PHOTOOXYGENATION OF TRIPHENYL PYRYLIUM AND THIOPYRYLIUM CATIONS

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The formal replacements of a -CH= group of benzene by $-\overset{+}{O}=$ and $-\overset{+}{S}=$ groups give 6π non-benzenoid aromatic systems, pyrylium and thiopyrylium cations, respectively. Both the cations are supposed to be resonance hybrids of Kekulé-type structures (A) and carbonium ion structures (B) in the ground state.
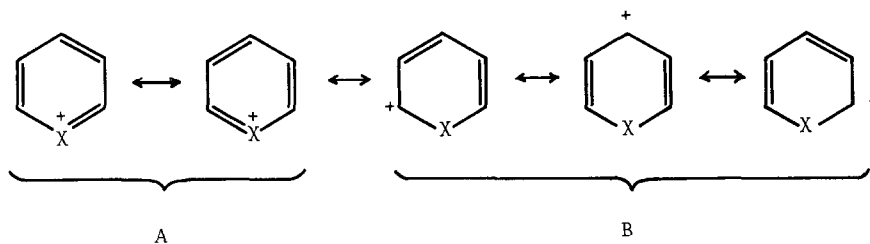
It is well known that aromatic hydrocarbons such as anthracene, rubrene and tetracene undergo photooxygenations.[1] Recently, the reactions of a few non-benzenoid aromatic compounds such as tropone and heptafulvene have been reported.[2] For these cases, a number of papers have provided evidence that singlet oxygen is the reactive species.[3] On the other hand, van Tamelen and Cole reported very recently that the ground state oxygen reacts with the excited triplet cation in the photooxygenation of trityl cation.[4] We are interested in the photooxygenations of pyrylium and thiopyrylium cations because of the presence of two possible mechanisms for the reactions. One is the mechanism that the ground state cations react with singlet oxygen, in which the Kekulé-type structures dominantly contribute to the resonance hybrids, and another is that the excited triplet cations react with the ground state oxygen, in which

the carbonium ion structures are of much importance.

The cations employed in this study are 2,4,6-triphenyl pyrylium (1) and thiopyrylium (2) cations as the form of perchlorate.
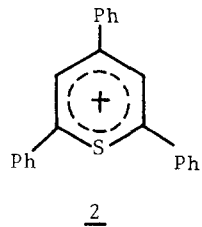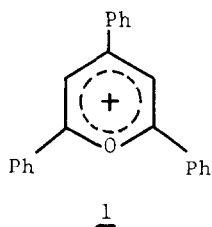
This is the first case of the photooxygenations of non-benzenoid aromatic cations. The reactions were carried out under oxygen atomosphere in a pyrex vessel at room temperature using a 450W high pressure mercury lamp as an external light source in methanol, ethanol and isopropanol. After 20 hours irradiation, the solvent was evaporated under reduced pressure, and the residue was gaschromatographed. The results are summarized in Table 1.

Table 1

Photooxygenation of 1 and 2 in methanol, ethanol and isopropanol.

Cation	Solvent	Product[*1] (Yield[*2], %)				
	MeOH	3(trace),	4(28),	5(19),		6(39)
1	EtOH	3(trace),	4(19),	5(7),	7(26),	6(33)
	iso-PrOH	3(10),	4(14),	5(8),	8(25),	6(27)
2	MeOH	9(trace),	4(43),	5(26),		6(17)

*1 The products were analyzed by glpc and identified by comparison with the ir spectra and retention times on glpc of their authentic materials. Numbers correspond to the following products; 3: Phenol, 4: Benzaldehyde, 5: Methyl benzoate, 6: Benzoic acid, 7: Ethyl benzoate, 8: Isopropyl benzoate, 9: Thio-phenol.

*2 Biphenyl was used as an internal standard.

When 1 in methanol was irradiated in the presence of methylene blue as a sensitizer under oxygen atomosphere, with the light of wavelength longer than 450 mµ, where methylene blue absorbs light, 1 was recovered quantitative-ly. Also in case of 2, the starting material was recovered. A possibility that 1 and 2 behave as a quencher was excluded by the following experiment; the attempted photooxygenation of tetramethylethylene in the presence of methylene blue and 1 or 2 gave the hydroperoxide of tetramethylethylene. From these results, it was found that 1 and 2 in the excited triplet state (10) react with the ground state oxygen, but those in the ground state not with singlet oxygen. Quite a different behavior of 1 and 2 from that of other non-benzenoid aromatic compounds[2] in the photooxygenations clearly in-dicates the considerably much contribution of the carbonium ion structures to the ground state of 1 and 2. This is reasonable since singlet oxygen is generally admitted to be electrophilic.[5]

A probable reaction course consistent with the above observation is shown as follows;
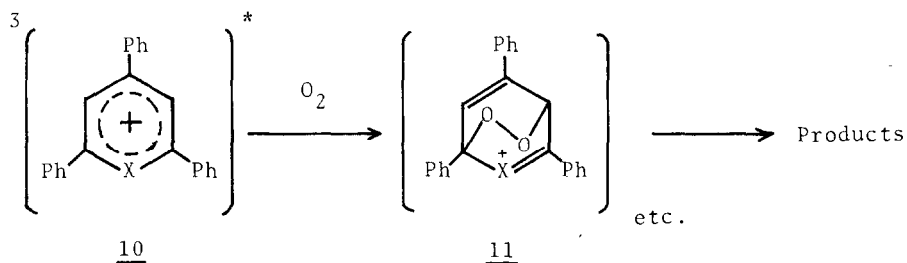
The products would be obtained by the complicated fragmentation of the reaction intermediate peroxides,(11). Although it was unsuccessful to trap the peroxides by irradiation of 1 in the presence of triphenylphosphine, the method of para-localization energy proposed by Brown[6] suggested the possibili-ty for 11 to exist as the reaction intermediate.[7] The fragmentation process

of the peroxides to the products is under investigation.

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(7) In the case of 2, the para-localization energy is obtained to be $3.41(-\beta)$,
    wich is nearly equal to $3.31(-\beta)$ for anthracene.