malism, based on variational transition-state theory, for finding this barrier. Implementation of Truhlar's canonical variational theory[6] (CVT) requires a somewhat arbitrarily defined reaction path from reactants to products which passes through the saddle point. The barrier is determined as a point on this path. Our path is parametrized by the H_1H_2 distance.[7] Next, the force constant matrix is evaluated at regular intervals along the path to create a free energy curve whose maximum corresponds to the TS. We have done this[8] at five geometries: H_1H_2 = 20.0 (reactants), 1.60, 1.40, 1.31, 1.20 Å. Free energies were calculated from the partition functions as a function of H_1H_2 distance and temperature, and the curves are shown in Figure 2. The internal rotation was treated by assuming a potential of $^1/_2 V_0(1 - \cos n\sigma)$ where n = 3 for ethyl radical and n = 2 in the saddle point region. V_0 is the calculated barrier height. The classical hindered rotation partition function was then calculated and the quantum mechanical partition function estimated by the method of Pitzer and Gwinn.[9]

The most striking feature of the results is that the TS structure shifts away from the saddle point toward the products at higher temperature. (Interpolated maxima are obviously uncertain, but the qualitative conclusion holds.) This can be understood simply by noting that entropy decreases from left to right in Figure 2, and $-T\Delta S^\ddagger$ tends to dominate $\Delta G^\ddagger$ at higher temperature. At 1100 K, for example, the 1.2-Å structure is 1.46 kcal higher than the saddle point in free energy, but 1.45 kcal lower in PE. Tightening the internal rotation accounts for 0.76 kcal, 1.46 kcal comes from vibration, 0.05 kcal from rotation, and 0.64 kcal from zero point energy. In general, *the TS structure shifts in the direction of lower entropy as the temperature is raised.*

One of several important consequences of this principle is that the Arrhenius activation parameters predicted by TST and CVT differ significantly as the temperature increases. At 900–1100 K CVT gives log $(A/M^{-1} s^{-1})$ = 11.2, E_a = 5.5 kcal/mol, whereas TST (obtained from Figure 2 by locating the TS at H_1H_2 = 1.31 Å at all temperatures) gives log A = 11.9, E_a = 6.4 kcal/mol.[10]

A large part of mechanistic chemistry is directed toward discovering the structure and properties of the TS. It is therefore important to keep in mind that properties determined at one temperature (e.g., reactivity–selectivity relations, charge distributions, etc.) may not be transferable to another temperature, especially if the barrier is low. For example, Giese[11] has studied the addition of carbenes to olefins and shown that the carbene selectivities converge on an isoselective temperature and are opposite on either side of that temperature. Houk[12] has shown that this phenomenon can be qualitatively modeled by a simple enthalpy/entropy competition along the reaction path which gives rise to a strong variation of TS structure with temperature. In theoretical investigations, the location of a saddle point on the PES is only the first step toward locating the TS. For low barriers (< ca. 5 kT) or flat barriers, *no claim of a TS structure can be believed without a variational search* (e.g., CVT[6]).

The temperature dependence of the TS structure is actually greater than Figure 2 suggests. At the saddle point the C_2H_4 moiety resembles ethyl radical more than ethylene, but the reverse is true at H_1H_2 = 1.2 Å, where C_1H_2 is now 1.30 Å. At this geometry C_1C_2 = 1.417 Å, C_1H_3 = 1.078 Å, and $H_3C_1C_2$ =

(7) Truhlar[6] recommends a steepest-descent path in mass-weighted cartesian coordinates. Our path is determined by varying the H_1–H_2 distance in small increments from the saddle point and requiring that the potential energy be a minimum at each incremental value of this distance.

(8) Translations and rotations were projected out before diagonalization of the force constant matrix. In the saddle point region the gradient direction then appeared as a large negative eigenvalue.

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116.7°, closer to their respective values in ethylene (1.335 Å, 1.073 Å, 121.8°) than in ethyl (1.536 Å, 1.084 Å, 110°). We conclude that at high temperature (> ca. 900 K) *the TS for this strongly exothermic reaction resembles the products more than the reactants and does so increasingly as the temperature is raised.*

Novel Dimerization Reaction of Bis(alkylthio)cyclopropenethiones Affording Tetrakis(alkylthio)thieno[3,4-c]thiophenes

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Because of its strain, aromatic character, and high reactivity, cyclopropenethione is of considerable current interest. Although a number of reactions have been reported, they are concerned with only two cyclopropenethiones, 2,3-diphenyl-[1] and 2,3-diamino-[2]substituted ones. Recently, we uncovered a new and unusual dimerization reaction of 2,3-bis(alkylthio)cyclopropenethiones (**1**) to give 1,3,4,6-tetrakis(alkylthio)thieno[3,4-c]thiophenes (**2**), derivatives of which are 10π nonclassical thiophenes containing tetravalent sulfur. The thieno[3,4-c]thiophene system has received much attention from synthetic and theoretical chemists,[3] but the synthetic work reported so far has been confined to the trapping of unstable 1,3-dimethyl- and 1,3-dicarbomethoxythieno[3,4-c]-thiophenes by N-phenylmaleimide and the synthesis of the isolable 1,3,4,6-tetraphenylthieno[3,4-c]thiophene by Cava and co-workers.[4] Herein, we now report the preparation of thieno[3,4-c]-thiophene **2** from **1** and the structure determination by x-ray crystallography.

a, R_1 = R_2 = t-Bu
b, R_1 = t-Bu, R_2 = Et
c, R_1 = t-Bu, R_2 = Me
d, R_1 = R_2 = i-Pr
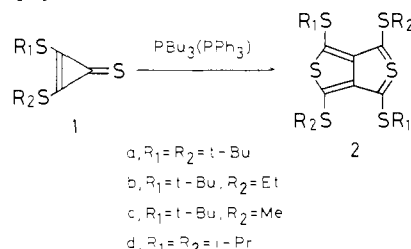
A benzene solution of 2,3-bis(*tert*-butylthio)cyclopropenethione (**1a**)[5] and 1.3 equiv of tributylphosphine was refluxed with stirring

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Table I. Melting Points and Spectral Data of 2a–d

product	mp, °C	IR (KBr), cm⁻¹	¹H NMR (CDCl₃), δ	UV (hexane) λmax, nm
2a	199.5–200.0 dec	2950, 1460, 1370, 1160	1.34 (s, 36 H)	255 (log ε 4.29), 305 (4.07), 506 (4.23)
2b	110.0–110.5 dec	2950, 1455, 1363, 1240, 1160	2.97 (q, 4 H, CH_2CH₃), 1.33 (s, 18 H, t-Bu), 1.32 (t, 6 H, CH₂CH_3)	258 (4.26), 303 (3.96), 515 (4.11)
2c	158.0–158.5 dec	2950, 1370, 1245, 1160	2.54 (s, 6 H, Me), 1.32 (s, 18 H, t-Bu)	259 (4.24), 304 (3.91), 534 (4.03)
2d	116.5–117.0 dec	2950, 1460, 1380, 1230, 1150, 1045	3.40 (sep, 4 H, CHMe₂), 1.26 (d, 24 H, Me)	258 (4.30), 301 (3.95), 505 (4.13)
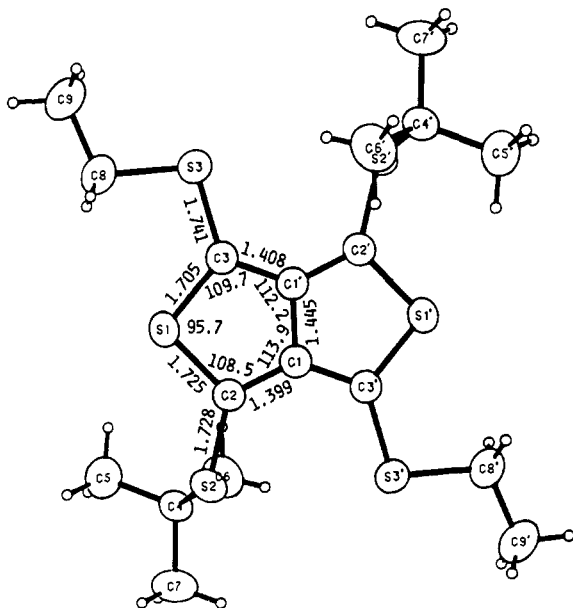
Figure 1. Molecular structure of **2b** with selected bond distances and angles. The estimated standard deviations are 0.002–0.003 Å for distances and 0.1–0.2° for angles.

for 4 h under nitrogen. The solvent was evaporated and the dark red residue was recrystallized from benzene–hexane to give **2a** as reddish purple crystals in 40% yield. Similarly, thieno[3,4-c]thiophenes **2b**, **2c**, and **2d** were prepared from cyclopropenethiones **1b**, **1c**, and **1d**, in 26%, 12%, and 38% yields, respectively. One reason for the poor isolated yields of **2a–d** (especially **2c**) is that they decompose slowly on exposure to air in the purification procedure. Potts and his co-workers[3d] have reported the ready addition of oxygen to 1,3,4,6-tetraphenylthieno[3,4-c]thiophene followed by decomposition. In our attempt to prepare 1,3,4,6-tetrakis(ethylthio)thieno[3,4-c]thiophene (**2e**) from 2,3-bis-(ethylthio)cyclopropenethione (**1e**) under similar conditions, the reaction solution turned dark red and showed the characteristic visible absorption at 507 nm suggesting the formation of **2e**, but the product could not be isolated owing to rapid blackening in the air. The result clearly indicates that the less bulky ethylthio groups are unable to hinder the addition of oxygen at 1,3,4,6-positions of the thieno[3,4-c]thiophene. Purified thieno[3,4-c]-thiophenes, **2a–d**, are stable for long periods at room temperature in the air. The melting points and spectral data are summarized in Table I.

The cycloaddition reactions of **2a** and **2d** with dimethyl acetylenedicarboxylate in refluxing xylene were examined. The former gave no cycloadduct, while the latter 5,6-dicarbomethoxybenzo-[c]thiophene (**3**) formed by extrusion of sulfur from the initial
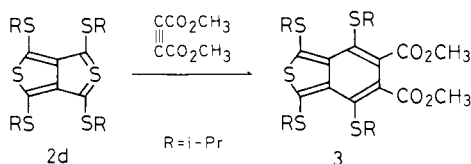
(5) Cyclopropenethiones **1a–e** were prepared according to the method of Weiss, Schlierf, and Schloter.[6]
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1:1 cycloadduct in 29% yield. The structural assignment of **3** was established by the IR, ¹H NMR, and mass spectra.[7] The failure of **2a** to undergo cycloaddition could be attributed to the steric protection provided by the tert-butylthio groups.

The crystals of **2b** suitable for an x-ray structure determination were obtained from ethanol. Crystal data: **2b**, C₁₈H₂₈S₆, triclinic, space group P1̄, a = 10.229 (1) Å, b = 10.870 (1) Å, c = 5.790 (1) Å, α = 102.00 (1)°, β = 103.20 (1)°, γ = 60.74 (1)°, Z = 1. The structure was solved by direct methods and refined by full-matrix least squares to final R value of 0.026. Figure 1 shows the molecular structure of **2b** with selected bond distances and angles.

Supplementary Material Available: Tables of general temperature factor expressions and observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

(7) Data for compound 3: mp 95.5–96.0 °C; IR (KBr) 2950, 1740, 1440, 1380, 1280, 1245, 1200, 1165 cm⁻¹; ¹H NMR (CDCl₃) δ 3.92 (s, 6 H), 3.43 (sep, 2 H), 3.32 (sep, 2 H), 1.27 (d, 12 H), 1.17 (d, 12 H); MS, m/e 546 (M⁺).

Pressure-Induced Torsional Isomerism in [n-Bu₄N]₂[Re₂X₈] (X = Br, I)

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The structural hallmark of the metal–metal quadruple bond, first characterized in [Re₂Cl₈²⁻],[1] is an eclipsed conformation of the two ML₄ halves of the molecule, despite the resulting steric interactions.[2] Twisted conformations, however, can be induced in certain cases by ligands bridging the two metal centers.[3] We wish to report evidence that high pressure applied to salts of both [Re₂I₈²⁻] and [Re₂Br₈²⁻] causes torsion from an eclipsed to a staggered conformation.

Crystals of [n-Bu₄N]₂[Re₂I₈][4] were suspended in a dispersed poly(methyl methacrylate)/dichloromethane medium, which was then evaporated, and a piece of the resulting film was placed under static pressure in a diamond anvil cell.[5] With increasing pressure a new band appears in the visible spectrum (see Figure 1), red-shifted from the well-known ¹(δ²) → ¹(δδ*) transition of the eclipsed form.[2] Analogous behavior is observed for [n-Bu₄N]₂-

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