tained: mp 116–117 °C; NMR ($CDCl_3$) δ 1.35 (s, 36 H, butyl) 2.94 (s, 4 H, CH_2CH_2), 6.97 (s, 4 H aromatic H); mass spectrum, m/e 408 (M^+). Anal. Calcd for $C_{28}H_{44}N_2$: C, 82.35; H, 10.78; N, 6.88. Found: C, 82.10; H, 10.99; N, 6.95.

Methyl fluorosulfate was prepared by the method described in the literature.[8] The compound was distilled under a nitrogen atmosphere at 92–94 °C (760 mmHg).

Reactions of 2 and 3 with FSO_3CH_3 under High Pressure. Various conditions were used for the reactions. A typical reaction procedure was as follows. A mixture of **2** (0.58 g, 3 mmol) and 0.38 g (3.3 mmol) of FSO_3CH_3 in 3.3 mL of dried methylene chloride was prepared in a drybox, placed in a Teflon capsule, and pressurized to 4000–4500 atm at 60 °C for several hours. After unreacted FSO_3CH_3 and methylene chloride were removed under reduced pressure, a mixture of 2,6-di-*tert*-butyl-4-methyl-*N*-methylpyridinium and 2,6-di-*tert*-butyl-4-methylpyridinium fluorosulfate was obtained. The NMR spectrum clearly showed two different proton peaks for *tert*-butyl in these two salts, δ 1.72 and 1.47, respectively. Treatment of the mixture with aqueous sodium bicarbonate and chloroform afforded 0.62 g of the *N*-methyl salt. Anal. Calcd for $C_{15}H_{26}NO_3SF$: C, 56.78; H, 8.20; N, 4.42. Found: C, 56.42; H, 8.31; N, 4.63.

Preparation and Properties of 2,6-Di-*tert*-butyl-4-methyl-*N*-methylpyridinium Iodide. 2,6-Di-*tert*-butyl-4-methyl-*N*-methylpyridinium fluorosulfate was allowed to exchange with I^- on Amberlite I ion-exchange resin: NMR ($CDCl_3$) δ 1.78 (s, 18 H, *t*-Bu) 4.63 (s, 3 H, *N*-methyl). The thermal properties of the iodide were investigated with a Du Pont thermal gravimetric analyzer under a nitrogen atmosphere. It was found that it started to decompose at around 125 °C.

Registry No. 2, 38222-83-2; **3**, 81142-31-6; (2,6-di-*tert*-butyl-4-pyridyl)methylene bromide, 81142-32-7; methyl fluorosulfate, 421-20-5; 2,6-di-*tert*-butyl-4,*N*-dimethylpyridinium fluorosulfate, 78008-53-4; 2,6-di-*tert*-butyl-4,*N*-dimethylpyridinium iodide, 78020-53-8; 2,6-di-*tert*-butyl-4,*N*-dimethylpyridinium perchlorate, 78008-52-3; 1,2-bis(2,6-di-*tert*-butyl-*N*-methylpyridinium)ethane fluorosulfate, 81142-34-9.

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[8] M. Fieser and L. F. Fieser, "Reagents for Organic Synthesis", Vol. III, Wiley-Interscience, New York, 1972, pp 202.

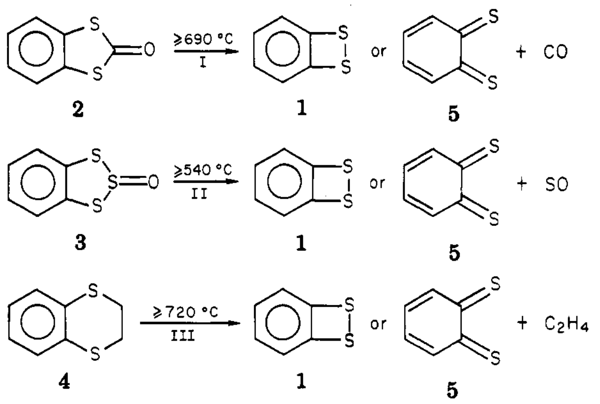
Communications

Photoelectron Spectrum and Infrared Spectrum of Thermally Generated Transient Benzodithiete[1]

Summary: Thermal routes to transient benzodithiete and 4-methylbenzodithiete are described, and the structure is proved from the gas-phase UV photoelectron spectrum and the infrared spectrum in an argon matrix.

Sir: 1,3-Benzodithiol-2-one loses carbon monoxide photochemically to give transient benzodithiete (**1**).[2] The sole property that has been known so far from this species is that it exhibits a weak UV absorption at 370 nm.[2] Below we describe new thermal pathways to **1** and contribute the full UV photoelectron and infrared spectra of the hitherto rather unexplored transient system.

We found that 1,3-benzodithiol-2-one (**2**),[3] 1,2,3-benzotrithiole 2-oxide (**3**),[4] and benzodithiene (**4**)[5] undergo the following smooth gas-phase reactions I to III in a variable-temperature photoelectron spectrometer (VTPES method[6]). The reactor of the spectrometer consisted of a stainless steel tube ca. 20 × 0.5 cm. Pressures and contact times were ca. 0.05 mbar and ca. 100 ms in all cases.



The recorded photoelectron spectra testify that the only byproducts are CO, SO, and C_2H_4 in reactions I, II, and III, respectively. Therefore **1** or dithiobenzoquinone (**5**) must have formed as the main product (assuming secondary reactions to be slow) in these reactions. As an example, Figure 1 shows the UV photoelectron spectrum of the products of reaction I.

Ab initio[7] (using the 4-31G basis set[8]) and semiempirical CNDO/S[9]–PERTCI[10] calculations[11] predict two ionizations

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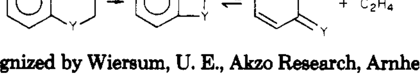
[1] Part 96 of "Theory and Application of Photoelectron Spectroscopy". Part 95: Märkl, G.; Rudnick, D.; Schulz, R.; Schweig, A. *Angew. Chem.*, **1982**, *94*, 211; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 221; *Angew. Chem. Suppl.* **1982**, 523.

[2] DeMayo, P.; Weedon, A. C.; Wong, G. S. K. *J. Org. Chem.* **1979**, *44*, 1977.

[3] For the synthesis of **2**, see ref 2. The photoelectron spectral data (vertical ionization potentials and assignments in parentheses) of **2** gathered in the present work are as follows: 8.68 (π), 9.21 (π), 10.00 (n_0), 10.92 eV.

[4] For the synthesis of **3**, see Steinle, K.; Schmidt, M. *Z. Naturforsch. B* **1972**, *27*, 83. The photoelectron spectral data (vertical ionization potentials and assignments in parentheses) of **3** obtained in the present work are as follows: 8.73 (π), 9.07 (π), 9.90 (π, S═O) eV.

[5] For the synthesis of **4**, see Parham, W. E.; Roder, T. M.; Hasek, W. R. *J. Am. Chem. Soc.* **1953**, *75*, 1647. The photoelectron spectral data are as follows (vertical ionization potentials and assignments in parentheses): 7.91 (π), 8.45 (π), 10.11 eV. The general applicability of thermal reactions of the type:



has been recognized by Wiersum, U. E., Akzo Research, Arnhem, Holland, 1980, personal communication.

[6] Schweig, A.; Vermeer, H.; Weidner, U. *Chem. Phys. Lett.* **1974**, *26*, 299. Schäfer, W.; Schweig, A. *Z. Naturforsch. A* **1975**, *30*, 1785. Schulz, R.; Schweig, A. *Angew. Chem.* **1981**, *93*, 603; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 570.

[7] The calculations were carried out by use of GAUSSIAN 76 with parts integrated from GAUSSIAN 80. GAUSSIAN 76: Binkley, J. S.; Whiteside, R. A.; Hariharan, P. C.; Seeger, R.; Pople, J. A.; Hehre, W. J.; Newton, M. D. *QCPE* **1978**, *No. 368*. GAUSSIAN 80: Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *No. 406*.

[8] Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. Hehre, W. J.; Lathan, W. A. *J. Chem. Phys.* **1972**, *56*, 5255.

[9] Schulte, K.-W.; Schweig, A. *Theor. Chim. Acta* **1974**, *33*, 19.

[10] Hase, H.-L.; Lauer, G.; Schulte, K.-W.; Schweig, A. *Theor. Chim. Acta* **1978**, *48*, 47.

0022-3263/82/1947-1979$01.25/0

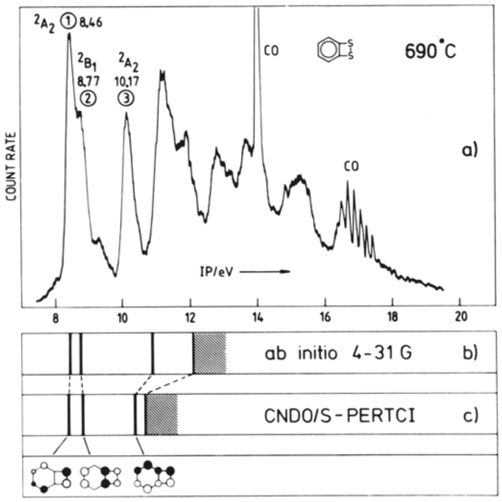


Figure 1. He–I photoelectron spectrum of (a) the reaction products of reaction I (cf. text), i.e., of benzodithiete (bands 1–3) and CO and (b and c) calculated vertical ionization potentials of benzodithiete, using the ab initio (4-31G basis set) method and the semiempirical CNDO/S–PERTCI method, respectively. Measured vertical ionization potentials (in electron volts) and assignments of bands are shown with the spectrum.

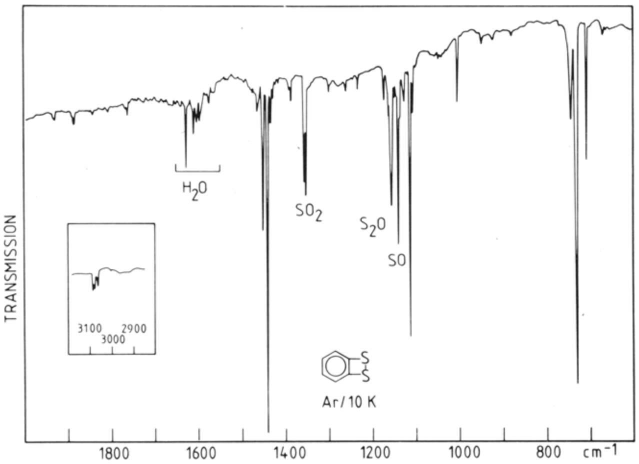


Figure 2. Infrared spectrum of the reaction products of reaction II (cf. text) in Ar at 10 K (inset: 3200–2800 cm^{-1} region).

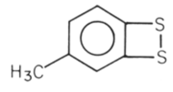
(one close to the other) below 10 eV for **1** and three for **5**. The measured spectrum (cf. Figure 1) exhibits two bands below 10 eV. This result as well as the agreement between the experimental and calculated vertical ionization energies (cf. Figure 1) vote for **1** (and not for **5**) as the species formed in reactions I–III.

To further buttress this result we repeated reactions I–III using a quartz reactor ca. 6 × 0.4 cm (ca. 10^{-5} mbar of pressure, contact times ca. <10 ms, temperatures ca. 100 °C higher than in the VTPES experiments), isolated the reaction products in an argon matrix at 10 K, and recorded the infrared spectra. As an example, the infrared spectrum of the products of reaction II is shown in Figure 2.

The infrared spectra of the products of reactions I–III exhibit the bands of CO, SO (along with those of its secondary products S_2O and SO_2), and C_2H_4, respectively, thus confirming the photoelectron spectral results. If the bands due to these respective byproducts are discarded from the product spectra, the resulting infrared spectra from all three reactions are in complete agreement. This finding perfectly parallels the aforementioned photoelectron spectral observations.

The infrared spectra of the main organic product (**1** or **5**) exhibit bands at 3080 (w), 1450 (m), 1440 (s), 1166 (d, w), 1111 (s), 1003 (m), 730 (s), and 707 (m) cm^{-1}. These absorptions (especially the one at 730 cm^{-1} along with the series of five weak combination bands in the range of 2000–1700 cm^{-1}) are characteristic for 1,2-disubstituted aromatic systems.[12] This result directly shows that **1** (and not **5**) has been formed in all three reactions.

To further back the results we generated 4-methylbenzodithiete (**6**) in reactions analogous to reactions I and II shown above. The photoelectron spectra obtained are nearly identical with those described above, with the bands due to **6** shifted by 0.2 eV to lower ionization potentials relative to the ones of **1**, as a consequence of the methyl substitution. The infrared bands of **6** at 10 K in argon occur at 1456 (s), 1392 (m), 1202 (w), 1147 (s), 1105 (m), 945 (w), 792 (s), and 720 (m) cm^{-1}. The strong absorption at 792 cm^{-1} is consistent with a strong absorption near 800 cm^{-1} expected for a 1,2,4-trisubstituted aromatic ring system.[12]



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The reaction products in the argon matrix are nearly colorless (with a faint touch of yellow) in accord with the above-mentioned UV absorption at 370 nm[2] and also with the calculated CNDO/S-PERTCI absorption at 321 nm [$^1A_1$ ($\pi \rightarrow \pi^*$) transition, 0.43 oscillator strength] for **1**. From the same sort of calculations, electronic absorptions at much longer wavelengths [$^1B_1$ ($n \rightarrow \pi^*$) 760 nm, $^1A_2$ ($n \rightarrow \pi^*$) 482 nm, and $^1B_2$($\pi \rightarrow \pi^*$) 370 nm (0.23 oscillator strength)] are to be expected for **5**. Consequently, the observed color is only explicable for **1** (and not for **5**).

Finally, it is worth noting that the infrared spectra show that the transient formed is stable up to 180 K. Between 180 and 200 K, the respective absorptions rapidly disappear.

In conclusion, transient benzodithiete was generated on three independent new thermal routes. New spectral data (ionization potentials from photoelectron spectroscopy and vibrational absorptions from infrared spectroscopy in an argon matrix) were gathered. Theoretical data (vertical ionization potentials and electronic absorptions) were provided for comparison from ab initio and semiempirical calculations, including electron correlation. All results are consistent with the formation of transient benzodithiete in the thermal decomposition reactions presented above.

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Registry No. 1, 81044-78-2; **2**, 62576-04-9; **3**, 36264-19-4; **4**, 6247-55-8; **6**, 81044-79-3.

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(11) All calculations are based on MNDO-optimized molecular geometries. For the MNDO method, see Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(12) See textbooks of infrared spectroscopy.