tolysis of either **1** or **3** in methanol–pyridine gives the *cis*-ether **9**.[23] These results suggest that the equilibrium between **10** and **11** lies heavily toward **10** and product formation reflects this equilibrium. That **4** and **5** also equilibrate in favor of **4** is support for this argument.

Further studies on the interconversion of these intriguing species are currently underway, particularly trapping of **6** with olefins.

Acknowledgment. We wish to thank the National Research Council of Canada for support of this research.

[23] The thermodynamic ratio for **9** and its trans isomer has not been determined.

[24] Alfred P. Sloan Fellow, 1972–1974.

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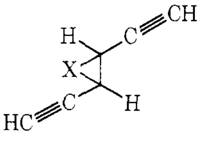
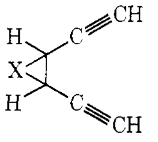
Competition between Sulfur Extrusion and Thermal Synthesis of Thienocyclobutadiene in the Pyrolysis of *cis*- and *trans*-1,2-Diethynylthiiranes. Dimerization of the Rearrangement Product to Bisthienocyclooctatetraene

Sir:

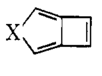
Thermal rearrangement of both cis and trans isomers of three-membered ring diacetylenes **1** and **2** affords[1,2] efficient syntheses of bicyclic triene **4** and furocyclobutadiene **5**. In principle, rearrangement of sulfur analog **3** should lead to thienocyclobutadiene **6**; this material is of interest because, despite recent syntheses[3,4] of substituted analogs **7–10**, preparation of the parent compound has not been recorded. We now wish to report the synthesis of **6** and its dimerization to the interesting 16π-electron bisthienocyclooctatetraene **12**. However, the pyrolysis of **3** is considerably more complicated than that of either **1** or **2**. Desulfurization overtakes C–C bond cleavage in the trans isomer, and this is the first instance in which the lower energy cis rearrangement[1,2] must be taken advantage of in order to successfully obtain the bicyclic triene. Besides the synthesis of **6** and **12**, our results provide some interesting insights into the mechanism of thermal desulfurization of thiiranes.



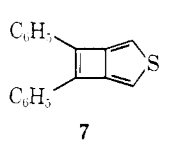
1T, X = CH_2
2T, X = O
3T, X = S



1C, X = CH_2
2C, X = O
3C, X = S



4, X = CH_2
5, X = O
6, X = S



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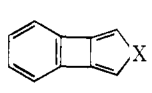
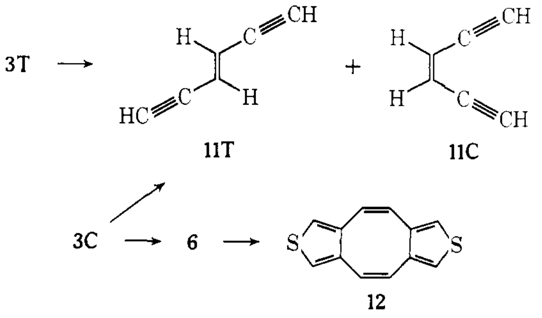


8, X = S
9, X = SO
10, X = SO_2

Only desulfurized olefins **11C** and **11T**[5] (Scheme I) can be isolated from solution pyrolysis of **3C** and **3T**[6] (toluene-d_8, 100°). Both reactions occur with greater than 90% retention of stereochemical configuration under these conditions, but the decomposition kinetics are complex. At nmr observable concentrations (~0.15 *M*) the reactions exhibit second-order kinetics initially; these change to first-order kinetics as the reactions proceed (*e.g.*, for **3T**, $k_2 = 3.9 \times 10^{-6}$ l./(mol sec), $k_1 = 1.18 \times 10^{-6}$ sec^{-1}; for **3C**, $k_2 = 1.03 \times 10^{-5}$ l./(mol sec), $k_1 = 1.03 \times 10^{-5}$ sec^{-1}). In a gas-phase nitrogen flow system, pyrolysis of **3T** is quantitative at 395° (15-sec contact time) and still gives only **11**, but under these conditions the reaction is considerably less stereoselective,[7] giving a 4:3 ratio of **11T** to **11C**. Flow pyrolysis of the cis isomer **3C** at 250° gave a 1:2 ratio of **11T** to **11C**, but admixed with them a new compound (**6**, ~5% yield, ~30% of the mixture of volatile products) which exhibited two resonances in the proton nmr (τ 3.25 and 3.99, acetone-d_6; τ 4.00 and 4.50, benzene-d_6). Compound **6** decomposes immediately on attempted chromatography or exposure to air. A mass spectrum could be obtained using break-seal techniques; this gave a parent peak at *m/e* 108; uv (cyclohexane) λ_{max} 286 and a higher wavelength band of considerable fine structure (12 peaks) extending to 442 mμ. Raney nickel desulfurization gave *cis*- and *trans*-1,2-dimethylcyclobutanes.

Scheme I



On standing at room temperature in benzene-d_6, the yellow solution decolorized and the nmr resonances due to **6** slowly disappeared at the expense of two new signals at τ 3.71 and 3.53. After 48 hr, the sealed nmr tube containing the sample was opened and a colorless oil isolated by preparative thin layer chromatography. On the basis of the nmr (*vide infra*), uv (diethyl ether,

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[1] (a) M. B. D'Amore and R. G. Bergman, *J. Amer. Chem. Soc.*, **91**, 5694 (1969); (b) M. B. D'Amore, R. G. Bergman, M. Kent, and E. Hedaya, *J. Chem. Soc., Chem. Commun.*, 49 (1972); (c) T. J. Henry and R. G. Bergman, *J. Amer. Chem. Soc.*, **94**, 5103 (1972).

[2] (a) K. P. C. Vollhardt and R. G. Bergman, *J. Amer. Chem. Soc.*, **94**, 8950 (1972); (b) R. G. Bergman and K. P. C. Vollhardt, *J. Chem. Soc., Chem. Commun.*, 214 (1973).

[3] P. J. Garratt and K. P. C. Vollhardt, *J. Amer. Chem. Soc.*, **94**, 7087 (1972).

[4] P. J. Garratt and K. P. C. Vollhardt, *J. Amer. Chem. Soc.*, **94**, 1022 (1972).

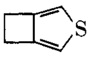
[5] (a) W. H. Okamura and F. Sondheimer, *J. Amer. Chem. Soc.*, **89**, 5991 (1967); (b) R. R. Jones and R. G. Bergman, *ibid.*, **94**, 660 (1972).

[6] Prepared either by the reaction of 1,2-diethynyloxiranes **2T** and **2C** with thiourea or by the reaction of diazopropyne with sulfur. For some analogies, see (a) R. D. Schuetz and R. L. Jacobs, *J. Org. Chem.*, **26**, 3467 (1961); (b) N. Latif and J. Fathy, *ibid.*, **27**, 1633 (1962); (c) A. Schönberg and E. Frese, *Chem. Ber.*, **95**, 2810 (1962).

[7] In order to assure ourselves that **11C** and **11T** were stable to cis–trans isomerization under the exact desulfurization reaction conditions, the following experiment was carried out. A sample of 50 mg of *trans*-thiirane **3T** doped with ~2 mg of tritiated olefin **11T** was subjected to pyrolysis. The pyrolysate was diluted with cold **11C** and **11T** and each olefin isolated by preparative gas chromatography. Scintillation counting showed that >99% of the radioactivity remained in the trans isomer **11T** and <1% was present in **11C**.

λ_{max} 258, 285 (sh) nm), and mass spectrum (molecular ion at *m/e* 216), this material was assigned the symmetrical dimer structure **12**.[8]

As in the case of its oxygen analog,[2a] the high-field chemical shift of the α protons in **6** relative to that in other substituted thiophenes (*e.g.*, **13**),[9] despite the



13

presence of an additional double bond, strongly indicates the contribution of a pronounced paramagnetic component to its ring current. The chemical shift in **12**, however, appears to be normal, suggesting that it exists in a nonplanar "tub" conformation, like cyclooctatetraene itself. The uv spectrum is also consistent with such a structure.

With regard to the mechanism of thiirane desulfurization,[10] the observation of complex kinetics under some conditions indicates that at relatively high concentrations a bimolecular process dominates; this competes with a somewhat slower unimolecular desulfurization which becomes the major pathway as the concentration of thiirane decreases during the reaction. This behavior provides kinetic evidence for the suggestion[10a] that thiirane desulfurizations can (in some cases at least) involve a more complicated mechanism than simple cheletropic extrusion of the sulfur atom. The apparently strong dependence of stereochemistry on temperature, however, suggests that these reactions cannot be classified as "stereospecific,"[10a] and mechanistic interpretation should perhaps be considered with this cautionary observation in mind.

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(8) For the oxygen analog, see J. A. Elix, M. V. Sargent, and F. Sondheimer, *J. Amer. Chem. Soc.*, **92**, 973 (1970), and ref 2a.

(9) (a) P. J. Garratt and D. N. Nicolaides, *J. Chem. Soc., Chem. Commun.*, 1014 (1972); (b) S. W. Longworth and J. F. W. McOmie, *ibid.*, 623 (1972).

(10) (a) E. M. Lown, H. S. Sandhu, H. E. Gunning, and O. P. Strausz, *J. Amer. Chem. Soc.*, **90**, 7164 (1968); (b) H. E. Gunning and O. P. Strausz, *Advan. Photochem.*, **4**, 143 (1966); O. P. Strausz, H. E. Gunning, A. S. Denes, and I. G. Csizmadia, *J. Amer. Chem. Soc.*, **94**, 8317 (1972).

(11) (a) Alfred P. Sloan Foundation Fellow, 1970–1972; (b) Camille and Henry Dreyfus Teacher-Scholar, 1970–1975.

Book Reviews

Organic Reactions and Orbital Symmetry. By T. L. Gilchrist and R. C. Storr (University of Liverpool). Cambridge University Press, London. 1972. viii + 271 pp. £1.80 (UK); $6.95 (USA).

This book presents a good cross section of cycloreaction chemistry in a highly readable manner. Introductory chapters on classifications and experimental indicators for reaction mechanisms, and on theoretical treatments of concerted processes, are followed by descriptive accounts of electrocyclic isomerizations, cycloadditions, and sigmatropic rearrangements. A brief coverage of substitutions, additions, and eliminations completes the text.

It may be recommended to readers at every level of familiarity with the cycloreaction literature: it informs efficiently and provokes thought effectively through a judicious alternation between specific examples and summarizing generalizations.

Inevitably, "Organic Reactions and Orbital Symmetry" and other recent books on similar matters, such as those by Anh, Lehr and Marchand, Maier, Wieland and Kaufmann, and Woodward and Hoffmann, are in part duplicative; yet no one of them is redundant. Each has a unique emphasis, balance, and level of mechanistic sophistication.

John E. Baldwin, *University of Oregon*

Selective Ion Sensitive Electrodes. By G. J. Moody and J. D. R. Thomas (University of Wales). Merrow Publishing Co., Watford, Herts, England (U.S. Distributor: Bonn Industries, Inc., Plainfield, N. J. 07061). 1972. vii + 140 pp. $6.90.

In this short, concise monograph, Moody and Thomas survey various characteristics of the ion-selective electrodes which have appeared since Ross rekindled interest in this area with the 1967 publication of the performance of the liquid ion exchange electrode for calcium ion. The authors make no pretext at presenting a theoretical framework or historical development. Their primary concern is the methods by which electrode selectivity is determined and the tabulation of various properties of the many commercially available electrodes. It is written as a practical guide to the selection and use of ion-selective electrodes. The book suffers from lack of depth and a paucity of specific examples with experimental details of the actual use of these electrodes. If one's bookshelf already contains Helferich's "Ion Exchange," Eisenman's "Glass Electrodes of Hydrogen and Other Cations," and Durst's Special Publication No. 314 (NBS), this book would be a suitable companion as a guide to the characteristics of commercially available electrodes.

George Baum, *Corning Glass Works*

Metal Pi-Complexes. Volume II: Complexes with Mono-Olefinic Ligands. Part 1: General Survey. By M. Herberhold (Technical University of Munich). American Elsevier, New York, N. Y. 1972. xv + 643 pp. $86.00.

The stated objective of this monograph is to survey completely the literature concerning monoolefin π complexes of transition metals from 1830 (when W. C. Zeise first described his platinum–ethylene complexes) through 1968. Part 1 is mainly descriptive in nature and is devoted to syntheses and properties of the complexes. It is to be followed by Part 2 which is to be devoted to spectroscopy, structure, and bonding in the monoolefin π complexes.

The book begins with a brief introduction which is followed by a short historical survey of olefin–transition metal complexes. Next there is a chapter which surveys the various methods used to synthesize olefin–transition metal complexes. Chapter IV describes the known nonfunctionally substituted olefin–π complexes. It is organized according to groups of the periodic table, beginning with group VIb metals and ending with a discussion of group Ib metal complexes.

Finally, Chapter V describes the complexes of functionally substituted monoolefins. Here the organization is according to functional group. Virtually all types of functionally substituted olefins are included (*e.g.*, cyanoolefins, α,β-unsaturated carbonyl compounds, haloolefins, vinyl alcohols, ethers and esters, allyl compounds, unsaturated amines, phosphines, arsines, and sulfides). Chapters IV and V together contain 85 tables which list spectral and physical properties for many of the compounds discussed.

In the opinion of this reviewer, this book represents a very sig-