Figure 2. UV (—), ORD (- - -), and CD (···) spectra of trans-olefin III.

References and Notes

(1) A. C. Cope, C. R. Ganellin, H. W. Johnson, Jr., T. V. van Auken, and H. J. S. Winkler, *J. Am. Chem. Soc.*, **85**, 3276 (1963); A. C. Cope, and A. S. Metha, *ibid.*, **86**, 5626 (1964); G. Krow, *Top. Stereochem.*, **5**, 31 (1970); M. Tichy and J. Sicher, *Tetrahedron Lett.*, 4609 (1969); M. Rösner and G. Köbrich, *Angew. Chem.*, **87**, 715 (1975).

(2) G. Schroeter and H. Müller, *Ber.*, **62**, 645 (1929); R. D. Haworth, *J. Chem. Soc.*, 1125 (1932).

(3) J. E. McMurry and M. P. Fleming, *J. Am. Chem. Soc.*, **96**, 4708 (1974); J. E. McMurry, *Acc. Chem. Res.*, **7**, 281 (1974); H. Wynberg, K. Lammertsma, and L. A. Hulshof, *Tetrahedron Lett.*, 3749 (1975); E. J. Corey, R. L. Danheiser, and S. Chandrasekaran, *J. Org. Chem.*, **41**, 260 (1976).

(4) In the case of II and III, only one of the possible enantiomers is shown in Scheme I.

(5) In the 100-MHz ^{1}H NMR spectra of both cis-II and trans-III isomers, multiplets were observed for the protons in the 1,1',2,2',3,3' positions. (II: δ 1.7–3.1; III: δ 1.6, 2.2, and 2.7). For the cis isomer an AB system was observed for the protons in the 9,9',10,10' positions.

(6) Ch. Goedicke and H. Stegemeyer, *Ber. Bunsenges. Phys. Chem.*, **73**, 782 (1969); H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules", Academic Press, New York, N.Y., 1967, Chapter 14 and 18.

(7) The first report of the use of (+)-TAPA[8a] in chromatographic separation of optical isomers is due to Klemm et al.[8b] Gil-Av et al.[8c] have recently reported its use in HPLC for the resolution of helicenes. We have applied the technique independently to the resolution of heterohelicenes.[8d]

(8) (a) M. S. Newman and D. Lednicer, *J. Am. Chem. Soc.*, **87**, 4765 (1965); (b) L. H. Klemm and D. Reed, *J. Chromatogr.*, **3**, 264 (1960); (c) F. Mikes, G. Boshart, and E. Gil-Av, *J. Chem. Soc., Chem. Commun.*, 99 (1976); (d) H. Numan, R. Helder, and H. Wynberg, *Recl. Trav. Chim. Pays-Bas*, **95**, 211 (1976).

(9) N. H. Andersen, C. R. Costin, and J. R. Shaw, *J. Am. Chem. Soc.*, **96**, 3692 (1974); C. C. Levin and R. Hoffmann, *ibid.*, **94**, 3446 (1972); A. D. Scott and A. D. Wrixon, *J. Chem. Soc. D*, 1182 (1969); *Tetrahedron*, **26**, 3695 (1970); A. Moscowitz, *Proc. R. Soc. London*, **297**, 16 (1967), and references cited therein.

(10) Dreiding models of the intermediate Ti complexes as suggested by McMurry and co-workers[3] indicate that, in going from the precursors of III and IV to the olefins, the formation of IV is disfavored due to steric hindrance.

(11) (a) Whether we view II as an "open helicene", a "chiral and rigid stilbene", or a novel helical conjugated π-system is a matter of semantics. (b) R. Martin, *Angew. Chem.*, **86**, 727 (1974); W. H. Laarhoven and Th. J. H. M. Cuppen, *Tetrahedron Lett.*, 163 (1971); R. H. Martin, Ch. Eyndels, and N. Defay, *ibid.*, 2731 (1972).

(12) I. Agranat and Y. Tapuhi, *J. Am. Chem. Soc.*, **98**, 615 (1976); H. O. Kalinowsky and H. Kessler, *Top. Stereochem.*, **7**, 295 (1973); I. R. Gault, W. D. Ollis, and I. O. Sutherland, *Chem. Commun.*, 269 (1970).

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Received July 13, 1976

above conditions, but in the presence of (−)-trans-2,3-methylenedioxybutane as solvent gave cis-isomer II as the only olefinic product. This product was nevertheless optically inactive.

Some additional aspects of the structures of the cis and trans olefins need to be mentioned. The structure of II resembles that of a heptahelicene (more accurately a tetrahydroheptahelicene) with a double bond replacing an aromatic ring. The olefin III has a double helix structure and resembles a double pentahelicene with a double bond replacing two aromatic rings.[11a] Both chiral as well as achiral double helix structures have been reported in the helicene case.[11b] The role of π-bond torsion has been the subject of many investigations,[1,9] although almost all of the attention has been focused on trans-cyclooctene. NMR studies connected with π-bond torsion have been reported for systems such as bisfluorenylidene and bianthrone, but no stable enantiomers have been obtained thus far.[12] To our knowledge, olefins II and III represent the first instance in which a dl-cis and dl-trans form of one inherently dissymmetric olefin have been isolated and resolved into enantiomers.

The isomerization and racemizations of II and III may furnish further information about the torsional distortion in both olefins. This complex series of interconversions will be the subject of further investigations.

Acknowledgment. The authors wish to thank Dr. R. Helder and Dr. H. Numan for their assistance during the HPLC resolutions, Dr. H. Hiemstra for recording and interpreting the NMR spectra, and the Netherlands Organization for Pure

Synthesis and Spectral Data of a Stable, Optically Active 1,2-Dioxetane

Sir:

Some years ago the synthesis and structure proof of the stable 1,2-dioxetane, derived from adamantylideneadamantane,[1] was reported. Subsequently this molecule has been studied in considerable detail.[2] Using the same olefin moiety, we have now prepared and characterized an *optically active* 1,2-dioxetane.[3]

In addition to the criteria we enumerated for the successful synthesis of the adamantylideneadamantane-1,2-dioxetane[1] (electron-rich olefin; avoidance of "ene" reaction and no steric hindrance), stereochemical considerations played a crucial role in our present synthetic strategy. (i) The possible difficulties in resolving a 1,2-dioxetane made us decide to prepare an optically active (and if possible optically pure) olefin, as precursor of the 1,2-dioxetane. (ii) Condition i requires either the synthesis of an olefin with a functional group allowing resolution, or the synthesis of an optically active olefin precursor. (iii) The position and nature of the substituent, which imparts chirality
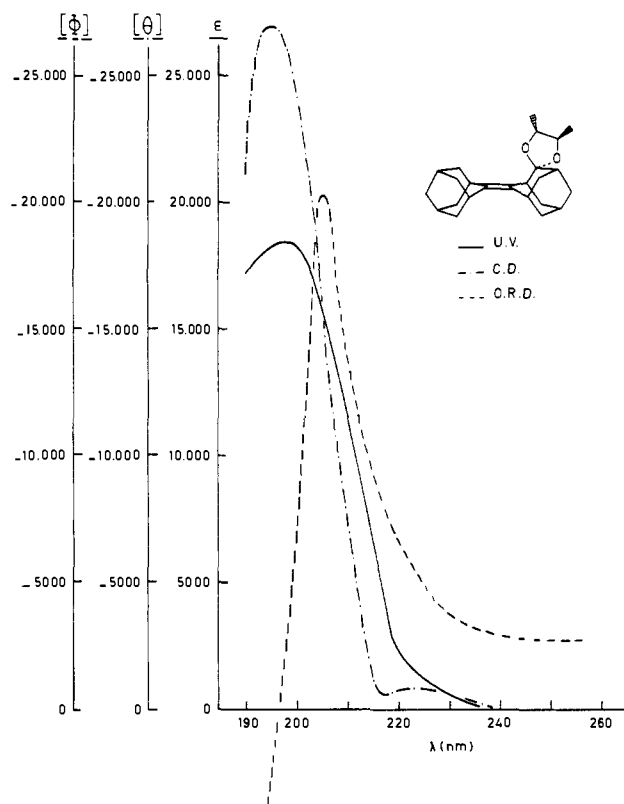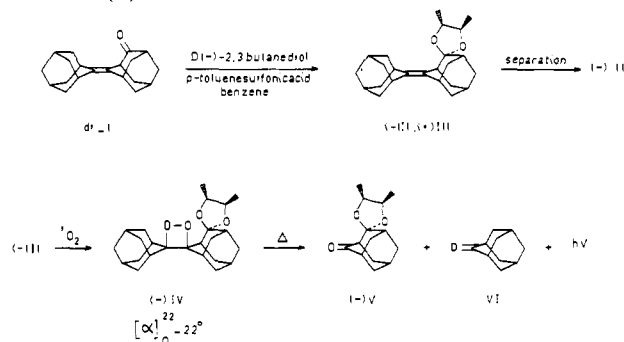
Figure 1. UV, ORD, and CD spectra (in n-hexane) of olefin ketal (−)-II.[17]

Scheme I. Synthetic Route to the Optically Active 1,2-Dioxetane (−)-IV.

on the olefin, is not trivial. The substituent must not interfere with 1,2-dioxetane formation either sterically or electronically and need to be selected in such a fashion that it exerts a maximum chiral perturbing influence on the n–π* transition of one of the thermal decomposition products of the 1,2-dioxetane (the chiral ketone) for purposes of possible measurements of circular polarization of luminescence[4] (CPL). These considerations have led us to the synthesis described below in Scheme I.[5]

The racemic unsaturated ketone I[6] (see Scheme I) was transformed into a mixture of two diastereomeric ketals[7] II and III by treatment with an excess of optically pure (−)-2,3-butanediol,[8] $[\alpha]_{578}^{22}$ −13.7°. Extensive and difficult separation[9] of these two diastereomers, using preparative GLC,[10] allowed the isolation of the olefin ketal (−)-II,[11] $[\alpha]_{578}^{22}$ −45°, c 0.075 (n-hexane), purity 95%, mp 96–99 °C, and the diastereomeric olefin ketal (+)-III;[11] $[\alpha]_{578}^{22}$ +33°, c 0.076 (n-hexane), mp 66.5–68.0 °C. The olefin ketal (−)-II was converted into the desired 1,2-dioxetane (−)-IV[12] in 60% yield, using the same method as previously described.[1] Dioxetane (−)-IV is a crystalline white compound with the following data:
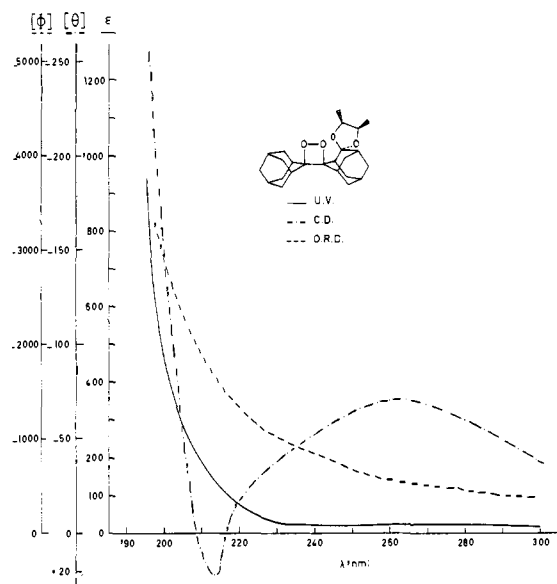
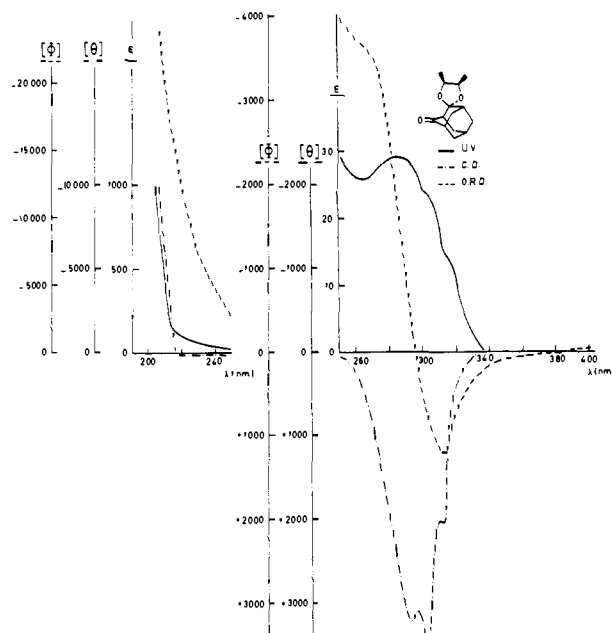Figure 2. UV, ORD, and CD spectra (in n-hexane) of 1,2-dioxetane (−)-IV.[17]

Figure 3. UV, ORD, and CD spectra (in n-hexane) of Ketone (−)-V.[17]

$[\alpha]_{578}^{22}$ −22°, c 0.12 (n-hexane); ^{1}H NMR (CDCl₃) δ 3.66–3.38 (2 H), 2.66–2.46 (4 H), 2.20–1.30 (22 H) 1.21–1.04 (6 H); ^{13}C NMR δ 97.6 and 96.9 (carbons of 1,2-dioxetane ring), 110.2 and 77.5 (carbons of ketal group); IR (CCl₄) 1110 cm⁻¹ (ketal), no carbonyl absorption; mass spectrum, molecular ion at m/e 386 and peaks at m/e 370 and 354, due to loss of one and two oxygen atoms and at m/e 236 and 150, corresponding to the adamantanone VI and the adamantanone ketal (−)-V molecular weights. Additional proof of structure was obtained by thermal decomposition, which led to beautiful chemiluminescence, and the isolation by GLC[10] of the two expected ketones, adamantanone VI and the new optically active ketone (−)-V;[11] $[\alpha]_{578}^{22}$ −12°, c 0.12 (n-hexane).

The ORD and CD spectra of the 1,2-dioxetane (−)-IV, shown in Figure 2, are to our knowledge the first data of the kind. Of significance is the distinct Cotton effect at 265 nm. This characteristic 1,2-dioxetane transition, previously observed as a weak maximum in the UV spectrum, must there-

fore be an optically active π^* (OO)–σ^* (OO) 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]

References and Notes

(1) 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 $^1O_2$ 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.
(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.

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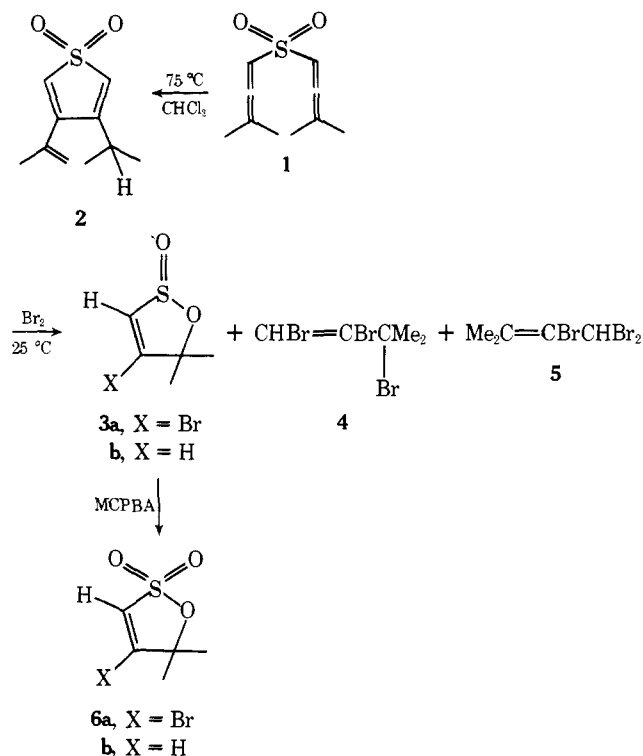*Department of Organic Chemistry, The University Groningen, The Netherlands*

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]

1

2

$\xrightarrow[\text{25 °C}]{\text{Br}_2}$

+ $CHBr{=}CBrCMe_2$ + $Me_2C{=}CBrCHBr_2$

Br

4

5

3a, X = Br
b, X = H

MCPBA

6a, X = Br
b, X = H

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-