7314 *J. Am. Chem. Soc.* **1982**, *104*, 7314–7316

$(MeCp)_2V_2S_4Fe(CO)_3$ (**3**).[13] Compound **3**, typically isolated in ca. 45% yield, was diamagnetic and, unlike **2**, air-stable in solution. $^1H$ NMR and IR spectroscopy, mass spectrometry, and its derivative chemistry indicated the structure shown in Scheme I.[14] The trigonal bipyramidal $M_3S_2$ core is a familiar motif in metal sulfide cluster chemistry; however, the bridging $\mu$-$\eta^2$-$S_2$ is unusual for organometallic sulfide clusters.[15] The $\mu$-$S_2$ ligand in **3** is of particular interest because it represents a reactive cluster-bound functional group.[16] Thus treatment of **3** with $Pt(C_2H_4)(PPh_3)_2$ ($CH_2Cl_2$ solution, 10 min, 25 °C) gave the tetranuclear cluster $(MeCp)_2V_2S_4Fe(CO)_3Pt(PPh_3)_2$ in quantitative yield (scheme).[17] This preliminary experiment suggests that **2** is a potential precursor to a wide range of heteronuclear sulfide cluster compounds.

Treatment of green $CH_2Cl_2$ solutions of **3** with P-*n*-$Bu_3$ (1 equiv, 5 min, 25 °C) afforded red $(MeCp)_2V_2S_3Fe(CO)_3$ (**4**) isolated in 75% yield as a crystalline solid after chromatographic workup and crystallization from $CH_2Cl_2$–$CH_3OH$.[18] The structure of this derivative was elucidated by using single-crystal X-ray diffraction methods (Figure 1).[19] The metals are arrayed as an approximate isosceles triangle, the two Fe–V distances being 2.82 ± 0.01 Å. Two $\mu_3$-S ligands bridge the three metals while one sulfide lies in the $FeV_2$ plane and spans the V···V edge. The iron atom is seven-coordinate. The V···V distance of 2.51 Å is 0.15 Å shorter than that in **1** but 0.05 Å longer than the V–V distances in $(C_5H_5)_2V_2(CO)_5$[20] and $(C_5H_5)_2V_2(CO)_4PPh_3$.[21] The short V···S(3) distances of 2.23 (1) Å (cf. 2.45 Å in $Cp_2V(SPh)_2$[22]) suggest partial multiple bonding between these sites as a means of alleviating the electron deficiency of the vanadium atoms.

Compound **4** is *formally* a 44-$e^-$ cluster as the desulfurization of **3** converted a 6-$e^-$ $\mu$-$\eta^2$-$S_2$ ligand (cf. $Fe_2(\mu$-$S_2)(CO)_6$[23]) to a 2-$e^-$ $\mu$-S ligand. The impact of this change appears to be localized at the vanadium centers. Thus the conversion of **3** to **4** is accompanied by a 0.8 ppm downfield shift in the $^1H$ NMR chemical shift of the cyclopentadienyl ring protons. In contrast, the $\nu_{CO}$ patterns for **3** and **4** (high-resolution FT IR, cyclohexane solution) are virtually superimposable.

On the basis of our synthetic studies, a rich chemistry of the cyclopentadienylvanadium sulfides appears assured.[24] Furthermore, the predilection of vanadium for electron-deficient configurations suggests that the reactivity of this new generation of cyclopentadienyl metal sulfides will prove distinctive in comparison with analogous compounds involving the later transition metals.

**Acknowledgment.** We thank the National Science Foundation for support (NSF CHE 81-06781). Mass spectra were obtained by Carter Cook and his associates in the University of Illinois Mass Spectrometry Laboratory, which is supported by the National Cancer Institute. T.B.R. is a recipient of a Camille and Henry Dreyfus Teacher–Scholar Award.

**Registry No.** **1**, 83587-83-1; **2**, 83587-84-2; **3**, 83587-85-3; **4**, 83587-86-4; $(MeCp)_2V_2S_4Fe(CO)_3Pt(PPh_3)_2$, 83587-87-5; V, 7440-62-2.

**Supplementary Material Available:** Tables of selected bond distances and angles, positional parameters, thermal parameters, and final observed and calculated structure factor amplitudes (27 pages). Ordering information is given on any current masthead page.

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(13) Anal. C, H, Fe, V. IR (cyclohexane) 2028.5 (s), 1978.5 (s), 1969.5 (s) $cm^{-1}$; $^1H$ NMR (360 MHz, $CDCl_3$) $\delta$ 4.95 (m, 2 H), 4.94 (m, 2 H), 1.97 (s, 3 H); field desorption mass spectrum, *m/e* 528 ($M^+$).

(14) The structure of **3** has been confirmed by a preliminary X-ray diffraction study. The relationship between **3** and **4** will be covered in a forthcoming full paper.

(15) The cluster $Mo_3S_{13}^-$ contains three $\mu$-$\eta^2$-$S_2$ ligands; many metal dimers and linear chain compounds (e.g., ref 11) also feature this moiety: Müller, A.; Jostes, R.; Cotton, F. A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 875.

(16) Anal. C, H, Fe, V. IR (toluene) 2013.5 (s), 1954 (br) $cm^{-1}$; $^1H$ NMR (90 MHz, $CDCl_3$) $\delta$ 7.32 (m, 15 H), 5.49 (m, 2 H), 5.41 (m, 2 H), 1.90 (s, 3 H); fast-atom bombardment mass spectrum, *m/e* 1163 ($C_{48}H_{44}FeP_2PtS_4V_2^+$).

(17) Day, V. W.; Lesch, D. A.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1982**, *104*, 1290. Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125. Braunstein, P.; Jud, J.-M; Tiripicchio, A.; Tiripicchio-Camellini, M.; Sappa, E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 307.

(18) Anal. C, H, Fe, V. IR (cyclohexane) 2028.5 (s), 1979.0 (s), 1970.0 (s) $cm^{-1}$; $^1H$ NMR (360 MHz, $CDCl_3$) $\delta$ 5.98 (s, 2 H), 5.55 (s, 2 H), 2.10 (s, 3 H); field desorption mass spectrum, *m/e* 496 ($M^+$).

(19) $(C_5H_4CH_3)_2V_2S_3Fe(CO)_3$ (**4**) crystallizes in the monoclinic space group $P2_1/C$ with $a = 10.397$ (2) Å, $b = 25.504$ (7) Å, $c = 14.135$ (4) Å, $\beta = 102.63(2)°$, $V = 3658$ (2) Å$^3$, $Z = 8$, $\mu = 20.93$ $cm^{-1}$ (Mo K$\alpha$, $\lambda$ 0.710 69 Å). A total of 9301 reflections ($3° < 2\theta < 55°$) were collected on a Syntex $P2_1$ diffractometer of which 8422 were unique. Of these reflections, 5040 with $F_o > 3\sigma(F_o)$ were used in the subsequent solution and refinement. The final discrepancy factors are 3.8% and 5.1% for $R$ and $R_w$, respectively.

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(24) For examples of cyclopentadienylchromium sulfido clusters see: Pasynskii, A. A.; Eremenko, I. S.; Ellert, O. G.; Novotortsev, V. M.; Rakitin, Yu. V.; Kalinnikov, V. T.; Shklover, V. E.; Struchkov, Yu. T. *J. Organomet. Chem.* **1982**, *234*, 315.

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# Stereochemical Consequences of Photosensitized and Electrode-Catalyzed Oxygenations of Stereoisomeric Di-*tert*-butylbi(bicyclo[3.3.1]non-9-ylidene)

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*Received July 6, 1982*

A number of electron-rich compounds react with singlet oxygen differently than do less electron-rich compounds.[1] In particular, [2 + 2] cycloaddition of singlet oxygen to produce dioxetanes occurs only with electron-rich olefins.[2-5] Recently, Foote,[6] Schaap,[7] Nelsen,[8] and Clennan[9] showed that dioxetanes once thought to be characteristic of singlet oxygen are also produced by electron transfer, e.g., cyanoaromatic-sensitization of several polyaryl olefins and electrode-catalyzed oxygenation of adamantylideneadamantane (**1**).

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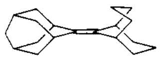
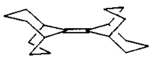
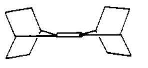
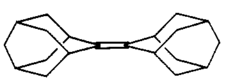
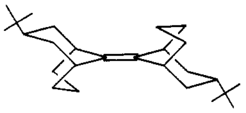
Table I, Dye- and DCA-Sensitized Photooxygenation and Electrode-Catalyzed Oxygenation

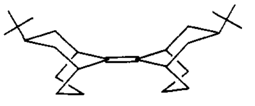
| olefins | $E_p$ vs. SCE,[a] V | yields of dioxetanes,[b] % | | | coulombic data[f] | | |
|---|---|---|---|---|---|---|---|
| | | $^1O_2$[c] | DCA[d] | $-e$, $^3O_2$[e] | time, min | charge, C | av chain length[g] |
| 1 | 1.52 | 98 | 66 | 87 | 15 | 0,46 | 78 |
|  4 | 1,53 | 92 | 59 | 72 | 20 | 0,68 | 58 |
|  5 | 1,54 | 100 | 21 | 80 | 200 | 7.60 | 5 |
|  6 | 1,86 | 15 | NR[h] | NR | | | |

[a] At a Pt electrode; solvent MeCN containing 0.1 M TBAP; scan rate 200 mV/s; full-scale deflection +2,0 V. [b] Isolated yields. For physical and spectroscopic data of dioxetanes, see ref 21. [c] Each olefin (0,20 mmol) in 20 mL of $CH_2Cl_2$ containing TPP was photolyzed for 3 h. [d] Each olefin (0,20 mmol) in 20 mL of MeCN–$CH_2Cl_2$ (2:1) containing DCA was photolyzed for 4 h. [e] Exhaustive electrolysis was conducted by using 0.4 mmol of olefin in 30 mL of 0.1 M TBAP–$CH_2Cl_2$ solution with a C electrode, [f] Coulombic meter was simultaneously operated. [g] Average chain length = (theoretical coulombs for an one-electron process/coulombs passed) – 1. [h] No reaction,

As a result, it is not clear when [2 + 2] cycloaddition of singlet oxygen goes by way of electron transfer from electron-rich substrates to singlet oxygen. Bartlett and Schaap's earlier masterful investigation of stereospecific dioxetane formation of diethoxyethylene[3a–c] indicates that electron transfer is not always operative, because electron transfer must produce an open intermediate that should rotate internally and lose its configuration, In spite of continuous interest in strained electron-rich olefins such as **1**,[5c,10] a proper stereochemical study has not been done yet. We now present the results of dye- and 9,10-dicyanoanthracene (DCA)-sensitized photooxygenations and electrode-catalyzed oxygenation of two stereoisomeric di-*tert*-butylbi(bicyclo[3.3.1]non-9-ylidenes) **2** and related olefins.


1


*anti*-2


*syn*-2

The two stereoisomers of **2**[11] were synthesized as a mixture (ca, 1:1) by the coupling of the geminal dibromide of the corresponding ketone with Simmons–Smith reagent;[5c,12] the mixture was separated by preparative HPLC.[13] Assignment of the stereochemistry followed from the X-ray crystal analysis of the *anti*-**2** isomer.[14]

The dye-sensitized photooxygenation was carried out under conditions[10g,15] that gave dioxetane as the only product and no trace of epoxide; i.e., a solution under bubbling oxygen of **2** (0.20 mmol) in 20 mL of methylene dichloride containing TPP (tetraphenylporphine) was photolyzed in a water-cooled Pyrex tube with a 300-W halogen lamp. The DCA-sensitized photooxygenation was conducted similarly with DCA and acetonitrile–methylene dichloride (2;1) as the sensitizer and the solvent.[6] The electrode-catalyzed oxygenation was accomplished by the method reported by Clennan.[9] A solution of 20 mL of 0.1 M tetra-*n*-butylammonium perchlorate and 0.2 mmol of **2** in $CH_2Cl_2$ under bubbling oxygen was subjected to constant-potential electrolysis (1.6 V vs. SCE) at a carbon electrode. The oxygenations were monitored by thin-layer chromatography, and final reaction mixtures were separated by column chromatography over silica gel–carbon tetrachloride without elution of the polar materials such as epoxide and ketone.

The TPP- and DCA-sensitized photooxygenation of *anti*-**2** gave a single dioxetane, *cis,trans*-**3**, mp 127–130 °C. The observation of two *tert*-butyl absorptions in equal intensity in the $^1H$ NMR spectrum (at 0.85 and 0.90 ppm in $CDCl_3$) as well as evidence in the $^{13}C$ NMR spectrum for two dioxetane ring carbons (at 95.5 and 95.3 ppm in $CDCl_3$) established the cis,trans structure. Photooxygenation of *syn*-**2** by either TPP or DCA gave two dioxetanes, *cis,cis*-**3**, mp 167.5–169 °C, and *trans,trans*-**3**, mp 140.5–144 °C, respectively (Scheme I). For each dioxetanes, a single *tert*-butyl absorption in the $^1H$ NMR (at 0.85 and 0.95 ppm in $CDCl_3$) and a single dioxetane ring carbon absorption in the $^{13}C$ NMR (at 95.3 and 95.9 ppm in $CDCl_3$) confirmed either the cis,cis or the trans,trans structure.[16] These two isomers were tentatively distinguished on the basis of the preferential attack of reagent ($O_2$) from the less hindered face of the olefins. Indeed, in all cases, the yields of *cis,cis*-**3** were always superior to those of *trans,trans*-**3**.

In contrast the electrode-catalyzed oxygenations of either isomeric olefin gave mixtures of all three dioxetanes, in which *cis,cis*-**3** and the mixture of *cis,trans*-**3** and *trans,trans*-**3** could be separated by chromatography. The ratio of the dioxetanes in the latter mixture was easily determined by $^1H$ NMR integration.

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(10) (a) Schaap, A. P.; Faler, G. R. *J. Am. Chem. Soc.* **1973**, *95*, 3381. (b) Shuster, G. B.; Turro, N. J.; Steinmetzer, H. C.; Schaap, A. P.; Faler, G.; Adam, W.; Liu, J. C. *Ibid.* **1975**, *97*, 7110. (c) Numan, H.; Wieringa, J. H.; Wynberg, H.; Hess, J.; Vos, A. *J. Chem. Soc., Chem. Commun.* **1977**, 591. (d) Bartlett, P. D. *Chem. Soc. Rev.* **1976**, *5*, 149. (e) Bartlett, P. D. *ACS Symp. Ser.* **1978**, *No. 69*, 15. (f) Jefford, C. W.; Boschung, A. F. *Tetrahedron Lett.* **1976**, 4771. (g) Jefford, C. W.; Boschung, A. F. *Helv. Chim. Acta* **1977**, *60*, 2673. (h) Jefford, C. W.; Knopfel, W.; Smith, L. C.; Kohmoto, S.; Almqvist, K. A.; Estrada, M. J.; Barchietto, G. In "Oxygen and Oxy-Radicals in Chemistry and Biology"; Rodgers, M. A. J., Powers, E. L., Eds.; Academic Press: New York, 1981; p 397.

(11) *anti*-**2**: mp 214–216 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 0.85 (s, 18 H), 1.75 (m, 22 H), 2.90 (brs, 4 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 131.7 (s), 42.1 (d), 35.2 (t), 33.9 (t), 32.8 (s), 32.2 (d), 27.2 (q), 22.6 (t); MS 356 ($M^+$). *syn*-**2**: mp 143–146 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 0.85 (s, 18 H), 1.75 (m, 22 H), 2.90 (brs, 4 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 131.7 (s), 42.2 (d), 53.4 (t), 33.7 (t), 32.9 (s), 32.2 (d), 27.1 (q), 22.6 (t); MS 356 ($M^+$). Calcd for $C_{26}H_{44}$: C, 87.56; H, 12.43. Found: *anti*-**2**, C, 87.77; H, 12.28; *syn*-**2**, C, 87.70; H, 12.66.

(12) Keul, H. *Chem. Ber.* **1975**, *108*, 1207.

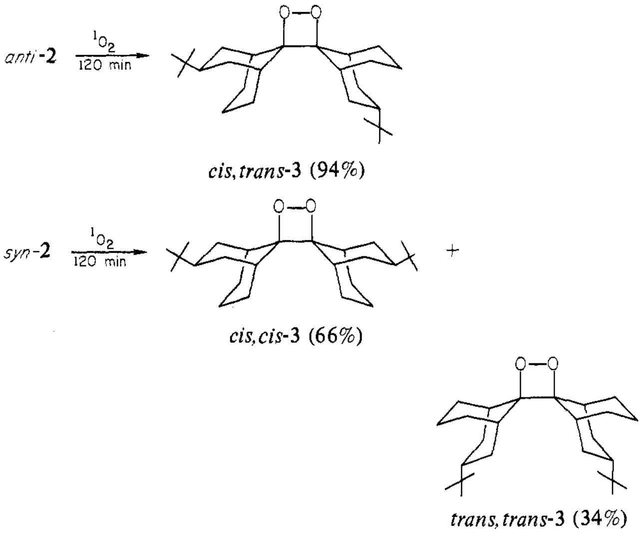
(13) A liquid chromatograph LC-08 (Nippon Bunseki Kōgyō Co. Ltd.) to which was attached a recycling system for longer passage was used with almost 30 recycles. The mixture of *syn*- and *anti*-**2** could be separated as two peaks (the former fraction is *anti*-**2**, the latter is *syn*-**2**). Column; JAIGEL-1H (20 mm × 600 mm × 2); carrier solvent, $CHCl_3$.

(14) The X-ray analyses were performed by Dr. K. Ueno of the Research Institute for Polymer and Textiles and is to be published.

(15) When Rose bengal was used as sensitizer in acetone–$CH_2Cl_2$ (1:1), epoxide could become the predominant product, but dye bleaching occurred rapidly in this system. One day was needed to complete the reaction under the same conditions. Thus, the formation of epoxide does not appear to be a direct reaction of singlet oxygen.[10g] Nevertheless, we confirmed that stereospecific epoxidation also occurred, and the result is to be published.

(16) All three dioxetanes showed the beautiful blue chemiluminescences by heating above 150 °C. Calcd for $C_{26}H_{44}O_2$: C, 80.35; H, 11.41. Found *cis,trans*-**3**, C, 80.32, H, 11.68; *cis,cis*-**3**, C, 80.13; H, 11.59; *trans,trans*-**3**, C, 80.43; H, 11.65.

Scheme I



$anti\text{-}2 \xrightarrow[420\ \text{min}]{\text{DCA},\ ^3O_2} cis,trans\text{-}\mathbf{3}\ (49\%) + \text{recovered } \mathbf{2}\ (25\%)$

$syn\text{-}2 \xrightarrow[300\ \text{min}]{\text{DCA},\ ^3O_2} cis,cis\text{-}\mathbf{3}\ (27\%) + trans,trans\text{-}\mathbf{3}\ (22\%) + \text{recovered } \mathbf{2}\ (15\%)$

$anti\text{-}2 \xrightarrow[300\ \text{min}]{-e^-,\ ^3O_2} cis,trans\text{-}\mathbf{3}\ (34\%) + cis,cis\text{-}\mathbf{3}\ (24\%) + trans,trans\text{-}\mathbf{3}\ (21\%) + \text{recovered } \mathbf{2}\ (11\%)$

$syn\text{-}2 \xrightarrow[80\ \text{min}]{-e^-,\ ^3O_2} cis,trans\text{-}\mathbf{3}\ (23\%) + cis,cis\text{-}\mathbf{3}\ (51\%) + trans,trans\text{-}\mathbf{3}\ (11\%) + \text{recovered } \mathbf{2}\ (9\%)$

Clearly, the dye-sensitized photooxygenations of *anti*- and *syn*-**2** are stereospecific in the fashion anticipated for the concerted cycloaddition of singlet oxygen. In contrast, the electrode-catalyzed oxygenation is not stereospecific, and this behavior is consistent with the Barton-type mechanism[17] involving the reaction of cation radical and $^3O_2$, already suggested by Nelsen[8] and Clennan.[9] Furthermore, in this case $^{13}C$ NMR spectra of recovered olefin demonstrated that extensive isomerization occurred under the same conditions, The same isomerization of the olefins was observed in the exhaustive electrolysis of *anti*- and *syn*-**2** under an argon atmosphere, So, as anticipated isomerization takes place in the cation-radical species. To our surprise, the DCA-sensitized photooxygenation, proceeding presumably by way of cation radical–$O_2^{-}\cdot$ reaction (Foote mechanism), occurred stereospecifically, In this case recovered olefin retained its configuration. In contrast to this result, Foote has reported that isomerization of starting olefin occurs in the DCA-sensitized photooxygenation of stilbene,[6c] Therefore, our results seem to indicate a borderline behavior; i,e,, singlet oxygen and electron transfer oxygenations are competitive, as suggested very recently by Foote,[18] To elucidate further the similarities and differences among the three mechanism (singlet oxygen and Foote- and Barton-type), we have examined the oxygenations of several other olefins (Table I), Olefins **4**–**6**[19] have fairly low oxidation potentials and showed similar reactivity except for **6**, which was inert to both DCA-sensitized and electrode-catalyzed oxygenations. Work is in progress to define further the characteristics of the electron-transfer oxygenations.

**Acknowledgment.** This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education (No, 57030049),

**Registry No. 1**, 30541-56-1; *anti*-**2**, 83665-47-8; *syn*-**2**, 83709-00-6; *cis,cis*-**3**, 83665-48-9; *cis,trans*-**3**, 83709-01-7; *trans,trans*-**3**, 83709-02-3; **4**, 83665-49-0; **5**, 55993-21-0; **6**, 51689-29-3.

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(17) (a) Barton, D. H. R.; Haynes, R. K,; Leclerc, G.; Magunas, P, D.; Menzies, I. D. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2055. (b) Tang, R.; Yue, H. J.; Wolf, J. F.; Mares, F. *J. Am. Chem. Soc*, **1978**, *100*, 5248. (c) Landis, M. E.; Madoux, D. C. *Ibid.* **1979**, *101*, 5106,

(18) On this point, Foote indicated that singlet oxygen can be produced from DCA in the interaction with olefins on the basis of the product distribution and the solvent isotope effects, identical with those from rose bengal sensitized reactions; see ref 6c, Abstracts of 15th Symposium of Oxidation Reactions, Nagoya, Japan, 1981, p 101, and private communication with C. S. Foote.

(19) Olefins **4**–**6** were prepared from the pyrolyses of corresponding thiadiazolines at 150 °C in $n$-$Bu_3P^{20}$ and purified by preparative GLC.

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(21) Physical data of **1** and **6** are consistent with the literature.[5c,10a,10b] **4**: mp 132–135 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 2.10 (m, 24 H), 2.60 (brs, 4 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 96,0 (s), 95.1 (s). **5**: mp 130–132 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 1.90 (m, 24 H), 2.60 (brs, 4 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 95.4 (s).

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# On the Mechanism of Oxidation of Hydroxycyclohexadienyl Radicals with Molecular Oxygen

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It is well recognized that molecular oxygen efficiently oxidizes cyclohexadienyl radicals to arenes,[1] On the basis of the kinetic evidence, Dorfman et al.[2] proposed a mechanism for the oxidation of hydroxycyclohexadienyl radical (**1**), formed by the reaction of hydroxyl radical with benzene, with molecular oxygen, In this mechanism a peroxy radical (**2**) formed by the addition of oxygen with **1** plays a role in giving rise to phenol with the liberation of hydroperoxy radical as shown in Scheme I,

In the course of our studies on the free radical aromatic hydroxylation with hydroxyl radical generated from $\alpha$-azohydroperoxide (**3**)[3–5] in anhydrous organic media (Scheme II), we have found that the isomer distribution ratio of phenols formed by this reaction varies with the concentration of oxygen introduced, Such phenomena of the variation of the isomer ratio under oxygen have also been reported in the aromatic hydroxylation with Fenton's reagent[6] and by radiolysis of water,[7–9] In order to explain the variation of the isomer ratio of phenols, we have proposed a mechanism involving peroxy radicals **5** and **6** and dihydrodiols **7** and **8** (see Scheme III), In the hope of elucidating the mechanism, we have undertaken in the present study the aromatic hydroxylation with **3** (see Scheme II) under $^{18}O_2$, This report describes our observations on the $^{18}O$ incorporation into aromatics and offers a mechanistic interpretation for this reaction.

To a toluene solution (4 mL) of $\alpha$-azohydroperoxide (**3**; 0,04 mmol) in a Pyrex tube (10 × 100 mm) was introduced $^{18}O_2$ (99% contents; 10,9 mg) through a vacuum line, and then the tube was sealed, The mixture was irradiated with a high-pressure mercury

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