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EFFECT OF LIGHT WAVELENGTH ON PHOTOOXYGENATION OF HEXAMETHYLBENZENE

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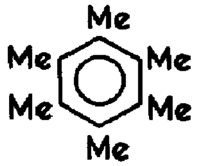
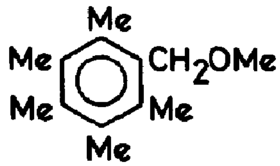
Abstract: Irradiation of the charge transfer complex of hexamethylbenzene with oxygen at 313 nm in a mixture of methanol and benzene afforded methoxymethylpentamethylbenzene and methoxypentamethylbenzene.

There has been discrepancy between the reported results on dye-sensitized photooxygenation of hexamethylbenzene(I).[1,2] Wasserman et al. reported that irradiation of I in a mixture of methanol and benzene in the presence of methylene blue(MB) in a Pyrex flask with a sun lamp afforded the monoether(II), diether(III), and phthalide(IV) as isolable products.[1] The reaction was explained as autoxidation of I initiated by excited MB.[1] On the other hand, recently van den Heuvel et al. reinvestigated this photooxygenation by irradiating I with MB or rose bengal with light longer than 520 nm, and isolated, as a sole product, the peroxide(V), which certainly resulted from 1,4-addition and ene-reaction of singlet oxygen with I.

We now wish to report our findings on the photooxygenation of I showing that the reported discrepancy originates from difference of excited species participating in the reaction depending on the effective wavelength of incident light.


I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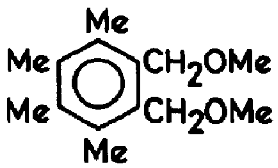
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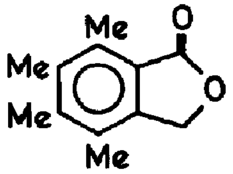
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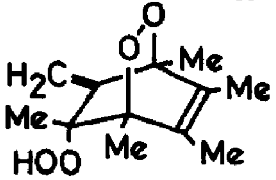
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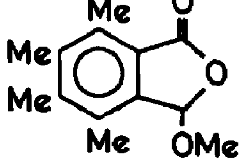
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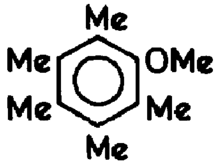
VII

The longest wavelength absorption maximum of I is at 278 nm in cyclohexane. However, on saturation of the solvent with oxygen a new absorption band appeared in the range of 285-360 nm (λ_{max}: 291 nm), and this band disappeared reversibly on introduction of argon to exclude oxygen. The new band is reasonably attributed to a charge transfer(CT) complex between I and oxygen[3] in view of the previous reports on the formation of CT complexes between electron-rich aromat compounds and oxygen.[4] Consequently, when mercury lamps are employed as a lig source, 254-nm light is expected to excite I directly and 313-nm light to exci the CT complex.

Irradiation of I (1.00 g) under oxygen in the presence of MB (0.05 g) in methanol-benzene(1:1) (700 ml) with a 650-W tungsten-bromine lamp through a Py wall (effective in the visible region) led to consumption of I (68%) and gave (57%)[5] as reported by van den Heuvel et al.[2]

Direct irradiation of I (1.44 g) under oxygen in methanol-acetonitrile(1: (200 ml) with a 160-W low pressure mercury lamp through a quartz wall (effecti at 254 nm) for 12 h led to oxidative degradation of I (conversion: 67%). Colu chromatography of the reaction mixture afforded IV (5%) and its derivative(VI) (2%) as isolable products, possibly through direct excitation of I followed by its reaction with oxygen.

Irradiation of I (3.00 g) in methanol-benzene(1:1) (360 ml) under oxygen with a 400-W medium pressure mercury lamp through a Pyrex wall (effective at 3 nm) for 31 h (conversion: 98%) afforded II (24%) together with the pentamethyl anisole(VII) (5%) probably through excitation of the CT complex. Furthermore, in an attempt to reproduce the reaction condition employed by Wasserman et al. photooxygenation of I (2.00 g) was carried out in the presence of MB (0.03 g) under illumination for 7.5 h with the medium pressure lamp through a Pyrex wal leading to II (13%) and VII (4%), but none of V (conversion: 99%).

These results would indicate that, even in the presence of MB, unless visible light is efficiently utilized, excitation of the CT complex of I with oxygen plays an important role in the overall reaction and singlet oxygen scarcely participates in the reaction.

Investigation concerning the detailed mechanism and extending photochemic behaviour of the CT complex is now in progress.

References and Notes

1) H. H. Wasserman, P. S. Mariano, and P. M. Keehn, J. Org. Chem., 36, 1765(19
2) C. J. M. van den Heuvel, H. Steinberg, and Th. J. de Boer, Recl., J. Roy. Netherl. Chem. Soc., 96, 157 (1977).
3) Mesitylene and durene also exhibited CT bands with oxygen.
4) M. Tamres and R. L. Strong, in "Molecular Association," Vol. 2, ed. by R. Foster, Academic Press, London (1979), p. 397.
5) In the present work, all products were separated by column chromatography a tlc on silica gel, and identified on the basis of spectral data. The yield denote those actually isolated and are based on I consumed.
6) The use of a mixture of methanol and benzene as a solvent did not lead to oxidation of I probably owing to light absorption by benzene.

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