

Figure 1.

pyrazoles were generally low when employing this procedure (Table I). Since HBr or HI is liberated, on formation or pyrazoles 16, and it is known that pyrazoles are acid sensitive,¹⁰ the thermolyses were undertaken under low-pressure conditions in the hopes of removing the pyrazole species as they were formed (procedure B). Some increase of yield occurred (Table I).

Further attempts at enhancing the yield involved the use of a stirred mixture of the phosphonium salts and equimolar amounts of sodium benzoate. A further increase of one of the yields was experienced (Table I).

In one further experiment, the phosphonium salt 13c and sodium benzoate were ground together instead of just mixed together, and there was a significant increase in yield over the comparable vacuum procedure (B).

Overall there are some generalities which were evident. Where R² (in 13) was methyl only pyrazole 16 was found. Where R² (in 13) was phenyl both pyrazoles 16 and 17 were formed. In all of the experiments tried, where the R³ groups were the same, the overall yields of the two phenyl-substituted pyrazoles obtained (16 + 17, R² = Ph) were greater than the comparable yields of methyl-substituted pyrazoles (16, R² = Me).

Spectral Characteristics. Compound 17 shows the following ¹H NMR data as referred to in Figure 1: ¹H NMR δ 6.72 (s, 1 H, H_A), 7.0–7.7 (m, 12 H, Ar and vinyl H). Compounds 16 exhibit ¹H NMR in the following regions: δ 6.22–6.47 (s, 1 H, H_A), 2.18–2.24 (s, 3 H, where R² = CH₃), 3.67–3.74 (s, 3 H, where R³ = CH₃), 4.56–4.60 (br s, 2 H, CH₂ where R³ = allyl), 5.04–5.16 (d, 1 H, J = 10, (E)-H₂C=CH— where R³ = allyl), 4.96 (d, 1 H, J = 17, (Z)-H₂C=C— where R³ = allyl), 5.90–5.91 (m, 1 H, H₂C=CH— where R³ = allyl), 7.0–7.7 (m, 12 H, —CH=CHC₆H₅).

The ¹³C NMR for compound 17 is as follows (see Figure 1): ¹³C NMR δ 149.2 (C3), 100.3 (C4), 147.0 (C5), 117.7 (C6).

For compounds 16 the ¹³C NMR appears in the following regions: ¹³C NMR δ 148.8–149.6 (C3), 102.7–103.4 (C4), 139.5–144.0 (C5), 120.4–121.3 (C6), 10.9–11.1 (R² = CH₃), 36.0–36.7 (R³ = CH₃) and 51.7–51.8 (R³ = CH₂CH=CH₂), 117.0–117.1 (R³ = CH₂CH=CH₂).

Experimental Section

General Methods. Dry nitrogen was routinely used as the atmosphere in all reactions. All glassware was baked at 110–120 °C for at least 1 h before use. Melting points are uncorrected and were obtained with a Thomas-Hoover apparatus. The ¹H, ¹³C, and ³¹P NMR of approximately 10% (w/v) solutions in CDCl₃ were obtained on a Bruker Spectrospin Model AM 250 or WM 250. Chemical shifts are reported in parts per million (δ scale) vs. tetramethylsilane (phosphoric acid for ³¹P NMR) as an internal standard. The following abbreviations have been used in reporting NMR data: coupling constant in hertz (J); singlet (s); doublet (d); doublet of doublets (dd); triplet (t); quartet (q); and multiplet (m). Precise mass spectra were recorded on a Du Pont 21-492B instrument with a resolution of 3300 or 5000. Acetonitrile was dried over calcium hydride and distilled over P₂O₅. Eastman Chromagram (silica gel with fluorescent indicator on polyethylene) precoated sheets were used in thin-layer chromatography. Baker silica gel (60–200 mesh) and EM 774 silica gel for column chro-

matography were used for product separation.¹¹

The following compounds were prepared by known methods: (2-methyl-7-phenyl-3,4-diaza-2,3,6-heptatrienyliene)triphenylphosphorane⁶ (3a) and (2,7-diphenyl-3,4-diaza-2,4,6-heptatrienyliene)triphenylphosphorane⁶ (3b).

Pyrolysis of Salts. Procedure A. The salts 13 (1.5–2.0 g) were placed in a 250-mL thick-walled glass bottle¹² under nitrogen. The bottle was sealed and placed in a 240 °C oil bath just until all of the salt had melted. The bottle was then cooled to room temperature and the residue was separated by column chromatography to isolate the pyrazoles 16 and 17 which were shown to be pure by TLC. Pyrazole 17 was recrystallized from ethanol, mp 154 °C. All of the pyrazoles 16 were oils. The precise mass of all of the compounds 16 and 17 were within ± 0.003 of theory.

Pyrolysis of Salts. Procedure B. The salts 13 (0.5 g) were placed in a distillation flask equipped with a magnetic stirrer. The salt was rinsed down from the sides of the flask with methylene chloride. The flask was connected to a vacuum pump equipped with a cold trap, and the methylene chloride was removed. The pressure was reduced to 0.5 mmHg, and the flask was heated in a hot oil bath (200 °C) until the salt was completely melted. After cooling, the residue inside the flask was separated by column chromatography to isolate the pyrazoles 16 and 17.

Pyrolysis of Salts. Procedure C. The salts 16 (0.5 g) and equimolar amounts of sodium benzoate were placed in a distillation flask equipped with a magnetic stirrer. The reaction was undertaken in the same manner as described for the previous procedure.

In the reaction with 13b, the reaction was also undertaken after intimately mixing 13b and the sodium benzoate by grinding to a fine powder with a mortar and pestle.

Registry No. 13a, 96688-86-7; 13b, 96688-87-8; 13c, 96688-88-9; 13d, 96688-89-0; 16a, 96688-90-3; 16b, 96688-91-4; 16c, 96688-92-5; 16d, 96688-93-6; 17, 96688-94-7.

(11) Chromatographic technique used was that of Taber, D. F. *J. Org. Chem.* 1982, 47, 1351.

(12) This thick-walled glass bottles used in procedure A were Kimble Glass Co. centrifuge bottles (Cat. No. 14700).

Chemistry of Sulfenic Acids. 6.^{1,2} Structure of Simple Sulfenic Acids Generated by Flash Vacuum Pyrolysis

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The importance of transient sulfenic acid (RSOH) intermediates in organic and bioorganic sulfur reactions is now well recognized.³ In principle, two tautomeric structures, 1a and 1b, can be considered for sulfenic acids.



Despite the fact that these species have been of interest for more than three-quarters of a century their structure remains unclear. The reason for this is that in the rare case where stable sulfenic acids have been isolated they

(1) Part 5: Davis, F. A.; Awad, S. B.; Jenkins, R. H.; Billmers, R. L.; Jenkins, L. A. *J. Org. Chem.* 1983, 48, 3071.

(2) These results were taken from: Billmers, R. L. Ph.D. Thesis Drexel University, 1984.

(3) (a) For reviews on the chemistry of sulfenic acids, see: Kice, J. L. *Adv. Phys. Org. Chem.* 1980, 17, 65. Hogg, D. R. *Compr. Org. Chem.* 1979, 4, 261. (b) For leading references to the biological reactions of sulfenic acids, see: Davis, F. A.; Billmers, R. L. *J. Am. Chem. Soc.* 1981, 103, 7016.

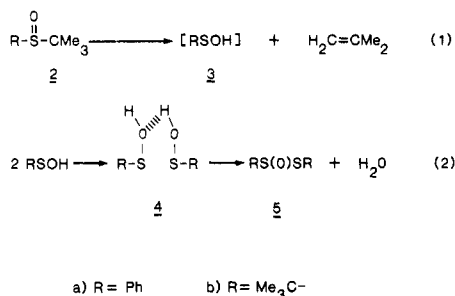
(10) Paquette, L. A. "Principles of Modern Heterocyclic Chemistry"; W.A. Benjamin, Inc.; New York, 1968; p 195.

were sufficiently encumbered with polar functionalities that the proton could not be located with any degree of certainty.

Bruice and Sayigh concluded from the solution infrared spectrum of anthraquinone-1-sulfenic acid that it has the O-protonated form, **1a**.⁴ Microwave studies by Penn and Block showed that methanesulfenic acid, in the gas phase, exists exclusively as **1a** (R = Me).⁵ The infrared spectra of 2-oxoazetidine-4-sulfenic acids⁶ and 9-triptycenesulfenic acid⁷ suggest that these sulfenic acids also have structure **1a**.

Shelton and Davis, on the other hand, attributed absorptions at 3400 and 2600 cm^{-1} in the solution infrared spectrum of 2-methyl-2-propanesulfenic acid (*t*-BuSOH) to the presence of both **1a** and **1b**, respectively.⁸ Ozone and oxygen atoms react with hydrogen sulfide (H_2S) and methanethiol (MeSH) in argon matrices to give both forms of the sulfenic acids.⁹ These assignments were based on infrared absorptions at 3600–3595 and 1096 cm^{-1} which were attributed to the O–H and S=O stretching vibrations of **1a** and **1b**, respectively. 1,3,6-trimethyl-lumazine-7-sulfenic acid, in the solid state, apparently prefers structure **1b** (SH, 2500 cm^{-1} , and S=O, 1050 cm^{-1}) but in solution structure **1a**.¹⁰ An ab initio configurational interaction method applied to HSOH and H_2SO concluded that both can exist as stable species.¹¹ HSOH was found to be more stable than H_2SO .

Our studies have shown that flash vacuum pyrolysis (FVP) of sulfoxides **2**, with condensation of the pyrolyzate on a cold finger cooled to liquid nitrogen temperatures, affords labile sulfenic acids **3**, in good concentration under conditions where they are stable and convenient for study (eq 1).^{1,12} The principal reaction of sulfenic acids gen-



erated in this manner, on warming of the cold finger, is dimerization to thiosulfates (RS(O)SR) (eq 2). We, as well as others, have suggested that hydrogen-bonded dimer **4** is a prerequisite for formation of the thiosulfate **5**.^{1,5,12}

We describe here the results of studies on the structure of simple sulfenic acids, **3a,b** using a modified FVP apparatus for measuring low-temperature infrared spectra. Benzenesulfenic acid (**3a**) and 2-methyl-2-propanesulfenic acid (**3b**), generated by FVP of **2a,b** are deposited on the NaCl window of an Air Products Cryo-tip. The infrared spectra of **3a,b** collected in this manner, are then moni-

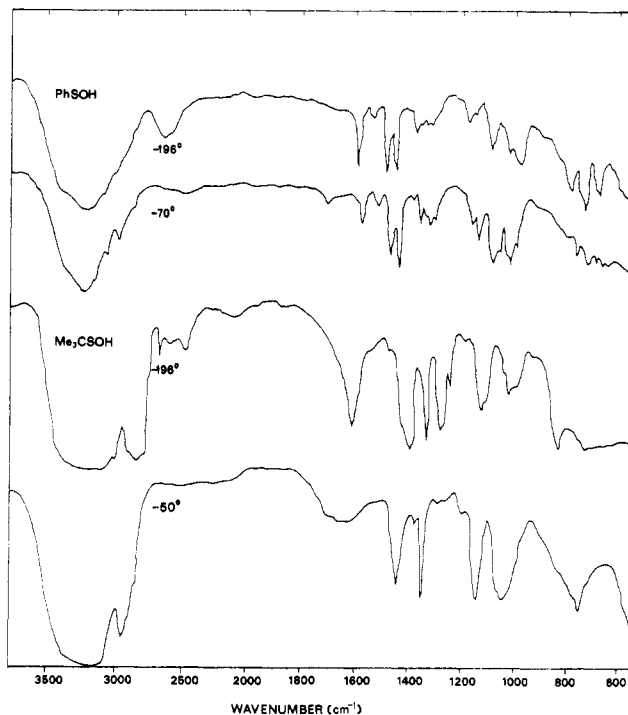


Figure 1. Infrared spectra of benzenesulfenic acid (**3a**) and 2-methyl-2-propanesulfenic acid (**3b**) at -196 and -70 or -50 $^{\circ}\text{C}$.

tored as a function of temperature.

At ca. -196 $^{\circ}\text{C}$ sulfenic acids **3a,b** display broad OH absorptions centered at 3300 and 3250 cm^{-1} , respectively (Figure 1). We attribute these absorptions to the presence of the O-protonated sulfenic acid (**1a**) and the hydrogen-bonded dimer **4**. The infrared spectra of **3a,b** also display weaker absorptions maxima at 2600 and 2630 cm^{-1} and at 1000 and 1060 cm^{-1} , respectively (Figure 1). The former values are in good agreement with those reported by others for the S–H stretching vibrations of sulfenic acids thought to have structures **1b** (vide infra).^{8–10} Additional support for the OH and SH assignments is the infrared spectrum of deuterium-labeled benzenesulfenic acid (**3a**, PhSOD). For labeled benzenesulfenic acid (**3a**) the absorptions attributed to O–D (**1a**) and S–D (**1b**) structures are shifted to 2435 and 1905 cm^{-1} , respectively. These values agree quite well with calculated values of 2408 and 1864 cm^{-1} , based on the reduced masses of H and D, considering that these calculations do not take into account hydrogen-bonding effects.^{13,14}

The assignment of the bands at 1000 and 1060 cm^{-1} to the S=O stretching vibration of **1b** is less clear because of the possibility of other absorptions obscuring this region.¹⁵ However, these maxima do change (vide infra) on warming of the sample window.

The infrared spectra of sulfenic acids **3a,b** remain unchanged on warming of the sample window to about -70 to -50 $^{\circ}\text{C}$, at which time the SH absorptions slowly disappear. The absorption at 1000 cm^{-1} in **3a** broadens and is displaced to about 1080 cm^{-1} . The maxima at 1060 cm^{-1}

(13) The X–D position was calculated with the following equation:¹⁴

$$\frac{\text{X-D}}{\text{X-H}} = \left(\frac{2 + 2M_x}{2 + M_x} \right)^{1/2}$$

(14) Rao, C. N. R. "Chemical Application of Infrared Spectroscopy"; Academic Press: New York, 1963; Chapter 1.

(15) The low-temperature infrared spectra (Figure 1) have absorptions due to 2-methylpropene (eq 1). The possibility that some thiosulfate is formed at temperatures below -70 to -50 $^{\circ}\text{C}$ cannot be rigorously excluded. Small amounts of sulfoxides **2a,b** may also have survived the FVP conditions.

(4) Bruice, T. C.; Sayigh, A. B. *J. Am. Chem. Soc.* **1959**, *81*, 3416.

(5) Penn, R. E.; Block, E.; Revell, L. K. *J. Am. Chem. Soc.* **1978**, *100*, 3622.

(6) Chou, T. S.; Burgdorf, J. R.; Ellis, A. L.; Lammert, S. R.; Kukulja, S. P. *J. Am. Chem. Soc.* **1975**, *96*, 1609. Bachi, M. D.; Gross, A. *J. Org. Chem.* **1982**, *47*, 897.

(7) Nakamura, N. *J. Am. Chem. Soc.* **1983**, *105*, 7172.

(8) Shelton, J. R.; Davis, K. E. *Int. J. Sulfur Chem.* **1973**, *8*, 205.

(9) Smardzewski, R. R.; Lin, M. C. *J. Chem. Phys.* **1977**, *66*, 3197. Tevault, D. E.; Mowery, R. L.; Smardzewski, R. R. *Ibid.* **1981**, *74*, 4480.

(10) Heckel, A.; Pfeleiderer, W. *Tetrahedron Lett.* **1983**, 5047.

(11) Besnainou, S.; Whitten, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 7444.

(12) Davis, F. A.; Jenkins, R. H., Jr.; Rizvi, S. Q. A.; Yocklovich, S. G. *J. Org. Chem.* **1981**, *46*, 3467.

in **3b** is displaced to 1068 cm^{-1} . Cooling the sample window back to $-196\text{ }^\circ\text{C}$ fails to restore these infrared absorptions. At -40 to $-20\text{ }^\circ\text{C}$ dehydration takes place (eq 2) to give the corresponding thiosulfonates **4a,b**. These thiosulfonates 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 $-50\text{ }^\circ\text{C}$. 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 $620\text{ }^\circ\text{C}$ 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 $\pm 5\text{ }^\circ\text{C}$. 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 produce 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 $0\text{ }^\circ\text{C}$ 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 ($3 \times 75\text{ mL}$) and dried over anhydrous MgSO_4 . Removal of the solvent under vacuum gives an oil, which is distilled at 40 – $41\text{ }^\circ\text{C}$ (0.1 torr) [lit.¹⁶ bp $55\text{ }^\circ\text{C}$ (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

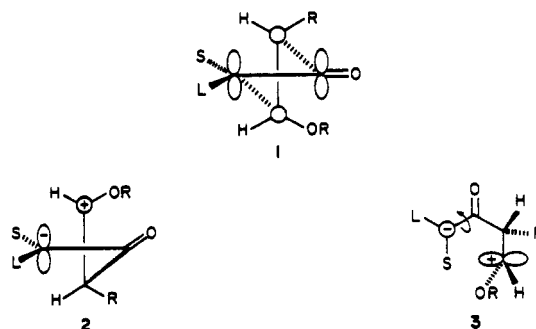
Cyanoketenes. Cycloaddition of *tert*-Butylcyanoketene to Silyl Enol Ethers—A Nonconcerted Reaction

Summary: The mechanism of the cycloaddition of *tert*-butylcyanoketene to silyloxy 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 silyloxy enol alkenes. Data are presented which show the reaction to proceed by a stepwise pathway¹ 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



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 react 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. Krepacki, L. R.; Hasaner, 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. Reynolds, 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.; Dieffenbacher, A.; Dreiding, A. S. *Helv. Chim. 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.