system, tungstenacyclobutane complexes are close in energy to alkylidene complexes, the actual species that predominates depending upon the extent of substitution of the tungstencyclobutane ring.

**Acknowledgment.** R.R.S. thanks the National Science Foundation for support through Grant CHE 84-02892. C.J.S. thanks the Science and Engineering Research Council (U.K.) for a NATO postdoctoral fellowship. We also thank the Biomedical Research Support Shared Instumentation Grant Program, Division of Research Resources, for funds to purchase the X-ray diffraction equipment (NIH Grant S10RR02243-01).

**Registry No.** W(CBu-*t*)(NHR)(dimethoxyethane)$Cl_2$, 101347-96-0; W(CHBu-*t*)(NR)(dimethoxyethane)$Cl_2$, 101375-06-8; W(CHBu-*t*)(NR)$(OR_F)_2$, 101249-40-5; $\overline{CH_2CH_2CH_2W}(NR)(OR_F)_2$, 101249-41-6; $\overline{W[CH(SiMe_3)CH(SiMe_3)CH_2]}(NR)(OR_F)_2$, 101347-97-1; W(CBu-*t*)(dimethoxyethane)$Cl_3$, 83416-70-0; $Me_3SiNH$-2,6-$C_6H_3Pr$-$i_2$, 78923-65-6; $LiOCMe(CF_3)_2$, 98171-13-2; W(CHEt)(NR)$(OR_F)_2$, 101249-42-7; W(O)(NR)$(OR_F)_2$, 101315-93-9; ethylene, 74-85-1; *tert*-butylethylene, 558-37-2; vinyltrimethylsilane, 754-05-2; *cis*-3-hexene, 7642-09-3; *trans*-5,5-dimethyl-3-hexene, 690-93-7; *cis*-2-pentene, 627-20-3; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; 3-hexene, 592-47-2; methyl oleate, 112-62-9.

**Supplementary Material Available:** Preparative, analytical, and spectroscopic details for all isolable compounds, along with final atomic coordinates and structure factor tables (31 pages). Ordering information is given on any current masthead page.

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# 6-Cyanotetracyclo[5.5.0.0$^{2,4}$.0$^{3,5}$]dodeca-6,8,10,12-tetraene: A Novel Heptalene Valence Isomer

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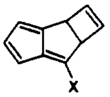
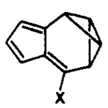
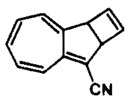
Recent research in this laboratory, beginning with the first synthesis of a pleiadiene isomer[1] in 1973, has been directed toward attainment of a synthetic representation of valence isomers of nonalternant hydrocarbons. Among the relevant species are the azulene isomers **1a**,[2] **1b**,[3] **2a**,[4] and **2b**[3] and the heptalene isomer **3**,[5,6] which contain nonalternant pentafulvene and heptafulvene chromophores,[7] respectively. Therefore, these studies are complementary to those of the well-documented benzene isomers.[8] In this paper we disclose the successful synthesis and some properties of the fourth example of our series, 6-cyanotetracyclo[5.5.0.0$^{2,4}$.0$^{3,5}$]dodeca-6,8,10,12-tetraene (cyanoheptalvalene)[9] (**4**), which is significant since this carbon skeleton has recently been postulated as an intermediate in thermal heptalene–heptalene transformations[10] but has never been isolated. The synthetic achievement completes a series of valence isomers of azulene and heptalene and opens the way for comparative studies on the detailed chemical and physical properties of these prototype molecules.



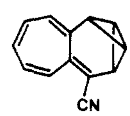
**1a**, X = $OCH_3$
**1b**, X = H



**2a**, X = $OCH_3$
**2b**, X = H

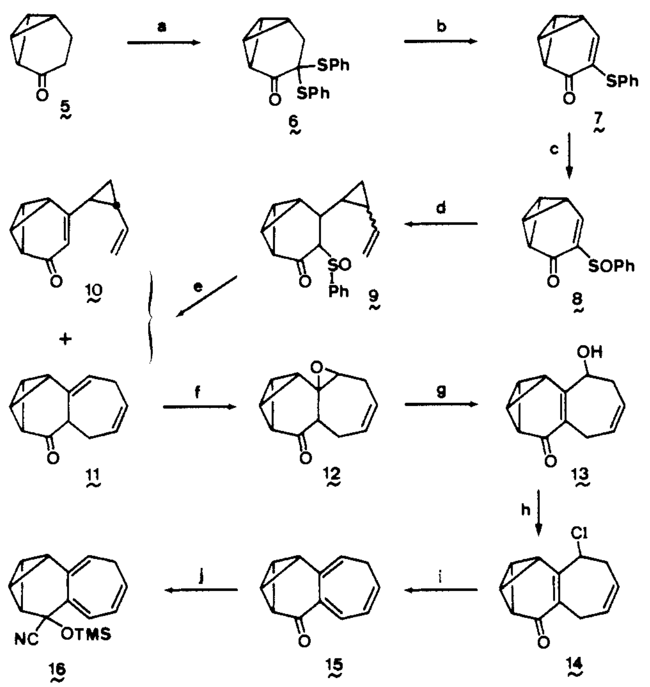


**3**



**4**

**Scheme I**[a]



[a] (a) 2.1 equiv of $LiN(i\text{-}C_3H_7)C_6H_{11}$ in THF–HMPA, then 2.2 equiv of $PhSSO_2Ph$ in THF, 0 °C, 1 h, 45%; (b) 1.1 equiv of mCPBA in $CH_2Cl_2$, −30 °C, 3 h, 62%; (c) 1.1 equiv of mCPBA in $CH_2Cl_2$, −78 °C, 1 h, 84%; (d) 3.0 equiv of 1-lithio-2-vinylcyclopropane in ether–THF, −78 °C, 1 h, 96%; (e) 0.3 equiv of $(MeO)_3P$ in benzene, 70 °C, 2.5 h, 77%; (f) 1.1 equiv of mCPBA in $CH_2Cl_2$, −78 → 0 °C, 2 days, 65%; (g) 3.2 equiv of *t*-BuOK in ether, −78 °C, 1 h, 80%; (h) 2.8 equiv of *n*-$Bu_3P$ and 5.9 equiv of $CCl_4$ in $CH_2Cl_2$, room temperature, 0.5 h, 88%; (i) 4.4 equiv of DBU in THF, room temperature, 3 h, 90%; (j) 2.7 equiv of $Me_3SiCN$, KCN/18-crown-6 complex in benzene, room temperature, 1 h, 99%.

Initially we planned to construct the bicyclobutane skeleton required for the synthesis of **4** through oxa-di-$\pi$-methane rearrangement[11] of an appropriately designed tricyclic $\beta,\gamma$-unsaturated ketone in an approach modeled after our previous synthesis of **2a**[4] and **2b**.[3] However, all attempts at these photoconversions gave unsatisfactory results. Consequently, in our successful approach outlined in Scheme I,[12] tricyclo[4.1.0.0$^{2,7}$]heptan-3-one (**5**),[13] which contains a bicyclobutane system, was used as a starting material.

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[1] (a) Murata, I.; Nakasuji, K. *Tetrahedron Lett.* **1973**, 47. (b) Pagni, R. M.; Watson, C. R., Jr. *Ibid.* **1973**, 59. (c) For a Dewar-type isomer, see: Meinwald, J.; Samuelson, G. E.; Ikeda, M. *J. Am. Chem. Soc.* **1970**, *92*, 7604.

[2] Sugihara, Y.; Sugimura, T.; Murata, I. *J. Am. Chem. Soc.* **1982**, *104*, 4295.

[3] Sugihara, Y.; Sugimura, T.; Murata, I. *J. Am. Chem. Soc.* **1984**, *106*, 7268.

[4] Sugihara, Y.; Sugimura, T.; Murata, I. *J. Am. Chem. Soc.* **1981**, *103*, 6738.

[5] Sugihara, Y.; Wakabayashi, S.; Murata, I. *J. Am. Chem. Soc.* **1983**, *105*, 6718.

[6] For a full paper on **1**–**3**, see: Murata, I.; Sugihara, Y.; Sugimura, T.; Wakabayashi, S. *Tetrahedron*, in press.

[7] Sugihara, Y.; Wakabayashi, S.; Murata, I.; Jinguji, M.; Nakazawa, T.; Persy, G.; Wirz, J. *J. Am. Chem. Soc.* **1985**, *107*, 5894.

[8] (a) van Tamelen, E. E.; Pappas, S. P. *J. Am. Chem. Soc.* **1963**, *85*, 3297. (b) Breslow, R.; Napierski, J.; Schmidt, A. H. *J. Am. Chem. Soc.* **1972**, *94*, 5906. (c) Katz, T. J.; Wang, E. J.; Acton, N. *J. Am. Chem. Soc.* **1971**, *93*, 3782. (d) Katz, T. J.; Acton, N. *J. Am. Chem. Soc.* **1973**, *95*, 2738.

[9] We propose a trivial name "heptalvalene" for the carbon skeleton of **4**.

[10] Bernhard, W.; Brügger, P.; Daly, J. J.; Englert, G.; Schönholzer, P.; Hansen, H.-J. *Helv. Chim. Acta* **1985**, *68*, 1010.

[11] Givens, R. S.; Oettle, W. F. *J. Chem. Soc., Chem. Commun.* **1969**, 1164. Givens, R. S.; Oettle, W. F.; Coffin, R. L.; Carlson, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 3957. Givens, R. S.; Oettle, W. F. *Ibid.* **1971**, *93*, 3963. For a review, see: Hixon, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531.

[12] All new compounds described in this paper gave satisfactory IR, $^1H$ NMR, and MS spectral data. Crystalline compounds are further characterized by combustion analyses.

[13] Ipaktschi, J. *Chem. Ber.* **1972**, *105*, 1996.

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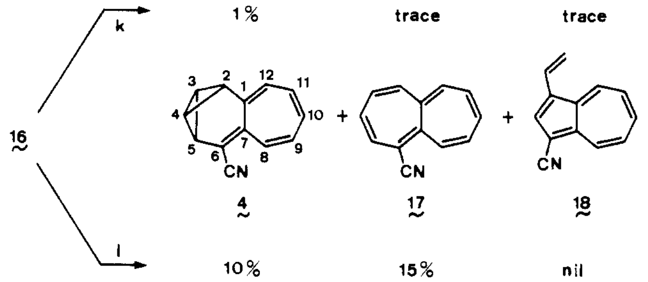
**Scheme II**[a]



[a] (k) 4.8 equiv of $POCl_3$ and 0.5 equiv of 4-(dimethylamino)pyridine in pyridine, 60 °C, 3 h; (l) 7.1 equiv of $POCl_3$ and 4.5 equiv of DBU in pyridine, 60 °C, 2–3 h.

Compound **5** was doubly sulfenylated[14] to **6** (an oil) in 45% yield by treatment with lithium cyclohexylisopropylamide and $PhSSO_2Ph$. Oxidation of **6** with mCPBA followed by elimination of benzenesulfenic acid during workup gave **7** (mp 97–99.5 °C) in 62% yield. At this juncture, the next subgoal of the synthetic effort involved annelation of a seven-membered ring via Michael addition of an appropriate five-carbon unit. To this end, reaction of **7** with a mixture of *cis*- and *trans*-1-lithio-2-vinylcyclopropane[15] was examined. This reaction, however, led to the undesired 1,2-addition product. Therefore, **7** was first oxidized with mCPBA to give sulfoxide **8** (mp 121.5–123.5 °C) as an efficient Michael acceptor in 84% yield. Unlike **7**, **8** was susceptible to a smooth Michael addition of the same reagent to yield the desired product **9** (an oil) in 96% yield which, without purification, on treatment with $(MeO)_3P$ in benzene at 70 °C gave the tetracyclic ketone **11** (an oil, 47% yield) through elimination of benzenesulfenic acid followed by Cope rearrangement, together with the uncyclized *trans*-cyclopropyl derivative **10** (an oil, 30% yield). With the tetracyclic ketone **11** in hand, completion of the synthesis required introduction of an additional double bond. Thus, compound **11** was converted into trienone **15** in the following manner. Regioselective epoxidation of **11** with mCPBA under controlled conditions gave epoxide **12** (an oil, bp 80 °C (bath temp) (0.1 torr), 65% yield). Ring opening of **12** with *t*-BuOK gave **13** (mp 126.5–127.5 °C) in 80% yield. Finally, treatment of **13** with $n$-$Bu_3P/CCl_4$[16] in $CH_2Cl_2$ gave **14** (mp 124–125 °C, 88% yield) which was dehydrochlorinated with DBU to afford a 4:1 mixture of **15** and its double-bond isomer as an oil in 90% yield.[17] Introduction of nitrile functionality was effected by treatment of the mixture, without separation, with $Me_3SiCN$ and KCN/18-crown-6 complex[18] to give cyanohydrin silyl ether **16** (an oil) quantitatively.

A few points in the last step (Scheme II) require comment. Thus, usual treatment of **16** with $POCl_3$ in pyridine[19] either in the presence or absence of 4-(dimethylamino)pyridine gave mainly a polymeric material along with small amounts of the desired **4**, 1-cyanoheptalene (**17**),[5] and 1-cyano-3-vinylazulene (**18**).[20] Furthermore, **16** almost remains intact upon treatment with $POCl_3$/pyridine in the presence of TMEDA. However, **4** was obtained in 10% yield by heating **16** at 60 °C with $POCl_3$ and DBU in pyridine. Although **4** is a slightly labile oil, the TLC and spectroscopic data[21] fully support the sufficient purity and the structure.

The $^1H$ and $^{13}C$ NMR signals at the 3- and 4-positions of **4** ($\delta_H$ 1.68, $\delta_C$ −12.6) appear at higher magnetic field by 1.79 and 52.7 ppm, respectively, compared with those of azulvalene **2b** ($\delta_H$ 3.47, $\delta_C$ 40.1).[3,4] This is reminiscent of the similar behavior between octavalene ($\delta_H$ 1.27, $\delta_C$ −13.4) and benzvalene ($\delta_H$ 3.53, $\delta_C$ 48.3) and is reasonably rationalized[22] by noting the difference in symmetry of the LUMO's between heptafulvene and pentafulvene. Actually, the reduction potential of **4** (−1.61 V)[23] is quite similar to that of 8-cyano-10,10-dimethylbicyclo[5.3.0]deca-1,3,5,7-tetraene (−1.59 V).[7] The data suggest that there exists no appreciable mixing between the bonding orbitals of the bicyclobutane moiety and the vacant orbitals of the 8-cyanoheptafulvene moiety and support experimentally the above rationalization.

On thermolysis, **4** undergoes quantitative isomerization to **17** with first-order kinetics in the temperature range 339.8–363.3 K (by $^1H$ NMR monitoring in benzene-$d_6$).[24] From an Arrhenius plot ($r$ = 0.9986), the activation parameters, $\Delta H^{\ddagger} = 26.1 \pm 0.7$ kcal/mol, $\Delta S^{\ddagger} = -1.3 \pm 0.9$ eu, $E_a = 27.2 \pm 0.7$ kcal/mol, and $\log A = 12.7 \pm 0.4$ are obtained. These data suggest that the heptalvalene **4** isomerizes directly to the heptalene **17** without any intervention of **3** ($E_a(\mathbf{3} \rightarrow \mathbf{17}) = 33.1$ kcal/mol[5]). Thus far the known examples of such direct aromatization confirmed experimentally are confined to benzvalene[25,26] and azulvalene.[2,4] Especially noteworthy is the substantially lower activation energy observed for the isomerization of **4**. Interpreting the rate enhancement remains an interesting problem.

As in the case of **3**, **4** shows anti-Kasha fluorescence originating from the $S_2$ state[7] and undergoes photoisomerization to **17** upon excitation to the $S_2$ state with selected monochromatic light (365 nm).[7] Further studies are currently in progress on the electronic

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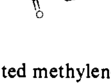
(14) Trost, B. M.; Salzman, T. N.; Hiroi, K. *J. Am. Chem. Soc.* **1976**, *98*, 4887.

(15) Piers, E.; Nagakura, I. *Tetrahedron Lett.* **1976**, 3237. Marino, J. P.; Browne, L. J. *Ibid.* **1976**, 3245.

(16) Downie, I. M.; Holms, J. B.; Lee, J. B. *Chem. Ind.* (*London*) **1966**, 900. Hooz, J.; Gilani, S. S. H. *Can. J. Chem.* **1968**, *46*, 86.

(17) According to $^1H$ NMR ($CDCl_3$, 100 MHz) and IR spectra, the mixture consists of **15** (major) [$\delta$ 7.23 (1 H, d, $J$ = 6.0 Hz), 6.26 (1 H, dd, $J$ = 9.3, 6.0 Hz), 5.60 (1 H, dt, $J$ = 9.3, 6.8 Hz), 5.22 (1 H, t, $J$ = 6.8 Hz), 2.82–3.10 (4 H, m), 2.28 (2 H, t, $J$ = 6.8 Hz); $\nu_{C=O}$ 1690 $cm^{-1}$ (s)] and its isomer (minor) [$\delta$ 6.72 (1 H, ddd, $J$ = 11.0, 5.5, <1 Hz), 6.52 (1 H, dt, $J$ = 11.0, ~1 Hz)], remaining olefinic proton signals are overlapped with those of **15** [3.27 (2 H, t, $J$ = 2.5 Hz), 2.78 (1 H, dt, $J$ = 4.5, 2.5 Hz), 2.69 (1 H, dt, $J$ = 4.5, 2.5 Hz), 2.50 (2 H, d, $J$ = 6 Hz); $\nu_{C=O}$ 1665 $cm^{-1}$ (m)]. The structure of the minor isomer was tentatively assigned as i. Comparison of



the relative areas of well-separated methylene proton resonances ($\delta$ 2.28 for **15** and 2.50 for i) in this spectrum indicates a 4:1 mixture.

(18) Evans, D. A.; Truesdale, L. K.; Carrol, G. L. *J. Chem. Soc., Chem. Commun.* **1972**, 55. Stork, G.; Kraus, G. *J. Am. Chem. Soc.* **1976**, *98*, 6747.

(19) Oda, M.; Yamamuro, A.; Watabe, T. *Chem. Lett.* **1979**, 1427.

(20) **18**: green crystals, mp 82–84 °C (from hexane); MS, $m/z$ 179 ($M^+$, 80%), 178 (100), 177 (33); IR (KBr) 2200, 980, 900 $cm^{-1}$; UV/vis (cyclohexane) $\lambda_{max}$ 242, 283, 301, 306, 320 (sh), 364, 379, 392, 401, 564 (sh), 586 (sh), 606, 640, 663, 713, 747 nm; $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$ 8.58 (d, 1 H, $J$ = 9.6 Hz), 8.54 (d, 1 H, $J$ = 9.6 Hz), 8.29 (s, 1 H), 7.82 (t, 1 H, $J$ = 9.6 Hz), 7.44 (t, 1 H, $J$ = 9.6 Hz), 7.43 (t, 1 H, $J$ = 9.6 Hz), 7.20 (dd, 1 H, $J$ = 17.5, 11.0 Hz), 5.82 (dd, 1 H, $J$ = 17.5, 1.2 Hz), 5.40 (dd, 1 H, $J$ = 11.0, 1.2 Hz).

(21) **4**: a red oil, bp 60–75 °C (0.3 torr); MS, $m/z$ 179.0730 ($M^+$), calcd for $C_{13}H_9N$ 179.0735; IR (neat) $\nu_{CN}$ 2200 $cm^{-1}$; UV/vis (cyclohexane) $\lambda_{max}$ 232 ($\log \epsilon$ 4.04), 357 (4.01), 371 (4.03), 392 (3.80), 430 (2.66), 461 (2.66), 499 (2.57), 544 (2.41), 597 (2.00), 660 nm (1.37); $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$ 6.61 (m, 1 H, H-8), 5.91–6.17 (m, 4 H, H-9–12), 2.94 (dt, 1 H, $J$ = 4.5, 2.5 Hz, H-2 or -5), 2.73 (dt, 1 H, $J$ = 4.5, 2.5 Hz, H-5 or -2), 1.68 (t, 2 H, $J$ = 2.5 Hz, H-3, -4); $^{13}C$ NMR ($CDCl_3$, 22.5 MHz) $\delta$ 143.4, 142.0, 134.7, 131.2, 131.0, 129.0, 120.1, 96.0, 44.8 ($J_{^{13}CH}$ = 161 Hz, C-2 or -5), 35.7 ($J_{^{13}CH}$ = 168 Hz, C-5 or -2), −12.6 ($J_{^{13}CH}$ = 217 Hz, C-3, -4).

(22) Christl, M.; Lang, R. *J. Am. Chem. Soc.* **1982**, *104*, 4494. Christl, M.; Herbert, R. *Org. Magn. Reson.* **1979**, *12*, 150.

(23) The cyclic voltammetry was carried out in DMF at −60 °C with 0.1 M $n$-$Bu_4NClO_4$ as the supporting electrolyte, with a platinum working electrode and SCE reference electrode. The peak separation for the cathodic and anodic waves was 190 mV at a sweep rate of 100 mV/s.

(24) A solution of **4** in benzene-$d_6$ in the presence of a small amount of TMEDA was degassed and sealed in vacuo in an NMR tube. Thermolysis were performed and analyzed in the same way as described in ref 5. First-order rate constants: $k^{339.8} = 1.60 \times 10^{-5}\ s^{-1}$, $k^{347.3} = 3.30 \times 10^{-5}\ s^{-1}$, $k^{355.8} = 8.62 \times 10^{-5}\ s^{-1}$, $k^{363.3} = 2.17 \times 10^{-4}\ s^{-1}$.

(25) Turro, N. J.; Renner, C. A.; Katz, T. J.; Wiberg, K. B.; Connon, H. A. *Tetrahedron Lett.* **1976**, 4133. Dewar, M. J. S.; Kirschner, S. *J. Am. Chem. Soc.* **1975**, *97*, 2932.

(26) Naphthvalene is reported to give no naphthalene and only benzofulvene on solution thermolysis;[8c] however, a recent reinvestigation has shown that naphthvalene does in fact give naphthalene thermally under certain conditions. Kjell, D. P.; Sheridan, R. S. *Tetrahedron Lett.* **1985**, *26*, 5731. For thermolysis of anthracenovalenes, see: Gandillon, G.; Bianco, B.; Burger, U. *Ibid.* **1981**, *22*, 51.

structure by PE spectroscopy and the detailed photochemical behavior of **4**.

**Acknowledgment.** This research was partially supported by a grant from the Itoh Science Foundation.

**Registry No.** **4**, 101493-51-0; **5**, 37939-70-1; **6**, 101493-52-1; **7**, 101493-53-2; **8**, 101493-54-3; **9**, 101493-55-4; **10**, 101493-56-5; **11**, 101493-57-6; **12**, 101493-58-7; **13**, 101493-59-8; **14**, 101493-60-1; **15**, 101493-61-2; **16**, 101493-62-3; **17**, 87306-22-7; **18**, 101493-64-5; i, 101493-63-4; PhSSO$_2$Ph, 1212-08-4; *cis*-1-lithio-2-vinylcyclopropane, 60711-85-5; *trans*-1-lithio-2-vinylcyclopropane, 60711-84-4.

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# Thioozonide Decomposition: Sulfur and Oxygen Atom Transfer. Evidence for the Formation of a Carbonyl *O*-Sulfide Intermediate

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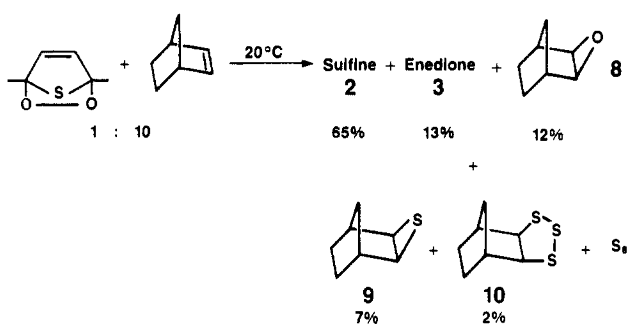
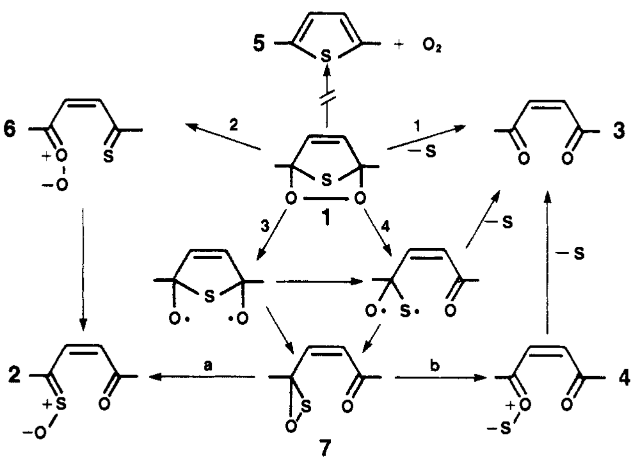
*Received August 16, 1985*

The chemistry of ozonides is of considerable interest from a practical and theoretical viewpoint.[1] Thioozonide **1**, formally the monosulfur-substituted ozonide of dimethylcyclobutadiene, has been proposed as an intermediate in the room temperature photooxidation of 2,5-dimethylthiophene.[2] Subsequent low-temperature studies confirmed this structural assignment.[3] When **1** is allowed to warm to room temperature, it rearranges to a mixture of sulfine **2** and *cis*- and *trans*-3-hexene-2,5-diones (**3c** and **3t**). Recent examination of the thermal decomposition of **1** has led to a proposed mechanism[4] involving a carbonyl sulfide **4** as an intermediate along the sulfur expulsion pathway to **3c**; however, no experimental support for this hypothesis was given. Carbonyl *O*-sulfides have also been implicated as intermediates from the photolysis of oxathiiranes.[5] We now wish to report evidence[6] for the formation of **4** during the decomposition of **1** and that elemental sulfur (S$_8$) is formed during the reaction by concatenation of sulfur atoms or fragments (S$_2$, S$_3$, etc.).



When a 0.25 M solution of 2,5-dimethylthiophene (**5**) was irradiated for 15 min at -50 °C in an aerated solution of CDCl$_3$ containing methylene blue, a quantitative conversion to thioozonide **1** was obtained as determined by $^1$H NMR (-40 °C). The absorptions for dimethylthiophene **5** were replaced by new singlets at 2.12 (6 H) and 6.46 (2 H) ppm. Warming the solution to room temperature (20 °C) resulted in the formation of both sulfine **2** (67%) and *cis*-3-hexene-2,5-dione (**3c**) (33%). As the reaction proceeded, some rearrangement of **3c** to the trans isomer **3t** was also observed. The identity of the products was confirmed by spectroscopic analysis[7] and in the case of **3c** and **3t** by comparison with authentic materials.[8] A plot of -ln [**1**] vs. time for the 0.25 M case gave a straight line ($r^2$ = 0.996) indicating a first-order process with a half-life of 23 min ($T$ = 20 ± 1 °C); however, the mechanism of decomposition must be more complicated since preliminary measurements show a dependence on starting substrate concentration and traces of oxygen ($[\mathbf{1}]_0$ = 0.09 M, $t_{1/2}$ = 12 min; $[\mathbf{1}]_0$ = 0.43 M, $t_{1/2}$ = 57 min). Further studies are under way to define rigorous conditions that give reproducible rate constants.

**Scheme I**



In Scheme I several possible mechanistic routes for the formation of **2** and **3c** are given. Initial steps may include (1) cheletropic expulsion of sulfur, (2) retro-1,3-dipolar cycloaddition, (3) O-O bond homolysis, and (4) O-O bond cleavage with simultaneous $\beta$-scission. Retro-[4 + 2] cycloaddition to regenerate thiophene and singlet oxygen is not observed. Pathway 2 would involve the generation of a carbonyl oxide intermediate **6** which might transfer oxygen internally and lead to sulfine **2**. Polar solvents would be expected to favor the formation of a dipolar species and decomposition of **1** in methanol has been shown to increase the yield of sulfine **2** to 85%, at the expense of enedione formation.[4] Direct singlet sulfur expulsion (path 1) is energetically unlikely but cannot be rigorously excluded on the basis of available experimental observations. Such an expulsion pathway may involve the release of concatenated sulfur species (S$_2$, S$_3$, S$_4$, etc.).[8] Pathways 3 and 4 potentially lead to the same oxathirrane intermediate and are in principle distinguishable by kinetic analysis.[10] The formation of an oxathiirane from the biradicals produced in steps 3 and 4 is reasonable based on CASSCF calculations (double-$\zeta$ plus bond polarization functions).[11] The calculation reproduced the experimental geometry of the sulfine (thioformaldehyde *S*-oxide) and predicted its observed stability. All other

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(6) We believe that this is the first nonspectroscopic evidence for the formation of a carbonyl sulfide intermediate. Other attempts to trap such a species with dipolarophiles were unsuccessful. See ref 5.

(7) Sulfine **2**: $^1$H NMR (CDCl$_3$) $\delta$ 2.31 (s, 3 H), 2.47 (s, 3 H), 6.52 (2 H, A portion of AX quartet, $J$ = 9.8 Hz), 7.74 (2 H, X portion of AX quartet, $J$ = 9.8 Hz); $^{13}$C NMR (CDCl$_3$, $^1$H decoupled) $\delta$ 30.4 (degenerate), 122.4, 128.1, 193.0, 196.8; MS, $m/e$ 144 (M$^+$, 6.5%), 102 (10.1), 101 (49.8), 87 (16.6), 59 (6.9), 43 (100), 42 (8.5). *cis*-3-Hexene-2,5-dione (**3c**): $^1$H NMR (CDCl$_3$) $\delta$ 2.32 (s, 6 H), 6.31 (s, 2 H); $^{13}$C NMR (CDCl$_3$) $\delta$ 29.1, 135.2, 200.0; MS, $m/e$ 112 (M$^+$, 11.2%), 97 (18.9), 69 (15.8), 43 (100). *trans*-3-Hexene-2,5-dione (**3t**): $^1$H NMR (CDCl$_3$) $\delta$ 2.39 (s, 6 H), 6.81 (s, 2 H); $^{13}$C NMR (CDCl$_3$) $\delta$ 27.3, 137.2, 198.1.

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