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Photooxygenation Reactions of 4-Flavanols and Benzylic-type Alcohols

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On irradiation in benzene under oxygen atmosphere *cis*- and *trans*-4-flavanols gave flavanones with significant structural effects on the yield: A high cis/trans selectivity and enhancement effect by electron-donating substituents. A series of benzylic-type alcohols showed similar substituent effects. The structure-reactivity relationships were explained in terms of the stereoelectronic requirements for favorable overlapping of intermediates. In order to infer the active oxidant species, the above photoreactions were compared with the oxidations by singlet oxygen and superoxide ion. The involvement of superoxide ion or its related species such as electron transfer complex $R^{+\cdot}\cdots O_2^{-\cdot}$ was suggested. The effects of additives and solvents were also investigated.

A detailed study has been reported on the photooxidation reaction of a series of benzylic-type alcohols in DMSO under oxygen atmosphere, showing a special effects of DMSO or the formation of a charge transfer complex.[1] On the other hand, a high stereoselectivity has been observed for the thermal oxidations of secondary alcohols[2] and a series of 4-chromanols[3] with chromium trioxide, which has been attributed to both the stereoelectronic effect and the strain relief. A significant cis/trans selectivity has also been observed in the oxidation of cis and trans isomers of 4-flavanols with the triplet state benzophenone, which has been explained in terms of the stereoelectronic requirements or favorable overlapping of the radical intermediates.[4]

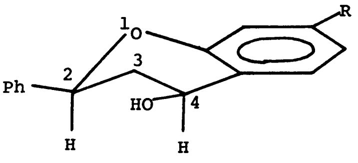
The present paper reports on the structural effects in the photooxygenation reactions of 4-flavanols **1**—**3** and the related benzylic-type alcohols **4**—**11** (Chart 1).

Results and Discussion

Photooxygenation Reactions. Table 1 summarizes the yields of flavanones formed in the photooxidations of 4-flavanols under oxygen atmosphere, in benzene (benzene/O_2), in benzene-diphenyl sulfone (benzene-DPSO/O_2), and in dimethyl sulfoxide (DMSO/O_2), respectively. No reaction products were detected from a benzene solution of **1a** after bubbling through with oxygen gas for 8.5 h in the dark, while only a trace amount of flavanone was detected by TLC analysis on irradiation under nitrogen atmosphere in place of oxygen.

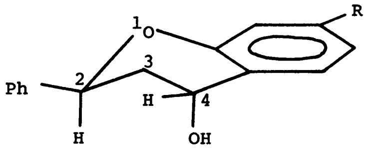
In the above photoreactions two points may be noted as to the structural effects of the substrates: (i) the cis isomers (**1a, 2a, 3a**) show higher reactivities compared with the corresponding trans isomers (**1b, 2b, 3b**), (ii) electron donating substituents at the 7-position facilitate the reaction. The latter (ii) implies the electrophilic nature of the intermediates while the former (i) suggests the conformational requirements for the substrates and/or intermediates.

Table 2 shows relative reactivities of a series of benzylic-type alcohols (hereafter denoted as benzylic alcohols) in the photooxidations in benzene/O_2, in benzene-DPSO/O_2, and in DMSO/O_2, respectively.



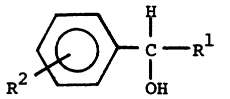
2,4-cis-4-Flavanols

1a R = H
2a R = Cl
3a R = OMe



2,4-trans-4-Flavanols

1b R = H
2b R = Cl
3b R = OMe



Benzylic alcohols

4 R^1 = Me R^2 = H
5 R^1 = Me R^2 = p-Cl
6 R^1 = Me R^2 = p-OMe
7 R^1 = Me R^2 = m-OMe
8 R^1 = Me R^2 = o-OMe
9 R^1 = Me R^2 = o,p-$(OMe)_2$
10 R^1 = H R^2 = H
11 R^1 = t-Bu R^2 = H

Chart 1.

Table 1. Photooxidations of 4-flavanols under different conditions

4-Flavanol	Percent yield of flavanone		
	Benzene/$O_2$$^{a)}$	Benzene-DPSO/$O_2$$^{b)}$	DMSO/$O_2$$^{c)}$
1a	22	34	20
1b	Trace	Trace	Trace
2a	35	44	22
2b	4	Trace	Trace
3a	53	d)	71
3b	12	d)	11

a) 4-Flavanol 0.04 mol dm^{-3} in benzene, under O_2 atmosphere, irradiation time 8 h. b) 4-Flavanol 0.04 mol dm^{-3}, diphenyl sulfone (DPSO) 0.04 mol dm^{-3} in benzene, under O_2 atmosphere, irradiation time 8 h. c) 4-Flavanol 0.025 mol dm^{-3} in dimethyl sulfoxide, under O_2 atmosphere, irradiation time 15 h. d) Photolyzed mixture solutions were too complex to analyze.

Table 2. Photooxidations of benzylic alcohols

Photooxidation system	Benzylic alcohol	Consumption of alcohol/%	Yield of acetophenone/%
Benzene/$O_2$$^{a)}$	**4**	12	12
	5	20	10
	6	32	29
	7	16	8
	8	10	8
	9	19	10
Benzene-DPSO/$O_2$$^{b)}$	**4**	51	45
	5	58	27
	6	98	19
DMSO/$O_2$$^{c)}$	**4**	10	10
	10	29	23$^{d)}$
	11	0	0

a) Benzylic alcohol 0.04 mol dm^3 in benzene, under O_2 atmosphere, irradiation time 10 h. b) Benzylic alcohol 0.04 mol dm^{-3}, diphenyl sulfone (DPSO) 0.04 mol dm^3 in benzene, under O_2 atmosphere, irradiation time 10 h. c) Benzylic alcohol 0.025 mol dm^{-3} in dimethyl sulfoxide, under O_2 atmosphere, irradiation time 15 h. d) Benzoic acid was also formed in 6% yield.

Table 3. Yields of acetophenones in the oxidation of benzylic alcohols with $O_2^{-}\cdot$$^{a)}$

Benzylic alcohol	Percent yield of acetophenone at				
	1 h	2 h	4 h	8 h	16 h
4	4	6	12	16	21
5	4	5	7	13	16
6	16	22	32	45	64
7			12		15
8			2		3
9			5		6
5/**6**$^{b)}$			6/37		13/55

a) Benzylic alcohol 3.3×10^{-2} mol dm^{-3}, KO_2 0.19 mol dm^{-3}, 18-Crown-6 3.3×10^{-2} mol dm^{-3} in benzene, under N_2 atmosphere, for 16 h at room temperature. b) A mixture solution of **5** and **6** each in 3.3×10^{-2} mol dm^{-3} were oxidized with $O_2^{-}\cdot$.

Relative reactivities of the *p*-substituted benzylic alcohols in benzene/O_2 show similar tendency (**4**<**5**<**6**) to that of 4-flavanols (**1a**<**2a**<**3a**). Although relative consumption rates in benzene–DPSO/O_2 also show similar tendency, the large gaps between the consumption of the substrates and the yield of acetophenones prevent detailed inspection.

On the other hand, ortho and meta substituents tend to lower the reactivity (**8**, **9** compared with **4**, **6**). Comparison of **4**, **10**, and **11** in DMSO/O_2 shows that bulky groups on the benzylic carbon depress the reaction in spite of the electron-donating ability, implying predominant role of steric factors over the stabilities of intermediates (*e.g.*, benzylic radicals).

Oxidations with Singlet Oxygen and Superoxide Ion. In order to infer the active oxidant species involved in the photooxygenation reactions, it seemed reasonable to compare the reactivities with those in the oxidations by singlet oxygen and superoxide ion, respectively. Oxidation of 4-flavanols by singlet oxygen gave the corresponding flavanones with high cis/trans selectivities (Table 4) which are comparable with those in Table 1. However, the substituent effect of the reactiviy order (**1a**>**2a**>**3a**) is the reverse to that in Table 1, thus suggesting different mechanisms. In the oxidation of 4-flavanols (R) with singlet oxygen in *t*-butyl alcohol, which is fairly polar solvent, superoxide ion may be generated from singlet oxygen *via* CT interaction[5,6] and act as the oxidant species, *e.g.*,

$$R + {}^1O_2 \rightleftharpoons R^{+}\cdot + O_2^{-}\cdot \longrightarrow RO_2 \rightarrow \rightarrow \text{products.}$$

Then, the difference in the reactivity order (Tables 1 and 4) may be due to the difference in the active oxidant species between superoxide ion (in *t*-butyl alcohol) and polar CT complexes (in benzene).

No sufficient data were available for the oxidation of 4-flavanols with superoxide ion (Table 4); the reaction in benzene gave mixtures too complex to analyze, except for **1a** and **1b** which show rather low cis/trans selectivity. In addition, reactions were complicated by the concomitant rearrangement reaction (ring opening). Thus, **1a**, **1b**, **2a**, and **2b** gave the corresponding 2′-hydroxychalcones stoichiometrically while **3a** and **3b** led to highly complex mixtures incapable of analysis.

As alternatives to the 4-flavanols, a series of benzylic alcohols may serve to see the structure-reactivity relationships in the superoxide ion oxidation. Table 3 illustrates the yields of acetophenone produced in the superoxide oxidation in benzene, showing that the reaction is fairly clean. The substituent effects on the reactivity are comparable to those in the photooxygenation reaction in benzene (Table 2). Thus, electron-donating substituents at the *p*-position facilitate the reaction (**4**—**6** and **5**/**6**), whereas the substituents at the ortho or meta position retard (**7**—**9**). From the similarities in the structure-reactivity relationships (Tables 1—3), it seems probable that the active oxidant species,

Table 4. Oxidations of 4-flavanols with $O_2^{-\cdot}$ and $^1O_2$

Oxidant and solvent	4-Flavanol	Consumption of flavanol/%	Yield of flavanone/%	Yield of chalcone/%
$O_2^{-\cdot}$/Benzene[a)]	**1a**	17	7	5
	1b	10	3	4
$O_2^{-\cdot}$/DMSO[b)]	**1a**	12	Trace	12
	1b	14	Trace	14
	2a	15	Trace	15
	2b	15	Trace	15
$^1O_2$/*t*-BuOH[c)]	**1a**		53	
	1b		Trace	
	2a		34	
	2b		Trace	
	3a		28	
	3b		Trace	

a) 4-Flavanol 0.025 mol dm^{-3}, KO_2 0.25 mol dm^{-3}, 18-Crown-6 0.025 mol dm^{-3} in benzene, for 2 h at room temperature. b) 4-Flavanol 0.025 mol dm^{-3}, KO_2 0.08 mol dm^{-3}, 18-Crown-6 0.025 mol dm^{-3} in dimethyl sulfoxide, for 3 h at room temperature. c) 4-Flavanol 0.13 mol dm^{-3}, Rose Bengal 3.3×10^{-4} mol dm^{-3} in *t*-butyl alcohol, irradiated with a W-lamp (300 W) for 5 h. Similar results were obtained with thionine sensitizer in place of Rose Bengal.

Table 5. Photooxidation of **4** in the presence of DPSO[a)]

DPSO added $\times 10^3$ mol dm^{-3}	Consumption of alcohol/%	Yield of acetophenone/%
0	4	4
2	9	9
4	11	11
8	17	17
10	22	19
20	20	20
40	25	25
80	40	32

a) 1-Phenylethanol 0.04 mol dm^{-3} in benzene, under O_2 atmosphere, irradiated for 10 h. A fairly worn-out light source (100-W Hg lamp) was employed in this irradiation and the intensity was much lower than that of the one used elsewhere in the present study.

involved in the photooxygenation reaction in benzene, is superoxide ion or its related species such as CT complexes. In fact 4-flavanols (**1a**, **3a**, and **3b**) in methanol under oxygen atmosphere showed broad enhancements of the UV-absorption in the region of 220—350 nm, which are ascribable to the charge transfer absorption.

Effects of Solvent and Additives. Photooxygenation of **1a** in different solvents under comparable conditions showed a wide variation in the yield of flavanone (%); ethyl acetate (100%), acetonitrile (61%), benzene (54%), DMSO (45%), 1,2-dimehoxyethane (13%), *t*-butyl alcohol (8%), DMF (trace).

Solvent polarity has been shown to play the key role in partitioning active species between the types of ion pairs and CT cmplexes present in solution.[6—9)] The reactivity order shown here is not in the order of solvent polarity, hence superoxide ion mechanism is of minor importance at least in less polar solvents.

Photooxidation of **4** in benzene/O_2 was significantly facilitated by the addition of small amounts of diphenyl sulfone (DPSO). Both the consumption of **4** and the yield of acetophenone were increased with increasing addition of DPSO (Table 5). The enhancement effect may be relevant to charge transfer phenomena as has been implied earlier in the photooxidation of benzylic alcohols in DMSO/O_2.[1)]

Table 6. Effects of additives on the yield of flavanone in the photooxidation of **1a** under oxygen atmosphere[a)]

Additive mol dm^{-3}	Percent yield of flavanone[b)] at 2 h	4 h	6 h	8 h	10 h
Nil	Trace	10	19	29	41
		12	24	30	
DABCO/0.02	0	0	0	Trace	
DTBP/0.02	Trace	22	37	58	
DMB/0.02	Trace	Trace	13	26	
TNM/0.02	76	100	100		
DPSO/0.04	24	43			
DPSO/0.04+DTBP/0.02	47				
DPSO/0.04+DMB/0.02	38				

a) In benzene solution of **1a** 0.02 mol dm^{-3}. DABCO: 1,4-diazabicyclo[2.2.2]octane, DTBP: 2,6-di-*t*-butylphenol, DMB: *p*-dimethoxybenzene, TNM: tetranitromethane, DPSO: diphenyl sulfone. b) Determined from the ^{1}H-NMR signal intensities at $\delta=5$.

The effects of other additives were also examined including 1,4-diazabicyclo[2. 2. 2]octane (DABCO) as a powerful detector for singlet oxygen,[5)] 2,6-di-*t*-butylphenol (DTBP) for free radicals,[10)] tetranitromethane (TNM) for superoxide ion,[11)] and *p*-dimethoxybenzene (DMB) as a competitor for the presumed CT complex formation of **1a** with O_2.[6)] Table 6 shows the additive effects on the percent yield of flavanone formed in the photooxidation of **1a** in O_2-saturated benzene. Insufficient supply of O_2 during photolysis gave somewhat different results. Thus, comparable irradiation of **1a** in sealed ampuls, after bubbling through with O_2 gas for 30 min, gave flavanone in 19% (additive/nil), 16% (DABCO/0.02 mol dm^{-3}), a trace (DMB/0.02 mol dm^{-3}), a trace (DTBP/0.02 mol dm^{-3}), respectively. Further, irradiation under air, in place of O_2 gas, led to no significant amount of the product.

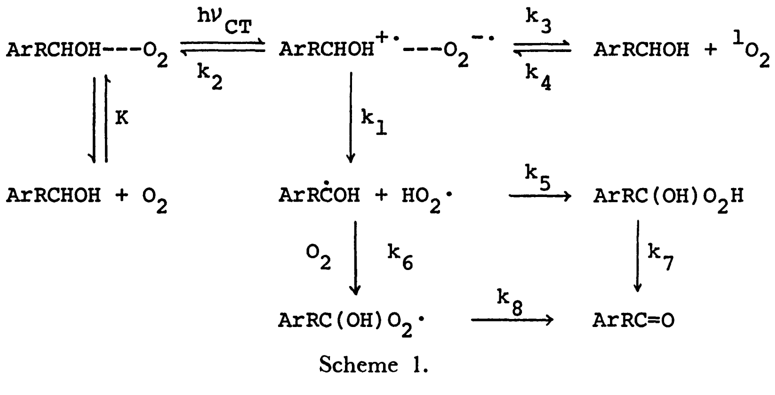
The remarkable enhancement effect by TNM implies the important role of CT interaction, while the strong depression by DABCO suggests the involvement of singlet oxygen. However, the photoreaction in sealed ampuls (O_2-insufficient conditions) was little subject to DABCO, hence singlet oxygen does not necessarily act as the oxidant species in its own form. The presence or absence of the depression by DABCO, depending on excess or deficiency of O_2, also implies that singlet oxygen is formed indirectly, *via* equilibria including complex formation which would become significant only in the presence of a large excess of O_2 (Scheme 1). The depression effect by DMB can be explained in terms of the competitive complex formation with oxygen species, which would be more significant in O_2-insufficient solution (Scheme 2). Also, it is notable that the photoreaction was enhanced by the combined addition of DPSO and DMB, as compared to the single addition of either, suggesting electron transfer sensitization by the additives.

Speculation on the Mechanism. Direct evidence has been reported for the generation of radical ions in electron transfer photooxygenation reactions in highly polar solvents.[7] In nonpolar solvents such as benzene, however, no such ion pair formation seems to occur but highly polar CT complexes are often formed.[6,12] The present photooxygenation reactions in benzene/O_2 can be explained in terms of Scheme 1, which is essentially similar to those proposed for the electron transfer photooxygenations of ethers,[13] amines,[12,14] and alkylbenzenes,[14,15] except for the inefficient generation of ion pairs in the present photoreaction. Here, ArRCHOH $\cdots O_2$ represents a contact pair between the substrate and oxygen in their ground states which is implied by the enhanced UV-absorption(250—300 nm). On excitation this will lead to a CT complex ($ArRCHOH^{+\cdot}\cdots O_2^{-\cdot}$), which will then undergo back electron transfer (k_2), proton transfer (k_1) to give the substrate radicals $ArR\dot{C}OH$, or the reversible formation of singlet oxygen (k_3, k_4). In the presence of DABCO efficient quenching of $^1O_2$ would occur to depress the photoreaction. The overall reaction efficiency will be governed by the ratio k_1/k_2 which in turn depends on the structure of the relative stability of $ArR\dot{C}OH$, if the subsequent processes (k_5, k_6) occur irreversibly. The in-cage radical coupling reaction (k_5) would proceed rapidly and little scavenged by added radical inhibitors such as DTBP.

In the presence of excess O_2 the out-of-cage reaction (k_6) would also occur efficiently before scavenged by DTBP. Disproportionation of the peroxyl radical (k_8) and decomposition of the hydroperoxide (k_7) will lead to the final products. The reactivity ratio of **3a**/**1a** or **4**/**6** is in the range of 2-3 (Tables 1 and 2), which corresponds to the Hammet reaction constant of $-0.6 \leqq \rho \leqq 1.4$, being consistent with the intermediacy of the substrate radicals.

The structure-reactivity relationships may be explained in terms of the stereoelectronic effects of the radical intermediates, assuming that the reaction efficiency is mainly determined by the ratio k_1/k_2 or the stability of the radical intermediate. Since the hydrogen atom on the 4-position is assigned to quasi-axial for the *cis*-4-flavanols **1a**—**3a** and quasi-equatorial for the trans isomers **1b**—**3b**,[16] the transition states or the 4-hydroxy-4-flavanyl radical intermediates would have conformations as [A] and [B], respectively (Chart 2). For the conformer [A] the *p*-type orbital on the 4-position is capable of overlapping with both the hydroxyl and phenoxyl groups. The conformer [B] is incapable of such coplanar overapping and less stable. Thus the cis/trans selectivity in Table 1 can be explained by the stereoelectronic effects of the intermediates. The substituent effects of benzylic alcohols (Table 2) may be explained in a similar manner. Thus, in the absence of ortho substituents the benzylic radicals can have the coplanar configuration [C] to allow favorable overapping with both the aryl and the hydroxyl groups. In the presence of ortho substituents such coplanarity would be sterically hindered, leading to unstable intermediates [D]. The methoxyl group at the meta position would destabilize the benzylic radicals due to its inductive effect while incapable of resonance effect, resulting in the slight depression of the product formation (**7** in Table 2). Photooxidations in DMSO/O_2 and in benzene-DPSO/O_2 show structure-reactivity relationships apparently similar to those in benzene/O_2, suggesting similar intermediates, $ArR\dot{C}OH$.

Highly complicated features are suggested for the



Scheme 1.

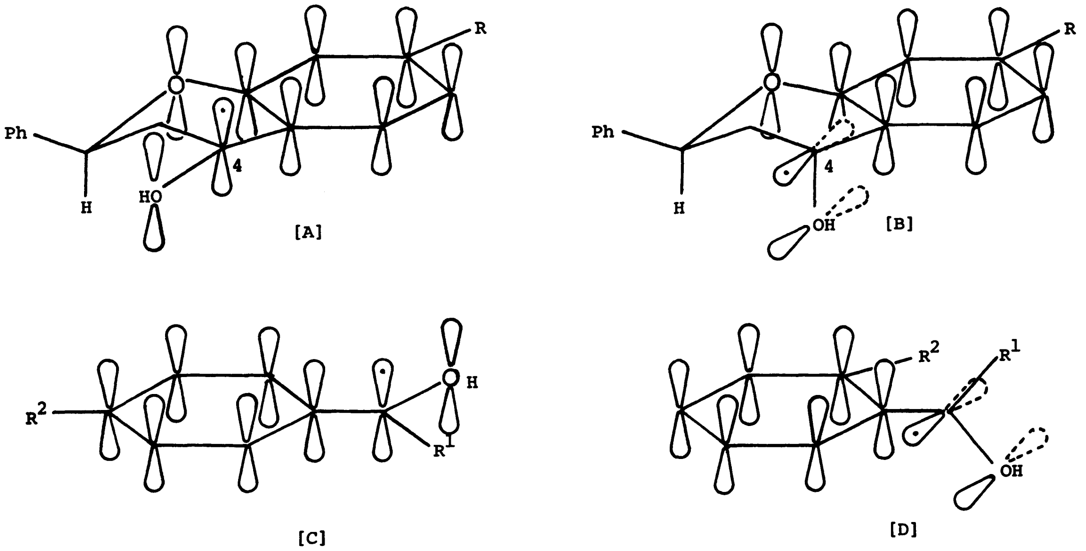
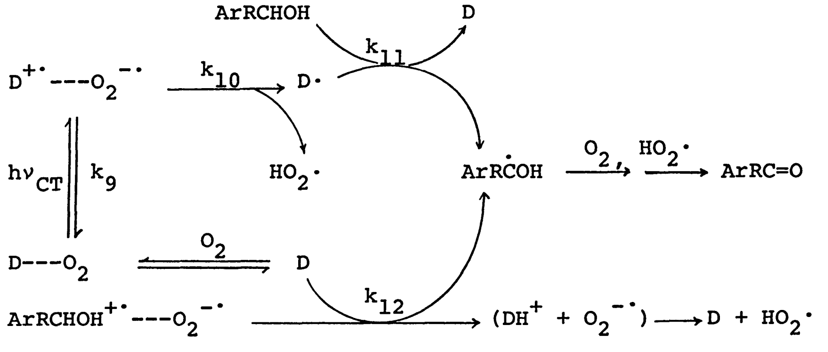
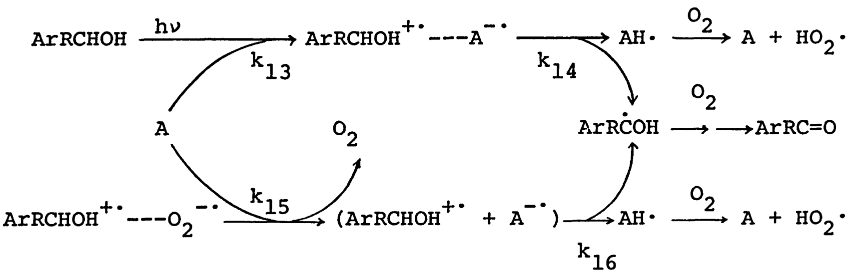


Chart 2.



Scheme 2.



Scheme 3.

effects of additives, since many of the additives can act on the various species present in the systems. For example, DTBP can be a good competitor for electron transfer interaction as well as a powerful scavenger of free radicals. It may also act as a carrier and/or initiator in free radical reactions.

Crude mechanisms are tentatively proposed for the effects of electron donors (Scheme 2) and electron acceptors (Scheme 3), respectively. In the presence of a good electron donor (D) such as DMB or DTBP, a CT complex of D ($D^{+\cdot}\cdots O_2^{-\cdot}$) may be formed on CT excitation of a contact pair ($D\cdots O_2$). These processes would not seriously affect the formation of $ArRCHOH\cdots O_2$ and $ArRCHOH^{+\cdot}\cdots O_2^{-\cdot}$, in the presence of excess O_2.

Subsequent proton transfer (k_{10}) will give radical D· which may undergo hydrogen abstraction from the substrates (k_{11}) to give the radical $ArR\dot{C}OH$. Alternatively, proton transfer from $ArRCHOH^{+\cdot}\cdots O_2^{-\cdot}$ to D may proceed (k_{12}) to facilitate the formation of $ArR\dot{C}OH$, thus eventually enhancing the product formation. The enhancement effects of D may be also due to the increased solubility or concentration of O_2 gas *via* contact pair formation.

In the presence of a good electron acceptor (A) such as TNM or DPSO, on the other hand, another type of CT complex ($ArRCHOH^{+\cdot}\cdots A^{-\cdot}$) may be formed ($k_{13}$), followed by proton transfer (k_{14}) to give $ArR\dot{C}OH$ (Scheme 3). Alternatively, electron transfer from $ArRCHOH^{+\cdot}\cdots O_2^{-\cdot}$ to A may occur (k_{15}).

Subsequent proton transfer (k_{16}) will lead to $ArR\dot{C}OH$, thus eventually facilitating the photoreaction.

Experimental

Apparatus and Procedure. The light source for irradiation was a 100-W high pressure mercury lamp (Rico). The UV absorption and proton NMR spectra were measured with a Hitachi 200-10 UV-spectrophotometer and a Hitachi R-24 NMR spectrometer (60 MHz), respectively. The product mixtures were chromatographed over Caster wax or PEG-20 M on 60—80 mesh Chromosorb WAW (3 mm×3 m), by the use of a Shimadzu GC-4CM-PF with a FID deteactor and nitrogen carrier gas. All melting points and boiling points were uncorrected.

Materials. While 2,4-*cis*-4-flavanols **1a**, **2a**, and **3a** were prepared by the reduction of the corresponding flavanones with sodium borohydride,[17,18] 2,4-*trans*-4-flavanols **1b**, **2b**, and **3b** were obtained from **1a**, **2a**, and **3a**, respectively, by treatment with phosphorous tribromide followed by alkaline hydrolysis.[18] **1a**: Colorless needles from methanol, mp 147.5—148 °C; **1b**: colorless needles from benzene-petroleum benzine, mp 115—116 °C; **2a**: colorless needles from ethanol-water, mp 103—103.5 °C; **2b**: colorless needles from hexane-benzene, mp 49.5—51.5 °C; **3a**: colorless needles from methanol, mp 100—101 °C; **3b**: colorless needles from benzene-petroleum benzine, mp 110—111 °C. 1-Phenylethanol **4** was of guaranteed grade commercially available (Wako Chemicals), while **5**—**9** were prepared by the reduction of the corresponding *p*-substituted acetophenones with sodium borohydride.[9] The purities were confirmed by GLC analysis. **5**: Bp 96.5—97 °C/5 mmHg†; **6**: bp 110.5 °C/4 mmHg; **7**: bp 94 °C/2.5 mmHg; **8**: bp 100 °C/5 mmHg; **9**: colorless needles from ether-petroleum ether, mp 41.5—42.5°C. Diphenyl sulfone, acetophenone, DABCO and DTBP were of the purest grade commercially available. Benzene and other solvents were distilled before use.

Photooxygenation Reactions. Typical procedures will be described below. A 25 ml benzene solution containing 0.04 mol dm^{-3} substrate was bubbled through with oxygen gas for 30 min, then irradiated at room temperature while stirring with a magnetic stirrer under oxygen atmosphere for 8—10 h. The photolyzed mixtures from 4-flavanols were analyzed by ^{1}H NMR spectroscopy after the removal of the solvent. Relative yields of flavanones and 4-flavanols recovered were calculated from the relative intensities of the protons at the C-2 position of flavanones and those at the C-4 or C-2 positions of 4-flavanols. Besides flavanones, trace amounts of 2′-hydroxychalcones were detected by TLC analysis on silica gel-benzene. The photoproducts from benzylic alcohols (**4**—**11**) were determined on GLC by comparing with corresponding acetophenones commercially available (acetophenone, 4′-chloro- and 4′-methoxyacetophenones) or prepared by known methods.[20] 3′-Methoxyacetophenone: Bp 134—135.5 °C/24 mmHg; 2′,4′-dimethoxyacetophenone: Colorless needles from benzene, mp 39—40 °C; 2′-methoxyacetophenone: Bp 132—135 °C/25 mmHg.

Oxidation by Superoxide Ion. A 30 ml benzene solution containing 18-Crown-6 (0.25 g, 1.0 mmol) and a benzylic alcohol (1.0 mmol) was mechanically stirred while bubbling through with nitrogen gas, then added potassium peroxide (0.40 g, 5.3 mmol) and continued stirring until the color changed into orange (*ca.* 15 h). Water was added and shaken, then the organic layer was condensed and analyzed on GLC as described above. Similarly, 4-flavanols were oxidized under nitrogen atmosphere in a 20 ml benzene solution containing a 4-flavanol (1.0 mmol), 18-Crown-6 (1.0 mmol), and potassium peroxide (10 mmol) for 2 h, or in a 20 ml DMSO solution containing a 4-flavanol (1.0 mmol), 18-Crown-6 (0.76 mmol), and potassium peroxide (2.8 mmol) for 3—5 h. The products were analyzed by NMR spectroscopy as described above.

Oxidation of 4-Flavanols by Singlet Oxygen. A 15 ml solution of *t*-butyl alcohol containing a 4-flavanol (2 mmol) and Rose Bengal or thionine (5 mg) as a sensitizer was irradiated with a 300-W tungsten lamp for 5 h while stirring with magnetic stirrer under oxygen atmosphere.

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References

1) T. Sato, H. Inoue, and K. Hata, *Bull. Chem. Soc. Jpn.*, **40**, 1502 (1967).

2) H. Kwart and P. S. Francis, *J. Am. Chem. Soc.*, **81**, 2116 (1959).

3) S. Yamaguchi, K. Kabuto, Y. Kikuchi, and N. Inoue, *Bull. Chem. Soc. Jpn.*, **44**, 3487 (1971).

4) M. Suzuki, J. Amano, M. Morioka, H. Mizuno, and R. Matsushima, *Bull. Chem. Soc. Jpn.*, **50**, 1169 (1977).

5) C. Quannes and T. Wilson, *J. Am. Chem. Soc.*, **90**, 6527 (1968); C. S. Foote, E. R. Peterson, and K. W. Lee, *ibid.*, **94**, 1032 (1972); C. F. Denke and N. I. Krinsky, *ibid.*, **98**, 3041 (1976); T. Thomas and C. S. Foote, *Photochem. Photobiol.*, **27**, 683 (1978).

6) J. Eriksen and C. S. Foote, *J. Am. Chem. Soc.*, **102**, 6083 (1980).

7) I. Saito and T. Matsuura, *J. Am. Chem. Soc.*, **103**, 188 (1981).

8) A. P. Schaap, K. A. Zaklika, B. Kaskar, and L. W. M. Fung, *J. Am. Chem. Soc.*, **102**, 389 (1980).

9) L. T. Spada and C. S. Foote, *J. Am. Chem. Soc.*, **103**, 391 (1981).

10) C. S. Foote, S. Wexler, and W. Ando, *Tetrahedron Lett.*, **1965**, 4111.

11) W. Bors, M. Saran, E. Lengfelder, C. Michel, C. Fuchs, and C. Frenzel, *Photochem. Photobiol.*, **28**, 629 (1978).

12) H. Tsubomura, T. Yagishita, and H. Toi, *Bull. Chem. Soc. Jpn.*, **46**, 3051 (1973).

13) C. von Sonntag, K. Neuwald, H. P. Schuchmann, F. Weeke, and E. Janssen, *J. Chem. Soc., Perkin. Trans. 2*, **1975**, 171.

14) M. Kojima, H. Sakuragi, and K. Tokumaru, *Tetrahedron Lett.*, **22**, 2889 (1981).

15) K. Onodera, H. Sakuragi, and K. Tokumaru, *Tetrahedron Lett.*, **21**, 2831 (1980).

16) H. L. Tökes and R. Bognar, *Tetrahedron*, **29**, 909 (1973); J. W. C. Lewis, *Aust. J. Chem.*, **21**, 2059 (1968).

17) A. Löbenwein, *Ber.*, **57**, 1515 (1924).

18) A. B. Kulkarni, *Indian J. Chem.*, **8**, 119 (1970).

19) K. B. Wiberg and T. M. Shryne, *J. Am. Chem. Soc.*, **77**, 2774 (1955); A. C. Davies, E. E. Edwin, J. Kenyon, and A. Walsh, *J. Chem. Soc.*, **1957**, 3158.

20) R. N. Goel, A. C. Jain, and T. R. Seshadr, *Proc. Indian Acad. Sci.*, **48**, 180 (1958).

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† 1 mm Hg≈133.322 Pa