fore be an optically active π^* (00)–σ^* (00) transition, if we adopt Turro's nomenclature.[13]

In the ORD and CD spectra, as pictured in Figures 1 and 3, the signs of the Cotton effects of the olefin ketal (−)-II and the optical active ketone (−)-V are in accord with one another and with an absolute configuration as drawn in Scheme I, using the olefin octant rule of Scott and Wrixon[14] and the ketone octant rule.[15] The anistropy factor (g factor) for the n–π^* transition of the ketone (−)-V as determined from the CD and UV spectra was found to be 0.04. Although this value is smaller than that for hydrindanone[4] (g 0.2), on which successful CPL measurements have been performed, the value is large enough to encourage us to attempt CPL measurements during the thermal decomposition of this 1,2-dioxetane.[18]

Sufficient evidence exists that animal species use the polarization of skylight as an aid for orientation.[16] With this in mind the possibility must be considered that bioluminescence is circularly polarized. To our knowledge no one has either suggested this possibility or measured this phenomenon. The stable and optically active 1,2-dioxetane (−)-IV presents a model compound to test whether circular polarization of chemiluminescence can be measured.[18]

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(9) The mixture of diastereomeric olefin ketals (−)-II and (+)-III could have been used in the synthesis of a mixture (of possibly four) optically active diastereomeric 1,2-dioxetane ketals. However, this increases the difficulties in characterization of the compound.
(10) Separation was carried out on an 8 ft column packed with 15% UCW 982 on Chromosorb WAW–DMCS 30–60 mesh at 260 °C for the olefin ketals and at 240 °C for the ketones.
(11) All new compounds had spectral data in agreement with their structures.
(12) Even though the olefin ketal (−)-II was virtually optically pure, the addition of $^1O_2$ to (−)-II may furnish two diastereomeric 1,2 dioxetanes. Fortunately this can not interfere with the formation of one pure decomposition product, namely ketone (−)-V (and not its diastereomer). This is of importance, since CPL measurements might be difficult on a diastereomeric mixture of ketones, the effective dissymmetry of which might be low.
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(17) Note that scale notations (+, −) have been inverted for convenience only.
(18) Note Added in Proof. We have recently observed this circular polarization of luminescence. H. P. J. M. Dekkers, H. Numan, and H. Wynberg, submitted for publication.

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An Unexpected Sulfone to Sulfinate Transformation. Electrophilic Fragmentation–Cyclization of Diallenic Sulfones and Propargylic Allenesulfinates to α,β-Unsaturated γ-Sultines

Sir:

In contrast to the vast amount of work performed so far on monoallenes,[1] the study of diallenic systems has received little attention in the past.[2,3] Recently, we have shown that bis-γ,γ-dimethylallenyl sulfone (1) undergoes a facile and novel cyclization on heating at 75 °C to the thiophene 1,1-dioxide derivative 2, in quantitative yield.[3] In continuation, we have investigated the addition of various electrophiles to the diallenic sulfone 1, with the hope of observing some type of intramolecular participation in the course of reaction.

Surprisingly, we have found that addition of a carbon tetrachloride solution of bromine to sulfone 1 at room temperature resulted in spontaneous and quantitative fragmentation of the sulfone, with formation of the cyclic α,β-unsaturated sulfinate (γ-sultine[4]) 3a (X = Br), and the tribromo products 4 and 5. Analogously, we have found that treatment of sulfone 1 with trifluoroacetic acid at room temperature gives rise to γ-sultine 3b (X = H). Besides the standard spectral evidence, the structures of the sultines 3a and 3b have also been confirmed by their ^{13}C NMR spectra[6] as well as by oxidation to the corresponding sultones 6a and 6b.[7]
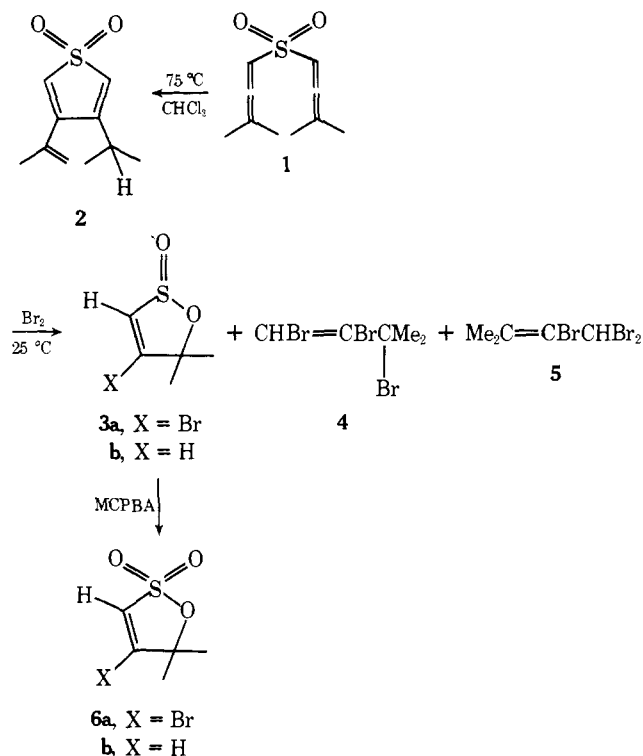
While the rearrangement of acyclic sulfinates to sulfones is fairly common,[3,8] and is thermodynamically a favored process,[9] several reports on the rearrangement of cyclic sulfones to sultines have also been published in the last decade. The first rearrangements of this type were reported to occur under electron impact of various benzo- and dibenzothiophene dioxides.[10] More recently, the rearrangement of thiete 1,1-dioxide to 5H-1,2-oxathiole 2-oxide, the parent substance of 3, on heating at high temperatures in solution or in the vapor phase, was reported.[5a] However, it is interesting to note that no sultine 3b could be obtained from the flash thermolysis of 2,2-dimethylthiete 1,1-dioxide.[5a] The results have been rationalized in terms of a mechanism involving vinyl sulfene as a reactive intermediate, which is formed and reacts in a con-

certed manner. Apparently, the release of ring strain present in the starting material provides considerable driving force. A similar rearrangement in this respect is that of *cis-* and *trans-*2,4-diphenylthietane 1,1-dioxides to *cis-* and *trans-*3,5-diphenyl-1,2-oxathiolane (2,3)-*cis-*2-oxides, respectively, on treatment with *tert-*butyoxymagnesium bromide, which is stereospecific with respect to the phenyl group but stereoselective with respect to the oxygen atoms on sulfur.[5c,d] No firm decision, between an anion–diradical mechanism and a concerted S → O 1,2-anionic shift, could be made from the available evidence. However, we are not aware of any literature reports on the conversion of sulfone to sulfinate under electrophilic conditions such as those employed by us.

We have considered it of interest to find out whether the rearrangement of **1** to **3** is not preceded by an isomerization of **1** to an acyclic sulfinate, such as for example α,α-dimethylpropargyl γ,γ-dimethylallenesulfinate (**7**). Although highly unlikely, this ester could in principle arise by a reversal of the [2,3]-sigmatropic rearrangement of **7** to **1**.[3,11] However, no ester **7**; nor any other sulfinate could be detected, even when the reaction of **1** with bromine was carried out at dry ice–acetone temperature, or when the reaction of **1** in TFA was interrupted at different intervals before completion. Nevertheless, since under the conditions used for the conversion of sulfone **1** the reactions of sulfinate **7** itself, yield **3a** and **3b**, at a very fast rate, it is not possible to exclude the intermediacy of **7**, in the rearrangement of **1** to **3**, as yet.

7
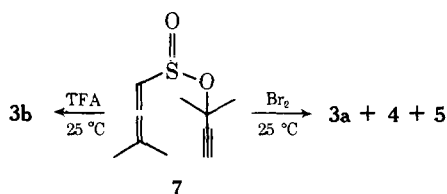
We tentatively suggest that both the fragmentation–cyclization of **1** as well as that of **7** take place by essentially the same mechanism as depicted in Scheme I, for the reactions with bromine.

Scheme I
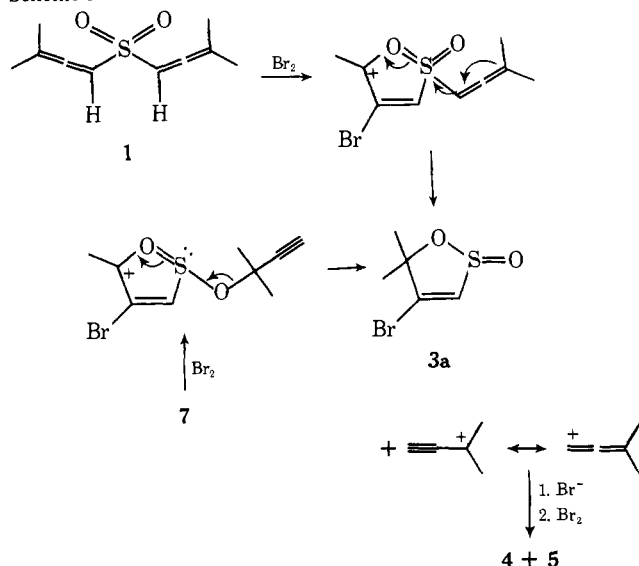
This mechanism, which bears some resemblance to that suggested by Durst and co-workers[5f,g,i] for the formation of γ-sultines by reaction of *tert-*butyl γ-hydroxyalkyl sulfoxides with SO_2Cl_2 or NCS in methylene chloride, is supported by several observations. First, treatment of either α,α-dimethylpropargyl or γ,γ-dimethylallenyl bromide with bromine gives the same mixture of **4** and **5**, as obtained in the reaction of **1**.

Second, reaction of either the unsubstituted diallenyl sulfone or of propargyl allenesulfinate did not result in the fragmentation–cyclization reported above for sulfone **1** and ester **7**, under the same conditions. Similarly, no γ-sultine was obtained on treatment of γ,γ-dimethylallenyl *p*-tolyl sulfone[8] with bromine, while γ,γ-dimethylallenyl *tert-*butyl sulfone gave compound **3a** and *tert-*butyl bromide. These results indicate that in the absence of a departing stable carbocation such as α,α-dimethylpropargyl or *tert-*butyl, no fragmentation and subsequent cyclization are possible under the mild conditions employed. This observation parallels with that made for the analogous fragmentation of benzyl and *tert-*butyl sulfoxides on reaction with *N*-halogenosuccinimides.[5e–g] It is worthwhile noting that oxidation of sulfinate **7** gave the corresponding sulfonate, which on treatment with bromine and TFA was transformed to sultones **6a** and **6b**, respectively.

Finally, as an interesting and natural extension, which also demonstrates the generality of the work described above, we have found that α,α-dimethylpropargyl phenyl γ,γ-dimethylallenephosphinate (**8**)[12] undergoes spontaneous and quantitative fragmentation–cyclization to 4-bromo-5,5-dimethyl-2-phenyl-1,2-oxaphosphol-3-ene 2-oxide (**9**), under similar conditions to those employed with sulfone **1**.
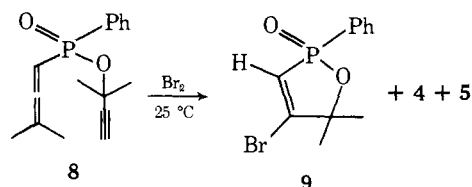
It appears to us that the results described above have not only considerable synthetic potential but also mechanistic significance. Besides the mechanistic aspects of this novel and unique fragmentation–cyclization, we are presently engaged on an examination of its occurrence under nonelectrophilic conditions, and on an exploration of its scope by a study of other diallenic and related systems.

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(6) ^{13}C chemical shifts ($CDCl_3$) in parts per million relative to Me_4Si: **3a**, δ 26.57, 28.83 (two diastereotopic methyl carbons), 99.17 (C–O), 133.25 (C–SO), 140.66 (C–Br); **3b**, δ 26.95, 29.36 (two diastereotopic methyl carbons), 100.48 (C–O), 133.75 (C–SO), 145.50 (C-4).

(7) The two new sultones, **6a** (mp 36–37 °C) and **6b** (mp 93–93.5 °C), gave satisfactory elemental analyses as well as IR, NMR, and mass spectral data in accord with the assigned structures.

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Solution Structures and Dynamics of Ir$_4$(CO)$_{12-x}$(PPh$_2$Me)$_x$ (x = 1-4)[1]

Sir:

Presently available evidence[2] suggests that the cluster compounds M$_4$(CO)$_{12}$ (M = Co, Rh, Ir) maintain the same structures in solution as in the solid state: **1** for Co$_4$(CO)$_{12}$[3] and Rh$_4$(CO)$_{12}$,[4] **2** for Ir$_4$(CO)$_{12}$.[4] However, the configurations adopted by their derivatives together with the occurrence and mechanisms of carbonyl mobility in such tetranuclear clusters remain problems of current interest. Complete scrambling of the carbonyl ligands over the tetrarhodium framework of Rh$_4$(CO)$_{12}$ has been demonstrated,[5] and the intermediacy of an unbridged form (**2**), as proposed by Cotton,[5,6] is consistent with available data.[7] However, spectral data reported for carbonyl scrambling in structurally related RhCo$_3$(CO)$_{12}$ are incompatible with the intervention of **2**, and concerted interchange of bridging and terminal carbonyls has been proposed.[8] Carbonyl mobility could not be established for Co$_4$-(CO)$_{11}$P(OMe)$_3$[9] or Co$_4$(CO)$_{12}$[9,10] due to ^{59}Co quadrupolar effects. A previous study of some Ir$_4$(CO)$_8$L$_4$ derivatives demonstrated carbonyl site exchange, but the molecular configurations were not well established and no mechanistic evidence was forthcoming.[11] Following up on a new method for the preparation of derivatives of Ir$_4$(CO)$_{12}$,[12] we report here

^{31}P and ^{13}C NMR data that establish the solution structures of the series Ir$_4$(CO)$_{12-x}$(PPh$_2$Me)$_x$ (x = 1-4)[13] and present variable temperature ^{13}C NMR spectra that delineate the carbonyl scrambling processes in Ir$_4$(CO)$_{11}$PPh$_2$Me.

1   2
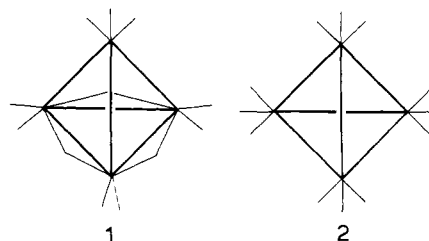
Crystalline Ir$_4$(CO)$_{10}$(PPh$_3$)$_2$ and Ir$_4$(CO)$_9$(PPh$_3$)$_3$ adopt configurations **4** and **5**, respectively.[14] In **4** one PPh$_3$ ligand is in a radial position (P$_2$) with respect to the bridging carbonyls and one PPh$_3$ ligand (P$_1$) is axial. Configuration **5** has two radial ligands (P$_2$P$_2'$) and one axial ligand (P$_1$). The ^{31}P{^{1}H} NMR spectrum[15] of Ir$_4$(CO)$_{10}$(PPh$_3$)$_2$ displays two resonances of equal intensity at −17.6 and 15.0 ppm and the spectrum of Ir$_4$(CO)$_9$(PPh$_3$)$_3$ shows two resonances of intensity 2:1 at −20.0 and 17.4 ppm. These data suggest that structures **4** and **5** are maintained in solution and that the radial phosphorus ligand signals appear at lower field than those of the axial phosphorus ligands. Accordingly, Ir$_4$(CO)$_{11}$PPh$_3$, which shows a ^{31}P signal at 13.0 ppm, is assigned structure **3** with an axial PPh$_3$ ligand.[16] Ir$_4$(CO)$_{11}$(PPh$_2$Me) (31.5 ppm), Ir$_4$(CO)$_{10}$(PPh$_2$Me)$_2$ (5.7, 28.2 ppm, 1:1), and Ir$_4$(CO)$_9$(PPh$_2$Me)$_3$ (5.2, 25.0 ppm, 2:1) display completely analogous ^{31}P spectra and are assigned structures **3, 4,** and **5,** respectively. Ir$_4$(CO)$_8$(PPh$_2$Me)$_4$ shows three resonances of intensity 1:2:1 (7.4, 39.8, 59.9 ppm), as previously reported.[11] Since the signal of relative intensity 2 is in the high field region associated with axial substitution, structure **6** is assigned.

Limiting ^{13}C{^{1}H} NMR spectra recorded for the PPh$_2$Me derivatives are fully consonant with these configurations (see Table I).[17,18] Certain general features of the data allow unusually detailed assignments for metal cluster carbonyl spectra. (i) Low-field resonances due to three bridging carbonyls (a, a', b) are seen in each case. These signals shift ~10 ppm further downfield for each substitution at an adjacent iridium atom. (ii) Signals for terminal carbonyls positioned approximately in the basal plane (radial positions d, d', f) are 7-15 ppm

Table I. ^{13}C NMR Data for Ir$_4$(CO)$_{12-x}$(PPh$_2$Me)$_x$, x = 1-4

Shift^a	Mult (rel int)	Assign	Shift^a	Mult (rel int)	Assign
	Ir$_4$(CO)$_{11}$PPh$_2$Me			Ir$_4$(CO)$_{10}$(PPh$_2$Me)$_2$	
206.8	m (2)	a,a'	217.6	m (1)	a'
196.2	m (1)	b	206.8	m (1)	a or b
173.2	d (1)^b	f	205.6	m (1)	a or b
171.1	s (2)	d,d'	175.0	m (1)	f
158.3	s (2)	c,c'	172.6	d (1)^d	d
157.1	s (2)	e,e'	160.9	s (1)	e,e' or c
155.9	d (1)^c	g	159.8	d (1)^e	g
			159.7	s (1)	e,e' or c
			158.7	d (1)^f	c'
			156.3	s (1)	e,e' or c
	Ir$_4$(CO)$_9$(PPh$_2$Me)$_3$			Ir$_4$(CO)$_8$(PPh$_2$Me)$_4$	
217.8	m (2)	a,a'	223.4	m (1)	b
217.1	m (1)	b	218.4	m (2)	a,a'
176.6	dt (1)^g	f	178.2	dd (2)^j	d,d'
165.7	d (1)^h	g	171.1	dd (2)^k	e,e'
160.7	d (2)^i	c,c'	164.5	dd (1)^l	f
159.9	s (2)	e,e'			

^{a} Chemical shifts in ppm relative to internal Me$_4$Si. ^{b} J(P-f) = 4 Hz. ^{c} J(P-g) = 26 Hz. ^{d} J(P$_2$-d) = 15 Hz. ^{e} J(P$_1$-g) = 24 Hz. ^{f} J(P$_2$-c') = 6 Hz. ^{g} J(P$_2$-f) = 14 Hz, J(P$_1$-f) = 9 Hz. ^{h} J(P$_1$-g) = 25 Hz. ^{i} J(P$_2$-c) = 3 Hz. ^{j} J(P$_1$-d) = 9 Hz, J(P$_2$-d) = 15 Hz. ^{k} J(P$_1$-e') = 32 Hz, J(P$_3$-e') = 4 Hz. ^{l} J(P$_3$-f) = 33 Hz, J(P$_2$-f) = 8 Hz.