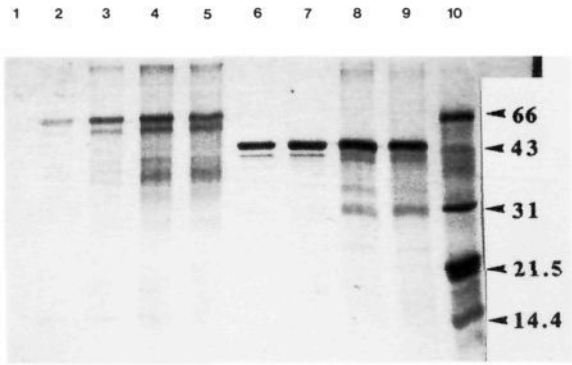

Figure 3. Peroxonitrite-generated hydroxyl radical. To samples of BSA and enolase in O_2-saturated 10 mM NaH_2PO_4, pH 7.0, was added directly either 2, 20, or 40 mg of ONOOK/KNO_3 generating 22, 220, and 440 nmol of HO•, respectively. BSA was present at a concentration of 0.30 mg/mL and enolase at a concentration of 0.23 mg/mL. After BHZ derivatization, 0.5 μg of protein/lane was loaded, separated, and then Western blotted. The strepavidin-AP/BCIP/NBT visualized blots are shown. Lane 1: untreated BSA control (biotinylation omitted, no bands apparent). Lane 2: untreated, BHZ-derivatized BSA control. Lane 3: 22 nmol of HO•/0.15 mg of BSA. Lane 4: 220 nmol of HO•/0.15 mg of BSA. Lane 5: 440 nmol of HO•/0.15 mg of BSA. Lane 6: untreated, BHZ-derivatized enolase control. Lane 7: 22 nmol of HO•/0.10 mg of enolase. Lane 8: 220 nmol of HO•/0.10 mg of enolase. Lane 9: 440 nmol of HO•/0.10 mg of enolase. Lane 10: biotinylated molecular weight standards.

and *p*-nitro blue tetrazolium chloride (NBT). Comparison of the Western blots for the two proteins using samples exposed to the two different HO•-generating methods (Figures 2 and 3) indicates that addition of the peroxonitrite reagent results in protein damage directly analogous to that produced radiolytically.

The streptavidin-AP-probed Western blots show that the majority of the newly formed BHZ-derivatized carbonyl moieties are present in the unfragmented protein, indicating that side-chain oxidation giving carbonyl substitution occurs more frequently than protein scission. This is consistent with the observation that side-chain H atom abstraction by HO• predominates over α-hydrogen abstraction in amino acids.[13]

The advantages of the peroxonitrite solid solution as a HO• source are numerous. The solid solution is remarkably stable; irradiated KNO_3 solid has been kept under ambient conditions for months with no observed decrease in yellow color or reactivity. The peroxonitrite can be quantified by dissolution in 0.1 M NaOH using $\epsilon_{302} = 1670\ cm^{-1}\ M^{-1}$.[14] This quantitation permits reproducible amounts of HO• to be generated in separate experiments.

Another advantage is the rapid disproportionation of the other radical product, NO_2•, which proceeds by the two steps

$$2NO_2^{\bullet} \rightarrow N_2O_4$$

$$N_2O_4 + H_2O \rightarrow NO_3^- + NO_2^- + 2H^+$$

which have rate constants $9 \times 10^8\ M^{-1}\ s^{-1}$ and $1 \times 10^3\ s^{-1}$, respectively.[15] By contrast, Fenton chemistry, which requires H_2O_2, generates HO_2• by the reaction of HO• with H_2O_2[16] and potentially generates hypervalent iron-oxo and nucleophilic iron-coordinated peroxo moieties. The large number of reactive species makes it difficult to determine the reaction sequences that generate the observed products. If the site-directed iron-EDTA protein cleavage systems[17] generate diffusible HO•, significant oxidative damage to neighboring amino acids should be observed in addition to cleavage. The lack of such surrounding damage would corroborate the proposal of Rana and Meares[18] that the protein fragmentation observed with a site-specific iron-EDTA conjugate is the result of a nucleophilic reaction.

A final major advantage of the single reagent system is enhanced control over the time and place of HO• generation. The time scale of exposure to HO• radical with the peroxonitrite reagent is on the order of several seconds beyond the time required for dissolution. This provides the potential for probing transient phenomena with half-lives as short as 10 s. The present results suggest the interesting possibility of generating HO• inside a cell by microinjection of the peroxonitrite-containing solid and investigating damage to the cellular components. This localization of effect would be impossible with either radiolysis or Fenton chemistry.

Acknowledgment. We thank Frank Johnson for initial investigations and Dr. John Leith for his assistance with the ^{137}Cs irradiations. The ^{137}Cs source is supported by Grant RR-01997. V.E.A. is a fellow of the Sloan Foundation.

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Cyclorearrangement and Cycloolefination of Keto Bis-sulfones. A Sulfone Analogue of a Pinacol Reduction-Rearrangement

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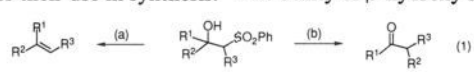
The utility of organosulfones as basic building blocks initially stemmed from their ease of deprotonation to generate nucleophiles followed by reductive cleavage.[1] The recent discovery of the displacement of an arylsulfonyl group by a nucleophile mediated by a Lewis acid[2-4] or a transition metal complex[5] significantly enhances their use in synthesis. The utility of β-hydroxy sulfones



as olefination intermediates (eq 1a)[6] and their prospects for Wagner-Meerwein shifts (eq 1b)[7] suggest versatile cyclization

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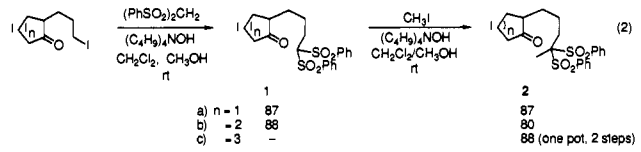
methodology requiring intramolecular addition of a sulfone-stabilized anion to a carbonyl group—a process thwarted by the lack of chemoselectivity in the deprotonation of a keto sulfone.[8] On the other hand, a geminal bis-sulfone permits easy chemoselective alkylation α to the sulfone in the presence of a carbonyl group (eq 2). Reductive cyclization of the bis-sulfones **1** and/or **2** would



1

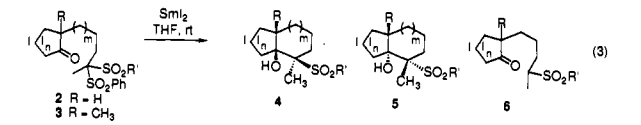
a) n = 1 87
b) = 2 88
c) = 3 –

2

87
80
88 (one pot, 2 steps)

provide a convenient strategy to these important building blocks. We wish to report the development of such a cyclization reaction and the subsequent Wagner–Meerwein shifts in a protocol that might be characterized as the sulfone analogue of a pinacol reduction–rearrangement.

In line with our notion of a pinacol type reduction, we initially subjected **2a** to low-valent titanium,[9] but unsuccessfully. On the other hand, the excellent success of lanthanides for reductive cyclization,[10,11] notably in the work of Molander,[12] led us to add **2a** to freshly prepared SmI_2 (kept in the presence of excess Sm) in THF at room temperature (eq 3).[13] The desired product **4a**[14]

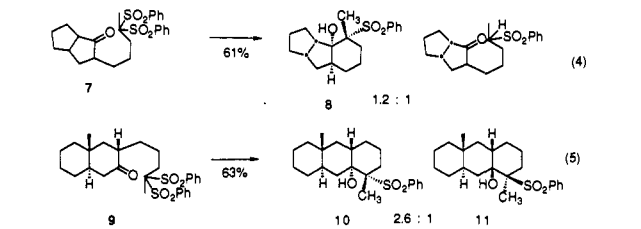


2 R = H
3 R = CH3

4 5 6

2a	m = 1	n = 1	R' = Ph	90%	2	-	1
2b	1	2	Ph	71%	2.3	1	-
2c	1	3	Ph	80%	2.6	1	-
2d	2	2	Ph	92%	–	ONLY	-
3e	1	2	Ph	91%	3	1	-
3f	1	2	CH_3	57%	5.2	1	-

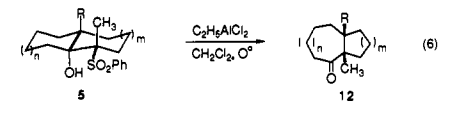
is obtained in 60% yield as a single diastereomer with the only byproduct being that of simple desulfonylation, **6a**. Another cyclopentanone substrate (**7**) shows similar behavior (eq 4), whereas, cyclohexanones (eq 3, substrates **2b**, **2d**, **3e**, **3f**; eq 5) and a cycloheptanone (eq 3, substrate **2c**) are devoid of this complication. X-ray crystallography establishes the stereochemistry of **4a** and **5c**. Correlation of the spectral and chromato-



7 8 9 10 11

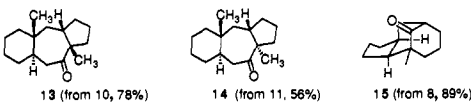
graphic properties of these compounds to the other products allows their assignment as depicted. The cis stereochemistry of the hydroxyl and sulfone substituents in all products suggests that, *in spite of the widespread belief that sulfones are poor Lewis bases,*[15] *samarium coordinates with both the carbonyl and sulfone oxygens in the transition state for cyclization.* The excellent chemoselectivity for cleavage of the aryl sulfone (**3f**, eq 3) correlates with the lower reduction potential for an aryl versus alkyl sulfone.

Conformationally rigid *trans*-β-hydroxy sulfones undergo pinacol type rearrangements in the presence of aluminum Lewis acids with very high regioselectivity to form bicyclic ketones **12** (eq 6)[16] through **15** on the basis of a trans periplanar arrangement of the migrating bond and the sulfone leaving group. On the other



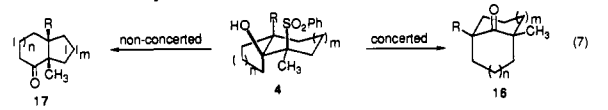
5 12

b) R = H	m = 1	n = 1	100% (86%)
c) H	1	2	97% (60%)
d) H	2	1	80% (77%)
e) CH_3	1	1	98% (75%)



13 (from 10, 78%) 14 (from 11, 56%) 15 (from 8, 89%)

hand, the conformationally less rigid *cis*-β-hydroxy sulfones give mixtures of bridged (**16**)[14] and fused (**17**)[14] bicycles (eq 7).[16] Whereas the former arises by the expected trans periplanar migration, the cis ring juncture of the fused bicycles suggests a nonconcerted pathway for their formation. Choice of Lewis acid

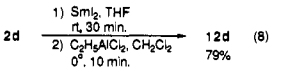


17 4 16

1	a) R = H	m = 1	n = 1	– (85%)	4
1	b) H	1	2	100% (88%)	2
1	c) H	1	3	99% (86%)	1.5
1	e) CH_3	1	2	89%	1

can switch the mechanism from a concerted to a nonconcerted pathway. For example, $Al(OSO_2CF_3)_3$[17] switches the rearrangement of **5e** from the previously observed formation of the fused bicycle **12e** (eq 6) to formation of the bridged bicycle **16e** as the major product (90%, **16e**:**12e** = 3:1), a product arising from the nonconcerted pathway for a trans-fused β-hydroxy sulfone. $Al(OSO_2CF_3)_3$ buffered with $C_2H_5AlCl_2$ is required to effect the rearrangement of **4e** and may account for the larger amount of the nonconcerted product (eq 7).

The protocol for cyclorearrangement does not require purification of the intermediate β-hydroxy sulfones. For example, the keto bis-sulfone **2d** provides an overall isolated yield of the fused bicyclic ketone **12d** of 79% (eq 8). The utility of the β-hydroxy



2d 12d 79%

sulfones as precursors to olefins (eq 1a) converts the protocol of pinacol type reduction–reductive cleavage into a cycloolefination to add to the cyclorearrangement protocol[18] (eq 9) from the same readily available keto bis-sulfones. The diversity stems from the availability of sulfones to function as chemical chameleons—nucleophiles or electrophiles, depending upon their chemical environment.[2]

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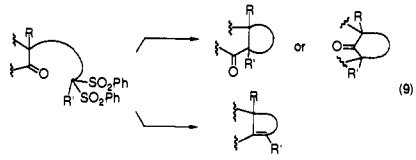

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health for their generous support of our programs and Merck Sharp and Dohme Research Laboratories for the X-ray structures. Mass spectra were provided by the Mass Spectrometry Facility, University of California at San Francisco, supported by the NIH Division of Research Resources.

Supplementary Material Available: Listings of characterization data for **4**, **5**, **8**, **10–12**, and **13–16** and X-ray data for **4a** and **5c** (4 pages). Ordering information is given on any current masthead page.

Spectroscopic Observation of a Thermal C–H Bond Insertion Reaction at 5 K: Intramolecular Rearrangement of $Fe(CO)_3(\eta^2\text{-}C_3H_6)$ To Produce $HFe(CO)_3(\eta^3\text{-}C_3H_5)$

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We report direct observation of the rearrangement of a coordinatively-unsaturated (η^2-alkene)metal complex to yield a coordinatively-saturated (η^3-allyl)metal hydride complex. This observation is significant in two distinct mechanistic contexts: alkene isomerization[1] and C–H bond activation.[2] Although several (η^3-allyl)metal hydrides have been well characterized,[3,4] few of the corresponding coordinatively-unsaturated (η^2-alkene)metal complexes have been characterized[5] because of their rapid rearrangement to (η^3-allyl)metal hydrides. Recent studies of C–H bond activation resulted in the direct observation of *inter*molecular C–H bond insertion reactions.[2a,6] Our studies result in direct observation of an *intra*molecular C–H bond insertion reaction that is remarkably facile, occurring thermally at temperatures as low as 5 K.

Photolysis (260 ± 10 nm, 30 min) of $Fe(CO)_4(\eta^2\text{-}CH_2{=}CHCH_3)$ (**1**),[7-9] matrix-isolated in either argon or methylcyclohexane (MCH) at 10 K,[10] results in a decrease in intensity of the carbonyl infrared absorptions of **1** with concomitant appearance of free CO (2132 cm^{-1}) and several new carbonyl infrared absorptions (Figure 1, Table I). The absorptions at 2064 and 1998 cm^{-1} are due to $HFe(CO)_3(\eta^3\text{-}CH_2CHCH_2)$ (**4**), which has been previously characterized by IR spectroscopy in an MCH glass at 90 K[8] and by ^1H and ^{13}C NMR spectroscopy in fluid MCH-d_{14} at 160 K.[4] The absorption at 2046 cm^{-1} is due to $^{\bullet}Fe(CO)_3(\eta^3\text{-}CH_2CHCH_2)$ (**5**).[11] The absorptions at 2038 and 1959 cm^{-1}

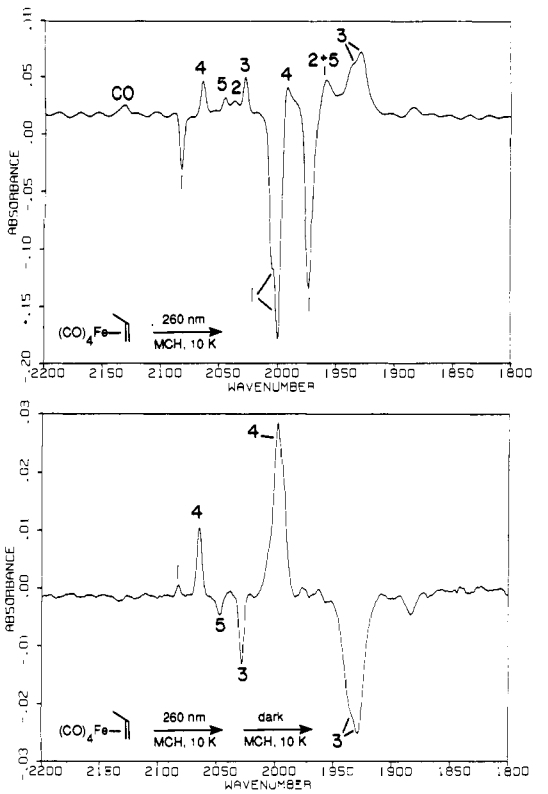
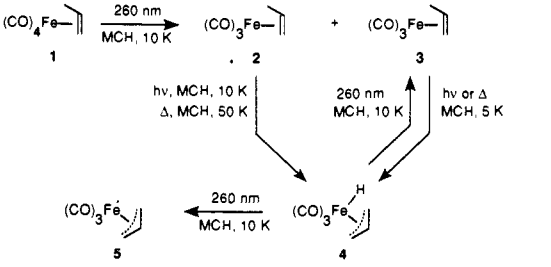


Figure 1. IR difference spectrum showing spectral changes observed upon photolysis (260 ± 10 nm, 30 min, 45% conversion) of $Fe(CO)_4(\eta^2\text{-}CH_2{=}CHCH_3)$ (**1**) in MCH at 10 K (top). The spectrum shows the disappearance of **1** and the appearance of **2–5** and free CO. IR difference spectrum showing spectral changes observed on allowing the matrix to stand in the dark at 10 K (6 h) (bottom). The spectrum shows the disappearance of **3** and **5** and the growth of hydride **4**. (The absorption at 1884 cm^{-1} is tentatively identified as a trace amount of $Fe(CO)_2(\eta^2\text{-}CH_2{=}CHCH_3)$).



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(11) We confirmed this assignment by independently generating **5** from $[Fe(CO)_3(\eta^3\text{-}CH_2CHCH_2)]_2$ in MCH: Murdoch, H. D.; Lucken, E. A. C. *Helv. Chim. Acta* **1964**, *47*, 1517–1524. Muetterties, E. L.; Sosinsky, B. A.; Zamaraev, K. I. *J. Am. Chem. Soc.* **1975**, *97*, 5299–5300. Putnik, C. F.; Welter, J. J.; Stucky, G. D.; D'Aniello, M. J.; Sosinsky, B. A.; Kirner, J. F.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 4107–4116.

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