fore be an optically active $\pi^*(00)-\sigma^*(00)$ 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 Wrixon¹⁴ and the ketone octant rule.¹⁵ The anistropy factor (g factor) for the $n-\pi^*$ 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 hydrindanone⁴ (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

Acknowledgment. We thank Dr. J. Wieringa, Drs. K. Lammertsma, and Drs. C. B. Troostwijk for their contribution in the early and frustrating phases of this work. We thank Professor R. M. Kellogg for stimulating discussions and valuable suggestions.

References and Notes

- J. H. Wieringa, J. Strating, H. Wynberg, and W. Adam, *Tetrahedron Lett.*, 169 (1972).
- (2) G. B. Schuster, N. J. Turro, H. C. Steinmetzer, A. P. Schaap, G. Faler, W. Adam, and J. C. Liu, *J. Am. Chem. Soc.*, 97, 7110 (1975).
- (3) To our knowledge no stable optically active 1,2-dioxetane has been described previously.
- (4) For measurements of circular polarization of luminescence (CPL) see: (a) C. A. Emeis and L. J. Oosterhoff, *Chem. Phys. Lett.*, **1**, 129, 268 (1967);
 (b) H. P. J. M. Dekkers and L. E. Closs, *J. Am. Chem. Soc.*, **98**, 2210 (1976);
 (c) C. K. Luk and F. S. Richardson, *ibid.*, **96**, 2006 (1974); (d) A. Gafni and I. Z. Steinberg, *Photochem. Photobiol.*, **15**, 93 (1972).
- (5) A number of alternate routes to an optically active 1,2-dioxetane were considered and tried prior to the successful route, described in this paper. For example, a route via the recently characterized bornanylidenebornanes failed: H. Wynberg, K. Lammertsma, and L. A. Hulshof, *Tetrahedron Lett.*, 3749 (1975).
- (6) J. H. Wieringa, J. Strating, and H. Wynberg, *Tetrahedron Lett.*, 4579 (1970).
- (7) Only (-)-II is drawn in Scheme I.
- (8) E. J. Corey and R. B. Mitra, J. Am. Chem. Soc., 84, 2938 (1962).
- (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 ¹O₂ 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.
- (13) N. J. Turro and P. Lechtken, Pure Appl. Chem., 33, 363 (1973).
- (14) A. I. Scott and A. D. Wrixon, *Tetrahedron*, 28, 933 (1972), and earlier papers.
- (15) W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, J. Am. Chem. Soc., 84, 4013 (1961); G. Snatzke and G. Eckhardt, Tetrahedron, 26, 1143 (1970).
- (16) R. Wehner, Sci. Am., July, 106 (1976).
- (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.

Hans Wynberg,* H. Numan

Department of Organic Chemistry, The University Groningen, The Netherlands Received July 13, 1976

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 -sultine⁴) **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 ¹³C NMR spectra⁶ 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 1,1dioxide to 5*H*-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 concerted 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 \rightarrow 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 iceacetone 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.



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^{5/,g,i} for the formation of γ -sultines by reaction of *tert*-butyl γ -hydroxyalkyl sulfoxides with SO₂Cl₂ or NCS in methylene chloride, is supported by several observations. First, treatment of either α, α -dimethyl-propargyl 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 sulfone⁸ 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.

Acknowledgment. Financial support by the Israel Commission of Basic Research is gratefully acknowledged.

References and Notes

- For reviews on this subject see (a) J. D. Roberts and C. M. Sharts, Org. React., 12, 1 (1962); (b) K. Griesbaum, Angew. Chem., Int. Ed. Engl., 5, 933 (1966); (c) D. R. Taylor, Chem. Rev., 67, 317 (1967); (d) J. E. Baldwin and R. H. Fleming, Fortschr. Chem. Forsch., 15, 281 (1970); (e) T. Okamoto, Bull. Inst. Chem. Res., Kyoto Univ., 50, 450 (1972).
 (2) (a) L. Skattebøl and S. Solomon, J. Am. Chem. Soc., 87, 4506 (1965); (b)
- (2) (a) L. Skattebøl and S. Solomon, J. Am. Chem. Soc., 87, 4506 (1965); (b) J. F. Harris, Jr., Tetrahedron Lett., 1359 (1965); (c) W. D. Huntsman and H. J. Wristers, J. Am. Chem. Soc., 89, 342 (1967); (d) F. Toda, H. Ishihara, and K. Akagi, Tetrahedron Lett., 2531 (1969); (e) H. Hopf, Angew. Chem., Int. Ed. Engl., 9, 732 (1970); (f) T. J. Henry and R. G. Bergman, J. Am. Chem. Soc., 94, 5103 (1972); (g) W. R. Roth, M. Heiber, and G. Erker, Angew. Chem., Int. Ed. Engl., 12, 504 (1973); (h) W. Grimme and H. J. Rother, *ibid.*, 12, 505 (1973); (i) C. M. Bowes, D. F. Montecalvo, and F. Sondheimer, Tetrahedron Lett., 3181 (1973).
- (3) S. Braverman and D. Segev, J. Am. Chem. Soc., 96, 1245 (1974).
- (4) The name "sultine" for a cyclic sulfinate was first suggested in the literature by D. C. Dittmer, R. S. Henion, and N. Takashina, *J. Org. Chem.*, 34, 1310 (1969). For subsequent reports related to sultine chemistry see ref 5.
 (5) (a) F. King, P. de Mayo, C. L. McIntosh, K. Piers, and J. D. H. Smith, *Can.*
- (5) (a) F. King, P. de Mayo, C. L. McIntosh, K. Piers, and J. D. H. Smith, *Can. J. Chem.*, **48**, 3704 (1970); (b) D. N. Harpp and J. G. Gleason, *J. Org. Chem.*, **36**, 1314 (1971); (c) R. M. Dodson, P. D. Hammen, and R. A. Davis, *ibid.*, **36**, 2693 (1971); (d) R. M. Dodson, P. D. Hammen and J. Y. Fan, *ibid.*, **36**, 2703 (1971); (e) F. Jung and T. Durst, *J. Chem. Soc., Chem. Commun.*, 4 (1973); (f) N. K. Sharma, F. Jung, and T. Durst, *Tetrahedron Lett.*, 2863 (1973); (g) F. Jung, N. K. Sharma, and T. Durst, *J. Am. Chem. Soc.*, **95**, 3420 (1973); (h) F. Jung, M. Molin, R. van Dew Elzen, and T. Durst, *ibid.*, **96**, 935 (1974); (i) T. Durst, N. K. Sharma, M. Molin, and F. Jung, Vith International Symposium on Organic Sulfur Chemistry, Bangor, England, July 1–5, 1974, Abstract C-15; (j) G. W. Astrologes and J. C. Martin, *J. Am. Chem. Soc.*, **97**, 6909 (1975); (k) D. C. Dittmer, G. C. Levy, and G. E. Kuhlman, *ibid.*, **91**, 2097 (1969).
- (6) ¹³C chemical shifts (CDCl₃) in parts per million relative to Me₄Si: **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.

- (8) For leading references see S. Braverman and H. Mechoulam, *Tetrahedron*, 30, 3883 (1974).
- (9) For an explanation of the direction of this and other O → S 1,2 shifts see E. G. Miller, D. R. Rayner, and K. Mislow, J. Am. Chem. Soc., 88, 3139 (1966).
- (10) E. K. Fields and S. Meyerson, J. Am. Chem. Soc., 88, 2836 (1966); J. H. Bowie, D. H. Williams, S.-O. Lawesson, J. Ø. Madsen, C. Nolde, and G. Schroll, *Tetrahedron*, 22, 3515 (1966); O. N. Porter, Aust. J. Chem., 20, 103 (1967); R. D. Chambers and J. A. Cunningham, *Chem. Commun.*, 583 (1967); D. C. Dittmer and F. A. Davis, J. Org. Chem., 32, 3872 (1967).
- (11) Pertinent evidence for a somewhat similar process, the concerted and reversible [2,3]-sigmatropic rearrangement of certain allylic sulfoxides to sulfenates, has been reported: S. Braverman and Y. Stabinsky, *Isr. J. Chem.*, **5**, 71p (1967); S. Braverman, *Int. J. Sulfur Chem., Part C*, **6**, 149 (1971); R. Tang and K. Mislow, *J. Am. Chem. Soc.*, **92**, 2100 (1970).
- (12) A. P. Boisselle and N. A. Meinhardt, J. Org. Chem., 27, 1828 (1962).

Samuel Braverman,* David Reisman

Department of Chemistry, Bar-Ilan University Ramat-Gan, Israel Received April 21, 1976

Solution Structures and Dynamics of

 $Ir_4(CO)_{12-x}(PPh_2Me)_x (x = 1-4)^1$

Sir:

Presently available evidence² 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 Co₄- $(CO)_{11}P(OMe)_3^9$ or $Co_4(CO)_{12}^{9,10}$ due to ⁵⁹Co quadrupolar effects. A previous study of some Ir₄(CO)₈L₄ 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

Table I. ¹³C NMR Data for $Ir_4(CO)_{12-x}(PPh_2Me)_x$, x = 1-4

³¹P and ¹³C NMR data that establish the solution structures of the series $Ir_4(CO)_{12-x}(PPh_2Me)_x$ (x = 1-4)¹³ and present variable temperature ¹³C NMR spectra that delineate the carbonyl scrambling processes in $Ir_4(CO)_{11}PPh_2Me$.



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 PPh₃ 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_2P_2') and one axial ligand (P_1) . The ³¹P {¹H} NMR spectrum¹⁵ 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 ³¹P signal at 13.0 ppm, is assigned structure 3 with an axial PPh₃ ligand.¹⁶ $Ir_4(CO)_{11}(PPh_2Me)$ (31.5 ppm), $Ir_4(CO)_{10}(PPh_2Me)_2$ (5.7, 28.2 ppm, 1:1), and $Ir_4(CO)$ ₉(PPh₂Me)₃ (5.2, 25.0 ppm, 2:1) display completely analogous ³¹P spectra and are assigned structures 3, 4, and 5, respectively. $Ir_4(CO)_8(PPh_2Me)_4$ 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 ¹³C {¹H} NMR spectra recorded for the PPh₂Me 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

Shift ^a	Mult (rel int)	Assign	Shift ^a	Mult (rel int)	Assign
	$Ir_4(CO)_{11}PPh_2Me$			$Ir_4(CO)_{10}(PPh_2Me)_2$	
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) °	g	159.8	d (1) ^e	g
		6	159.7	$\overline{\mathbf{s}}(1)$	e.e' or c
			158.7	$d(1)^{f}$	c'
			156.3	$\frac{1}{s(1)}$	e.e' or c
	$Ir_4(CO)_9(PPh_2Me)_3$			$Ir_4(CO)_8(PPh_2Me)_4$	-,
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 $(1)^{i}$	f
159.9	s (2)	e,e'		、	

^a Chemical shifts in ppm relative to internal Me₄Si. ^b J(P-f) = 4 Hz. ^c J(P-g) = 26 Hz. ^d J(P₂-d) = 15 Hz. ^e J(P₁-g) = 24 Hz. ^f J(P₂-c') = 6 Hz. ^g J(P₂-f) = 14 Hz, J(P₁-f) = 9 Hz. ^h J(P₁-g) = 25 Hz. ⁱ J(P₂-c) = 3 Hz. ^j J(P₁-d) = 9 Hz, J(P₂-d) = 15 Hz. ^k J(P₁-e') = 32 Hz, J(P₃-e') = 4 Hz. ^f J(P₃-f) = 33 Hz, J(P₂-f) = 8 Hz.