Tetrahedron Letters No.57, pp. 4987-4990, 1970. Pergamon Press. Printed in Great Britain.

PHOTOINDUCED REACTIONS. XLIV.

REACTIVITY OF SINGLET OXYGEN TOWARD METHOXYBENZENES.[1)]

Isao Saito and Teruo Matsuura

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan.

(Received in Japan 27 October 1970; received in UK for publication 10 November 1970)

It is well known that, in the dye-sensitized photooxidation of olefins and dienes involving singlet oxygen, electron-donating substituents increases the reaction rate.[2)] In accordance with this, we previously reported the first example of the addition of singlet oxygen to some t-butylated methoxybenzenes.[3)] We now wish to report that the substitution of methoxyl groups to a benzene ring in appropriate positions causes the addition of singlet oxygen to the aromatic nuclei.

A series of methoxybenzenes(Ia~Il) was photooxidized in methanol solution containing rose bengal as a sensitizer.[4)] Among them, Ig and Ii~Il consumed smoothly an equimolar amount of oxygen, while Ia~If and Ih were found to be unreactive. Relative rates of photooxidation of Ig and Ii~Il were compared with the values of the half-wave oxidation potentials ($E_{1/2}$) and the frequencies of charge-transfer band ($\bar{\nu}_{c.t.}$) with tetracyanoethylene(TCNE) obtained by Zweig *et al*[5),6)](Table I).

Within the reacted methoxybenzene(Ig and Ii~Il) there is a good correlation between $E_{1/2}$ and the relative rate of photooxidation, while with the exception of 1,2,4-trimethoxybenzene (Ig) the frequency of charge-transfer maxima ($\bar{\nu}_{c.t.}$) is also linearly related to the relative rate (Fig. 1). It has already been demonstrated that, in a series of methoxybenzenes, $E_{1/2}$ or $\bar{\nu}_{c.t.}$ has a linear relation to π-ionization potential.[5)] Therefore, it may be concluded that the reactivity of Ig and Ii~Il is related to π-ionization potential. The Kearns selection rule predicts that, in the concerted addition of singlet oxygen ($^1\Delta g$) to olefins or dienes, molecules having lower π-ionization potential should be more reactive.[7)] These results indicate that the methoxybenzenes which have lower π-ionization potential are more reactive to singlet ($^1\Delta g$) oxygen.[8)]

Table 1. Relative Rate of Photooxidation of Methoxybenzenes.

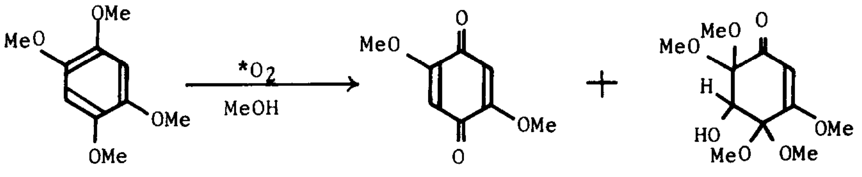
Compound		Relative Rate[a]	$E_{1/2}$(oxid),V,vs s.c.e[b] in CH_3CN	$\bar{\nu}_{c.t.}$[c] cm^{-1} $\times 10^3$
Anisole	(Ia)	0	+ 1.76	19.7
1,2-Dimethoxybenzene	(Ib)	0	1.45	16.9
1,3-Dimethoxybenzene	(Ic)	0	——	18.2
1,4-Dimethoxybenzene	(Id)	0	1.34	16.1
1,2,3-Trimethoxybenzene	(Ie)	0	1.42	19.4
1,3,5-Trimethoxybenzene	(If)	~ 0[d]	1.49	18.2
1,2,4-Trimethoxybenzene	(Ig)	0.086	1.12	14.6
1,2,3,4-Tetramethoxybenzene	(Ih)	0	1.25	17.9
1,2,3,5-Tetramethoxybenzene	(Ii)	0.150	1.09	16.5
1,2,4,5-Tetramethoxybenzene	(Ij)	1.0	0.81	12.5
Pentamethoxybenzene	(Ik)	0.185	1.07	16.4
Hexamethoxybenzene	(Il)	0.030	1.24	19.5

[a] Determined by competitive reactions at 20±4° by the known method[2a]. Error limits ±10%. [b] Reference 5. [c] With tetracyanoethylene in CH_2Cl_2.[6] [d] The compound was photooxidized at a negligible slow rate.

Some of the reaction products were isolated and characterized. Photooxidation of 1,2,4,5-tetramethoxybenzene(Ij) in methanol gave 2,5-dimethoxy-p-benzoquinone(II) (5 %) and an enone III (20 %) $C_{11}H_{18}O_7$[9]; mp 126°. The spectral properties of III are as follows; λ^{EtOH}_{max} 254 nm (logε 3.94); ν^{nujol}_{max} 3450, 1670, 1620 cm^{-1}, τ_{TMS}(in DMSO-d_6) 4.63 (s, 1H), 4.75 (d, J=5Hz, OH), 5.91 (d, J=5Hz, -$\overset{|}{C}$H-OH), 6.24 (s, 3H), 6.70 (s, 6H)[10], 6,76 (s, 3H), 6.92 (s, 3H). Acid hydrolysis of III in aqueous methanol gave an o-quinone IVa(15 %) $C_7H_6O_5$; mp 213-214°; λ^{EtOH}_{max} 450 nm (logε 2.86), 380 nm (logε 3.26), 290 nm (logε 4.12); ν^{nujol}_{max} 3400, 1710, 1670, 1640, 1610 cm^{-1}; τ_{TMS}(in acetone-d_6) 6.13 (s, 3H), 4.20 (s, 1H) 1.88 (s, OH), 1.72 (s, OH). Reduction with hydrosulphite and subsequent methylation with diazomethane of di-acetate IVb gave V, which was identical with the authentic sample.[11] The above results are in accordance with the structure III for the enone.

Photooxidation of pentamethoxybenzene(Ik) in methanol yielded a diketone VI(57 %); $C_{11}H_{16}O_7$; mp 120-122°; λ^{EtOH}_{max} 286 nm (logε 3.86), 214 nm (logε 3.80); $\nu^{CHCl_3}_{max}$ 1770(broad), 1680, 1610 cm^{-1}; τ_{TMS}(in $CDCl_3$) 4.10(1H), 6.04(3H), 6.42(6H), 6.44(6H), all appears as singlet. Treatment of VI with o-phenylenediamine gave an adduct VII ; $C_{17}H_{20}O_5N_4$; mp 146°;

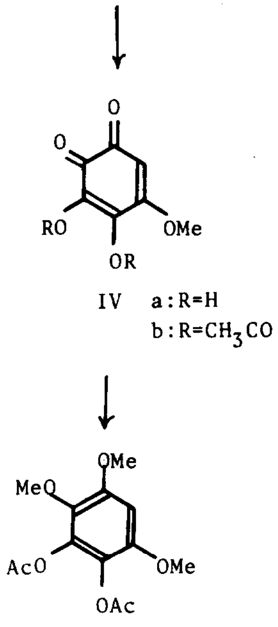
λ_{max}^{EtOH} 368 nm (logε 4.13), 354 nm (logε 4.17), 280 nm (logε 4.41), 250 nm (logε 4.16), 222 nm (logε 4.48); ν_{max}^{nujol} 1650, 1560 cm^{-1}; τ_{TMS}(in $CDCl_3$) 1.80~2.50 (m, 4H), 3.95 (s, 1H), 6.05 (s, 3H), 6.41 (s, 6H), 6.42 (s, 6H). Hydrogenation (Pd-C) of VI in ethanol gave 3,4,5-trimethoxycatechol VIII[11]. The results led us to assign the structure VI for the diketone. The structure of other products and the mechanism of the reaction are under investigation.



Ij

II

III



IV a:R=H
b:R=CH_3CO

V

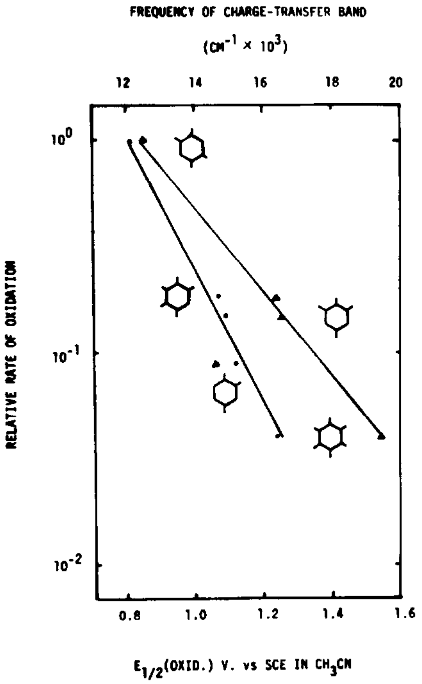
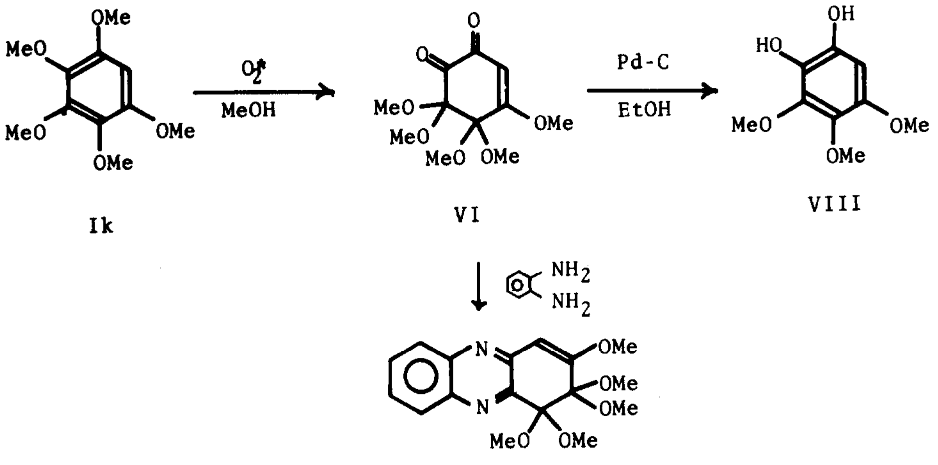


Figure 1. Semilog plot of the relative rate of photooxidation of methoxybenzenes (Ig, Ii ~ Il) vs. half-wave oxidation potentials (●) and frequency of charge-transfer maxima with TCNE (▲).



Ik VI VIII

VII

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7. D. R. Kearns and A. U. Khan, Photochem. Photobiol., **10**, 193 (1969); D. R. Kearns, J. Am. Chem. Soc., **91**, 6554 (1969). They have shown that, in some substituted olefins, there is a good correlation between ionization potential and reactivity toward singlet oxygen.
8. Oxidation with singlet oxygen generated from hydrogen peroxide and hypochlorite could not be applied to the methoxybenzenes (Ig and Ii～Il), which were found to be easily oxidized with hydrogen peroxide alone in methanol to give corresponding quinones.
9. Satisfactory microanalyses were obtained for all new compounds and the molecular formulas were confirmed by mass spectrometic analyses.
10. This peak appears as two lines (τ 6.53 and 6.55) in $CDCl_3$.
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