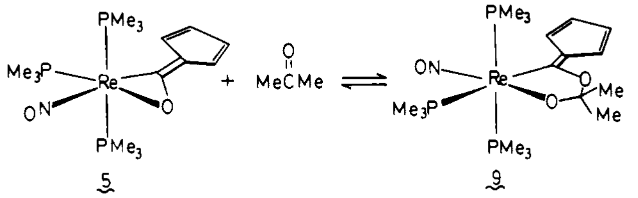
with structure **5** in which the ketene carbon is cis to all three phosphorus ligands.[11]

Significantly higher yields of **5** were obtained from photolysis of **3** and PMe_3 than were obtained from thermal reaction. When a toluene solution of **3** (2.64 mmol, 0.31 M) and PMe_3 (34.4 mmol, 4.05 M) was photolyzed in a Rayonet photochemical reactor at 366 nm for 112 h, at 59% yield of ketene complex **5** was isolated. Methane (66%) was also observed.[12]



The ketene complex **5** reacts with acetone solvent over the course of 48 h at 25 °C to form a high yield of the 1:1 adduct **9**[13] resulting from insertion of acetone into the Re–O bond of **5**. The reaction is analogous to the addition of $(C_6H_5)_2C{=}C{=}O$ to $\{(\eta^5\text{-}C_5H_5)_2Ti(Ph_2C_2O)\}_2$, which leads to insertion of the C=O bond of the ketene into the Ti–O bond.[2a]

The ^1H NMR of acetone adduct **9** in benzene-d_6 consists of multiplets at δ 7.36 (2 H), 6.96 (1 H), and 6.90 (1 H) assigned to the four protons of the cyclopentadiene ring, a singlet at δ 1.36 assigned to the *gem*-dimethyl protons, a doublet at δ 1.02 (J = 7.9 Hz) assigned to the unique PMe_3 ligand, and a three-line pattern ($J_{PH} + J_{P'H}$ = 6.8 Hz) at δ 1.19 assigned to the equivalent *trans*-PMe_3 ligands. In the related 1:1 adduct of **5** with 2-butanone, the *trans*-PMe_3 ligands are no longer equivalent and resonances due to three different PMe_3 ligands are seen as δ 1.50 (three lines, $J_{PH} + J_{P'H}$ = 6.8 Hz), 1.47 (three lines, $J_{PH} + J_{P'H}$ = 6.8 Hz), and 1.61 (d, J = 8.1 Hz).[14] In the $^{13}C\{^1H\}$ NMR (CD_2Cl_2) of **9**, there is a doublet (J_{PC} = 55 Hz) at δ 238.2 assigned to the carbon bonded to rhenium, which is trans to the unique PMe_3 ligand.[11,13]

The formation of **9** from **5** and acetone was shown to be reversible by heating a 0.036 M benzene-d_6 solution of **9** at 80 °C for 4 h. Periodic observation by ^1H NMR indicated the clean conversion of **9** to **5** and free acetone with a half-life of ~60 min at 80 °C.

The conversion of η^5-C_5H_5 complex **3** into the cyclopentadienylidene ketene complex **5** probably proceeds via the observed intermediate η^1-C_5H_5 bisphosphine adduct **4**. The mechanism for formation of **5** is necessarily complex due to the large number of bonds that must be broken or formed in the process. Cleavage of the Re–CH_3 bond and formation of methane might occur either by protonation of the Re–CH_3 bond or by reductive elimination from an intermediate CH_3ReH species. Cleavage of the C–H bond of the cyclopentadiene unit could occur either by base abstraction or insertion of Re into the α-CH bond of an η^1-C_5H_5Re species; alternatively, migration of the η^1-C_5H_5 unit to CO might preceed C–H cleavage by either base abstraction or Re β-H elimination from a Re–CO–C_5H_5 species. Formation of the new carbon–carbon bond of the ketene complex could occur either by migration of an η^1-C_5H_5 ligand to CO or by coupling of an intermediate cyclopentadienylidene ligand with coordinated CO.[1b,3d] Whatever the mechanism, it is becoming clear that a great deal of interesting chemistry is resulting from PMe_3-induced η^5-$C_5H_5 \rightleftarrows \eta^3$-$C_5H_5 \rightleftarrows \eta^1$-$C_5H_5$ transformations.

Acknowledgment. Support from the Department of Energy, Division of Basic Energy Sciences, is gratefully acknowledged.

Registry No. 3, 38814-45-8; **5**, 85283-03-0; **9**, 85283-04-1.

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[11] For rhenium compounds, trans J_{PC} is typically 40–60 Hz and cis J_{PC} is typically 5–10 Hz: Anglin, J. R.; Calhoun, H. P.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 2281–2289. However, we are unable to definitively assign the configuration of **5** since cases are known in which cis J_{PC} is greater than trans J_{PC}: Flood, T. C.; Jensen, J. E.; Statler, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4410–4414.

[12] In a related experiment in benzene-d_6, the ^1H NMR before photolysis indicated complete conversion of **3** to **4**, which was indefinitely stable at 32 °C in the dark. Photolysis at 366 nm and 32 °C for 80 h led to formation of 67% **5**. In addition, equal intensity multiplets at δ 6.44, 6.27, and 2.71 were observed and are assigned to cyclopentadiene (30%).

[13] **9**: $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −45 °C, 0.09 M $Cr(acac)_3$) δ 238.3 (d, J_{PC} = 55 Hz), 135.8, 122.5, 117.1, 116.4, 115.9 109.3, 29.8, 18.0 (d, J_{PC} = 23.2 Hz), 15.0 (three-line pattern, $J_{P'C} + J_{PC}$ = 27.8 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40 °C, 0.09 M $Cr(acac)_3$) δ −34.1 (three-line pattern with $J_{PP'} + J_{PP''}$ = 31.2 Hz), −38.9 (d, J = 15.6 Hz) relative to external H_3PO_4; IR (Nujol) 1647 (s), 1494 (s), 1350 (m), 1253 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{37}O_3NP_3Re$: C, 36.36; H, 6.27; N, 2.36. Found: C, 36.26, H, 6.27; N, 2.35. *m/e* calcd 595.1538, obsd 595.1548.

[14] A referee suggested that **9** might be a simple adduct with a coordinaged acetone ligand and a bent NO ligand. However, this structure is inconsistent with our new data on the 2-butanone adduct of **5**. Moreover, our earlier NMR data for **9** showed an upfield shift of the *gem*-dimethyl protons relative to free acetone in benzene (δ 1.36 vs. 1.54); for comparison, a downfield shift has been seen for the methyl groups of coordinated acetone in $(C_5H_5)Re(CO)(NO)(O{=}C(CH_3)_2)^+$.[15] In addition, the large upfield shift of the acetone carbonyl from δ 206 in acetone to δ 135.8 in the ^{13}C NMR of **9** is most consistent with our proposed formulation.

[15] Sweet, J. R.; Graham, W. A. G. *Organometallics* **1982**, *1*, 982–986.

Synthesis, Characterization, and Reaction Chemistry of a Bis(iodosylbenzene)-Metalloporphyrin Complex, $[PhI(OAc)O]_2Mn^{IV}TPP$. A Complex Possessing a Five-Electron Oxidation Capability

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Received October 29, 1982

The current interest in high-valent manganese porphyrin complexes derives from the ability of these materials to activate hydrocarbons[1] and water[2] under very mild conditions. Rigorous investigation of these activation processes has been hindered by the lack of availability of purified forms of these highly reactive complexes. Recently, we reported the preparation, purification, and characterization of a monomeric manganese(IV) complex, $Mn^{IV}TPP(OCH_3)_2$,[3,4] two types of dimeric manganese(IV) complexes, $[XMn^{IV}TPP]_2O$, **1**, X = N_3^- and OCN^-,[5] and $[YMn^{IV}TPP(OIPh)]_2O$, **2**, Y = Cl^- and Br^-,[6] and a manganese(V) complex, $NMn^{V}TpMPP$.[7] The dimeric manganese(IV) complexes enabled us to establish a detailed mechanism for alkane functionalization by **1** and **2**.[8] We report here the synthesis, characterization, and reaction chemistry of a new type of manganese(IV) complex, $[PhI(OAc)O]_2Mn^{IV}TPP$, **3**, which hydroxylates alkanes and epoxidizes olefins. This complex contains both a transition metal (Mn) and a nonmetal ion (I) in unusual oxidation states. The high-valent iodine and manganese atoms provide this complex with a five-electron oxidation capability.

(Tetraphenylporphinato)manganese(III) acetate, $Mn^{III}TPP(OAc)$, was dissolved in chlorobenzene and oxidized in the presence of 6 equiv of glacial acetic acid with 3 equiv of iodosylbenzene. A slight excess of iodosylbenzene above the 2.5

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* After June 1, 1983 address correspondence to this author at the Department of Chemistry, Emory University, Atlanta, Georgia 30322.

[1] (a) Hill, C. L.; Schardt, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 6374–6375. (b) Groves J. T.; Kruper, W. J., Jr.; Haushalter, R. C. *Ibid.* **1980**, *102*, 6375–6377. (c) Hill, C. L.; Smegal, J. A. *Nouv. J. Chim.* **1982**, *6*, 287–289. (d) Tabushi, I.; Koga, N. *Tetrahedron Lett.* **1979**, 3681–3684. (e) Tabushi, I.; Yazaki, A. *J. Am. Chem. Soc.* **1981**, *103*, 7371–7373. (f) Tabushi, I.; Koga, N. *Ibid*, **1979**, *101*, 6456–6458.

[2] (a)Carnieri, N.; Harriman, A. *J. Photochem.* **1981**, *15*, 341–346. (b) Harriman, A.; Porter, G. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 1543–1552. (c) Porter, G. *Proc. R. Soc. London, Ser. A* **1978**, *A362*, 281–303. (d) Tabushi, I.; Kojo, S. *Tetrahedron Lett.* **1975**, 305–308.

[3] Abbreviations: TPP, TpMPP are the tetraphenylporphinato and the tetrakis(*p*-methoxyphenyl)porphinato dianion ligands, respectively.

[4] Camenzind, M. J.; Hollander, F. J.; Hill, C. L. *Inorg. Chem.* **1982**, *21*, 4301–4308.

[5] Schardt, B. C.; Hollander, F. J.; Hill, C. L. *J. Am. Chem. Soc.* **1982**, *104*, 3964–3972.

[6] Smegal, J. A.; Schardt, B. C.; Hill, C. L. *J. Am. Chem. Soc.*, in press.

[7] Hill, C. L.; Hollander, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 7318–7319.

[8] Smegal, J. A.; Hill, C. L. *J. Am. Chem. Soc.*, in press.

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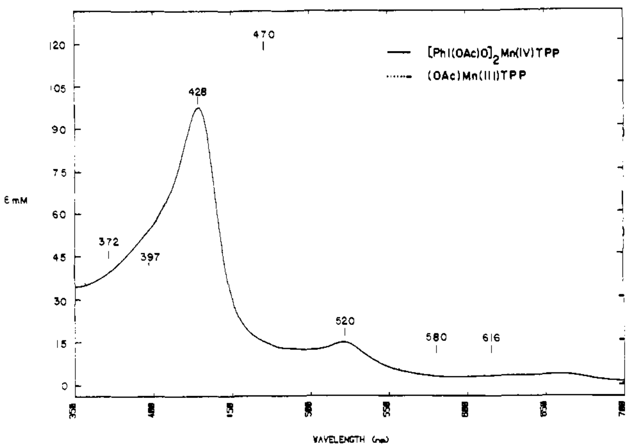


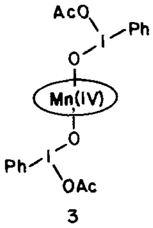
Figure 1. Visible absorption spectra of 3 and $Mn^{III}TPP(OAc)$. Spectra were recorded as 1 mM solutions in benzene at 25 °C.

equiv necessary to yield the isolated product was used to ensure complete oxidation. The resulting red-brown mixture was filtered into a receiver cooled to −35 °C. Addition of hexane to the stirred, chilled solution precipitated purple microcrystalline product, **3**, in 60% yield. Recrystallization from CCl_4/hexane at −30 °C provided analytically pure product.[9]

The visible absorption spectrum of **3** displays a broad absorption at 428 and at 520 nm (Figure 1) The resolved absorption band at 520 nm is characteristic of a monomeric manganese(IV) porphyrin and is similar to that displayed by the complex $Mn^{IV}TPP(OMe)_2$.[4] In the dimeric iodosylbenzene complexes, **2**, this band is present as a broad shoulder at 502 nm.[6]

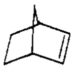
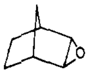
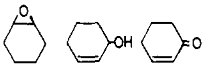
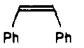
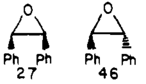
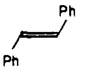
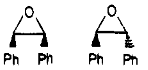
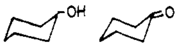
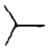
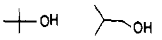
The infrared spectrum of **3** (KBr pellet) displays two absorption bands attributable to the acetate moiety: ν(C=O) at 1610 cm^{-1} and ν(C—O) at 1300 cm^{-1}, indicating an esterlike unidentate binding mode for acetate.[10,11] An absorption at 582 cm^{-1} that shifts to 550 cm^{-1} in the complex prepared from ^{18}O-labeled iodosylbenzene can be assigned to a Mn–O–I stretch.[6] The Mn–O–Mn stretching fundamental readily observed in **1** and **2** is absent in **3**.[5,6]

The variable-temperature magnetic susceptibility of **3** was determined in the solid state at a field strength of 5000 G from 5 to 300 K. A plot of $1/\chi_M$ vs. temperature yielded a straight line with a temperature intercept of −0.4 K, indicating Curie–Weiss behavior. On the basis of the equation $\mu_{eff} = 2.83[\chi_M(T-\theta)]^{1/2}$ and for $\theta = -0.4$ K, values for μ_{eff} ranged from 3.71 ± 0.02 μ_B at 5 K to 3.83 ± 0.02 μ_B at 300 K. On the basis of this result, we can assign a d^3 high-spin Mn(IV) porphyrin ground electronic state to **3**. All the data are consistent with but do not prove a structure for **3** as shown in the diagram.



3

Table I. Hydrocarbon Oxidation by 3[a]

substrate	products	% yield[b]
Ph_3P	$Ph_3P=O$	99
		67
	 34 22 2	58
	 27 46	73
	 <1 37	37
	 23 2	25
	 19 <1	19

[a] All reactions were run anaerobically at 25 °C with substrate present in at least 10-fold excess. Dichloromethane was used as solvent for the triphenylphosphine and cyclohexene reactions, chlorobenzene for the stilbene reactions, and benzene for the alkane oxidations. Approximately 2 equiv of iodobenzene were recovered in all reactions. [b] Yields are based on 2.5 two-electron oxidizing equiv for 3.

The reaction of **3** with various hydrocarbons and triphenylphosphine in relatively inert solvents at room temperature produced the products and yields listed in Table I. Approximately 2 equiv of phenyl iodide and 1 equiv of $Mn^{III}TPP(OAc)$ were produced in all these reactions. The formation of 2.5 equiv of triphenylphosphine oxide from the oxidation of triphenylphosphine by **3** demonstrates the five-electron oxidizing capability of **3** and confirms the presence of two trivalent iodine atoms in the complex.[12] Since **3** contains only two transferable oxygen atoms, the additional oxygen required by the observed yield of triphenylphosphine oxide may result from water present in the reaction. When the complex $Mn^{IV}TPP(OCH_3)_2$ was reacted with triphenylphosphine under the identical conditions, 0.6 equiv of triphenylphosphine oxide were observed, indicating that the $Mn^{IV}TPP$ moiety is capable of oxidizing triphenylphosphine to triphenylphosphine oxide under the reaction conditions utilized although the complex itself may be lacking in transferable oxygen atoms. The oxidation of *trans*-stilbene by **3** produced only *trans*-stilbene oxide in 37% yield, while the oxidation of *cis*-stilbene gave a 1.7:1 ratio of *trans*- to *cis*-epoxide in a total yield of 73%.[1b,13] The lower overall yield of epoxide from *trans*-stilbene is best explained by steric constraints at the activating site.[13a] The loss of stereospecificity in the oxidation of *cis*-stilbene is in accord with a radical intermediate that freely rotates about a C–C single bond.[1b]

The oxidation of alkanes is also effected by **3** in fair yields. Similar yields of alcohol products are producted from the oxidation of these substrates by the dimeric iodosylbenzene complexes, **2**.[6] With the dimeric complexes, however, good yields of halogenated products are also produced. In the reactions of **3** with hydrocarbons, acetate functionalization is not observed. The oxidation of isobutane by **3** indicates a high selectivity toward tertiary hydrogens.

We previously proposed a mechanism of alkane oxidation by the dimeric iodosylbenzene complexes which involved hydrogen atom abstraction from the substrate by an oxomanganese porphyrin complex formed from **2**.[8] Nearly identical product distributions in the reactions of both the dimeric complexes **2** and

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(9) Anal. Calcd for $C_{60}H_{44}N_4I_2MnO_6$: C, 58.79; H, 3.62; N, 4.57; I, 20.70. Found: C, 58.88; H, 3.60; N, 4.59, I, 20.16.

(10) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley: New York, 1978; pp 232–233.

(11) In the relevant compound $PhI(OAc)_2$, ν(C=O) is 1625, 1640 cm^{-1} and ν(C—O) is 1275 cm^{-1}. Bell, R..; Morgan, K. J. *J. Chem. Soc.* **1960**, 1209–1214.

(12) The designation of iodine in these complexes as I(III) is based on the common use of this formalism for describing tricoordinate iodinanes. In this formalism covalent iodine compounds such as $(C_6H_5)_3I$ and iodobenzene are assumed to have iodine in the 3+ and 1+ oxidation states, respectively. See: Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Wiley: New York, 1972; p 488.

(13) The stereochemistry of stilbene epoxidation by high-valent Cr and Fe porphyrin complexes has been reported by Groves and co-workers: (a) Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032–1033. (b) Groves, J. T.; Kruper, W. J., Jr. *Ibid.* **1979**, *101*, 7613–7615.

3 with alkanes and alkenes strongly suggest that similar functionalization mechanisms are operable for both types of complexes.[8]

Acknowledgment. Support of this work by the donors of the Petroleum Research Fund, administered by the Americal Chemical Society, and the National Science Foundation (Grant No. CHE-7909730) is acknowledged.

Registry No. 3, 85282-35-5; $\mathrm{Mn^{III}TPP(OAc)}$, 58356-65-3; $\mathrm{PPh_3}$, 603-35-0; bicyclo[2.2.1]hept-2-ene, 498-66-8; cyclohexene, 110-83-8; *cis*-stilbene, 645-49-8; *trans*-stilbene, 103-30-0; cyclohexane, 110-82-7; isobutane, 75-28-5.

New Probes for Electron-Transfer Processes. Evidence Supporting the Single-Electron-Transfer Mechanism in Additions of Carbanions to Dienones

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Received December 6, 1982

The question of whether carbanion additions to carbonyl compounds proceed via a single-electron-transfer (SET) pathway or a polar pathway has received much attention in recent years. Many of the studies in this area have sought to determine the operability of the SET pathway via the use of a variety of internal probes. These include, inter alia, cis-trans isomerizations of bulky enones[2] and the incorporation of "free radical clocks" in the carbanion.[3] In this communication we report on the development of a new probe for detecting SET processes and the use of this probe in elucidating the mechanism of carbanion additions to dienones.

The internal probe that we have used is the ethylenedioxy group. By placing this functional group on the α-carbon of a ketyl (radical anion), one introduces the possibility of carbon-oxygen bond scission. If the α-ethylenedioxyketyl in question is generated by a single electron transfer from a carbanion to an α-ethylenedioxy carbonyl compound, radical-radical anion combination is forced to compete with carbon-oxygen bond scission[4] (Scheme I). Since in direct carbanion additions to these substrates carbon-oxygen bond scission cannot be a competitive process, *the direct observation of products derived from carbon-oxygen bond scission in carbanion additions to α-ethylenedioxy carbonyl compounds would implicate the presence of a ketyl intermediate and would thereby provide strong support for the operability of the SET mechanism.*

In this regard we have studied the reactions of **1** with a variety of organometallics (see Table I). The most obvious fact that emerged from our studies is that significant amounts of **4** were produced in *all* of the cases investigated. This observation is, of course, completely consistent with the SET mechanism proposed in Scheme I. Similarly, the results obtained from the series *n*-butyllithium, *sec*-butyllithium, and *tert*-butyllithium are also compatible with the SET pathway, i.e., while the magnitude of k_3 is expected to decrease as the size of R· increases, the magnitude of k_2 has no direct relationship with R.

Scheme I

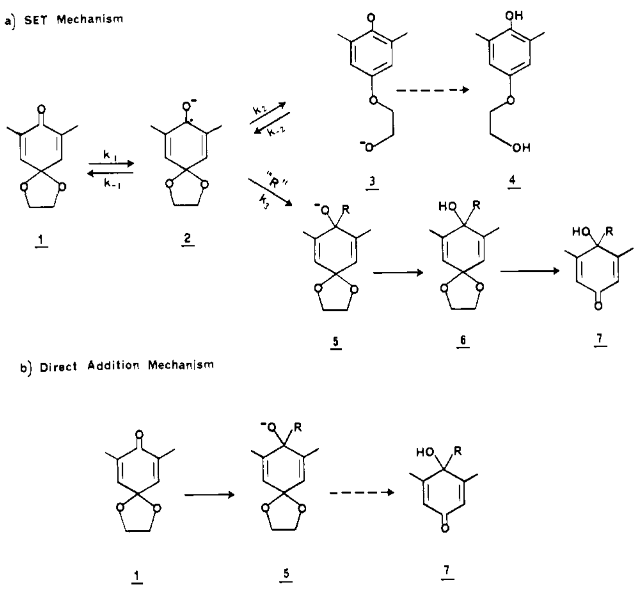

Table I

reagent	R	solvent	temp, °C	% 1^a	% 6^a	% 4^a
$(CH_3)_2CuLi$	CH_3^-	Et_2O	−78	15		85
CH_3Li	CH_3^-	Et_2O	−78 → 25	10	88	2
		THF	−78 → 25	7	90	3
		THF	−78		95	5
CH_3MgBr	CH_3^-	THF	−78 → 25	7	90	3
		THF	−78	2	95	3
n-C_4H_9Li	n-$C_4H_9^-$	Et_2O	−78 → 25	5	90	5
		THF	−78 → 25	4	95	1
		THF	0 → 25	8	46	46
n-C_4H_9MgBr	n-$C_4H_9^-$	THF	0	10	40	50
sec-C_4H_9Li	s-$C_4H_9^-$	THF	−78	30	26^b	44
t-C_4H_9Li	t-$C_4H_9^-$	THF/	−78	10		90
		TMEDA^c	−78 → 25	5	25^b	70
sec-C_4H_9Li	s-$C_4H_9^-$	THF/ TMEDA^c	−78 → 25	10	52	38

[a] Obtained via NMR spectroscopy. [b] Some ketal hydrolysis occurred during workup. Yield indicates the total amount of **6** and **7** that were produced. [c] Tetramethylethylenediamine (3 mol equiv equiv).

Unfortunately, although both of these observations are consistent with the SET mechanism, they do not rule out the possibility that the addition products (**6**) are formed by competitive direct carbanion addition. In order to answer this question, we examined the reaction of **1**[5] with 1-lithio-5-hexene (−78 → 25 °C). Since we have independently shown that this lithiate does not undergo any structural rearrangements,[6] the fact that *all* of the observed addition product, **6**, had R = cyclopentylcarbinyl clearly indicates the intermediacy of the 5-hexenyl radical,[7] which then undergoes a well-precedented rearrangement to the cyclopentylcarbinyl radical.[8] Radical/radical anion coupling produces **5**, which, upon quenching with a proton source, produces **6**. *These results taken as a whole not only demonstrate the operability of the SET mechanism with dienones but also rule out the possibility of any competitive direct carbanion addition.*

One additional point should be made. We had previously shown that quinols possessing general structure **7** could be produced by

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[1] Fellow of the Alfred P. Sloan Foundation, 1980–1984. Recipient of a Camille and Henry Dreyfus Teacher-Scholar Fellowship, 1981–1986.

[2] For example see: Ashby, E. C.; Wiesemann, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 310.

[3] For example, see: (a) Smith, J. G.; Irwin, D. C. *J. Am. Chem. Soc.* **1980**, *102*, 2757. (b) Ashby, E. C.; Bowers, J. S. *Ibid.* **1977**, *99*, 8504. See also: Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.

[4] Electron-transfer reactions involving γ-alkoxyenones rarely result in expulsion of the γ-alkoxy group from the intermediate radical anion. For example, see: Ruden, R. A.; Letterer, W. E. *Tetrahedron Lett.* **1975**, 2043. For an exception to this, see: Nilsson, A.; Ronlan, A.; Parker, V. D. *Ibid.* **1975**, 1107.

[5] A general method for the synthesis of quinone ketals, such as **1**, will be the subject of future reports.

[6] This lithiate was generated via a lithium-halogen exchange reaction involving 1-bromo-5-hexene, 2 equiv of *tert*-butyllithium, and 3 equiv of TMEDA in THF. If this mixture is quenched with trimethylsilyl chloride, 5-hexenyltrimethylsilane is cleanly produced.

[7] Because of the lack of radical byproducts observed, it is unlikely that this reaction produces a "free" 5-hexenyl radical. Instead, the radical is probably bound to a hexenyllithium aggregate and therefore less prone to participate in radical/radical or radical/molecule reactions.

[8] Walling, C.; Cioffari, A. *J. Am. Chem. Soc.* **1972**, *94*, 6059.

0002-7863/83/1505-2922$01.50/0