Unexpected Catalyzed C=C Bond Cleavage by Molecular Oxygen Promoted by a Thiyl Radical†

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Received August 31, 2000

Olefin oxidation with molecular oxygen, promoted by a transition metal catalyst and a thiophenol, involved C=C bond cleavage into the corresponding carbonyl derivatives. This new reaction proceeds under one atmosphere of oxygen, at room temperature, in the presence of an excess of thiophenol and a catalyst such as MnL_2 **3a** or $VClL_2$ **3c**. It was applied to aromatic and aliphatic olefins, as well as to functionalized or unfunctionalized acyclic compounds, providing the corresponding ketones and aldehydes in up to 98% yield. The synthetic interest of this catalytic oxidation was illustrated by a one-step preparation of the fragrance (−)-4-acetyl-1-methylcyclohexene **7e** in 73% isolated yield. The C=C bond cleavage probably results from a catalyzed decomposition of the *β*-hydroperoxysulfide intermediate **12** that is formed by the radical addition of thiophenol to the olefin in the presence of oxygen. Although an excess of the thiophenol was used, it was transformed into the disulfide which could then be reduced without purification in 83% overall yield, thereby allowing for recycling. In addition, the C=C bond cleavage under oxygen could be promoted by catalytic quantities of the thiyl radical, generated by photolysis of the disulfide; thus, in the presence of 0.1 equiv of bis(4-chlorophenyl) disulfide **4b** and 5% of the manganese complex **3a**, *trans*-methylstilbene **1b** gave, under radiation, benzaldehyde **6a** and acetophenone **7a** in up to 95% yield. This new reaction offers an alternative to the classical C=C bond cleavage procedures, and further developments in the fields of bioinorganic and environmental chemistry are likely.

Introduction

Considerable progress has been made in the field of catalytic olefin oxidation since the advent of industrial production of acetaldehyde[1] and ethylene oxide.[2] Consequently, numerous catalyzed epoxidation[3−5] or dihydroxylation reactions[6] and ketone[7] or α-hydroxyketone[8] syntheses are now recognized as classical methods. Moreover, from an ecological point of view, catalytic oxidations using hydrogen peroxide or molecular oxygen[9] have attracted increasing attention because of their environmentally friendly byproducts. Although catalytic oxidation of organic substrates by molecular oxygen is highly desirable for its simplicity, in most cases[10] it requires the use of an aldehyde,[11] 2-propanol, or a *β*-keto ester[12] in stoichiometric amounts.

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† This work was presented in part at the seventh International Symposium on Dioxygen Activation (ADHOC-99), July 19−23, 1999, York, UK.

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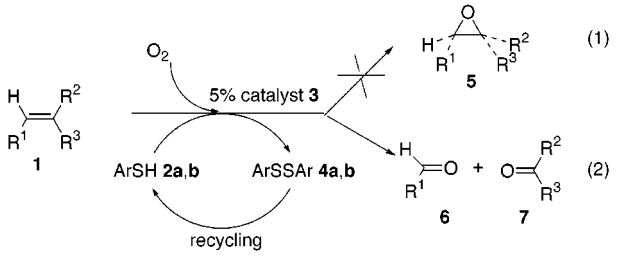
10.1021/jo0013148 CCC: $20.00
Published on Web 05/26/2001

Scheme 1

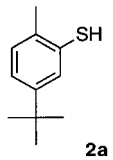


To investigate new reductants for the well-known catalyzed epoxidation of olefins by oxygen, we used the thiols **2**, expecting the formation of the disulfide **4**, which could then be easily recycled by simple reduction or irradiation (Scheme 1). However, using the thiophenol **2**, the catalytic oxidation of *trans*-stilbene **1** in the presence of the transition metal complex **3** did not give the expected epoxide **5** (Scheme 1, eq 1), but produced instead C=C bond cleavage in high yield (eq 2).

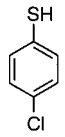
Although the oxidative cleavage of double bonds can be performed by $NaIO_4$ in the presence of osmium[13] or ruthenium tetraoxide,[14] only a few examples of catalytic oxidation using molecular oxygen as the terminal oxidant[15] have been reported. We now report here the unexpected C=C bond cleavage by molecular oxygen, promoted by thiophenol and related derivatives.

Results and Discussion

Cleavage of Aromatic Olefins. First, the reaction was investigated using *trans*-stilbene **1a** with oxygen (1 atm) in the presence of the thiophenols **2a** or **2b** and 5%



2a



2b

mol equiv of the transition metal complexes **3a**−**c** or of the salts ($MnCl_2$, $CoCl_2$). The complexes **3a**−**c** were prepared by mixing a solution of the corresponding transition metal chloride (1 equiv) with the ligand **10** (2 equiv), which was previously prepared by condensation of salicylaldehyde **8** with methyl serinate **9** (Scheme 2).

When the reaction was performed in acetone at room temperature in the presence of 4 equiv of the thiophenol **2a**[16] and 5% of the manganese complex **3a**, the conversion of stilbene **1a** was complete in 15 h, furnishing benzaldehyde **6a** in 70% yield (Table 1, entry 1). Under these conditions, no significant formation of the epoxide, diol, or benzoic acid was observed. Similar results were obtained using dichloromethane, ethyl acetate, toluene, methanol, or acetonitrile as the solvent. Without a catalyst, the conversion of stilbene was slower, and benzaldehyde was obtained in only 12% yield after 48 h (entry 2).

Table 1. C=C Bond Cleavage of Stilbene 1a with O_2

	reaction conditions[a]			PhCHO **6a**	
entry	ArSH	catalyst	acid	yield[b] (%)	time (h)
1	**2a**	**3a**	none	70	15
2	*c*	none	*c*	12	48
3	*c*	**3a**	H_3PO_4 (0.2 equiv)	75	6
4	*c*	$MnCl_2$	*c*	63	15
5	**2b**	**3a**	*c*	78	8
6	*c*	**3c**	*c*	94	4

[a] All reactions were carried out in acetone under 1 atm of oxygen at room temperature, with *trans*-stilbene **1a** (0.1M), catalyst (5% mol), and thiophenol **2** (4 equiv.). [b] Determined by GC. [c] Same as entry above.

When 0.2 equiv of phosphoric acid or a weak acid[17] were added to the reaction mixture, the reaction proceeded more rapidly, affording benzaldehyde in 75% yield after 6 h (entry 3). The C=C bond cleavage also occurred in the presence of 5% manganese(II) chloride or cobalt(II) chloride as the catalyst, since **1a** was completely consumed in 15 h, giving benzaldehyde **6a** in 63% yield (entry 4). On the other hand, when 4-chlorothiophenol **2b** was used, benzaldehyde was obtained in 78% yield in 8 h (entry 5). However, no appreciable improvement was observed with other aliphatic or aromatic thiols.[18] The best results were obtained using 4-chlorothiophenol **2b** with the vanadium catalyst $VClL_2$ **3c**. Thus, in acetone under oxygen at room temperature and in the presence of phosphoric acid (0.2 equiv), **1a** led to benzaldehyde **6a** in 94% yield in 4 h (entry 6).

It is noteworthy that the $NaBH_4$ reduction[19] of the crude disulfide **4a** (or **4b**) gave back the thiophenols **2a** or **2b** in 83% overall yields.

The oxidation of several aromatic olefins was studied (Table 2) using the best reaction conditions.

In the presence of the MnL_2 complex **3a** and thiophenol **2a**, conversion of *trans*-methylstilbene **1b** gave, in 4 h, benzaldehyde **6a** and acetophenone **7a** in 95% and 98% yields, respectively (entry 3). Monitoring the reaction mixture by GC showed that acetophenone formation was concomitant with olefin disappearance; however, benzaldehyde appeared more slowly and only reached a maximum after 4 h (Figure 1). It should be pointed out that complete conversion of the olefin required the consumption of 3 equiv of thiol over 2 h (Figure 1).

Although the reaction was slightly slower, very good

(10) For examples of catalytic olefin oxidation with oxygen and without any associated reductant, see: preparation of ethylene oxide,[2a] epoxidation or dihydroxylation, respectively, in the presence of a ruthenium porphyrin catalyst,[3b] or osmium: Döbler, C.; Mehltretter, G.; Beller, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 3026−3028.

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(16) Thiophenol **2a**, which was provided by Clariant SA (BP1, Trosly Breuil 60350, France), is nearly odorless.

(17) Use of formic, acetic, trichloroacetic, or benzoic acid gave also satisfactory yields.

(18) Use of 4-bromo-, 3,4-dichloro-, 2,3,5,6-tetrafluorothiophenol, 2-mercaptobenzoic acid, 2-mercaptonaphthalene, or 2-mercaptopyrimidine in the oxidation reaction often led to incomplete conversion of the olefin and formation of the aldehyde in poor yields. When thioethanol or dodecanethiol was used in the presence of 5% MnL_2 **3a**, stilbene **1a** did not react at room temperature after 24 h.

(19) Ookawa, A.; Yokohama, S.; Soai, K. *Synth. Commun.* **1986**, *16*, 819−825.

Scheme 2

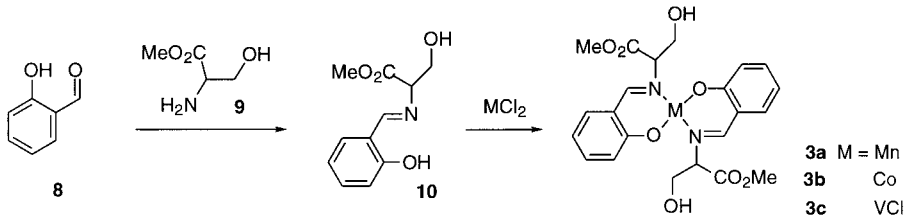


Table 2. Application to Various Aromatic Olefins

Entry	Olefin	Reaction conditions[a]	Products	yield[b] (%)	time (h)
1	Ph, Ph **1a**	**A**	H, O, Ph **6a**	75	6
2	Ph, Ph **1a**	**B**	H, O, Ph **6a**	94	4
3	Ph, Ph, Me **1b**	**A**	**6a**	95	4
			Me, O, **7a**, Ph	98	
4	Ph, Ph **1c**	**A**	**6a**	75	8
5	Ph **1d**	**A**	**6a**	83	8
6	Ph, Ph **1e**	**A**	Ph, O, Ph **7b**	95, 73[c]	10
7	**1f**	**A**	O, H, **6b**, O, H	13	20

[a] All reactions were carried out in acetone under 1 atm of oxygen at room temperature in the presence of 0.2 equiv of H_3PO_4; Conditions A: thiophenol **2a** (4 equiv), catalyst **3a** (5% mol); B: thiophenol **2b** (4 equiv), catalyst **3c** (5% mol). [b] Determined by GC. [c] Isolated yield.

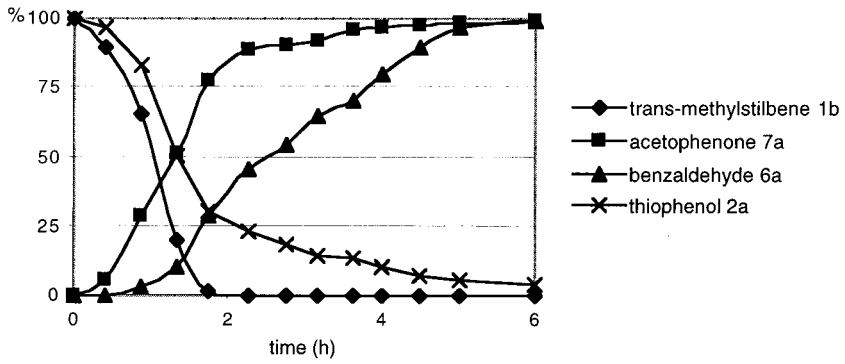


Figure 1. Kinetic study of the catalyzed C=C bond cleavage of *trans*-methylstilbene **1b** into acetophenone **7a** and benzaldehyde **6a**.

results were also obtained with CoL_2 **3b**, $Cr(acac)_3$, $Mn(acac)_2$, or $V(acac)_3$ as the catalysts.

Under standard conditions A, the reaction of *cis*-stilbene **1c** gave benzaldehyde in 75% yield in 8 h (entry 4). GC analysis of the reaction showed rapid conversion of the *cis*-**1c** into its *trans* isomer **1a** without any consumption of the thiophenol **2a** (Figure 2). Benzaldehyde was then formed at a rate corresponding to the disappearance of the thiophenol **2a**, and the yield reached 75% after 8 h (Figure 2). Ultimately the result was comparable to that obtained starting from *trans*-stilbene **1a** (entry 1).

The same conditions have also been successfully applied to styrene **1d** and diphenylethene **1e** (entries 5, 6).

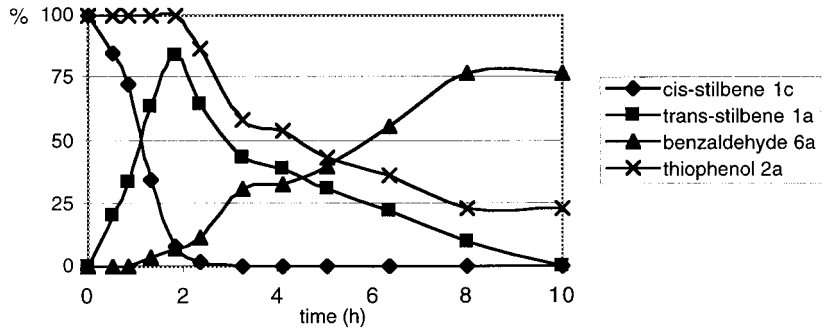
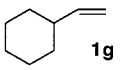
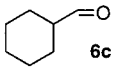
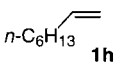
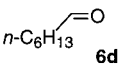
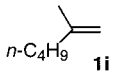
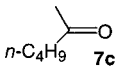
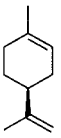
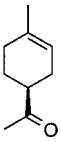


Figure 2. Kinetic study of the catalyzed C=C bond cleavage of *cis*-stilbene **1c** into benzaldehyde **6a**.

Table 3. Oxidation of Various Aliphatic Olefins

Entry	Olefin	Reaction conditions[a]	Product	yield[b] (%)	time (h)
1	 **1g**	A	 **6c**	34	144
2		B		58	24
3	 **1h**	B	 **6d**	58	24
4	 **1i**	B	 **7c**	74, 68[c]	4
5	 **1j**	B	 **7d**	68[c]	20
6	 **1k**	B	 **7e**	73[c]	15

[a] All reactions were carried out in acetone under 1 atm of oxygen at room temperature, using for conditions A: Mn-catalyst **3a** (5% mol)/thiophenol **2a** (5 equiv); B: V-catalyst **3c** (5% mol)/thiophenol **2b** (5 equiv). [b] Determined by GC. [c] Isolated yield.

However, in the case of the cyclic olefin **1f**, the expected dialdehyde **6b** was obtained in low yield (entry 7).

Cleavage of Aliphatic Olefins. Under the oxidation conditions A shown above, vinylcyclohexane **1g** reacted very slowly giving cyclohexanecarboxaldehyde **6c** in 34% yield after 6 days (Table 3, entry 1). Using 4-chlorothiophenol **2b** or ethyl acetate as the solvent, the reaction produced comparable results. The best conditions were obtained with the vanadium complex **3c**[20] as the catalyst, when the conversion of vinylcyclohexane **1g** reached 100% after 24 h, giving the cyclohexanecarboxaldehyde **6c** in 58% yield (entry 2). It should be noted that the appearance of cyclohexanecarboxaldehyde **6c** was not accelerated by the presence of an acid in the reaction mixture.

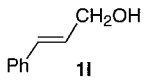
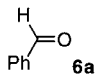
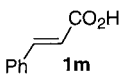
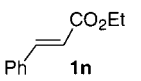
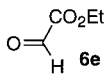
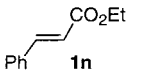
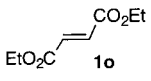
Using reaction conditions B as reported in Table 3, 1-octene **1h** led to heptanal **6d** in 58% yield over 24 h (entry 3), while 2-methyl-1-hexene **1i** gave 2-hexanone **7c** in 74% yield in only 4 h (entry 4). We also investigated the cleavage of several terpenes. β-Pinene **1j** gave nopinone **7d** in 68% isolated yield (entry 5), while more interestingly, the regioselective cleavage of the acyclic C=C bond of the (*S*)-(−)-limonene **1k** gave in one step and in 73% isolated yield the fragrance (*S*)-(−)-**7e**, which had been previously prepared in three steps and in 38% overall yield from **1k** (entry 6).[21]

Cleavage of Functionalized Olefins. Under the reaction conditions A, *trans*-cinnamic alcohol **1l**, cinnamic acid **1m**, and ethyl cinnamate **1n** underwent C=C bond cleavage, providing benzaldehyde **6a** in yields up to 73% (Table 4, entries 1−3). In the last case, the reaction was faster, and ethyl glyoxylate **6e** was obtained in 53% yield; however, when the reaction was carried out under the conditions B, the yields improved (entry 4). Finally, ethyl fumarate **1o** also underwent C=C bond cleavage, to form ethyl glyoxylate **6e** in 41% yield over 48 h (entry 5). Although the reaction was rather slow, these results demonstrate that our method for C=C bond cleavage is

(20) Use of commercialy available vanadium oxo bis (1-phenyl-1,3-dibutanedionate) or V(acac)$_3$ complexes led to similar results.

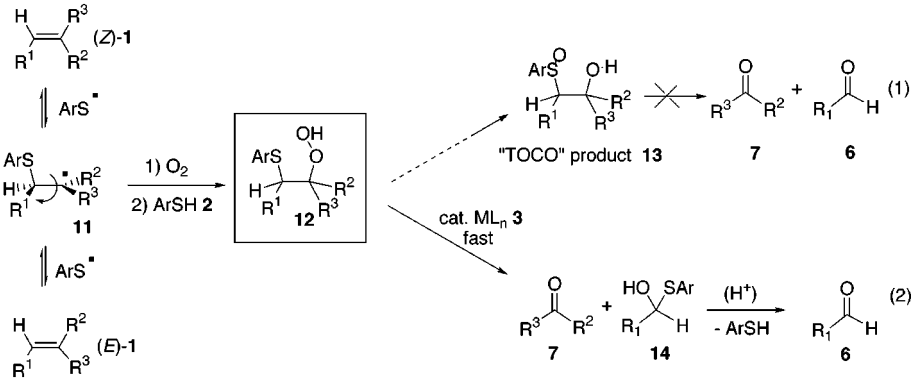
(21) Jo Davisson, V.; Dale Poulter, C. *J. Am. Chem. Soc.* **1993**, *115*, 1245−1260.

Table 4. Oxidation of Various Functionalized Olefins

Entry	Olefin	Reaction conditions[a]	time (h)	Products	yields[b,c] (%)	time (h)
1	 **1l**	A	16	 **6a**	61	16
2	 **1m**	A	22	**6a**	60	22
				6a	73	
3	 **1n**	A	3	 **6e**	53	10
4	 **1n**	B	1	**6a**	85	16
				6e	60	
5	 **1o**	A	48	**6e**	41	48

[a] All reactions were carried out in acetone under 1 atm of oxygen at room temperature; Conditions A: thiophenol **2a** (4 equiv)/Mn-catalyst **3a** (5% mol)/H_3PO_4 (0.2 equiv); B: thiophenol **2b** (5 equiv)/catalyst **3c** (5% mol)/without acid. [b] Determined by GC. [c] Based on unrecovered olefin.

Scheme 3



also effective with unsaturated compounds bearing electron-withdrawing substituents.

Mechanism of the C=C Bond Cleavage. It is known that addition of the thiyl radical ArS• to an olefin **1** is reversible, but the resulting radical **11** can be trapped by oxygen to provide the hydroperoxysulfide **12**, which then undergoes rearrangement to β-hydroxysulfoxide **13** ("TOCO" reaction; Scheme 3, eq 1).[22,23]

The fact that thiophenol was essential for the C=C bond cleavage and that the *cis*−*trans* isomerization of *cis*-stilbene **1c** into *trans*-stilbene **1a** was observed before any other reaction (Figure 2) are in agreement with the reversible addition of the thiyl radical to the olefin **1** (Scheme 3). The improvement observed with 4-chlorothiophenol **2b** also confirms this mechanism, since it is known that the thiyl radical polarity (i.e., *p*-ClPhS•) favored this addition.[23c,d]

On the other hand, since the β-hydroxysulfoxide **13** did not lead to the carbonyl products **6** and **7** (Scheme 3, eq 1), the carbon−carbon bond cleavage probably arises from the decomposition of the β-hydroperoxysulfide **12**, catalyzed by the transition metal complexes ML_n (eq 2). Thus, it is reasonable to assume that the decomposition of **12** provides the carbonyl compound **7** and the hemithioacetal **14**, leading to the aldehyde **6**. Consequently, the fact that the radical addition to the olefin occurs on the less substituted carbon atom (anti-Markovnikov) may explain the slower formation of the aldehyde **6** than of the ketone **7**, as observed in *trans*-methylstilbene **1b** (Figure 1). The regioselectivity and the better reactivity observed for the bond cleavage of limonene **1k**, and the acyclic olefins

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Scheme 4. Photoinduced C=C Bond Cleavage Catalyzed by the Disulfide 4b and the Transition Metal Complex 3a

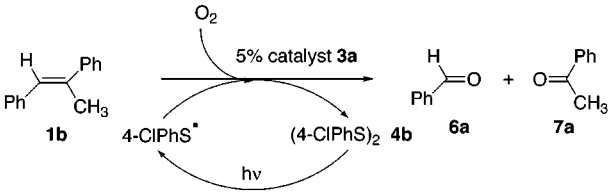

Table 5. Photoinduced C=C Bond Cleavage of *trans*-Methylstilbene 1b under Oxygen Bubbling

	reaction conditions[a]		products		
entry	**4b**/**1b** ratio	conversion time[b] (h)		yields[b](%)	time (h)
1	0.5	0.5	**6a**	73	0.5
			7a	95	1.5
2	0.25	0.5	**6a**	55	1
			7a	91	3
3	0.1	2	**6a**	40	2
			7a	95	8

[a] All reactions were carried out in ethyl acetate under oxygen bubbling, at room temperature, under radiation by medium-pressure mercury lamp through Pyrex. [b] Determined by GC.

1d,**e**,**g**−**j** (Table 2, 3), can also be interpreted by this mechanism.

Photoinduced C=C Bond Cleavage. Since thiyl radicals can be formed from aromatic disulfide photolysis,[22] we applied this activation process to promote the C=C bond cleavage by oxygen under totally catalytic conditions (Scheme 4).

In the absence of a catalyst, the photolysis of *trans*-stilbene **1a** under oxygen, performed by irradiation with a medium-pressure mercury lamp through Pyrex in the presence of thiophenol **2a**, led to the formation of the corresponding β-hydroxysulfoxide **13**.

Photolysis of *trans*-methylstilbene **1b** under oxygen in the presence of a catalytic amount of the manganese complex **3a** and bis(4-chlorophenyl)disulfide **4b** gave acetophenone **7a** and benzaldehyde **6a** with the speed of the reaction depending on the **4b**/**1b** ratio (Table 5).

Using 0.5 or 0.25 equiv of disulfide **4b**, the reaction proceeded quite rapidly, and acetophenone **7a** was obtained in up to 95% yield. The benzaldehyde yields reached 73%, but decreased under the oxidation conditions (entries 1, 2). When the reaction was carried out with 0.1 equiv of disulfide **4b**, the conversion of **1b** was slower and acetophenone was produced in good yield (95%), while benzaldehyde **6a** was formed in only 40% yield (entry 3).

Conclusion

We have herein reported the first example of a catalytic C=C bond cleavage, at room temperature, of olefins under an oxygen atmosphere into aldehydes and ketones in good to excellent yields. This new reaction resulted from transition metal catalyzed decomposition of the β-hydroperoxysulfide **12** formed in situ from thiyl radical addition to the double bond, followed by oxygen trapping. A study of the reaction showed that it can be performed in a majority of common solvents and catalyzed by various transition metal salts or complexes. It is particularly suited for acyclic substrates, and several examples showed that the reaction was compatible with other functional groups such as alcohols, esters, or acids. Promising selectivity was demonstrated by the cleavage of the acyclic double bond of limonene **1k**, which yielded in one step the ketone **7e** in 73% yield. Although this catalyzed C=C bond cleavage requires 4 equiv of thiophenol **2a** (or **2b**) as the coreagent, the disulfide produced as the byproduct can be readily reduced in very good yield, without any purification. Moreover, we have shown that a disulfide can be used as a catalytic thiyl radical precursor. Thus, by photolysis with a medium-pressure mercury lamp, 0.1 equiv of disulfide was sufficient to bring the reaction of *trans*-methylstilbene **1b** with oxygen to completion in 2 h, giving the corresponding carbonyl derivatives.

The present system for the oxidation of olefins catalyzed by transition metal complexes or salts offers an alternative to the classical C=C bond cleavage procedures, and new developments in the fields of bioinorganic and environmental chemistry are likely.

Experimental Section

General Procedures. Solvents were dried and freshly distilled under a nitrogen atmosphere over sodium/benzophenone for THF, CaH_2 for acetone, ethyl acetate, methylene chloride, chloroform, and acetonitrile, and sodium alcoholate for EtOH and *i*-PrOH. Oxygen gas was purchased from Air Liquide and used as received. 4-Chlorothiophenol, $Cr(acac)_3$, cinnamic acid, cinnamic alcohol, ethyl cinnamate, ethyl fumarate, dihydronaphthalene, (−)-limonene, β-pinene, *cis*- or *trans*-stilbene, *trans*-methylstilbene, styrene, 1,1-diphenylethene, $V(acac)_3$, VCl_3, and vanadium oxo bis(1-phenyl-1,3-dibutanedionate) were purchased from Aldrich, Acros, Avocado, and Fluka. All compounds were purified by either vacuum distillation or recrystallization before use. $MnCl_2$ and $CoCl_2$ were dried by heating at 100 °C.

GC analysis of reactions with aromatic olefins, cinnamic alcohol, and cinnamic acid were performed with dodecane (1%) as an internal reference using a Carlo Erba GC 6000 (Vega series 2), equipped with an Alltech AT-WAX (30 m × 0.32 mm i.d. × 0.5 μm film) column and fitted with a 1020 Perkin-Elmer integrator. The programming of temperature was carried out from 110 to 230 °C at 10 °C/min (hold 30 min). Oxidation of *trans*-stilbene was also analyzed on a DB-5 (J &W Scientific) (30 m × 0.32 mm i.d.) column with temperature program from 70 °C to 80 °C at 5 °C/min, 80 °C to 230 °C at 15 °C/min (hold 15 min). GC analyses of vinylcyclohexane, ethyl cinnamate, diethyl fumarate, limonene, 2-methylhexene, 1-octene, and β-pinene were performed with dodecane (1%) as an internal reference and using a Perkin-Elmer Autosystem. It was equipped with a RESTEK RTX 1- SE 30 (100% dimethylpolysiloxane; 30 m × 0.32 mm × 0.5 μm film) column and fitted to a 1020 Perkin-Elmer integrator. The oven temperature was programmed from 80 to 310 °C at 10 °C/min (hold 30 min). The ethyl glyoxylate was compared to an authentic sample of the corresponding hemiacetal with EtOH furnished by Clariant SA. GC-MS analyses were performed on a Nermag R10-10C mass spectrometer, coupled with a Varian gas chromatography equipped with Chrompack CP-Sil-5 (30 m × 0.25 mm i.d. × 0.25 μm film) column, with temperature program from 90 to 310 °C at 5 °C/min. All photolyses were conducted in a temperature-controlled water bath (25 °C), with a Mazda medium-pressure mercury 250 W lamp fitted with a Pyrex sleeve. Thin-layer chromatography was performed on silica chromagel (60 F_{254}; SDS) and exposed by UV or permanganate treatment. Flash chromatography was performed on silica gel (60ACC, 6−35 μm; SDS). All NMR spectra were recorded on a Bruker DPX 250 spectrometer using TMS as internal reference for ^1H and ^{13}C NMR. Melting points were measured on a Buchi melting point apparatus and are uncorrected. Optical rotation values were determined at 20 °C on a Perkin-Elmer 241 polarimeter. Infrared spectra were recorded on a Bruker Equinox 55. Mass spectral analyses were performed

on a NERMAG R10-10C and a JEOL MS 700 for exact mass, at the Mass Spectroscopy Laboratories of ENSCP and ENS Paris, respectively. The major peak *m*/*z* is mentioned with the intensity as a percentage of the base peak in brackets. Elemental analyses were measured with a precision superior to 0.3% at the Microanalysis Laboratory of P. & M. Curie University (Paris).

Preparation of Methyl 2-*N*-Salicylidene-3-hydroxypropanoate 10 Ligand and Its Corresponding ML_2 Complexes. Following a literature procedure,[12] in a 50 mL round-bottomed flask equipped with a magnetic stirrer, 1.09 g (7 mmol) of methyl D,L-serinate hydrochloride[24] was introduced in 35 mL of EtOH, and triethylamine (1.1 mL; 7.9 mmol) was added under stirring at room temperature. Then 0.75 mL of salicylaldehyde **8** (7 mmol) was added, and the mixture was stirred for 5 h. After removal of the solvent, the residue was purified by chromatography on silica gel using acetonitrile as eluent. The ligand was obtained as a yellow oil. R_f = 0.8 (acetonitrile); yield 1.45 g, 93%; IR (neat, ν cm^{-1}): 3444 (vs), 1740 (s), 1632 (w), 1279 (m); ^{1}H NMR ($CDCl_3$): δ 3.54 (3H, s, C*H*$_3$), 3.72 (1H, m, C*H*), 3.92 (2H, m, C*H*$_2$), 6.64−6.71 (2H, m, *H* arom), 7.04−7.12 (2H, m, *H* arom), 8.18 (1H, s, C*H*Ph), 12.50 (1H, sl, O*H*); ^{13}C NMR ($CDCl_3$): δ 52.6 (*C*H$_3$), 63.6 (*C*H$_2$O), 72.7 (*C*H), 117.2 (*C*H arom), 118.6 (*C* arom), 119.0 (*C*H arom), 132.1 (*C*H arom), 133.1 (*C*H arom), 160.9 (*C* arom), 168.6 (*C*HPh), 170.4 (*C*O$_2$Me); MS (EI; CH_4) *m*/*z* (relative intensity): 223(62), 192(26), 164(38), 132(100), 107(67), 77(29); HRMS (EI) calcd for $C_{11}H_{13}NO_4$: 223.0844; Found: 223.0844.

The complexes **3a**−**c** were prepared by mixing a solution of the ligand **10** (2 equiv) with the corresponding transition metal chloride (1 equiv) and were used without further purification.

C═C Bond Cleavage under Oxygen and in the Presence of Thiophenol. Typical Procedure. In a 25 mL round-bottomed flask equipped with a magnetic stirrer and a rubber septum containing the unsaturated compound **1a**−**o** (1 mmol) were added 22 mg of the ligand **10** (0.1 mmol) and 6.3 mg of $MnCl_2$ (conditions A), or 7.9 mg of VCl_3 (conditions B) and 10 mL of acetone. Then, 4 equiv of thiophenol **2a** (or **2b**; 4 mmol) was added, and the flask was subjected to three vacuum/O_2 cycles, before pressurizing to 1 atm with a balloon of O_2. After addition of 0.2 equiv of H_3PO_4, the reaction medium was stirred at room temperature and the reaction was monitored by GC. Upon completion, the reaction mixture was filtered through a short column of silica gel (3 cm), which was washed with 2 × 50 mL of EtOAc. After removal of the solvent, the residue was purified either by silica gel chromatography with cyclohexane as eluent or distilled under vacuum using a bulb to bulb Kugelrohr apparatus, to afford the carbonyl compound(s) and a residue containing the disulfide **4a** (or **4b**).

(1*R*,5*S*)-(+)-Nopinone 7d from (−)-β-Pinene 1j. In a 50 mL round-bottomed flask were introduced 19 mg of VCl_3 (0.12 mmol), 53.8 mg of ligand **10** (0.242 mmol), and 10 mL of acetone, under oxygen. After 20 min of stirring at room temperature, 326 mg of β-pinene **1j** (2.4 mmol; $[\alpha]_D^{20}$ = −19 neat), 1.39 g of 4-chlorothiophenol **2b** (9.6 mmol), and 15 mL of acetone were added and then stirred at room temperature for 20 h. After removing the solvent, the residue was distilled using a bulb to bulb Kugelrohr apparatus under vacuum (bp = 130 °C; 20 mmHg) to give 297 mg of the crude pinanone **7d**, which was repurified by silica gel chromatography using a mixture of pentane/diethyl ether (4:1) as eluent. Colorless oil. R_f = 0.2 (petroleum ether/diethyl ether); yield 226 mg, 68%; $[\alpha]_D^{20}$ = +36.5, lit.[25] $[\alpha]_D^{20}$ = +36.9 (*c* 4, MeOH); IR (neat, ν cm^{-1}): 2949 (s), 1711 (s); ^{1}H NMR ($CDCl_3$): δ 0.85 (3H, s, C*H*$_3$), 1.33 (3H, s, C*H*$_3$), 1.59 (1H, m, C*H*), 1.94−2.07 (2H, m, C*H*$_2$), 2.23−2.39 (2H, m, C*H*$_2$), 2.50−2.59 (3H, m). ^{13}C NMR ($CDCl_3$): δ 21.3 (*C*H$_2$CH$_2$CO), 22.0 (*C*H$_3$), 25.1 (CH*C*H$_2$CH), 25.8 (*C*H$_3$), 32.7 (*C*H$_2$CO), 40.3 (CH$_2$*C*HCH$_2$), 41.1 (*C*(CH$_3$)$_2$), 57.8 (*C*HCO), 214.6 (*C*O); MS (EI) *m*/*z* (relative intensity): 108 (60), 69 (*m*/2*z*; 100), 55 (86); MS (DCI; CH_4) *m*/*z* (relative intensity): 139 (MH^+); HRMS (DCI, CH_4) calcd for $C_9H_{15}O$ (MH^+): 139.1123; Found: 139.1125.

(*S*)-(−)-4-Acetyl-1-methylcyclo-1-hexene 7e from (*S*)-(−)-Limonene 1k. In a 50 mL round-bottomed flask were introduced 25 mg of VCl_3 (0.16 mmol), 71 mg of ligand **10** (0.32 mmol), and 15 mL of acetone, under oxygen. After 20 min of stirring at room temperature, 407 mg of (*S*)-(−)-limonene **1k** (3 mmol; $[\alpha]_D^{20}$ = −100 (*c* 10, EtOH), 2.16 g of 4-chlorothiophenol **2b** (14.95 mmol, 5 equiv), and 15 mL of acetone were added and stirred at room temperature for 15 h. After removal of the solvent, the residue was distilled using a bulb to bulb Kugelrohr apparatus under vacuum (bp = 120 °C; 1 mmHg), to give 430 mg of the crude ketone **7e** and 2.47 g of a residue, which was purified by chromatography using cyclohexane as eluent, to give the disulfide **4b** (1.88 g; yield 87%). The final purification of **7e** was carried out by silica gel chromatography using a mixture of pentane/diethyl ether (95:5) as eluent. Colorless oil. R_f = 0.4 (petroleum ether/diethyl ether 9:1); yield 300 mg, 73%; $[\alpha]_D^{20}$ = −97 (*c* 3.6, $CHCl_3$), lit.[21] $[\alpha]_D^{20}$ = −92 (*c* 6.3, $CHCl_3$); IR (neat, ν cm^{-1}): 2920 (s), 1709 (s), 1440 (m), 1362 (m), 1162 (m); ^{1}H NMR ($CDCl_3$): δ 1.65 (4H, m), 1.96 (3H, m, C*H*$_3$C═C), 2.18 (5H, m), 2.48−2.58 (1H, m, C*H*CO), 5.39 (1H, sl, C═C*H*); ^{13}C NMR ($CDCl_3$): δ 23.5 (*C*H$_3$C═C), 25.0 (*C*H$_2$), 27.1 (*C*H$_2$), 28.1 (CO*C*H$_3$), 29.6 (*C*H$_2$), 47.3 (*C*HCO), 119.3 (C═*C*H), 133.9 (C═*C*CH$_3$), 212.1 (*C*O); MS (EI) *m*/*z* (relative intensity): 138 (86), 123 (58), 95 (100); MS (DCI; CH_4) *m*/*z* (relative intensity): 139 (MH^+; 100), HRMS (DCI, CH_4) calcd for $C_9H_{15}O$ (MH^+): 139.1123; Found: 139.1120.

Photoinduced C═C Cleavage of *trans*-Methylstilbene 1b under Oxygen and in the Presence of the Disulfide 4b and the Mn-Complex 3a. Typical Procedure. In an annular Pyrex reactor, equipped with a diving mercury medium-pressure lamp 250 W, 194 mg of *trans*-methylstilbene **1b** (1 mmol), 6.3 mg of $MnCl_2$ (0.05 mmol), 22.3 mg of the ligand **10** (0.1 mmol), and 10 mL of EtOAc were introduced. The solution was irradiated under oxygen bubbling, and the reaction was monitored by GC.

Acknowledgment. S.J. gratefully acknowledges the Association Paul Neumann of the French Hoechst Society (now Clariant) for financial support, and thanks D. Mansuy and G. Mattioda for helpful discussions. We also thank J. Salaün for his help in the preparation of the manuscript, and N. Morin and N. Sellier for obtaining HRMS and GCMS data.

Supporting Information Available: Formation of 3-(2-carboxaldehyde phenyl)propanal **6b** and β-hydroxysulfoxide **13** by photolysis. Recycling of the disulfide **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0013148

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