in **3b** is displaced to 1068 cm^{-1}. Cooling the sample window back to −196 °C fails to restore these infrared absorptions. At −40 to −20 °C dehydration takes place (eq 2) to give the corresponding thiosulfinates **4a,b**. These thiosulfinates exhibit strong S=O absorptions at approximately 1080 and 1068 cm^{-1}, respectively.

We conclude from these studies that simple sulfenic acids, generated by FVP, can exist in both the O- and S-protonate forms **1a,b** in the temperature range −196 to −50 °C. Furthermore, the broad OH absorption in the region 3250–3300 cm^{-1} is consistent with formation of hydrogen-bonded dimer **4**, often postulated as being required for thiosulfinate formation.

Experimental Section

FVP of sulfoxides **2a,b** was carried out at 340 and 620 °C as previously described,[12] except that the sulfenic acids were collected on the sodium chloride window of an Air Products Inc. Model AC 2-110 Cryo-tip. The temperature of the Cryo-tip window was monitored using a copper–constantan thermocouple, estimated to be accurate to ±5 °C. Infrared spectra were measured on a Perkin Elmer Model 457 spectrometer referenced against a polystyrene film standard. Control experiments, pyrolysis in the absence of the sample and vaporization of **2a,b** in the absence of pyrolysis failed to produced OH absorptions in the 3300-cm^{-1} region.

Synthesis of 2-Methyl-2-propyl-d_9 Phenyl Sulfide. To a 100-mL round-bottomed flask equipped with magnetic stir bar is placed 50 mL of 75% aqueous (D_2O) sulfuric acid-d_2 (Aldrich) and the flask cooled to 0 °C in an ice bath. To the reaction mixture, with stirring, is added 1.0 g (0.012 mol) of 2-methyl-2-propanol-d_{10} (Aldrich) followed by dropwise addition over 30 min of 1.3 g (0.012 mol) of benzenethiol. After the addition is complete the ice bath is removed and the reaction mixture stirred for 1 h. At this time the reaction mixture is carefully poured into 100 g of ice (D_2O), and the solution is extracted with ether (3 × 75 mL) and dried over anhydrous $MgSO_4$. Removal of the solvent under vacuum gives an oil, which is distilled at 40–41 °C (0.1 torr) [lit.[16] bp 55 °C (0.15 torr)] to give 1.56 g (75%) of 2-methyl-2-propyl-d_9 phenyl sulfide. Proton NMR indicates that the sulfide contains >95% deuterium. This sulfoxide is oxidized to the sulfoxide, **2a**, as previously described.[11]

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Registry No. **2a**, 4170-71-2; **2b**, 2211-92-9; **3a**, 27610-20-4; **3b**, 4719-19-1; 2-methyl-2-propanol-d_{10}, 53001-22-2; benzenethiol, 108-98-5; 2-methyl-2-propyl-d_9 phenyl sulfide, 96808-03-6.

(16) Shelton, J. R.; Davis, K. E. *Int. J. Sulfur Chem.* **1973**, *8*, 197.

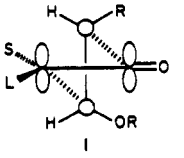
Communications

Cyanoketenes. Cycloaddition of *tert*-Butylcyanoketene to Silyl Enol Ethers—A Nonconcerted Reaction

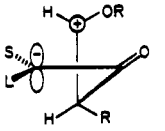
Summary: The mechanism of the cycloaddition of *tert*-butylcyanoketene to siloxy enol ethers is shown to proceed via a dipolar intermediate. This stepwise mechanism is operative even though experimental criteria are met which are normally used to argue in favor of a concerted mechanism.

Sir: Reported here is a study of the cycloadditions of *tert*-butylcyanoketene (TBCK) to siloxy enol alkenes. Data are presented which show the reaction to proceed by a stepwise pathway[1] even though the following three experimental observations were met, and these are commonly claimed as criteria for the concertedness of ketene/alkene cycloadditions: (1) the cycloadditions are stereospecific; (2) *cis*-alkenes generally react faster than their corresponding trans isomers; (3) for those cycloadditions employing an unsymmetrical ketene, the kinetic products are generally contrathermodynamic.

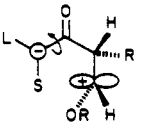
The above predictions come directly from the $2\pi s + 2\pi a$ transition state, **1** (L = large, S = small), associated with a concerted ketene/alkene cycloaddition.[2] However, they can also be rationalized with respect to the two-step variant of the above involving the zwitterion **2** or even with an



I



2



3

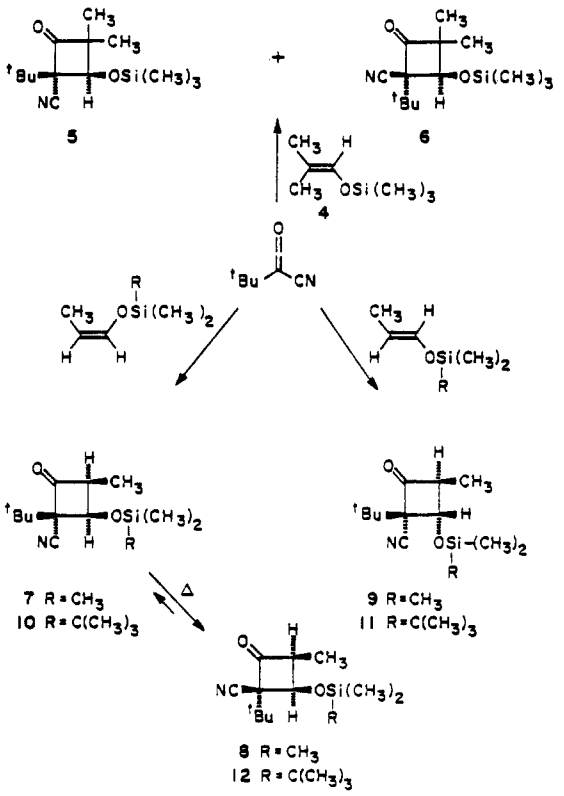
alternate mechanism in which zwitterion **3** is the ultimate intermediate.[12] For example, consideration of steric effects associated with **3** leads to the above predictions, i.e., (1) if ring closure is faster than bond rotation, the cycloadducts will be formed stereospecifically; (2) more steric strain would be relieved in the transition state leading to **3** starting with a *cis*-alkene than with the trans isomer and thus, the former should ract faster than the latter; (3) the contrathermodynamic products would result from the

(1) Little has appeared describing the reactions of ketenes with silyl enol ethers. That which has concerns haloketene cycloadditions, and here the available data do not allow a distinction to be made between a concerted or a stepwise mechanism. For examples, see the following key references: Brady, W. T.; Lloy, R. M. *J. Org. Chem.* **1978**, *44*, 2560. Krepski, L. R.; Hassner, A. *Ibid.* **1978**, *43*, 3173. Brady, W. T.; Lloyd, R. M. *Ibid.* **1980**, *45*, 2025. Brady, W. T.; Lloyd, R. M. *Ibid.* **1981**, *46*, 1322. Bellus, D.; Martin, P.; Sauter, H.; Winkler, T. *Helv. Chim. Acta* **1980**, *63*, 1130. Brady, W. T.; Watts, R. D. *J. Org. Chem.* **1981**, *46*, 4047. Raynolds, P. W.; DeLoach, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 4566.

(2) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781. For specific ketene/alkene cycloadditions, see, for example: Dominh, T.; Strauss, O. P. *J. Am. Chem. Soc.* **1970**, *92*, 1966. Brady, W. T.; Hoff, E. F.; Row, R.; Parry, R. H. *Ibid.* **1969**, *91*, 5679. Baldwin, J. W.; Kapacki, J. A. *Ibid.* **1969**, *91*, 5679. Baldwin, J. W.; Kapacki, J. A. *Ibid.* **1970**, *92*, 4874. Rey, M.; Roberts, S.; Dieffenbacker, A.; Dreiding, A. S. *Helv. Chem. Acta* **1970**, *53*, 417. Montaigne, R.; Ghosez, L. *Angew. Chem., Int. Ed. Engl.* **1968**, *80*, 194. Huisgen, R.; Feiler, L. A.; Oho, P. *Tetrahedron Lett.* **1968**, *80*, 194. Huisgen, R.; Feiler, L. A.; Oho, P *Tetrahedron Lett.* **1968**, 4485. Isaacs, N. S.; Stanbury, P. *R. J. Chem. Soc., Chem. Commun.* **1970**, 1061.

0022-3263/85/1950-2595$01.50/0

Scheme I



kinetically preferred ring closure of **3**, i.e., the indicated rotation mode would be more favorable since the smaller groups pass one another in the ring closure step.

Data presented will show that a dipolar mechanism involving zwitterion **2** is operative in the TBCK cycloaddition outlined here.

tert-Butylcyanoketene was generated in refluxing benzene in the presence of 1 equiv of the trimethylsilyl enol ether **4**.[3] The reaction was monitored by H^1 NMR and after 1 h the cyclobutanones **5** and **6** were present in the respective ratio of 1:1.2 (92%); this ratio changes to 1:2 after 2 h and was 1:4 after 10 h (Scheme I). Equilibration takes place much more rapidly in a more polar solvent. For example, when an acetonitrile solution of **5** and **6** (1:1.2) was refluxed for 2 h, the respective ratio of the cyclobutanones was 1:9, and this changed to 1:32 after 10 h. When the cycloaddition was accomplished at 25 °C by treating the enol ether with a preformed benzene solution of TBCK, the reaction was complete within 1 h and the ratio of the cyclobutanone **5** and **6** was respectively 3:2. This observation, along with the above equilibration data demonstrate the contrathermodynamic isomer to be the kinetic product of the cycloaddition. This product is reasonably assumed to have structure **5**. Confirmation of such was obtained by utilizing the previous observation that a cyano group deshields a cis, relative to a trans, disposed adjacent proton in cyclobutanones.[4] Thus, the chemical shift of the methine proton in **5** appears at δ 4.58 while that of **6** is at δ 4.21.

In a related experiment the cis and trans isomers of 1-(trimethylsiloxy)propene were independently treated with TBCK in benzene at ambient temperature to give respectively **7** (95%) and **9** (97%). It was further established that the *cis*-alkene reacts faster than the trans. For example, when a benzene solution containing 1 equiv of a 1:1 mixture of the geometric isomers of 1-(trimethylsiloxy)propene was treated with 0.5 equiv of TBCK at ambient temperature **7** and **9** were obtained in a ratio of 4:1. The cyclobutanone **7** was further established to be the contrathermodynamic isomer. That is, when a benzene solution of **7** was refluxed for 2 h a 1:4 mixture of **7** and **8** was realized. The cis stereochemistry at position-3 and -4 for both **7** and **8** was established from the coupling constant between the methine protons (8.43 and 7.90 Hz).[5] In comparison, the analogous methine protons in **9** show a J value of lower magnitude (6.3 Hz), an observation consistent with the assigned trans configuration.

It should be noted that **9** is stable in refluxing benzene (10 h) as would be expected for the assigned structure.[6] The observed formation of **9** is of particular significance since it would be the expected product to arise from either **1** ($2\pi s + 2\pi a$) or **2**, but not directly from **3**. Thus, these data meet those criteria normally employed to argue for a concerted cycloaddition, but such arguments are clearly not unambiguous. Indeed, further studies were conducted which show the above cycloadditions to proceed via a nonconcerted dipolar pathway in which the rate-determining step is formation of zwitterion **2**.

Significant evidence that the above cycloadditions proceed via a two-step pathway comes from an investigation of the cycloaddition of TBCK to *cis*- and *trans*-(*tert*-butyldimethylsiloxy)propene. Surprisingly, in this series, the *trans*-alkene reacts much faster than its cis isomer, an observation which is without a previous precedent in ketene/alkene cycloadditions. For example, a benzene solution of the *cis*-alkene and TBCK resulted in only 5% conversion to **10** (95% unreacted alkene) after 32 days at ambient temperature while the *trans*-alkene gave a 95% yield of **11** after only 12 h. This observation rules out the $2\pi s + 2\pi a$ concerted mechanism for the formation of **10** and **11** since such predicts the alkene reactivity to be cis > trans. At least for the *cis*-alkene, these data also rule out a mechanism in which the formation of a zwitterionic intermediate such as **2** is rate limiting. It is, however, consistent with a two-step mechanism in which ring closure of such a zwitterion is the kinetically slow step. Thus, these results strongly suggest the generalization that a two-step dipolar mechanism is operative for all of the TBCK/siloxyalkene cycloadditions described here.

Finally, a most interesting result which confirms the above generalization was obtained from a study of the thermolysis of *trans*-3-azido-2-*tert*-butyl-5-methyl-4-(trimethylsiloxy)cyclopent-2-en-1-one (**13**).[7] This vinyl azide is ideally suited to cleave to a zwitterionic intermediate as predicted from the previously reported structural requirements for such an ionization.[8] Furthermore, the initial ionization of **13** should give **14**, a zwitterion having exactly the same conformation as the generalized zwitterionic structure **3**. As noted above, direct ring closure of such a zwitterion might be expected to follow rotation mode a (Scheme II). Thus, the cyclobutanone **16** would

(3) Moore, H. W.; Weyler, W.; Duncan, W. G. *J. Am. Chem. Soc.* **1975**, *97*, 6187.

(4) Weyler, W.; Byrd, L.; Caserio, M. C.; Moore, H. W. *J. Am. Chem. Soc.* **1972**, *94*, 1027.

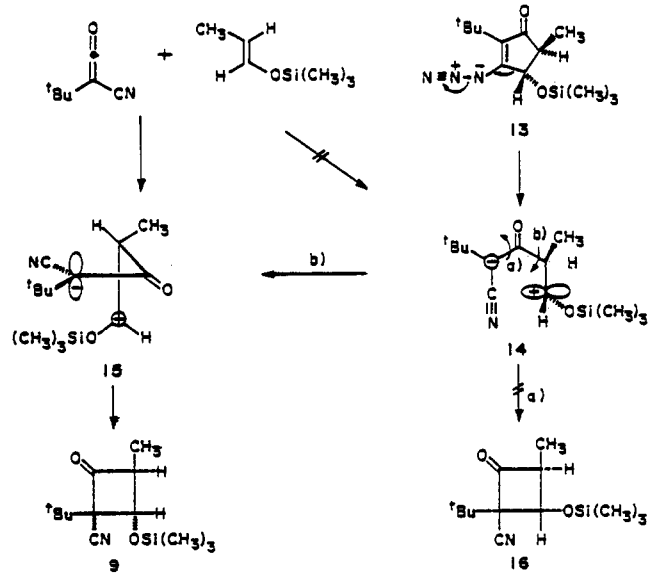
(5) Sutcliffe, L. H.; Walker, S. M. *J. Phys. Chem.* **1967**, *71*, 555.

(6) The stereostructure of **9** is further based upon ^1H NMR spectral comparison of 25 cyclobutanones. The details will be presented subsequently.

(7) Compound **13** was prepared from the known compound, 2-*tert*-butyl-3-chloro-5,5-dimethylcyclopentene-1,4-dione (Moore, H. W.; Wilbur, D. S. *J. Org. Chem.* **1980**, *45*, 4483) involving selectride reduction to the 4-hydroxy analogue, formation of the 3-azido derivative (tetramethylguanidinium azide), and silation (Me_3Si) to give **13**. Spectral and analytical data of **13** as well as the other new compounds described in this manuscript are in agreement with their assigned structures.

(8) Moore, H. W. *Acc. Chem. Res.* **1979**, *12*, 125.

Scheme II



be anticipated. However, it was observed that thermolysis of **13** (80 °C, benzene) gave **9** (91%), the same product obtained in the TBCK cycloaddition itself. As a result, if **14** does result from the thermolysis of **13**, it most likely releases steric interactions and undergoes conformational change to **15** (rotation mode b).[9,10] This then gives **9** upon ring closure. In a comparison experiment the cis isomer of **13** was subjected to thermolysis (80 °C, 30 min) in refluxing benzene. This resulted in **7**, **8**, and **9** (1:1.4:0.12), the same products as are observed when the cycloaddition of TBCK and *cis*-1-(trimethylsiloxy)propene was carried out in refluxing benzene.[11,12]

Taken together, these data provide strong evidence that the TBCK/siloxy enol ether cycloadditions described here are dipolar in character and specifically involve zwitterionic intermediate of structural type **2**. Furthermore, they provide a very important generalization. That is, caution should most certainly be exercized when utilizing one or more of the three experimental criteria noted above as necessarily providing solid evidence for a concerted cycloaddition.

Acknowledgment. We thank the National Science Foundation (CHE-8025567) for financial support of this work.

Registry No. **4**, 6651-34-9; **5**, 96504-33-5; **6**, 96504-34-6; **7**, 96504-35-7; **8**, 96612-31-6; **9**, 96612-32-7; **10**, 96504-36-8; **11**, 96612-33-8; *cis*-**13**, 96504-37-9; *trans*-**13**, 96504-38-0; TBCK, 29342-22-1; *cis*-1-(trimethylsiloxy)propene, 50300-18-0; *trans*-1-(trimethylsiloxy)propene, 39162-68-0; *cis*-(*tert*-butyldimethylsiloxy)propene, 96504-39-1; *trans*-(*tert*-butyldimethylsiloxy)propene, 96504-40-4.

(9) The nonconcerted nature of certain ketene/alkene cycloadditions was further revealed by a secondary kinetic isotope study recently presented by Holder, R. W.; Graf, N. A.; Duesler E.; Moss, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 2929.

(10) A crossover control showed that the azidocyclopentenone **13** was not simply cleaving to TBCK and the enol ether and that these were then undergoing cycloaddition. For example, thermolysis (80 °C) of the 5,5-dimethyl analogue of **13** in the presence of 1 equiv of *cis*-1-(trimethylsiloxy)propane gave a 3:2 mixture of respectively **7** and **5**. Yet when TBCK was generated in the presence of a 1:1 mixture of *cis*-1-(trimethylsiloxy)propene and 1-(trimethylsiloxy)-3-methylpropene, only **7** was observed.

(11) Here, the ketone (TBCK) was generated from the thermolysis (80 °C) of 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone in the presence of the silyl enol ether.

(12) Becker, D.; Brodsky, N. C. *J. Chem. Soc., Chem. Commun.* **1978**, 237.

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A Stereocontrolled Synthesis of 1,3,5-Tri-*O*-benzoyl-α-D-ribofuranose

Summary: The synthesis of a valuable carbohydrate intermediate, 1,3,5-tri-*O*-benzoyl-α-D-ribofuranose (**4**), has been achieved in a convenient, one-step process from commercially available 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose (**7**).

Sir: A great deal of interest has developed in the preparation of 2-deoxyfuranosyl nucleosides as a result of their reported antiviral and antitumor activity.[1] Of paramount importance to the synthesis of this series of nucleosides is a preparation of the carbohydrate portion in a manner which allows selective manipulation of the C_2 hydroxyl.[2]

Fletcher and co-workers[3a] during a study of the solvolysis of **3a,b** to **5** (see Scheme I) also obtained another product in 40% yield which was identified as the ortho acid **4'**. The structure of this material was correctly assigned in later work by the same authors[3b,c] as **4**. The four-step method of Fletcher is frequently quoted in the literature as the means of preparing the valuable intermediate **4** in about 40% yield. The mechanism proposed by Fletcher and Ness[3c] (see Scheme II) involves the formation of a 1,2-benzoxonium ion, **6**, which undergoes solvolysis with water.

We have prepared **4** by this method but found the yield varied from 0% to 40% for reasons that were not clear. A study of the solvolysis of **3a,b** to identify the problems associated with this reaction was carried out in acetone-d_6 and D_2O using 360-MHz ^1H NMR to follow the course of the reaction. While the β-bromo sugar **3b** reacted rapidly upon addition of D_2O, the α-bromo sugar **3a** reacted slowly. In the NMR spectrum the anomeric protons are for **3b**, a singlet at 6.7 ppm, **3a**, a doublet at 6.98 ppm, and **4**, a doublet at 6.45 ppm. In another experiment, **3a,b** was prepared in CD_2Cl_2, and then D_2O was added to this reaction mixture with vigorous stirring. NMR monitoring showed that **3b** was consumed in less than 2 h but **3a** was unreacted even after 5 days.

According to the mechanism proposed by Fletcher, it appeared to us that only the β-bromo anomer can form the desired product. Although Hanessian and Pernet[4] were able to prepare the anomerically pure chloro analogue of **3b**, bromination under various conditions gave at best 1:1 mixtures of anomers.

The brominations of either **7** or **2** previously reported were performed in the presence of acetic acid or with a

(1) (a) Watanabe, K. A.; Su, T.-L.; Reichman, U.; Greenberg, N.; Lopez, C.; Fox, J. J. *J. Med. Chem.* **1984**, *27*, 9. (b) Watanabe, K. A.; Su, T.-L.; Klein, R. S.; Chu, C. K.; Matsuda, A.; Lopez, C.; Fox, J. J. *J. Med. Chem.* **1983**, *26*, 152. (c) Wright, J. A.; Taylor, N. F.; Fox, J. J. *J. Org. Chem.* **1969**, *34*, 2632. (d) Su, T.-L.; Klein, R. S.; Fox, J. J. *J. Org. Chem.* **1982**, *47*, 1506.

(2) Chavis, C.; Dumont, F.; Wightman, R. H.; Ziegler, J. C.; Imbach, J. L. *J. Org. Chem.* **1982**, *47*, 202.

(3) (a) Ness, R. K.; Diehl, H. W.; Fletcher, H. G. *J. Am. Chem. Soc.* **1954**, *76*, 763. (b) Ness, R. K.; Fletcher, H. G. *J. Am. Chem. Soc.* **1954**, *76*, 1663. (c) Ness, R. K.; Fletcher, H. G. *J. Am. Chem. Soc.* **1956**, *78*, 4710.

(4) Hanessian, S.; Pernet, A. G. *Can. J. Chem.* **1974**, *52*, 1280.

0022-3263/85/1950-2597$01.50/0