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Preliminary communication

Boron photochemistry
VII. Photochemically induced electron transfer from tetraphenylborate anion to singlet oxygen

J.C. DOTY, P.J. GRISDALE, T.R. EVANS and J.L.R. WILLIAMS
Research Laboratories, Eastman Kodak Company, Rochester, New York 14650 (U.S.A.)

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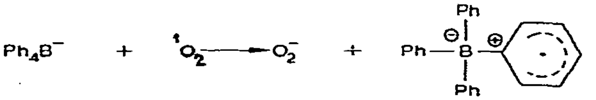
The "ate"-type photochemical rearrangement of tetraarylborate salts leads to the intramolecular formation of mixtures of biaryls and dihydrobiaryls[1,2], the ratio of which depends on the amount of triplet oxygen present during photolysis. We now report the rearrangement of sodium tetraphenylborate to biphenyl by the action of Rose Bengal-generated singlet oxygen. When a 0.25% solution of sodium tetraphenylborate in water containing 0.025% Rose Bengal was irradiated in the presence of oxygen a 75% yield of biphenyl was obtained. In the absence of either Rose Bengal or oxygen no appreciable photolysis occurred. Attempts to utilize singlet oxygen formed by reaction of bromine with hydrogen peroxide failed since there was direct attack of bromine on tetraphenylborate anion. Singlet oxygen generated from the mole ozonide of triphenylphosphite yielded the same products as those obtained from the photolysis of Rose Bengal-oxygen mixtures. The Rose Bengal-oxygen method is preferred since complicated intermolecular phenylation reactions involving triphenylphosphate occur when the ozonide method is used.

Since no photolysis occurred in the absence of oxygen, we at first believed that singlet oxygen produced by Rose Bengal was involved in a direct attack upon the tetraphenylborate anion. It was difficult to rationalize at what point singlet oxygen could attack the tetracoordinate tetraphenylborate anion, which is stable towards triplet oxygen. On the other hand, trigonal triphenylborane reacts rapidly with triplet oxygen owing to the presence of an empty *p*-orbital. We have postulated that variations of the product ratios for the unsensitized reactions in the absence and the presence of oxygen are due to the formation of an oxygen-sensitive trigonal boron intermediate[3]. A related process under these conditions would require that interaction between Rose Bengal and the tetraphenylborate anion yield a trigonal intermediate which would be attacked by singlet or triplet oxygen. However, the endothermic energy requirements rules out either singlet or triplet energy transfer processes from excited Rose Bengal to the borate anion.

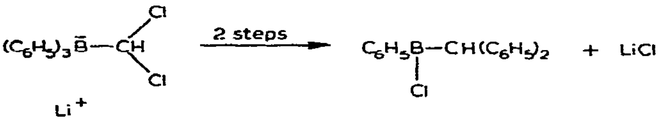
Thus we considered the attack of singlet oxygen on a phenyl group in the ground state of the tetraphenylborate anion. Cooper and Powell[4] have shown that protonation of sodium tetraphenylborate can occur at a point in one of the phenyl rings. Attack by singlet oxygen in one of the phenyl groups seems unlikely since oxygenated products such as hydroxybiphenyl are formed only in minor amounts. We have also considered that singlet energy transfer might occur from singlet oxygen to the tetraphenylborate anion. This is impossible since singlet oxygen in its highest energy state $(^1\Sigma_g^+)$ possesses only 37 kcal/mole and the $\pi \rightarrow \pi*$ transition of sodium tetraphenylborate requires approximately 102 kcal/mole.

A possible explanation of our results is prompted by the work of Geske[5] who showed that the electrooxidation and ceric ion oxidation of sodium tetraphenylborate proceed via electron-transfer mechanisms. Therefore, we propose that in the present case the process proceeds not by an energy-transfer mechanism but by an electron-transfer mechanism from the π-system of the tetraphenylborate anion to singlet oxygen. This would be the primary step in the pathway leading to biphenyl and would yield a cationic center adjacent to the boron atom.



The photochemical rearrangement of sodium tetraphenylborate to biphenyl and 1-phenyl-1,3-cyclohexadiene appears to occur also when an electron-deficient carbon bond to boron is produced[2,6].

Kōbrich and Merkle[7] have demonstrated intramolecular phenyl migration from boron to an electron-deficient carbon in the reaction of triphenylborane with dichloromethyllithium.



Further evidence for electron transfer has been found in our most recent experiments using 2,5-diphenyloxazole as the light-absorbing species. Irradiation under nitrogen of 0.1 molar solution of sodium tetraphenylborate in isopropanol containing 10% by weight of 2,5-diphenyloxazole yielded 29% biphenyl, 33% phenyl-1,4-cyclohexadiene and 28% 1,6-diphenylhexadienes[2] in a conversion of 94%. The fact that the energy of the singlet state of sodium tetraphenylborate lies at 104 kcal/mole and that of 2,5-diphenyloxazole at 84 kcal/mole rules out singlet energy transfer in favor of an electron-transfer process.

We are now studying the scope of these processes by varying both the light-absorbing species and the structural characteristics of tetraarylborate anions.

EXPERIMENTAL

Irradiations using Rose Bengal

Irradiations were carried out in a Pyrex-glass, double-jacketed reaction vessel. Cooling water was circulated through the inner jacket. The outer jacket, which was spaced 1 cm from the inner one, contained a solution prepared from 36 g of calcium chloride, 20 g of cupric chloride and 100 ml of dilute hydrochloric acid. A 150-W, medium-pressure Hanovia arc was placed in the source well. A 0.25% aqueous solution of sodium tetraphenylborate containing 0.025% of Rose Bengal was placed in the reaction vessel. Air was passed through the reaction solution during an irradiation period of 5 h.

A 75% yield of biphenyl (72% conversion) was obtained by isolation techniques previously described[1]. The unreacted tetraphenylborate anion was precipitated and isolated as the potassium salt.

Irradiations using 2,5-diphenyloxazole

The irradiations were carried out using a Pyrex-glass reaction vessel which was placed in a Rayonet 3500-Å photochemical reactor. Nitrogen was bubbled through the reaction medium during the irradiation. After 24 h of irradiation a solution of 0.1 *M* sodium tetraphenylborate in isopropanol containing 10% by weight (based on sodium tetraphenylborate) of 2,5-diphenyloxazole produced 29% biphenyl, 33% phenyl-1,4-cyclohexadiene and 28% of a mixture of 1,6-diphenylhexadienes at a conversion of 94%. The product isolation techniques were described previously[1]. The 2,5-diphenyloxazole was essentially unchanged as determined by absorption spectra taken before and after irradiation.

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