

involve a bimolecular reaction^{12a} between the diazo compound and the ozonide. Work on this aspect of these results is continuing. A summary of the photosensitized oxidations, phosphite ozonide oxidations, and some comparable experiments in which the desired ozonides were obtained by ozonolysis of the appropriate olefins is given in Table I.

The similarity of the ozonide stereoisomer distributions in a given ozonide obtained by the photosensitized oxidations and the phosphite ozonide oxidations¹⁴ suggests a common precursor to ozonide, most likely the zwitterion 2. The results in Table I also indicate that for 1,2-diisopropylethylene ozonide the photosensitized oxidations and the oxidation with phosphite ozonide 5 give an ozonide stereoisomer distribution which is closer to that obtained by ozonolysis of the trans olefin and distinctly different from that obtained from the cis olefin. These results thus parallel similar results reported earlier³ in the case of 1-(1-naphthyl)-1-phenyl-1-propene. In the case of the stilbene ozonides the new oxidations reported here give an ozonide stereoisomer distribution which is approximately the same as that obtained by ozonolysis of either olefin isomer. The relationship of these results to studies of the ozonolysis mechanism involving an ¹⁸O tracer¹⁵⁻²⁰ is under investigation.

The results obtained here suggest that singlet oxygen may react with a number of other systems containing an electron-rich center (e.g., azides, ylids, etc.). In addition, these new methods for producing zwitterions, uncomplicated by the conditions of the ozonolysis method, may permit us to examine other reactions of zwitterions (including other 1,3-dipolar additions) as well as to examine their nmr spectra and possibly obtain evidence for the existence of syn and anti isomers.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation through Grant No. GP 29373X.

(14) The one exception to this statement is the reaction of isopropyl-diazomethane with 4 at -40° . In this case the variation is believed to be a temperature effect which is being explored further.

(15) S. Fliszár and J. Carles, *J. Amer. Chem. Soc.*, **91**, 2637 (1969).

(16) P. R. Story, C. E. Bishop, J. R. Burgess, R. W. Murray, and R. D. Youssefyeh, *J. Amer. Chem. Soc.*, **90**, 1907 (1968).

(17) R. W. Murray and R. Hagan, *J. Org. Chem.*, **36**, 1103 (1971).

(18) P. R. Story, J. A. Alford, J. R. Burgess, and W. C. Ray, *J. Amer. Chem. Soc.*, **93**, 3042 (1971).

(19) C. W. Gillies and R. L. Kuczkowski, *J. Amer. Chem. Soc.*, **94**, 7609 (1972).

(20) C. W. Gillies, R. P. Lattimer, and R. L. Kuczkowski, *J. Amer. Chem. Soc.*, **96**, 1536 (1974).

D. P. Higley, R. W. Murray*

Department of Chemistry, University of Missouri-St. Louis
St. Louis, Missouri 63121

Received February 27, 1974

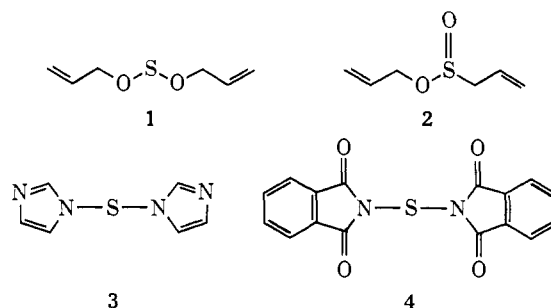
A New Synthesis of Allylic Sulfones and Their Conversion to Polyolefins. β -Carotene from Vitamin A

Sir:

The well-known Ramberg-Bäcklund olefin synthesis¹ should allow a conversion of diallylic sulfones to the corresponding trienes. Because none of the existing

(1) L. A. Paquette in "Mechanisms of Molecular Migrations," Vol. I, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1968, p 121.

syntheses appeared to be suitable for the preparation of such sulfones, we have prepared them by a new method from allyl alcohols and sulfur transfer agents. Some precedent for the chemistry to be discussed was available. Treatment of allyl alcohol with sulfur dichloride at -95° gave 2-propene 1-sulfinate (2) by rearrangement of the anticipated diallyl sulfoxylate (1).² 1,1'-Thio-dimidazole (3) combines with alcohols to yield alkyl sulfoxylate esters,³ and the more stable *N,N'*-thiodi-phthalimide (4)⁴ was found to react with a number of nucleophiles.⁵



Three experimental procedures were followed for the synthesis of allylic sulfones. In method A an allylic alcohol in ether or methylene chloride is added to sulfide 3 in the same solvent at $0-20^{\circ}$. Sulfide 3 may be prepared *in situ* from 1 equiv of sulfur dichloride and 4 equiv of imidazole and used directly as was done for the synthesis of sulfone 7a. With vitamin A, however, better yields are obtained using sulfide which had been isolated. In method B the lithium alkoxide is preformed with *n*-butyllithium in methylene chloride at 0° followed by addition of a slight excess of sulfide 4 at room temperature and stirring for 1 hr. Finally, a mixture of sulfide 4 and the allylic alcohol in either benzene or methylene chloride is stirred at room temperature for a few hours in the presence of suspended potassium carbonate or 1 equiv of triethylamine (method C). Sulfonates 6a, b, c, and 10 with intense ir absorption at $1120-1150\text{ cm}^{-1}$ are initially formed from the allylic (5a, b, c) and propargylic (9) alcohols presumably by [2,3]sigmatropic rearrangement of the sulfoxylic amide esters or the sulfoxylates. The sulfinate-sulfone rearrangement, accompanied by the appearance of intense ir absorption at $1300-1330\text{ cm}^{-1}$ proceeds only slowly at room temperature. More rapid transformation was accomplished by stirring methylene chloride solutions of crude sulfonates over silica gel at room temperature or by refluxing toluene solutions over potassium carbonate for approximately 40 min. Sulfoxylate esters were never encountered and no 3-sulfonylfuran was produced by [2,3] rearrangement of the sulfinate 13.⁶ Sulfones 7b and 7c were found to be mixtures of geometric isomers, but it is not clear yet whether this is the result of nonstereospecific 2,3-sigmatropic rearrange-

(2) Q. E. Thompson, *J. Org. Chem.*, **30**, 2703 (1965); N. S. Zefirov and F. A. Abdulvaleeva, *Vestn. Mosk. Univ., Khim.*, **24**, 135 (1969); *Chem. Abstr.*, **71**, 112345 (1969). Since submission of this manuscript, sulfone 11 has been prepared by a similar method; see S. Braverman and D. Segev, *J. Amer. Chem. Soc.*, **96**, 1245 (1974).

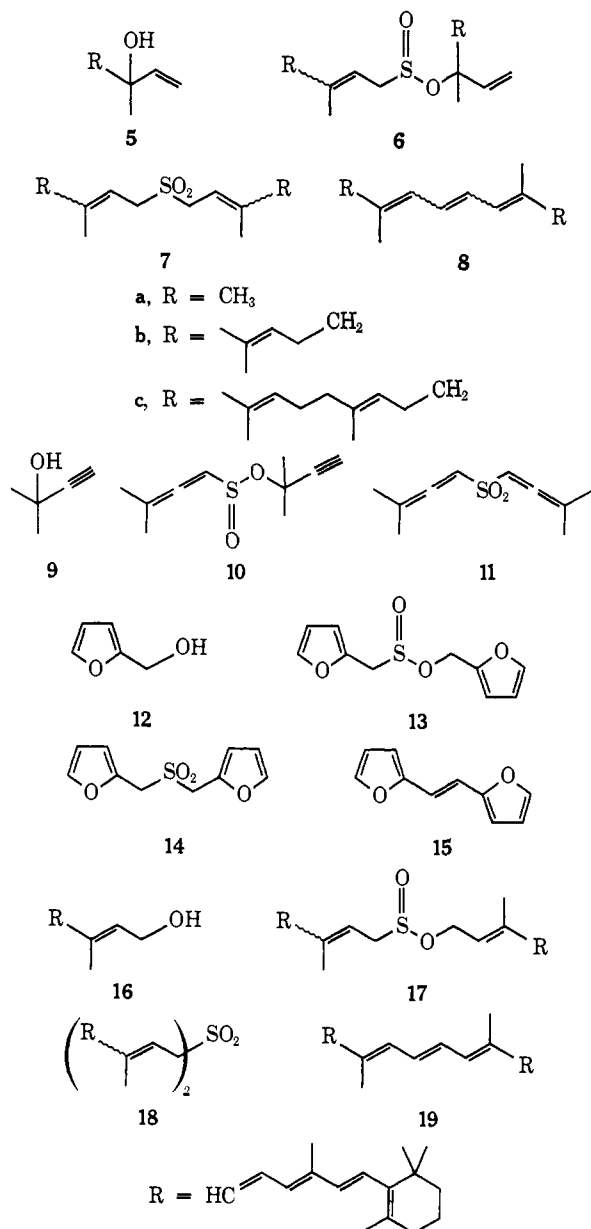
(3) L. Birkofer and H. Niedrig, *Chem. Ber.*, **99**, 2070 (1966); L. Birkofer, P. Richter, and A. Ritter, *ibid.*, **93**, 2804 (1960).

(4) M. V. Kalnins, *Can. J. Chem.*, **44**, 2111 (1966).

(5) D. N. Harpp and T. G. Back, *Tetrahedron Lett.*, 1481 (1972).

(6) S. Braverman and T. Globerman, *Tetrahedron Lett.*, 3023 (1973), reported the thermal isomerization of furfuryl arenedisulfonates to phenyl-3-furfuryl sulfones.

ments⁷ or subsequent isomerization of the sulfones. Vitamin A (16) afforded β -retinyl sulfone (18) in analogy



to the rearrangement of cinnamyl trichloromethane-sulfenate to cinnamyl trichloromethyl sulfoxide⁸ and β -ionyl *p*-toluenesulfinate to β -ionyl *p*-tolyl sulfone.⁹ In these cases an allylic shift would have resulted in loss of conjugation and/or increased steric interactions.

Carbon tetrachloride in the presence of potassium hydroxide¹⁰ at room temperature converted sulfones 7a, b, c, and 14 rapidly to the olefins 8a, b, c, and 15 (method D) (Table I). No dichlorocarbene adducts were detected. The Ramberg-Bäcklund reaction of

(7) The stereochemical outcome of the related sulfenate-sulfoxide and other [2,3]sigmatropic rearrangements depends on the substitution pattern of the double bonds: D. A. Evans, G. C. Andrews, T. T. Fujimoto, and D. Wells, *Tetrahedron Lett.*, 1389 (1973); P. A. Grieco, *J. Chem. Soc., Chem. Commun.*, 702 (1972); P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *J. Amer. Chem. Soc.*, 90, 4869 (1968); J. E. Baldwin, J. de Bernardis, and J. F. Patrick, *Tetrahedron Lett.*, 353 (1970); V. Rautenstrauch, *Helv. Chim. Acta*, 54, 739 (1971); K. B. Sharpless and R. F. Lauer, *J. Amer. Chem. Soc.*, 94, 7154 (1972).

(8) S. Braverman, *Int. J. Sulfur Chem., Part C*, 6, 149 (1971).

(9) G. Büchi and H. Wüest, unpublished.

(10) C. Y. Meyers, A. M. Malte, and W. S. Mathews, *J. Amer. Chem. Soc.*, 91, 7510 (1969).

Table I

Alcohol	Sulfone	Method of preparation	% yield	Olefin	Method of preparation	% yield
5a	7a mp 37–38°	A	83	8a	D	78 ^a
5a	7a	B	48			
5b	7b oil	B	66 ^b	8b	D	69 ^b
5c	7c oil	B	74 ^b	8c	D	89 ^b
9	11 mp 62°	B	28			
12	14 mp 76–78°	B	32	15	D	18 ^c
16	18 amorphous	A	46 ^b	19		
16	18	C	74 ^b	19	E	24 ^c

^a 3:1 mixture of geometric isomers by glc. ^b Undetermined mixture of isomers. ^c All-trans isomer.

sulfone 14 required 60° and failed for β -retinyl sulfone (18). A mixture of stereoisomeric β -carotenes was prepared by treatment of the α,α' -dianion¹¹ (produced with *n*-butyllithium or lithium diisopropylamide in tetrahydrofuran at 0°) with iodine or bromine (method E). Thermal or iodine catalyzed isomerization¹² gave crystalline all-*trans*- β -carotene. The new transformation of a sulfone dianion to an olefin with halogens may be viewed as proceeding through an α -halo sulfone analogous to the Ramberg-Bäcklund transformation or as a two-electron oxidation to the episulfone followed by loss of sulfur dioxide.

Acknowledgment. We thank the National Institutes of Health (Grant No. GM 09868) for financial support.

(11) E. M. Kaiser and C. R. Hauser, *Tetrahedron Lett.*, 3341 (1967).

(12) O. Isler, H. Lindlar, M. Montavon, R. Rüegg, and P. Zeller, *Helv. Chim. Acta*, 39, 249 (1956).

(13) National Institutes of Health, Predoctoral Fellow 1972–present.

George Büchi,* Roger M. Freidinger¹³

Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received February 22, 1974

Total Synthesis of *dl*-Shionone, a Tetracyclic Triterpene¹

Sir:

As an integral part of our program directed toward the total synthesis of polycyclic triterpenes,² we have investigated the total synthesis of the tetracyclic triterpene shionone (15)³—an interesting objective in itself and a useful model for some of the transformations necessary in a total synthesis of friedelin⁴ and its derivatives. The successful approach we report here for this total synthesis incorporates the tetracyclic ketone 10⁵

(1) This work was made possible through the support of the National Science Foundation and a grant from the Hoffman-LaRoche Foundation.

(2) (a) R. E. Ireland, M. I. Dawson, S. C. Welch, A. Hagenbach, J. Bordner, and B. Trus, *J. Amer. Chem. Soc.*, 95, 7829 (1973). (b) R. E. Ireland, S. W. Baldwin, D. J. Dawson, M. I. Dawson, J. E. Dolfini, J. E. Newbould, W. S. Johnson, M. Brown, R. J. Crawford, P. F. Hudrlík, G. H. Rasmussen, and K. K. Schmiegel, *J. Amer. Chem. Soc.*, 92, 5743 (1970).

(3) Y. Tarrahashi, Y. Moriyama, T. Tokahashi, F. Patil, and G. Ourisson, *Bull. Soc. Chim. Fr.*, 2374 (1966); T. Takahashi, T. Tsuyuki, T. Hoshimo, and M. Ito, *Tetrahedron Lett.*, 2997 (1967).

(4) E. J. Corey and J. J. Ursprung, *J. Amer. Chem. Soc.*, 78, 5041 (1956); G. Brownlie, F. S. Spring, R. Stevenson, and W. S. Strachan, *J. Chem. Soc.*, 2419 (1956).

(5) The structural formulas containing one or more asymmetric carbon atoms depict one enantiomer but refer to racemic compounds throughout. All intermediates were characterized by ir and nmr spectroscopy which are fully consistent with the structures shown. All new substances gave satisfactory combustion analyses.