalene remains η, π^* even in polar solvents.

Magnetic field effect on triplet sublevel relaxation: a novel method to probe the dynamics of short-lived triplet intermediates in photoreactions

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A mechanism is described whereby the influence of an external magnetic field on the relaxation between the sublevels of an electronically excited triplet state, which is subject to sublevel-selective deactivation, modulates the yield of photochemical products originating from such a triplet intermediate. A theory of this novel magnetic field effect is outlined and its first experimental application to determine the absolute decay constants of short-lived triplet exciplexes be-