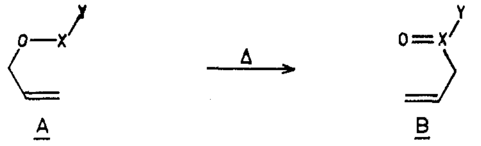
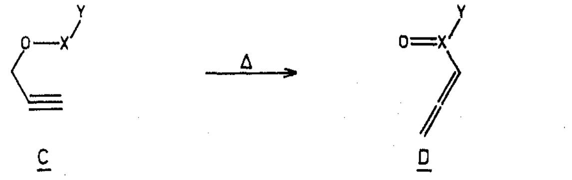
The Formation of an Unusual Bicyclic Sultone by Means of Thermally Induced Rearrangement of a Dipropargylic Sulfite

Summary: On pyrolysis the sulfite from 4,4-dimethyl-2-yne-1-pentanol undergoes a [2,3] sigmatropic rearrangement followed by intramolecular cycloaddition.

Sir: There is now adequate evidence that on thermal activation sigmatropic rearrangements occur readily with allylic (A → B, eq 1) and propargylic (C → D, eq 2) sulfenates (X = S; Y = R),[1] sulfoxylates (X = S; Y = OR),[2] and sulfinates (X = SO; Y = R).[2,3] Related rearrangements of sulfonium ylides also are known[4] and similar structural mobility likewise is seen in the transformations of propargylic sulfides to isomeric allenes.[5]



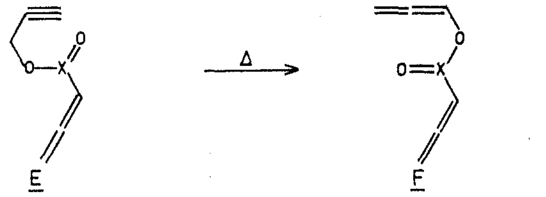
(1)



(2)

We report here evidence for what we believe to be the first example of sigmatropic rearrangement of a propargylic sulfite (C, X = SO, Y = OR), thereby setting the stage for a remarkable cycloaddition of an allene and an acetylene.

The experiment was carried out with a dipropargylic sulfite with the thought that there would be formed E, through a [2,3] sigmatropic process, or possibly F, from E through [3,3] sigmatropic conversion (eq 3), which compounds were anticipated to be particularly suitable substrates for realization of intramolecular cycloaddition. Such reactions have previously drawn our attention.[6]



(3)

Sulfite 1 (R = t-C_4H_9) was prepared as shown in eq 4.

$$\mathrm{R}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_3} \xrightarrow[\text{2. KOH/CaO}]{\text{1. PCl}_5} \mathrm{RC{\equiv}CH} \xrightarrow[\text{2. (CH}_2\text{O)}_n]{\text{1. CH}_3\text{Li}}$$

$$\mathrm{RC{\equiv}CCH_2OH} \xrightarrow[\mathrm{CCl_4/CO_2}]{\mathrm{SOCl_2}} \underset{\mathbf{1}}{(\mathrm{RC{\equiv}CCH_2O})_2\mathrm{SO}} \quad (4)$$

Pyrolysis of neat 1 above 180° leads to tarry material from which in 22% yield (not maximized) an isomeric substance, mp 141.3–141.4°,[10] was isolated. Consideration of the spectral data[7] in the light of reasonable mechanistic hypotheses led to 2 or 3. Attempts to probe chemically into the structure (see below) gave, however, no basis for a distinction.

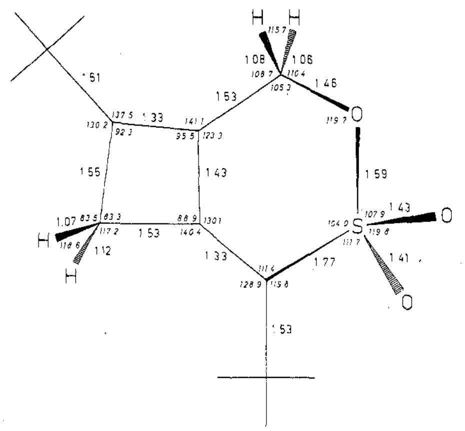


Figure 1. Bond distances in Å and angles in degrees for **3** (data for the *tert*-butyl groups are omitted).

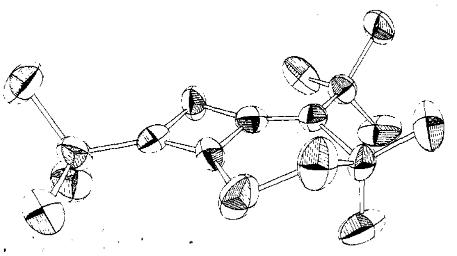
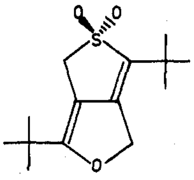


Figure 2. ORTEP plot of **3** (hydrogen atoms omitted).



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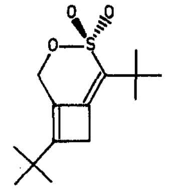
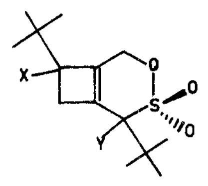


3

By x-ray diffraction the correct structure was shown to be **3**. The crystal data follow: triclinic, a = 9.82, b = 9.80, c = 7.96 Å, α = 84.9, β = 101.8, γ = 96.8°, U = 742 Å, Z = 2, space group $P\bar{1}$. The structure was solved by direct methods,[9] followed by a least-squares refinement with 1589 independent reflections, which were measured on an Enraf–Nonius four-circle diffractometer at room temperature using Mo Kα radiation. The weighted index R decreased to 0.121. Pertinent angles and bond lengths are depicted in Figure 1. An ORTEP plot of **3** is shown in Figure 2. The ring system present in **3** has never before been reported.

Compound **3** is remarkably stable. It is recovered unchanged on attempted hydrolysis with NaOH in dioxane–water or HCl in the same medium; it is stable to treatment with zinc in acetic acid, sodium in ethanol, hexachlorodisilane, potassium *tert*-butoxide in *tert*-butyl alcohol, or to N-bromosuccinimide under brominating conditions. It is stable to irradiation and pyrolysis. Several addition reactions do take place. Addition of bromine gives a single dibromide, mp 119.2–120.1°, which on the basis of spectral data[10] is assigned structure **4a** or **5a**. A rather unstable ad-



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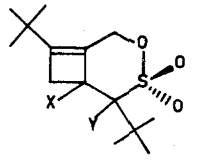
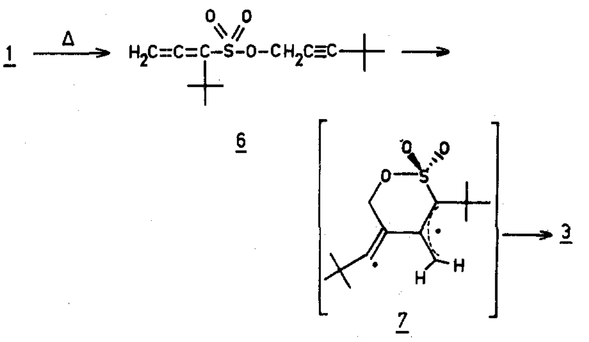


5

a. X = Y = Br
b. X = H, Y = I
c. X = H, Y = OH
d. X = Y = H

duct **4b** or **5b** is obtained with HI; this on treatment with $AgNO_3$ in THF–water affords unstable **4c** or **5c.** Treatment with triethylamine causes **4/5a** to revert to **3** whereas **4/5b** and **4/5c** revert to **3** on chromatography. Hydrogenation of **3** (Pd/C) gives a complex mixture of reduced products; reduction (Zn/HOAc) of **4/5b** gives **4/5d.** Ozonolysis of **3** produces a stable ozone addition product, mp 83.3–83.8° dec, the structure of which is under investigation.[10]

The structure of **3** makes probable that it is preceded by **6**, which we have been unable to observe, suggesting its great proclivity toward cycloaddition, even through the uncommon allene–acetylene mode.[11] It is likely that the latter reaction passes through diradical **7** (eq 5).[11a] A superficially



(5)

related reaction has been observed by Braverman and Segev.[2a] The structure **2** originally considered as an alternative would become accessible were **6** to undergo a subsequent [3,3] sigmatropic rearrangement (eq 3), followed by the well-known allene dimerization through a 2,2′-bisallyl diradical.[6,11g]

Further investigations are underway.

Acknowledgment. We are indebted to Professor Dr. A. Vos of the Department of Structural Chemistry of this university for making available equipment for crystallographic work.

Supplementary Material Available. A listing of crystallographic data (atomic coordinates and thermal parameters, interatomic distances, bond angles and least square planes) as well as physical data for **3**, **4/5a-*d*** and the ozone adduct will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journal Division, American Chemical Society, 1155 16th Street, N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JOC-75-3308.

References and Notes

(1) (a) S. Braverman and Y. Stabinsky, *Chem. Commun.*, 270 (1967); *Isr. J. Chem.*, **5**, 125 (1967). (b) P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4869 (1968). (c) R. Tang and K. Mislow, *ibid.*, **92**, 2100 (1970). (d) Also D. H. R. Barton and S. Prabhakar, *J. Chem. Soc., Perkin Trans. 1*, 781 (1974).

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(4) For example, (a) B. M. Trost and R. La Rochelle, *Tetrahedron Lett.*, 3327 (1968); (b) J. F. Baldwin, R. E. Hackler, and D. P. Kelly, *Chem. Commun*, 537, 538, 1083 (1968); (c) P. A. Grieco, M. Meyers, and R. S. Finkelhor, *J. Org. Chem.*, **39**, 119 (1974).

(5) H. Kwart and T. J. George, *Chem. Commun*, 433 (1970).

(6) (a) T. Beetz and R. M. Kellogg, *J. Am. Chem. Soc.*, **95**, 7925 (1973); (b) T. Beetz and R. M. Kellogg, paper in preparation.

(7) Spectral data for **3**: ^1H NMR (CCl_4) δ 1.15 [s, 9, $(CH_3)_3C{-}$], 1.33 [s, 9, $(CH_3)_3C{-}$], 3.15 (dd, 2, J = 3.5, 2.4 Hz, $-CH_2-$),[8] and 5.06 (dd, 2, J = 3.5, 2.4 Hz, $-CH_2$); ir (KBr) 1335 and 1155 cm^{-1} (sulfur–oxygen bonds); uv (C_2H_5OH) λ_{max} 246 nm (ϵ 8750). In the coupled ^{13}C NMR spectrum there is seen in addition to the $(CH_3)_3C{-}$ absorptions (relative to TMS) δ 158.1 (s, vinylidene C), 139.8 (s, vinylidene C), 132.7 (s, vinylidene C), 129.1 (s, vinylidene C), 68.2 (t, J_{CH} = 153 Hz, $-CH_2-$), and 36.5 (t, J_{CH} = 143 Hz, $-CH_2-$).

(8) Coupling constants confirmed by computer simulation [LAME: C. W. Haigh, *Annu. Rep. NMR Spectrosc.*, **4**, 311 (1971)].

(9) MULTAN computer program: G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr.*, **A27**, 368 (1971).

(10) Correct elemental analyses have been obtained for all new compounds save **4/5b,c,** which were too unstable for analysis, and **4/5d.** Spectral data were all in accord with the proposed structures. See also note concerning microfilm edition.

(11) Examples of this type of reaction are reported by (a) B. E. Kirk and D. R. Taylor, *J. Chem. Soc. Perkin Trans. 1*, 1844 (1974); (b) R. E. Banks, W. R. Deem, R. N. Hazeldine, and D. R. Taylor, *J. Chem. Soc., C*, 2051 (1966); (c) D. E. Applequist and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 4012 (1956); (d) Ya. M. Slobodin, Yu. A. Tallier, and I. Ismailova, *Zh. Org. Khim.*, **3**, 1529 (1967) (English translation, p 1484). (e) A failed attempt to realize this reaction has been reported by H. A. Staab and H-A. Kurmeier, *Chem. Ber.*, **101**, 2697 (1968). (f) The addition of benzyne to allenes could be considered a variant on this reaction: H. H. Wassermann and J. M. Fernandez, *J. Am. Chem. Soc.*, **90**, 5322 (1968); H. H. Wasserman and L. S. Keller, *Chem. Commun*, 1483 (1970). (g) For general references on allene cycloadditions, see J. E. Baldwin and R. H. Fleming, *Fortsch. Chem. Forsch.*, **15**, 281 (1970); D. Seebach, Houben-Weyl Methoden der Organischen Chemie, George Thieme Verlag, Stuttgart, 1971, IV/4, p 151 et seq.

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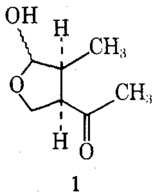
The Stereochemistry of Ester Dienolate Anions. A Stereoselective Route to Botryodiplodin

Summary: A three-step total synthesis of the antibiotic and antileukemic agent botryodiplodin by means of the stereoselective Claisen rearrangement of *cis*-crotyl senecioate is described.

Sir: A short, stereoselective total synthesis of the antibiotic and antileukemic agent botryodiplodin[1,2] (1) has been achieved by a route which also provides evidence for the configuration of ester dienolate anions. Several recent re-



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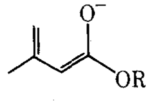
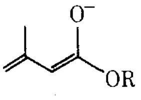
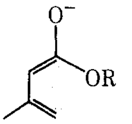


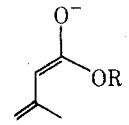
2, *E* (s-cis)



3, *E* (s-trans)



4, *Z* (s-cis)



5, *Z* (s-trans)