tion is energetically more favorable due to the lower charge repulsion to be overcome.

Research in progress is directed toward determining the scope of the method, particularly its applicability to more highly saturated molecules and to the synthesis of carcinogenic aromatic hydrocarbons and related compounds otherwise accessible only through tedious multistep procedures.

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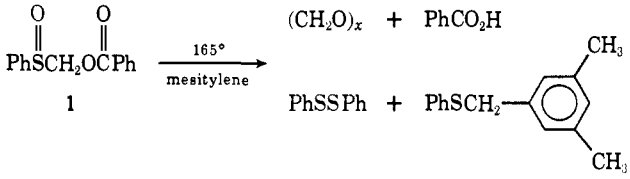
Mechanism of the Thermolysis of Benzoyloxymethyl Phenyl Sulfoxide. A New Sulfoxide Fragmentation Reaction

Sir:

Thermolysis of a sulfoxide may result in racemization, rearrangement, or fragmentation.[1-10] The most common fragmentations involve rearrangement to sulfenates followed by elimination of thiols to give aldehydes[4,5] or direct β elimination of sulfenic acids to give alkenes.[6-9] We recently reported an additional sulfoxide thermolysis reaction where methoxymethyl phenyl sulfoxide rearranged at 36° to a sulfenate, which then decomposed to phenyl benzenethiosulfinate and bismethoxymethyl ether.[11] The benzoyloxy analog (**1**),[12] however, was unreactive below 110°.

We now wish to report on the thermolysis of benzoyloxymethyl phenyl sulfoxide (**1**), for which a new sulfoxide fragmentation mechanism has been observed. An oxygen-18 labeling study indicates that the mechanism for the fragmentation does not involve a sulfenate intermediate.

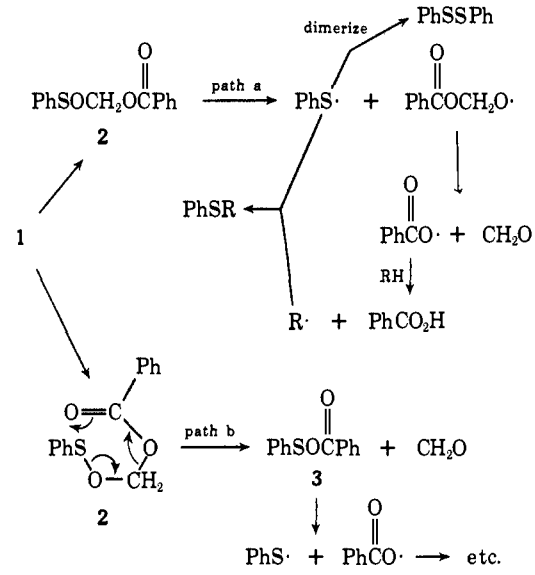


1

Thermolysis of **1** in *cis*-decalin at *ca.* 190° for 4 days gave phenyl disulfide (61%), benzoic acid (23%), some paraformaldehyde, and considerable carbon black. After refluxing in toluene for 10 days, less than 10% of **1** was converted to products. However, on refluxing in mesitylene for 5 days, **1** was completely converted in a clean reaction to phenyl disulfide (*ca.* 10%), 3,5-dimethylbenzyl phenyl sulfide (*ca.* 80%), benzoic acid (77%), and paraformaldehyde (83%).[13]

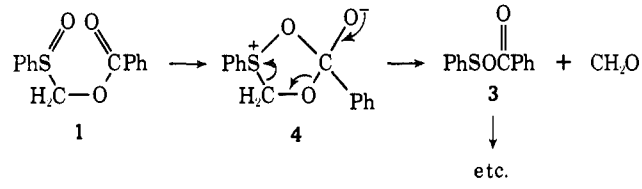
Two reaction mechanisms may be envisioned to explain the products isolated. The first (Scheme I) involves initial Meisenheimer rearrangement of **1** to benzoyloxymethyl benzenesulfenate (**2**) followed by fragmentation by either of two pathways. Path a involves homolytic cleavage of the S–O bond of **2**. Dimerization of the thiophenoxy radicals gives rise to phenyl disulfide. β-Scission of the benzoyloxymethoxy radical results in the formation of formaldehyde and benzoyloxy radical. Attack of the latter on solvent leads to benzoic acid and the sulfide. Path b involves a cyclic process leading to expulsion of formaldehyde with formation of an intermediate sulfenyl benzoate (**3**). Decomposition of **3** would give the other products. Some sulfenyl carboxylates have been isolated,[14] but **3** would be expected to decompose under the reaction conditions.

Scheme I



The second mechanism (Scheme II) involves direct attack of the sulfoxide oxygen on the carbonyl to give a cyclic zwitterionic intermediate (**4**), which could collapse with expulsion of formaldehyde to give benzene sulfenyl benzoate (**3**). A significant difference between these mechanisms is that the sulfoxide oxygen atom goes to the formaldehyde in Scheme I but to benzoic acid in Scheme II.

Scheme II



In order to distinguish between these mechanisms we have carried out the thermolysis of **1** labeled with ^{18}O

(1) R. Tang and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 2100 (1970).
(2) E. G. Miller, D. R. Rayner, H. T. Thomas, and K. Mislow, *ibid.*, **90**, 4861 (1968).
(3) S. Braverman, *Int. J. Sulfur Chem., Part C*, **6**, 149 (1971).
(4) W. Carruthers, I. D. Entwistle, R. A. W. Johnstone, and B. J. Millard, *Chem. Ind. (London)*, 342 (1966).
(5) D. B. Barnard-Smith and J. F. Ford, *Chem. Commun.*, 120 (1965).
(6) C. A. Kingsbury and D. J. Cram, *J. Amer. Chem. Soc.*, **82**, 1810 (1960).
(7) J. L. Kice and J. D. Campbell, *J. Org. Chem.*, **32**, 1631 (1967); D. W. Emerson, A. P. Craig, and I. W. Potts, Jr., *ibid.*, **32**, 102 (1967); D. W. Emerson and T. J. Korniski, *ibid.*, **34**, 4115 (1969).
(8) I. D. Entwistle, R. A. W. Johnstone, and B. J. Millard, *J. Chem. Soc. C*, 302 (1967).
(9) J. R. Shelton and K. E. Davis, *J. Amer. Chem. Soc.*, **89**, 718 (1967).
(10) D. C. Dittmer, G. C. Levy, and G. E. Kuhlmann, *ibid.*, **89**, 2793 (1967).
(11) T. J. Maricich and C. K. Harrington, *ibid.*, **94**, 5115 (1972).
(12) L. Horner and E. Jurgens, *Justus Liebigs Ann. Chem.*, **602**, 135 (1957).
(13) Products were identified by comparison of their melting points and ir and nmr spectra with those of authentic samples.
(14) D. H. R. Barton, Y. L. Chow, A. Cox, and G. W. Kirby, *J. Chem. Soc.*, 3571 (1965); C.-E. Hagberg, O. Bohman, and C. Engdahl, *Tetrahedron Lett.*, 3689 (1972); L. Field, P. M. Giles, Jr., and D. L. Tuleen, *J. Org. Chem.*, **36**, 623 (1971).

at the sulfoxide oxygen.[15] The results, summarized in Table I, show that essentially all of the ^{18}O label (>90%)

Table I. ^{18}O-Labeling Results

Compound	^{18}O (atom % excess)[a] Sample 1	Sample 2
*O O || || $PhSCH_2OCPh$	6.4[b]	6.5[b]
$PhCO_2H$	5.7[c]	6.1[c]
O || PhSOCPh	6.5[d]	6.4[d]

[a] Determined by direct mass spectrometry of the compounds; error = ±0.1%. [b] From *m/e* peaks 125/127 of **1**. [c] From molecular ion. [d] From *m/e* peaks 230/232 of **1**.

is found in the benzoic acid and indicate that the fragmentation reaction involves the cyclic zwitterionic intermediate of Scheme II. The slightly less than quantitative recovery of the ^{18}O label in benzoic acid may be the result of a small amount of exchange during work-up. The conclusion that all of the reaction follows Scheme II is supported by the observation that **1** fragments (probably thermally) in the mass spectrometer with loss of unlabeled formaldehyde to give *m/e* peaks 230/232 which are consistent with structure **3** containing all of the label.[16]

Acknowledgments. We wish to acknowledge the assistance of Dr. R. A. Upham of the University of Minnesota for performing the mass spectral analyses on our labeled compounds. We are indebted to the National Cancer Institute for support of this study (CA-13201-01).

(15) The method of sulfide oxidation with the pyridine–bromine complex and ^{18}O-enriched water was employed: S. Oae, Y. Ohnishi, S. Kozuka, and W. Tagaki, *Bull. Chem. Soc. Jap.*, **39**, 364 (1966).

(16) Mass spectral oxygen-18 analysis was not obtained for the paraformaldehyde because of its complex fragmentation pattern.

(17) National Science Foundation Undergraduate Research Participant, 1970.

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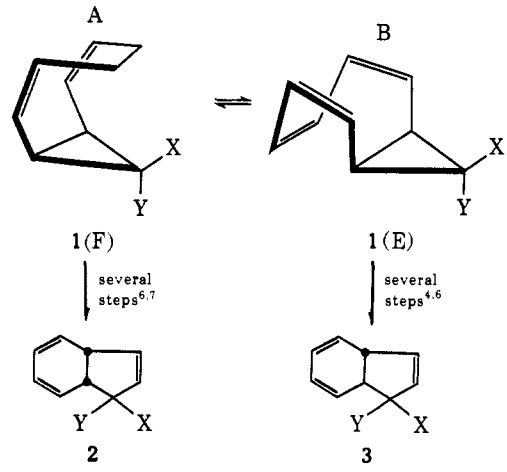
Thermal Bond Relocation of the *syn*- and *anti*-9-*tert*-Butylbicyclo[6.1.0]nona-2,4,6-trienes. Evidence for Strict Conformational Control

Sir:

A few years ago we stressed[1] the possible complexity of the seemingly straightforward, well documented,[2] conversion of *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**1**; X = Y = H) into *cis*-bicyclo[4.3.0]nona-2,4,7-triene (**2**; X = Y = H) insofar as orbital symmetry[3] demands that the resulting [4.3.0] bicycle be fused trans rather than cis.[1] The first mechanistic breakthrough with regard to this bond relocation dates to the subsequent discovery, by Staley and Henry,[4] that 9,9-dialkylbicyclo[6.1.0]nona-2,4,6-trienes do indeed thermolyze to the expected trans-fused bicyclo[4.3.0]nona-2,4,7-trienes and the consequent realization by these workers that reactant conformation influences the stereochemical outcome of the general [6.1.0] to [4.3.0] conversion.[5] This notion was effectively confirmed and further amplified by our own efforts in the area[6,7] which established that (i) of the two 9-methylbicyclo[6.1.0]nona-2,4,6-triene variants only the syn isomer produces a significant amount (32%) of trans-fused 8,9-dihydroindene skeleton on thermolysis,[6] (ii) the thermal bond relocation of the parent [6.1.0] triene is somehow intermediated by *cis,cis,trans,cis*-cyclononatetraene,[7] and (iii) path A of Scheme I (abbreviated) is favored over

Scheme I



path B by a $\Delta\Delta G^{\ddagger}$ term of *ca.* 4 kcal/mol.[6,7]

Presently, we disclose pertinent information with the sterically demanding *syn*- and *anti*-9-*tert*-butylbicyclo[6.1.0]nona-2,4,6-trienes which constitutes the first unambiguous realization of the conformationally controlled mechanistic dichotomy postulated in Scheme I. Moreover, the work detailed here serves to effectively counter recent criticism[8] of our mechanistic interpretation of the thermolytic behavior of *syn*-9-methylbicyclo[6.1.0]nona-2,4,6-triene (**1**; X = CH_3, Y = H).

The two novel stereoisomeric *tert*-butyl derivatives[9] were prepared as shown in Scheme II: **4** [white crys-

(1) A. G. Anastassiou, *J. Amer. Chem. Soc.*, **90**, 1527 (1968); see also W. Grimme, Habilitationsschrift, Koln, 1968.

(2) E. Vogel, *Angew. Chem.*, **73**, 548 (1961); **74**, 829 (1962).

(3) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(4) S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, **91**, 1239, 7787 (1969).

(5) For a critical evaluation of the problem, see S. W. Staley, *Intra-Sci. Chem. Rep.*, **5**, 149 (1971).

(6) A. G. Anastassiou and R. C. Griffith, *J. Chem. Soc. D*, 1301 (1971), 399 (1972).

(7) A. G. Anastassiou and R. C. Griffith, *J. Amer. Chem. Soc.*, **93**, 3083 (1971). In answer to a referee's comment, we note that as of this writing the above report contains the only *bona fide* example of cycloadditive trapping of *cis,cis,trans,cis*-CNT. We might recall in this context that the early mechanistic confusion associated with the formation of a cycloadduct incorporating a monocyclic C_9 moiety in the reaction of TCNE with *cis*-bicyclo[6.1.0]nona-2,4,6-triene (W. Okamura and T. W. Osborn, *J. Amer. Chem. Soc.*, **92**, 1061 (1970); C. S. Baxter and P. J. Garratt, *ibid.*, **92**, 1062 (1970)) has been effectively clarified with the recent demonstration (J. Clardy, L. K. Read, M. J. Broadhurst, and L. A. Paquette, *ibid.*, **94**, 2094 (1972)) that the stereochemical characteristics of the adduct are incompatible with its origination from *cis,cis,trans,cis*-CNT. In fact, Paquette and coworkers reasonably ascribe the formation of the said adduct to electrophilic addition of TCNE onto the *intact* [6.1.0]triene skeleton.

(8) M. B. Sohn, M. Jones, Jr., and B. Fairless, *J. Amer. Chem. Soc.*, **94**, 4774 (1972).

(9) Stereochemical assignments were made on the basis of the well documented tendency of the C-9 proton in an anti [6.1.0] stereoisomer to (i) resonate at higher field and (ii) exhibit a smaller coupling constant than its counterpart in the corresponding syn stereoisomer.