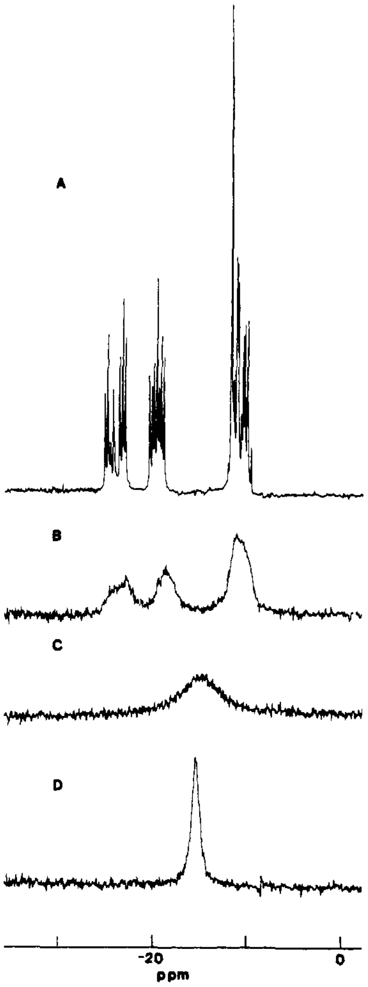
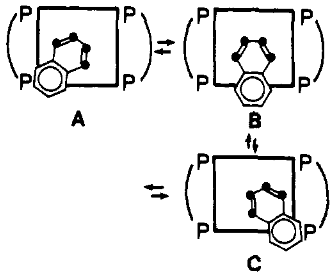


Figure 2. The $^{31}P-\{^1H\}$ NMR spectra of $TaCl(\eta^4-C_{10}H_8)(dmpe)_2$ in toluene-d_8: (a) −36 °C, (b) −15 °C, (c) 35 °C, and (d) 55 °C.

resolved into two multiplets (δ 3.4, 1 H, and δ 2.5, 1 H) in agreement with the lack of symmetry found for the ground state (Figure 1). Identical spectral details are observed for **2** and **3**.

These data are consistent only with rotation of naphthalene about the Ta–Cl axis, a mechanism which necessarily traverses the monocapped trigonal prismatic intermediate B.[11,12]



These observations constitute detection of the pentagonal bipyramid to monocapped trigonal prism interconversion via rotation of a pair of adjacent ligands about the common C_2 axis of the idealized geometries. That is, one of the equatorial and the two axial ligands in the pentagonal bipyramidal arrangement become the unique ligand and two of the four symmetry related vertices in the monocapped trigonal prismatic structure, respectively. By comparison of the discoincidence indices[13] for all plausible C_{2v} to D_{5h} paths, we have shown this mechanism to be that of least motion[14] for interconversion of the idealized geometries. Moreover, electronic barriers associated with this process are estimated to be small on the basis of symmetry arguments.[15] This mechanism is analogous to that suggested by Muetterties[16] and by Hoffmann et al.[2e]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE 75-19177 and CHE 76-05582) for support of this research.

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(6) Defined as $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.
(7) Other bis(dimethylphosphino)ethane structures are disordered; see ref 3h; U. A. Gregory, S. D. Ibekwe, B. T. Kilbourn, and D. R. Russell, *J. Chem. Soc. A*, 1118 (1971); I. W. Nowell, S. Rettig, and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 2381 (1972).
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(9) ^{31}P coupled spectra established that H(2), H(3) remain coupled to ^{31}P throughout the temperature range; H(6)–H(10) are not measurably coupled.
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(11) 1,2 or 1,3 shifts by themselves or coupled with rotation create, at best, one mirror plane.
(12) Intermediate B can be equally well represented by an ortho-quinoidal resonance form. This possibility is mitigated by observation of identical spectral behavior for $TaCl(1,3\text{-cyclohexadiene})(dmpe)_2$ (**4**). **4** was prepared in poor yield by prolonged reduction of $TaCl_2(dmpe)_2$[4] with sodium amalgam in the presence of excess cyclohexadiene and isolated by fractional crystallization. An analytically pure sample could not be obtained, but the proper ^1H and ^{31}P NMR and high-resolution mass spectral data were obtained.
(13) T. A. Halgren and W. N. Lipscomb, *Chem. Phys. Lett.*, submitted for publication.
(14) Using unit bond lengths and bond angles, as given in ref 2d.
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(16) E. L. Muetterties, "Boron Hydride Chemistry," Academic Press, New York, N.Y., 1975, p 28.

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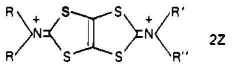
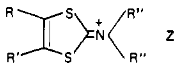
Received February 25, 1977

Thiapen Chemistry. 1.
Synthesis of 1,3,4,6-Tetrathiapentalene-2,5-bis(dialkyliminium) Salts

Sir:

We describe here the ready synthesis of anion salts of the novel 1,3,4,6-tetrathiapentalene-2,5-bis(dialkyliminium) ring system (**1**, abbreviated thiapendiiminium).[1] Previously, 2-dialkyliminium salts of 1,3-dithiole system (e.g., **2**) have been





2

1a: R = R′ = CH$_3$

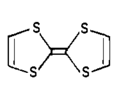
1b: R/R = R′/R′ = $\left(\mathrm{CH_2}\right)_4$

1c: R/R = R′/R′ = $\left(\mathrm{CH_2}\right)_5$

1d: R = CH$_3$; R′/R′ - $\left(\mathrm{CH_2}\right)_4$

shown to be useful precursors to a variety of dithiole derivatives,[2-5] most notably as intermediates in the preparation of electon-rich tetrathiafulvalenes (**3**, TTF).[6] TTF has gained recent prominence as an electron donor which forms anisotropic, organic charge-transfer conductors with suitable electron acceptors.[7,8]

Our interest in developing a synthetic entry into the thiapen ring system stemmed conceptually from the possibility of elaborating a variety of symmetrical derivatives using chemical methods already developed for the 1,3-dithiolium analogues.[2] For example, the interesting fused TTF molecule **4** can be viewed as a bis-capped species, approachable via suitable precursor thiapens such as **1**.



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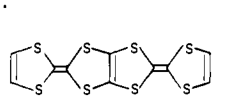
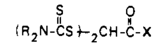


4

We have discovered that thiapendiiminium salts **1** can be prepared in virtually quantitative yield by acid induced cyclization of the bis(dithiocarbamates) of acetic acid derivatives, **5a–d.** The bis(dithiocarbamates) **5b** and **c** were readily synthesized from alkyl dihaloacetates by reaction in acetone or dioxane with salts of N,N-dialkyl dithiocarbamic acid dihydrate. Acid **5a** was prepared by reaction of dichloracetyl chloride with 2 mol equiv of the hydrated carbamate salt, whereas dialkylamide **5d** was obtained when 3 mol equiv of the carbamate nucleophile were employed.[9]



$$\left(\mathrm{R_2N\text{-}\overset{S}{\overset{\|}{C}}S}\right)_2\mathrm{CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}X}$$

5a: X = OH

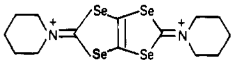
5b: X = OCH$_3$

5c: X = OCH$_2$CH$_3$

5d: X = N(CH$_3$)$_2$

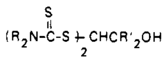
Cyclization of **5a, 5b, 5c** or **5d** proceeded on solution in 70% perchloric or concentrated sulfuric acid. The crystalline bisperchlorate salts **1** (Z = ClO$_4^-$) when dry were dangerously explosive, detonating violently on touch and should be treated with utmost caution. The corresponding bisulfate salts **1** (Z = HSO$_4^-$) were hydroscopic, but were stable when stored under nitrogen. Recrystallization from dry acetonitrile afforded the thiapendiiminium salts as colorless needles. The characterization of **1a** and **1d** followed from their spectral properties[10] (see below). For example, the IR spectrum (KBr) of perchlorate **1a**[11] was almost totally superimposable on the IR of 4-methyl-2-(N,N-dimethyiminium)-1,3-dithiole perchlorate[2] (**2**, R = H; R′ = R″ = CH$_3$), exhibiting major absorptions at 1605 (s), 1408 (m), 1250 (m), 1210 (m), 1090 (s, br), 780 (m), 620 (s). The ^{1}H NMR spectrum of **1a** in strong acids displayed a sharp N-methyl singlet[12] at $\delta \approx 3.7$. The ^{13}C NMR showed the expected equivalency of the vinyl and iminium carbons; however, nonequivalence of the N-methyl carbons was unexpectedly observed. This was also seen in the ^{1}H NMR spectrum when acetonitrile was employed as the solvent ($\Delta^{N\text{-methyl}} = 7.0$ Hz). Synthesis of the mixed bis(dialkyliminium) salt **1d**[13] appeared to rule out that nonequivalence was due to an environmental difference between the two iminium groups (R$_2$$^+$N=) in the molecule. The ^{13}C NMR spectrum of **1d** was a perfect composite of **1a** and **1b**, clearly showing the nonequivalence of the α carbons on each iminium group. While the reason for this nonequivalence of the α-N-alkyl carbons is presently not clear, a possible explanation may involve the waters of hydration which coordinate at the two positive iminium centers, either on the same or opposite sides of the thiapen ring system.

Piperidinium N,N-pentamethylenediselenocarbamate also reacted with methyl dichloroacetate to give methyl bis(N,N-pentamethylenediselenocarbamoyl)acetate which could be subsequently cyclized in concentrated H$_2$SO$_4$ or HClO$_4$ in low yield to the unstable 1,3,4,6-tetraselenapentalene-2,5-dipiperidinium salts (**6**).[14]



6

2-Dialkyliminium salts of the 1,3-dithiole system (**2**) have been converted into precursors suitable for coupling to TTF derivatives either by treatment with hydrogen sulfide to give the corresponding thiones[2,3,5] or by reduction (NaBH$_4$) and acid treatment to give the corresponding dithiolium cation salts.[3,5] Attempts to treat **1** in similar fashion have so far been unsuccessful, owing to facile ring opening that occurs on treatment with nucleophilic reagents. For example, treatment of **1** with water or alcohol instantly provided the ring-opened derivative **5a** or **5b,c,** respectively, in which H$_2$O or alcohol added across the central double bond of the thiapen ring system. Sodium borohydride reduction of **1** in 2-propanol gave 2,2′-bis(dialkyldithiocarbamoyl)ethanol (**7a**). With NaBD$_4$,



$$\left(\mathrm{R_2N\text{-}\overset{S}{\overset{\|}{C}}\text{-}S}\right)_2\mathrm{CHCR'_2OH}$$

R = alkyl

7a: R′ = H

7b: R′ = D

no deuterium incorporation in the 2 position was found, suggesting that an initial reaction involving the waters of hydration produced an intermediate which was subsequently reduced to the alcohol, **7b.**

The facile ring opening of the thiapendiiminium system with nucleophiles presently limits their synthetic potential as precursors to new TTF derivatives. Alternate thiapen derivatives[15] appear more promising in this regard.

Acknowledgments. We thank A. A. Fukushima and V. V. Patel for their competent technical assistance and T. Horikawa for running the ^{13}C NMR spectra.

References and Notes

(1) We have chosen the name tetrathiapentalene in analogy to the well-known pentalene hydrocarbon in much the same way as tetrathiafulvalene is used to designate the sulfur analogue of fulvalene. Adopting a thoughtful suggestion of Professor H. C. Brown, we now use the shortened form "thiapen" to broadly represent a general class of compounds of rich and varied chemistry that we will be describing in this and subsequent papers.

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(9) A more complete discussion of this reaction will be given in a later paper in this series.

(10) These salts as hydrates are difficult to analyze and their assignment is based on their spectral properties and comparison with model systems such as **2**.

(11) The KBr IR spectrum of perchlorate **1a** was performed before its explosive nature was appreciated.

(12) In fluorosulfonic acid this singlet remained almost invarient over a temperature range of −60 to +60 °C. No change was observed for **1a** in the ^{13}C NMR chemical shift difference ($\Delta^{N\text{-}Me}$ = 30 Hz) when the temperature was raised from 30 to 80 °C.

(13) A method for synthesizing mixed iminium salts (e.g., **1d**) will be described in a later paper.

(14) Characterization of **6** is based on the similarity of its spectral properties with **1c**. ^1H NMR (δ, CD_3CN): **6**, 1.78 (3 H, br s), 4.00 (2 H, br s); **1c**, 1.76 (3 H, br s), 4.03 (2 H, br s). The UV spectrum in 70% $HClO_4$ displays the expected bathochromic shift in going from **1c** to **6** (λ_{1c} 255 nm, λ_6 275 nm).

(15) See following paper in this issue by R. R. Schumaker and E. M. Engler.

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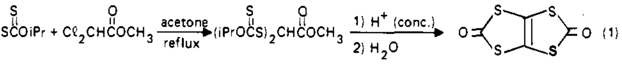
Received March 25, 1977

Thiapen Chemistry. 2. Synthesis of 1,3,4,6-Tetrathiapentalene-2,5-dione

Sir:

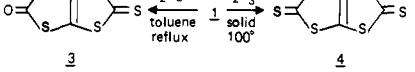
In the preceding communication,[1] a new heterocyclic ring system, 1,3,4,6-tetrathiapentalene (abbreviated thiapen) was prepared as a 2,5-bis(dialkyliminium) salt by reacting a dialkylcarbamate with methyl dichloroacetate, followed by cyclization in acid. Attempts to convert the iminium groups to functional groups suitable for the elaboration of tetrathiafulvalene derivatives[2] were unsuccessful. This problem has been circumvented by employing an *O*-alkyldithiocarbonate in place of the carbamate. This permits the preparation of 1,3,4,6-tetrathiapentalene-2,5-dione (**1**, abbreviated thiapendione), analogous with previous work on the preparation of 1,3-dithiole-2-ones.[3]

Reaction of methyl dichloroacetate with 2 mol equiv of potassium *O*-isopropyldithiocarbonate in refluxing acetone provided in quantitative yield methyl 2,2-bis(*O*-isopropyldithiocarbonyl)acetate (**2**)[4] as a light yellow oil. This material could be readily cyclized to the thiapen ring system[5] with concentrated H_2SO_4 at 0-5 °C and isolated as the 2,5-dione derivative (**1**) on addition to ice-water (eq 1). Crystallization from acetonitrile gives thiapendione **1** as long white needles in 70-80% yield (mp 150 °C; IR (KBr, cm^{-1}) 1727(m), 1678 (s), 973 (w); 914 (w); UV (λ_{max}, nm, methanol) 273, 222; mol wt calcd 207.878, found (mass spectroscopy) 207.878). Thiapendione is a central precursor for the preparation of a wide variety of novel organosulfur compounds. Some illustrative examples follow.



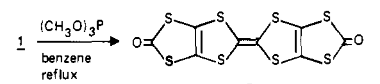
2 1

Depending on reaction conditiŏn, thiapendione can be converted on treatment with boron sulfide into either the mixed carbonyl-thiocarbonyl derivative **3** or the dithiocarbonyl derivative **4**. Thus, treatment of **1** with boron sulfide in refluxing toluene afforded **3** (mp 176-179 °C dec; IR (KBr, cm^{-1}) 1727 (w), 1700 (m), 1675 (m), 1083 (s), 968 (w), 900 (w); mol wt calcd 223.855, found (mass spectroscopy) 223.853) as the major product with minor amounts of **1** and **4** also present. These impurities could be separated by chromatography. When a solid mixture of **1** and boron sulfide is heated overnight at 100 °C, dithione **4** is obtained as a yellow solid (mp 207-210 °C dec; IR (KBr, cm^{-1}) 1068 (s), 959 (m), 900 (w), 776 (w); mol wt calcd 239.832, found (mass spectroscopy) 239.831).



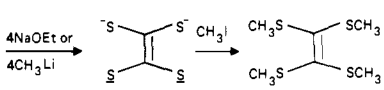
3 4

Treatment of **1** with trimethyl phosphite in refluxing benzene precipitated the dimerized system **5** (dithiapendione)[4] as a very insoluble olive powder in 75% yield (mp >360 °C; IR (KBr, cm^{-1}) 1740 (m), 1720 (s), 1700 (s), 1510 (w), 970 (w), 880 (w), 845 (w), 765 (w), 745 (m)). No higher coupled homologues (trimers, etc.) were detected, even under more strenuous reaction conditions.

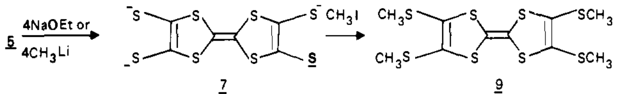


5

Reaction of **1** or **5** under nitrogen with 4 mol equiv of sodium ethoxide in refluxing ethanol or methyllithium in tetrahydrofuran at room temperature afforded the corresponding air-sensitive tetrathiolate salts[6] **6** and **7** which could be converted on addition of methyl iodide to the *known* compounds: tetrathiomethoxyethylene (**8**)[7] and tetrathiomethoxytetrathiafulvalene (**9**),[8] respectively.[9] TTF derivative **9** reacts with TCNQ in nitroethane at low temperature to give a blue-black 1:0.9 charge-transfer salt with a room temperature compaction conductivity of 2.5 × 10^{-4}Ω cm.

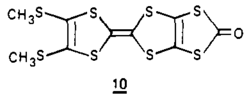


6 8



7 9

When only 2 mol equiv of sodium ethoxide or methyllithium are added to **5** and subsequently treated with methyl iodide, the half-opened dithiomethoxy derivative (**10**)[10] can be isolated in low yield after chromatography (mp 178 °C dec; IR (KBr, cm^{-1}) 2900 (m), 1660 (s), 1610 (m), 1420 (m), 965 (w), 875 (m), 765 (w) 750 (m); NMR (δ, $CDCl_3$) 2.40).[11]



10

While dimer **5**, a tetrathiafulvalene derivative, appears to be unreactive with TCNQ, monomer **1**, surprisingly, forms a 1:1 blue-black charge-transfer salt with TCNQ[4] with a room temperature compaction conductivity of 10^{-8}/Ω cm.

Further elaboration of the chemistry of thiapendione, including capping reactions with 1,3-dithiole derivatives,[12] will be reported shortly.

Acknowledgments. We thank A. A. Fukushima and V. V. Patel for their experimental assistance and R. Greene for carrying out the conductivity measurements.

References and Notes

(1) R. R. Schumaker and E. M. Engler, *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) A number of tetrathiafulvalene derivatives react with acceptors to form the most conducting organic solids presently known. Reviews: M. Narita and C. U. Pittman, Jr., *Synthesis*, 489 (1976); E. M. Engler, *Chem. Technol.*, 6, 274 (1976).

(3) E. Campaigne, R. D. Hamilton, and N. W. Jacobsen, *J. Org. Chem.*, **29**, 1708 (1964); I. D. Rae, *Int. J. Sulfur Chem.*, **1**, 59 (1971); A. K. Bhattacharya and