are listed in Table III. Intensities of three reflections were monitored after every 2 h of X-ray exposure. All intensity data were corrected for Lorentz and polarization factors. A Gaussian method[31] was employed to make the absorption correction by using 216 sampling points. Each structure amplitude was assigned a weight, $\omega_F = 1/\sigma_{F^2}$, where σ_F was obtained from counting statistics.[32]

The positions of the two chlorine and two phosphorus atoms were obtained from an E map evaluated by using the direct methods program MULTAN.[33] The remainder of the structure was obtained by successive difference Fourier syntheses. All hydrogen atoms were located from a difference Fourier map calculated at a later stage of least-squares refinement. All nonhydrogen atoms were given anisotropic thermal parameters, while the hydrogen atoms were refined isotropically. In the final cycles of refinement, the anomalous dispersion effects of Cu-radiation by Cl and P atoms were taken into account. Refinement was terminated when the maximum parameter shifts of the nonhydrogen atoms were less than 40% of their corresponding standard deviation. The final R factor for 5056 reflections included into the least-squares calculations is 0.054, while it is 0.091 for all 7433 reflections. All refinements were carried out by using a block diagonal least-squares method,[34] in which the quantity, $\sum \omega(kF_o - F_c)^2$, was minimized. Scattering factors for Cl, P, O, and C were taken from ref 35 while those of the hydrogen atoms were from Stewart, Davidson, and Simpson (1965).[36]

The final positional parameters along with equivalent isotropic thermal parameters for all nonhydrogen atoms are given in Table IV.

Acknowledgment. We gratefully acknowledge support of this work by the USPHS, National Cancer Institute, Grant CA 22770 (K.D.B.) and Grant CA 17562 (D.v.d.H.). We gratefully acknowledge the aid of Dr. Kurt Loening, Director of Nomenclature at Chemical Abstracts, in naming the compounds in this work.

Registry No. *meso*-**5a**, 80799-76-4; *meso*-**5b**, 80799-73-1; **6a**, 1663-45-2; **6b**, 6737-42-4; **6c**, 7688-25-7; **6d**, 27721-02-4; **6e**, 19845-69-3; **7a**, 81194-90-3; **7b**, 81194-91-4; **7c**, 81194-92-5; **7e**, 81194-93-6; **8a**, 81194-95-8; **8b**, 81194-97-0; **8c**, 81194-99-2; **8d**, 81195-01-9; **8e**, 81195-03-1; **9a**, 81195-05-3; **9b**, 81195-07-5; **9c**, 81195-09-7; **9d**, 81195-11-1; **9e**, 81195-13-3; **10**, 2071-20-7; **11**, 81195-14-4; **12**, 81195-16-6; **13**, 81205-74-5; **16**, 81195-17-7; **17**, 81195-19-9; **18**, 81195-21-3; **27**, 81195-22-4; **28**, 56771-37-0; **29**, 58191-14-3; 1-chloro-3-methyl-2-butene, 503-60-6; 1-bromo-3-methyl-2-butene, 870-63-3; 3-bromopropene, 106-95-6; 5-bromo-1-pentene, 1119-51-3; 4-bromo-1-butene, 5162-44-7; **19**, 81195-24-6; **21**, 81195-26-8; **23**, 81195-28-0.

Supplementary Material Available: A listing of anisotropic thermal parameters and hydrogen atom parameters (4 pages). Ordering information is given on any current masthead page.

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Carbon–Phosphorus Heterocycles. Synthesis, Separation, and Resolution of Stereoisomers of 1,1′-(1,2-Ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Diperchlorate. The Use of ^{31}P NMR Analysis To Monitor the Resolution

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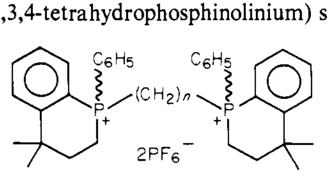
Contribution from the Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078. *Received October 2, 1981*

Abstract: The synthesis of the diastereomeric mixture of the title compound via polyphosphoric acid induced intramolecular alkylation of a strategically designed, open-chain precursor was recorded for the first time. The meso and (±) diastereomers were separated by fractional crystallization, and partial resolution of the (±) form was attained via the use of Ag hydrogen dibenzoyltartrates [L(+) and D(−)]. The ^{31}P NMR analysis was advantageously used to monitor the separation of diastereomers and the resolution of (±) form. Spectral data for all of the stereoisomers has been briefly discussed for these first members of the title compounds. Evidence is presented which strongly suggests that nonequivalence at phosphorus is induced in the meso isomer via the presence of a chiral anion such as hydrogen dibenzoyltartrate. The separation and resolution are the first recorded in this family of heterocycles also.

The preceding paper[1] described the synthesis of 1,1′-(α,ω-alkanediyl)bis(1,2,3,4-tetrahydrophosphinolinium) salts **1** (n = 1–6)



1

which were dissymmetric because of the presence of two asymmetric phosphorus atoms in the two rings. A search of the literature revealed that only simple C–P heterocycles containing one asymmetric phosphorus atom have been resolved into optical antipodes.[2-6] The first and *only* previous successful separation of diastereomers and resolution of an *open-chain* bis(phosphonium) salt **2** was recorded by Horner and co-workers.[7] Heretofore, no heterocyclic bis(phosphonium) salt containing two asymmetric phosphorus atoms in two rings has been separated into diastereomers or resolved into optical antipodes.[8] We report herein

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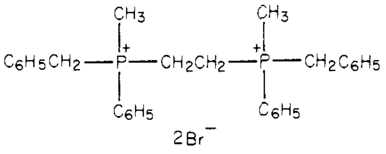
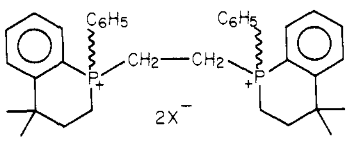


$C_6H_5CH_2-\overset{+}{P}(CH_3)(C_6H_5)-CH_2CH_2-\overset{+}{P}(CH_3)(C_6H_5)-CH_2C_6H_5 \quad 2Br^-$

2

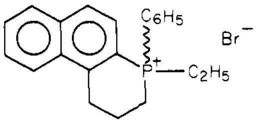
the first preparation of bis(phosphinolinium) salts **3–8** and the



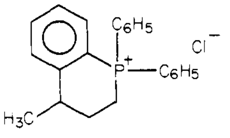
racemic and meso forms

3, X = ClO_4
4, X = $B(C_6H_5)_4$
5, X = Cl
6, X = I
7, X = L(+)-HDBT
8, X = D(−)-HDBT

separation and resolution of stereoisomers of a heterocyclic bis(phosphonium) salt **3** with the aid of silver hydrogen L(+)- and D(−)-benzoyltartrates[9] [Ag L(+)-HDBT and Ag D(−)-HDBT]. However, the confirmed carcinostatic activity of several members of the substituted 1,2,3,4-tetrahydrophosphinolinium salts **9** and **10**[10,11] also stimulated our interest in stereoisomers of **3–8** which are related structurally to **9** and **10**. The NSC number refers to that number assigned to that compound by National Cancer Institute. (The T/C refers to the ratio test animals to control and the test system is in brackets).



9
NSC-145185
T/C = 142
[P-388 system]



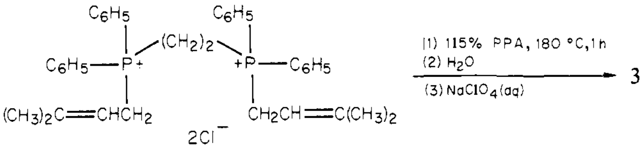
10
NSC-273810
T/C = 155
[3 PS31^c system]

Results and Discussion

Synthesis. The synthesis of **3** was accomplished as outlined in Scheme I. The open-chain precursor **11** was prepared from readily available bis(diphenylphosphino)ethane according to the procedure described in the previous paper.[1] The use of polyphosphoric acid (PPA) for annulation of C–P heterocycles has been well established.[12] Cyclization of the dichloride **11** in presence of 115% PPA at 180 °C followed by treatment with aqueous $NaClO_4$ resulted in the formation of **3** which was found to be a mixture of meso and (±) forms of **3** as expected from the two similar asymmetric phosphorus atoms in the molecule. The mixture of meso and (±) forms of **3** showed two ^{31}P NMR signals at +15.86 and +14.83 ppm, respectively, downfield from 85% phosphoric acid in $DCCl_3$ (with a drop of F_3CCO_2H added) corresponding to the two diastereomers.

Separation of Diastereomers. The separation of meso and (±) forms from the diastereomeric mixture of **3** was achieved by fractional crystallization using H_2CCl_2–ether and monitoring the process via ^{31}P NMR analysis. The much less soluble *meso*-**3** was isolated in pure form and melted at 291–293 °C. Several attempts to separate pure (±)-**3** from the fraction enriched with (±)-**3** were unsuccessful. Conversion of enriched (±)-**3** to enriched (±)-**4** [$2(C_6H_5)_4B^-$] was achieved by treatment of the former with a methanol solution of sodium tetraphenylborate. Fractional crystallization of the crude, enriched (±)-**4** with H_2CCl_2–ether was successful and (±)-**4** (mp 218–220 °C) was separated in pure form. For the resolution work, it was found convenient to employ dihalides as reactants with Ag L(+)-HDBT and D(−)-HDBT. Therefore both *meso*-**3** and (±)-**4** were converted into the respective dichlorides *meso*-**5** and (±)-**5** via passage of the former salts through a column of Dowex 1-X8 (Cl^-). Further proof of the structure of *meso*-**5** was obtained through metathesis to and characterization of *meso*-**6**, whereas (±)-**5** was converted to and characterized as (±)-**3** ($2ClO_4^-$; mp 256–258 °C).

Scheme I



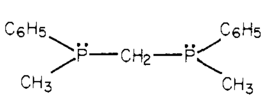
11

Resolution of (±)-5. Some success in the resolution of (±)-**5** was achieved by using Ag D(−)-HDBT and Ag L(+)-HDBT and monitoring the process via ^{31}P NMR analysis. Metathesis of (±)-**5** with Ag L(+)-HDBT in methanol gave a mixture of diastereomers from which it was possible by fractional crystallization ($HCCl_3$–ether) to obtain in pure form (−)-**7** [2L(+)-HDBT]: mp 151–153 °C dec; $[\alpha]^{21}_D = +60.5°$ (*c* 1.00, H_3COH). Following the same procedure, (+)-**8** [2D(−)-HDBT] was isolated and had a melting point of 147.5–149 °C dec and $[\alpha]^{21}_D = -60.0°$ (*c* 1.00, H_3COH). The stoichiometric inclusion of 1 equiv of water in the crystal of (+)-**8** [2D(−)-HDBT] was revealed by elemental analysis. Such an inclusion of solvent is not unknown with phosphonium salts.[4,13,14]

Metathesis of (−)-**7** [L(+)-HDBT] with $NaClO_4$ in methanol resulted in the formation of (−)-**3**: mp 262.5–264 °C; $[\alpha]^{21}_D = -18.5°$ (*c* 1.00, acetone). Following the same procedure, the other enantiomer (+)-**3** was obtained from (+)-**8** [D(−)-HDBT], and it had a melting point of 263–264 °C and $[\alpha]^{26}_D = +19.1°$ (*c* 1.00, acetone).

Since no simple experimental method exists to distinguish a meso isomer from the (±) isomer of a compound, the former isomer of **3** was subjected to similar experiments as employed in the resolution of (±)-5. The diastereomers *meso*-**7** [L(+)-HDBT] and *meso*-**8** [D(−)-HDBT], upon metathesis with $NaClO_4$ in H_3COH, gave the same *meso*-**3** with a rotation of 0° as expected. Elemental analysis revealed the inclusion of 1 equiv of water in the crystalline *meso*-**7** [L(+)-HDBT].

Identification of Diastereomers by Nuclear Magnetic Resonance. The meso and (±) forms of species containing two asymmetric atoms have different physical properties including NMR spectra.[15,16] Recently, systems in which two asymmetric phosphorus atoms were separated by one carbon atom, such as in bis(methylphenylphosphino)methane (**12**) and its *P,P'*-diselenide **13**, were recorded to exhibit different ^{31}P NMR signals for meso and (±) forms.[17] The diastereomeric mixture of **3** gave two ^{31}P NMR



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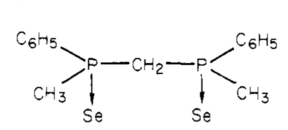

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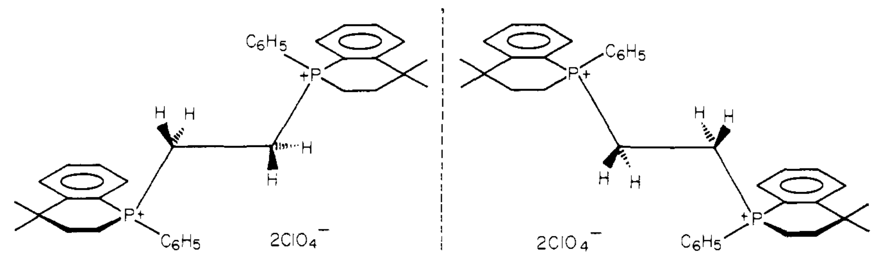
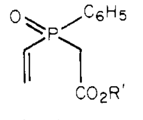


(±)-3

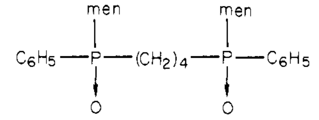
signals corresponding to *meso*-**3** and (±)-**3**. In contrast, each pure form [*meso*-**3**, (±)-**3**, (±)**4**, *meso*-**5**, and *meso*-**6**], after separation, exhibited one ^{31}P NMR signal. The meso isomer of each salt always showed a lone ^{31}P NMR signal *upfield* relative to the corresponding (±)-form, which may be due to differences in nonbonded interactions in the preferred conformation of the former as compared to those in the preferred conformation of the latter. The nature of the substituents attached to phosphorus further complicated the conformational analysis.

It is interesting to note that diastereomeric salts[18] containing chiral anions, (±)-**7** [L(+)-HBDT] and (±)-**8** [D(−)-HDBT], showed *two* ^{31}P NMR signals corresponding to the two diastereomers. The dipolar attraction between anions and cations of optically active molecules is considered to be important in resolution procedures. Such attraction between the chiral anions and the chiral phosphorus centers creates a chiral environment around each asymmetric phosphorus atom and results in two ^{31}P NMR signals, each signal corresponding to a phosphorus atom in a different environment. It was observed that a drop of trifluoroacetic acid (TFA) added to the solution of (±)-**7** or (±)-**8** in DCCl$_3$ made the two ^{31}P NMR signals collapse to *one* signal (Table I). This may be due to the replacement of chiral anion, L(+)-HDBT$^-$ [or D(−)-HDBT$^-$], by the trifluoroacetate anion. Each pure diasteromer (−)-**7** [L(+)-HDBT] or (+)-**8** [D(−)-HDBT] exhibited one ^{31}P NMR signal when dissolved in DCCl$_3$ or in DCCl$_3$ containing a drop of TFA. Recently it was reported[19] that the enantiomeric mixture of **14** containing a chiral ligand



14, R' = men

showed two ^{31}P NMR signals in benzene, and the pure enantiomer, after separation, showed a lone ^{31}P NMR signal. Two ^{31}P NMR signals observed for *meso*-**7** [L(+)-HDBT] or *meso*-**8** [D(−)-HDBT] in DCCl$_3$ (Table I) may also be explained via a similar argument. In the chiral environment created by dipolar attraction of chiral anions to the chiral phosphorus centers, the two phosphorus atoms must be able to exhibit different ^{31}P NMR chemical shifts. Valentine and co-workers[20] reported two ^{31}P NMR signals for the P-oxide of *meso*-**15** (*R*,*S*) in which a chiral ligand was



$$\mathrm{C_6H_5-\underset{\underset{O}{\downarrow}}{\overset{\overset{men}{|}}{P}}-(CH_2)_4-\underset{\underset{O}{\downarrow}}{\overset{\overset{men}{|}}{P}}-C_6H_5}$$

15

men = menthyl

directly attached to each phosphorus atom by a covalent bond (two different melting points were reported for this compound). In our examples, it was observed that the two ^{31}P NMR signals of *meso*-**7** and *meso*-**8** collapsed into one signal by the addition of a drop of TFA to the solution (DCCl$_3$), again apparently due to the destruction of the chiral environment around each phosphorus atom.

Table I. ^{31}P NMR Spectral Data for Diastereomeric Mixtures [(±)-7, *meso*-7, (±)-8, and *meso*-8]

compd	anion	^{31}P NMR data (ppm from 85% H$_3$PO$_4$) in	
		DCCl$_3$	DCCl$_3$ with a drop of TFA
(±)-7	L(+)-HDBT$^-$	17.03, 17.27	15.91
(±)-7	D(−)-HDBT$^-$	17.21, 17.45	15.98
meso-8	L(+)-HDBT$^-$	15.58, 15.62	15.06
meso-8	D(−)-HDBT$^-$	15.51, 15.54	15.07

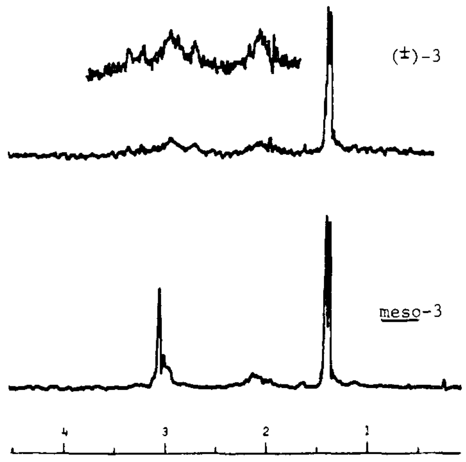
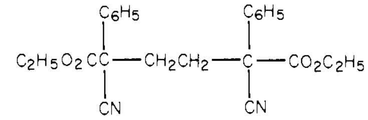


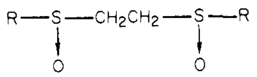
Figure 1. ^{31}P-decoupled ^{1}H NMR signals for CH_2 and CH_3 groups for compounds (±)-**3** and *meso*-**3**.

The ^{1}H NMR spectra of the diastereomers and enantiomers were complex because of severe overlap of the signals for the bridge CH_2 protons with those of the CH_2 protons in the phosphorinane ring. However, the *meso*-**3** and (±)-**3** showed perceptible differences in the ^{31}P-decoupled ^{1}H NMR spectra (Figure 1). In the case of *meso*-**3**, a singlet (δ 3.05) was observed to overlap with a multiplet, whereas (±)-**3** gave only a multiplet for CH_2 protons. Such a fortuitous singlet was detected for the bridge methylene protons in the meso form and a multiplet for the (±) form of the α,α'-diphenyl substituted adiponitrile **16**[21] and of γ-sulfoxides **17**



$$\mathrm{C_2H_5O_2C\underset{\underset{CN}{|}}{\overset{\overset{C_6H_5}{|}}{C}}-CH_2CH_2-\underset{\underset{CN}{|}}{\overset{\overset{C_6H_5}{|}}{C}}-CO_2C_2H_5}$$

16



$$\mathrm{R-\underset{\underset{O}{\downarrow}}{S}-CH_2CH_2-\underset{\underset{O}{\downarrow}}{S}-R}$$

17

(R = C$_6$H$_5$ or substituted phenyl).[22,23] We assume a heavy population of anti rotamer in solution for *meso*-**3** and (±)-**3** be-

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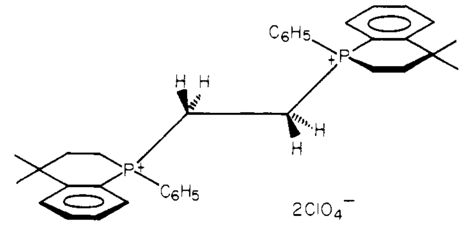
cause the electrostatic repulsion and bulkiness of attached groups should keep the two phosphorus atoms with like charges at the greatest distance from each other. This assumption was further substantiated by the single-crystal X-ray diffraction analysis of *meso*-**3** which revealed that the molecule assumed a near anti conformation in the solid state.[1] The bridge CH_2–CH_2 group would be expected to give an AA′BB′ type multiplet pattern both in *meso*-**3** and (±)-**3** since the two protons of each methylene group adjacent to asymmetric phosphorus atom are diastereotopic and therefore, in principle, anisochronous.[24] Moreover, the $^3J_{HH}$ trans values are larger than the $^3J_{HH}$ gauche values.[25] The anti rotamer of *meso*-**3** is a centrosymmetric molecule in which the H atoms trans to each other in the bridge are in identical environments whereas the trans-oriented protons in the ethylene bridge of the anti rotamer of (±)-**3** are in different environments due to a lack of symmetry in the molecule. Accordingly, a simplified spectrum (albeit a singlet) was observed for the bridge CH_2–CH_2 protons in *meso*-**3**. In the case of (±)-**3**, the ethylene protons gave the expected AA′BB′ multiplet. However, the signal overlap of the methylene protons in the phosphorinane ring with bridge CH_2 protons further complicated the analysis. Thus the phenomenon of a singlet for CH_2–CH_2 in a meso isomer with the required structure discussed may well be a distinguishing feature in such systems, assuming no extraordinary differences exist in the magnetic shielding for each of the sets of trans, geminal protons on one carbon. The ^1H NMR spectra of the enantiomers (+)-**3** and (−)-**3** were found to be identical with that of (±)-**3**, as expected.



meso-**3**

Experimental Section

General Data. Melting points were obtained on a Thomas-Hoover melting point apparatus and were uncorrected. The ^1H and ^{31}P NMR spectra (^1H decoupled) were recorded on a Varian XL-100(15) NMR spectrometer equipped with a Nicolet TT-100 PFT accessory operating at 100.1 MHz for ^1H and at 40.5 MHz for ^{31}P signals with $(CH_3)_4Si$ as internal standard for ^1H and 85% phosphoric acid as external standard for ^{31}P. Infrared spectral data were collected on a Perkin-Elmer 681 spectrophotometer with the samples in potassium bromide pellets. Elemental microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Rotations of optically active compounds were determined on a Rudolf Model 80 polarimeter at the sodium D line using a 1-dm cell. The designation *c* refers to concentration in g/100 mL. Unless otherwise specified, commercial reagent grade chemicals were used directly without further purification. The 115% polyphosphoric acid (PPA) was obtained from FMC Corp. Anhydrous solvents such as ether were dried over sodium and filtered prior to use. Dowex 1-X8 (Cl^-) was used as the packing in an anion-exchange column.

1,1′-(1,2-Ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Diperchlorate (3). A Mixture of (±)-3 and *meso*-3. The bis(phosphonium) dichloride **11** (3.0 g, 4.9 mmol) was slowly added to 60 g of 115% PPA at 180 °C with stirring for an additional 1 h. The solution was cooled to 120 °C and was slowly poured into 500 g of crushed ice with continuous stirring to give a homogeneous solution. Upon the addition of 40 mL of aqueous solution containing 15 g of $NaClO_4$, a heavy precipitate separated. The precipitate was filtered and washed profusely with water. Dissolution of the precipitate in H_2CCl_2 (ca. 25 mL), followed by dropwise treatment with ether, produced crude **3**. Reprecipitation (H_2CCl_2–ether) gave 2.5 g (69%) of **3**, mp 254–258 °C. The rather wide melting point range of **3** is understandable in view of the possible existance of the two diastereomers. The existence of the racemic and *meso* forms of **3** in the ratio ca. 5:4 in the mixture was indicated by the two ^{31}P NMR signals at +15.86 and +14.83 ppm, respectively, downfield from 85% phosphoric acid in $DCCl_3$ (with a drop of F_3CCO_2H added to it). The separation of *rac*-**3** and *meso*-**3** was accomplished as will be described.

Separation of *meso*-1,1′-(1,2-Ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Diperchlorate (*meso*-3). The diperchlorate mixture **3** (24.0 g, 0.3 mol) was dissolved in 350 mL of H_2CCl_2, and dry ether (ca. 50 mL) was added slowly until the solution became cloudy. The mixture became clear upon standing, and the solid which separated was filtered and dried to give 3 g of the first fraction, mp 286–288 °C. The filtrate was made cloudy by the dropwise addition of ether. After 2 h, the solid separated was collected by filtration to give 3.5 g of the second fraction, mp 284–286 °C. Reprecipitation of the resulting filtrate (dry ether) was repeated five more times, and the successive crops of diperchlorate were collected. Each of the five crops had a melting point of 282–284 °C (3.0 g), 258–260 °C (2.0 g), 248–250 °C (3.0 g), 238–240 °C (3.5 g), and 230–234 °C (2.5 g), respectively. The *meso*-3 was isolated by combining the first three fractions (9.5 g) and recrystallizing the latter from hot methanol (ca. 500 mL) to obtain 8.0 g (75%) of *meso*-**3**: mp 291–293 °C; IR (KBr) ν 1439 (P-C_6H_5), 1085 (ClO_4), 999 (P-C_6H_5) cm^{-1}; ^1H NMR ($DCCl_3$–TFA, 20:1) δ 1.37 (s, 6 H, CH_3), 1.42 (s, 6 H, CH_3), 1.62–3.38 (m, 12 H, CH_2), 7.38–8.04 (m, 18 H, ArH). The lone ^{31}P NMR signal at +14.85 ppm (85% phosphoric acid; $DCCl_3$–TFA, 20:1) confirmed the separation of the pure meso form.

Anal. Calcd for $C_{36}H_{42}P_2Cl_2O_8$: C, 58.78; H, 5.75; P, 8.72. Found: C, 58.85; H, 5.81; P, 8.59. The last four crops (11 g) enriched with racemic form were used to isolate *rac*-3.

Preparation and Separation of (±)-1,1′-(1,2-Ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Bis(tetraphenylborate) [(±)-4]. The racemic-enriched mixture from the last four fractions of diperchlorate **3** (11.0 g), from the above experiment, were combined and fractionally crystallized (hot CH_3OH). There resulted 1.4 g of a mixture of (±)-**3** and *meso*-**3** in the ratio of ca 11:1 as depicted by ^{31}P NMR analysis (+16.15 and +14.85 ppm). Further attempts to obtain the pure (±)-**3** were unsuccessful and hence enriched (±)-**3** was converted into enriched (±)-**4** as follows: The 11:1 racemic-enriched mixture of diperchlorates (1.4 g, 1.9 mmol) was dissolved in 100 mL of boiling methanol, and the solution was filtered into an aqueous solution (20 mL) containing 2 g of sodium tetraphenylborate. The resulting mixture was stirred for 30 min. The solid which separated was reprecipitated (H_2CCl_2–ether) to yield 2.1 g (94%) of **4**, mp 214–217 °C. The enriched racemic **4** (2.1 g, 1.8 mmol) was dissolved in 200 mL of H_2CCl_2, and the solution was filtered to remove any insoluble, floating solid. Dry ether was added dropwise until the solution became cloudy, and the mixture was allowed to stand overnight. Crystals separated and were filtered off and reprecipitated (H_2CCl_2–ether) to give 0.9 g (4% based on **3**) of shining crystals of (±)-**4**: mp 218–220 °C; IR (KBr) ν 1439 (P-C_6H_5), 1112 (P-C_6H_5), 998 (P-C_6H_5) cm^{-1}; ^1H NMR ($DCCl_3$–TFA, 20:1) δ 1.39 (s, 12 H, CH_3), 1.48–3.94 (m, 12 H, CH_2), 7.26–8.00 (m, 58 H, ArH). A lone ^{31}P NMR signal at +16.24 ppm (85% phosphoric acid; $DCCl_3$–TFA, 20:1) confirmed the achievement of the separation of pure racemic form of **4**.

Anal. Calcd for $C_{84}H_{82}P_2B_2$: C, 85.86; H, 7.03; P, 5.27. Found: C, 85.90; H, 7.04; P, 5.33.

(±)-1,1′-(1,2-Ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Dichloride [(±)-5]. The anion-exchange resin, Dowex 1-X8 (Cl^-) (40.0 g), was packed on a column (50 × 1.5 cm) and washed with 100 mL of solution of H_3CCN and H_2O (4:1). A solution of 2.0 g (1.7 mmol) of (±)-**4** in 200 mL of a solution of H_3CCN and H_2O (4:1) was passed through the column at a rate of 1 drop/min. This column was eluted with 200 mL of a solution of H_3CCN and H_2O(4:1), followed by washing with the same solvent mixture. All the eluates were combined and evaporated to dryness. The residue was dissolved in 30 mL of acetone and again evaporated to dryness. To the residue obtained was added 50 mL of H_2CCl_2, and the solution was dried (Na_2SO_4). Reprecipitation was effected by the addition of excess ether (30 mL) and allowing the solution to stand overnight. The solid separated was collected by filtration and reprecipitated (H_2CCl_2–ether) to give (±)-**5** [1.03 g (qt); mp 211–216 °C]. The bis(phosphonium) dichloride (±)-**5** was soluble in H_2O, H_3COH, and C_2H_5OH, but it was insoluble in ether. The product gave a positive halogen test $AgNO_3$). The dichloride, being hygroscopic, was characterized as its diperchlorate derivative (±)-**3**.

(±)-1,1′-(1,2-Ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Diperchlorate [(±)-3]. An aqueous solution (5 mL) containing 2.0 g of $NaClO_4$ was added dropwise to (±)-**5** (0.1 g, 0.16 mmol) in 2 mL of water at room temperature with stirring for 15 min. The solid formed was collected by filtration and dissolved in H_2CCl_2 (ca. 10 mL). The solution was dried (Na_2SO_4) and reprecipitated (H_2CCl_2–ether) to give 0.082 g (68%) of (±)-**3**: mp 256–258 °C; IR (KBr) ν 1438 (P-C_6H_5), 1085 (ClO_4), 998 (P-C_6H_5) cm^{-1}; ^1H NMR ($DCCl_3$–TFA, 20:1) δ 1.37 (s, 6 H, CH_3), 1.42 (s, 6 H, CH_3), 1.72–3.74

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(m, 12 H, CH_2), 7.30–8.04 (m, 18 H, ArH). The ^{31}P magnetic resonance absorption of (±)-**3** occurred at +15.93 ppm ($DCCl_3$–TFA, 20:1) relative to 85% phosphoric acid.

Anal. Calcd for $C_{36}H_{42}P_2Cl_2O_8$: C, 58.78; H, 5.75; P, 8.42. Found: C, 58.78; H, 5.89; P, 8.47.

***meso*-1,1′-(1,2-Ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Dichloride (*meso*-5).** A solution of 4.0 g (5.4 mmol) of *meso*-**3** (diperchlorate) in 250 mL solution of H_3CCN and H_2O (1:1) was passed through a column packed with Dowex 1-X8 (Cl^-) (40.0 g) which had been previously washed with a 100-mL solution of H_3CCN and H_2O (1:1). The column was eluted (rate of 2 drops/min) with 250 mL of H_3CCN and H_2O (1:1), followed by washing with 200 mL of the same solvent mixture. Evaporation of the eluant gave a residue which was dissolved in 30 mL of acetone. This solution was again evaporated to dryness, and the residue was dissolved in H_2CCl_2 (ca. 50 mL). The solution was dried (Na_2SO_4) and concentrated (ca. 30 mL). Ether (30 mL) was added, and the solution was allowed to stand overnight. A solid formed was filtered and reprecipitated (H_2CCl_2–ether) to give 3.3 g (qt) of *meso*-**5**, mp 257–259 °C. The *meso*-**5** was soluble in H_2O and C_2H_5OH but not in ether. It gave a positive halogen test ($AgNO_3$) and was characterized via its diiodide derivative, *meso*-**6**.

***meso*-1,1′-(1,2-Ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Diiodide (*meso*-6).** An aqueous solution (2 mL) containing 0.2 g (0.33 mmol) of *meso*-**5** was added dropwise to an aqueous solution (5 mL) containing 2.0 g of NaI at room temperature with stirring for 30 min. The solid formed was filtered and dissolved in H_2CCl_2 (ca. 10 mL). The solution was dried (Na_2SO_4), filtered, and concentrated (ca. 5 mL). Reprecipitation was effected by the dropwise addition of ether until the solution became cloudy. After the mixture was left standing overnight, a solid formed. This was filtered and reprecipitated (CH_3OH–ether) to give 0.2 g (77%) of *meso*-**6**: mp 324 °C dec; IR (KBr) ν 1438 (P-C_6H_5), 1115 (P-C_6H_5), 998 (P-C_6H_5) cm^{-1}; ^1H NMR ($DCCl_3$–TFA, 20:1) δ 1.37 (s, 6 H, CH_3), 1.43 (s, 6 H, CH_3), 1.58–3.62 (m, 12 H, CH_2), 7.42–8.38 (m, 18 H, ArH). The ^{31}P NMR spectrum of *meso*-**6** showed absorption at +15.13 ppm ($DCCl_3$–TFA, 20:1) relative to 85% phosphoric acid.

Anal. Calcd for $C_{36}H_{42}P_2I_2$: C, 54.70; H, 5.35; P, 7.84. Found: C, 54.81; H, 5.48; P, 7.60.

Silver Hydrogen L(+)- and D(−)-Dibenzoyltartrates (HDBTS). AgL(+)-HDBT and AgD(−)-HDBT were prepared according to the procedure described by Coyne and co-workers[26] from L(+)-dibenzoyltartaric acid monohydrate [mp 83–85 °C; $[\alpha]^{23}{}_D = +108°$ (*c* 3.00, acetone) (lit.[27] mp 84–86 °C, $[\alpha]^{25}{}_D = +109°$)] and D(−)-dibenzoyltartaric acid monohydrate [mp 87–89 °C, $[\alpha]^{23}{}_D = -110°$ (*c* 3.00, acetone) (lit.[28] mp 88–90 °C, $[\alpha]^{11}{}_D = -114.8°$)], respectively.

Resolution of (±)-1,1′-(1,2-Ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Dichloride [(±)-5]. Synthesis and Separation of (−)-1,1′-(1,2-Ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Bis[hydrogen L(+)-dibenzoyltartrate] [(−)-7]. The bis(phosphonium) dichloride (±)-**5** (0.4 g, 0.66 mmol) dissolved in 20 mL of H_3COH was slowly added to a suspension of AgL(+)-HDBT (0.62 g, 1.33 mmol) in boiling H_3COH (20 mL), and the mixture was boiled for a period of 1 h. The white AgL(+)-HDBT slowly dissolved during the reaction and AgCl precipitated. The mixture was cooled, and AgCl was filtered. The filtrate was evaporated to dryness, and the residue was dissolved in ca. 20 mL of H_2CCl_2. This solution was treated with activated charcoal and filtered. The filtrate was concentrated to ca. 10 mL, and excess (ca. 10 mL) dry ether was added. A solid separated was filtered and dried in vacuo to give 0.7 g of crude white (±)-**7** [L(+)-HDBT]: mp 152–154 °C dec; $[\alpha]^{24}{}_D = +92.5°$ (*c* 1.00, H_3COH). The ^{31}P NMR analysis of (±)-**7** displayed two signals at +17.26 and +17.03 ppm (1:1) and was indicative of the existence of two diastereomers in equal amounts in the reaction product (±)-**7** [L(+)-HDBT]. The diastereomers of (±)-**7** were separated by fractional crystallization. The (±)-**7** (0.4 g 0.32 mmol) dissolved in 20 mL of $HCCl_3$ was filtered to remove insoluble matter and concentrated to ca. 10 mL. Dry ether was added dropwise until the solution became cloudy. After the mixture had stood for 6 h, it was filtered to yield the first fraction of **7** (0.055 g, mp 149–151 °C dec). Two more fractions were obtained from the filtrate by reprecipitation using dry ether. Each of the fractions had a melting point of 150–152 °C dec (0.100 g) and 149–151 °C dec (0.045 g), respectively. These three fractions were combined and reprecipitated thrice ($HCCl_3$–ether) to yield 0.135 g (72%) of (−)-**7** [L(+)-HDBT]: mp 151–153 °C dec; $[\alpha]^{21}{}_D = +60.5°$ (*c* 1.00, H_3COH); IR (KBr) ν 1725 (C=O), 1438 (P-C_6H_5), 1114 (P-C_6H_5) cm^{-1}. The lone ^{31}P signal at +16.97 ppm ($DCCl_3$) relative to 85% phosphoric acid confirmed the separation of (−)-**7**.

Subsequent precipitations of this material failed to cause any variance in these analytical data.

Anal. Calcd for $C_{72}H_{68}O_{16}P_2$: C, 69.11; H, 5.48; P, 4.95. Found: C, 68.98; H, 5.46; P, 5.03.

Metathesis of (−)-1,2-Ethanediylbis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Bis[hydrogen L(+)-dibenzoyltartrate] [(−)-7] to the Corresponding Diperchlorate (−)-3. A solution of (−)-**7** [L(+)-HDBT] (0.08 g, 0.064 mmol) in 2 mL of H_3COH was added to an aqueous solution (5 mL) of $NaClO_4$ (2.0 g, 0.016 mol), and the solution was stirred for 30 min. The solid formed was collected by filtration, washed profusely with water, and dissolved in ca. 20 mL of H_2CCl_2. This solution was dried (Na_2SO_4) and concentrated (ca. 5 mL). Dry ether was added until the solution became cloudy, and the mixture was allowed to stand overnight. The solid was filtered and reprecipitated twice (H_2CCl_2–ether) to give 37 mg (79%) of pure enantiomer (−)-**3**: mp 262.5–264 °C; $[\alpha]^{22}{}_D = -18.5°$ (*c* 1.00, acetone); IR (KBr) ν 1438 (P-C_6H_5), 1085 (ClO_4), 998 (P-C_6H_5) cm^{-1}; ^1H NMR ($DCCl_3$–TFA, 20:1) δ 1.37 (s, 6 H, CH_3), 1.41 (s, 6 H, CH_3), 1.72–3.64 (m, 12 H, CH_2), 7.44–8.05 (m, 18 H, ArH). The ^{31}P NMR spectrum ($DCCl_3$–TFA, 20:1) exhibited a single signal at +16.03 ppm relative to 85% phosphoric acid.

Anal. Calcd for $C_{36}H_{42}P_2Cl_2O_8$: C, 58.78; H, 5.75; P, 8.42. Found: C, 58.78; H, 5.92, P, 8.40.

Resolution of (±)-1,1′-(1,2-Ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Dichloride [(±)-5]. Synthesis and Separation of (+)-1,1′-(1,2-Ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Bis[hydrogen D(−)-dibenzoyltartrate] [(+)-8]. The bis(phosphonium) dichloride (±)-**5** (0.4 g, 0.66 mmol) and silver hydrogen D(−)-dibenzoyltartrate (0.62 g, 1.33 mmol) were allowed to react in the same manner utilized for the L(+) isomer to give 0.55 g of (±)-**8** [D(−)-HDBT]: mp 151–153 °C dec; $[\alpha]^{24}{}_D = -91.5°$ (*c* 1.00, H_3COH). The ^{31}P NMR analysis of (±)-**8** [D(−)-HDBT] displayed two signals at +17.21 and 17.44 ppm (1:1), indicating the existence of two diastereomers in equal amounts in the reaction product (±)-**8** [D(−)-HDBT]. Four reprecipitations ($HCCl_3$–ether) of (±)-**8** [D(−)-HDBT] (0.4 g, 0.32 mmol) were sufficient to produce 85 mg (45%) of (+)-**8** with a constant melting point and constant specific rotation; mp 147.5–149 °C dec; $[\alpha]^{20}{}_D = -60.0°$ (*c* 1.00, H_3COH); IR (KBr) ν 1724 (C=O), 1439 (P-C_6H_5), 1112 (P-C_6H_5), 998 (P-C_6H_5) cm^{-1}; a lone ^{31}P NMR signal at +16.90 ppm (85% phosphoric acid; $DCCl_3$) shown by (+)-**8** further confirmed the separation of the pure diastereomer. The inclusion of 1 equiv of water was detected also (as revealed by elemental analysis) in crystalline (+)-**8**. Such inclusion of solvent is not uncommon with phosphonium salts.[4,13,14]

Anal. Calcd for $C_{72}H_{68}O_{16}P_2 \cdot H_2O$: C, 68.13; H, 5.56; P, 4.88. Found: C, 68.17; H, 5.50; P, 4.80.

Metathesis of (+)-1,1′-(1,2-Ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Bis[hydrogen D(−)-dibenzoyltartrate] [(+)-8] to the Corresponding Diperchlorate (+)-3. Utilizing the procedure previously described for metathesis, 0.06 g (0.048 mmol) of (+)-**8** and an aqueous solution (5 mL) of $NaClO_4$ (2.0 g, 0.016 mol) reacted to give, after two reprecipitations (H_2CCl_2–ether), 26 mg (74%) of (+)-**3**: mp 263–264 °C; $[\alpha]^{26}{}_D = +19.1°$ (*c* 1.00, acetone); IR (KBr) ν 1439 (P-C_6H_5), 1085 (ClO_4), 998 (P-C_6H_5) cm^{-1}; ^1H NMR ($DCCl_3$–TFA, 20:1) δ 1.36 (s, 6 H, CH_3), 1.40 (s, 6 H, CH_3), 1.70–3.64 (m, 12 H, CH_2), 7.44–8.02 (m, 18 H, ArH). The ^{31}P NMR spectrum of (+)-**3** showed absorption at +16.04 ppm ($DCCl_3$) relative to 85% phosphoric acid.

Anal. Calcd for $C_{36}H_{42}P_2Cl_2O_8$: C, 58.78; H, 5.75; P, 8.42. Found: C, 58.73; H, 5.88; P, 8.46.

***meso*-1,1′-(1,2-Ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Bis[hydrogen L(+)-dibenzoyltartrate] (*meso*-7).** The bis(phosphonium) dichloride, *meso*-**5** (0.5 g, 0.8 mmol) and silver hydrogen L(+)-dibenzoyltartrate (0.8 g, 1.7 mmol) were allowed to react in the same manner utilized for the resolution of (±)-**7** to give 0.95 g (95%) of *meso*-**7** [L(+)-HDBT]: mp 153–155 °C (dec; $[\alpha]^{24}{}_D = +92.5°$ (*c* 1.00, H_3COH); IR (KBr) ν 1724 (C=O), 1439 (P-C_6H_5), 1112 (P-C_6H_5) 998 (P-C_6H_5) cm^{-1}; ^1H-decoupled ^{31}P NMR ($DCCl_3$) +15.58, +15.62 ppm (relative to 85% phosphoric acid).

Anal. Calcd for $C_{72}H_{68}O_{16}P_2 \cdot H_2O$: C, 68.13; H, 5.56; P, 4.88. Found: C, 67.97; H, 5.56; P, 4.80.

Metathesis of *meso*-1,1′-(1,2-Ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Bis[hydrogen L(+)-dibenzoyltartrate] (*meso*-7) to the Corresponding Diperchlorate *meso*-3. Utilizing the procedure previously described for metathesis, 200 mg (0.16 mol) of *meso*-**7** [L(+)-HDBT] and 10 mL of an aqueous solution of $NaClO_4$ (2.0 g, 0.016 mol) reacted and gave, after two reprecipitations (H_2CCl_2–ether), 0.095 g (80%) of *meso*-**3**: mp 291–293 °C; $[\alpha]^{21}{}_D = 0°$ (*c* 1.00,

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acetone) which was identical to *meso*-**3** separated from the diastereomeric mixture of **3**.

***meso*-1,1′-(1,2-Ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Bis[hydrogen D(−)-dibenzoyltartrate] (*meso*-8).** Utilizing the procedure previously described for resolution of (±)-**5**, 0.5 g (0.8 mmol) of *meso*-**5** and 0.8 g (1.7 mmol) of silver hydrogen D(−)-dibenzoyltartrate reacted to give 0.75 g (75%) of *meso*-**8** [D(−)-HDBT]: mp 149–151 °C dec; $[\alpha]^{24}_{D} = -91.3°$ (*c* 1.00, H_3COH); IR (KBr) ν 1724 (C=O), 1440 ($P\text{-}C_6H_5$), 1112 ($P\text{-}C_6H_5$), 998 ($P\text{-}C_6H_5$) cm^{-1}; ^1H-decoupled ^{31}P NMR ($DCCl_3$) +15.51; +15.54 ppm (relative to 85% phosphoric acid).

Anal. Calcd for $C_{72}H_{68}O_{16}P_2$: C, 69.11; H, 5.48; P, 4.95. Found: C, 68.96; H, 5.44; P, 4.96.

Metathesis of *meso*-1,1′-(1,2-Ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Bis[hydrogen D(−)-dibenzoyltartrate] (*meso*-8) to the Corresponding Diperchlorate (*meso*-3). The phosphonium salt, *meso*-**8** [D(−)-HDBT] (200 mg, 0.16 mmol) and an aqueous solution (10 mL) of $NaClO_4$ (2.0 g, 0.016 mol) were allowed to react in the same manner utilized for metathesis of (−)-**7** [L(+)-HDBT] to give 0.085 g (75%) of *meso*-**3**, mp 291–293 °C, $[\alpha]^{24}_{D} = 0°$ (*c* 1.00, acetone) which was identical to *meso*-**3** separated from the diastereomeric mixture of **3**.

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Registry No. (±)-**3**, 80799-71-9; *meso*-**3**, 80799-73-1; (+)-**3**, 80799-75-3; (−)-**3**, 81207-46-7; (±)-**4**, 81207-47-8; (±)-**5**, 81207-48-9; *meso*-**5**, 80799-76-4; *meso*-**6**, 81207-49-0; (±)-**7**, 81207-50-3; *meso*-**7**, 81207-51-4; (−)-**7**, 81207-52-5; (±)-**8**, 81207-53-6; *meso*-**8**, 81207-54-7; (+)-**8**, 81219-01-4; **11**, 81194-90-3.

Synthesis and Thermal Decomposition of 1,3-Dithietane and Its *S*-Oxides[1-3]

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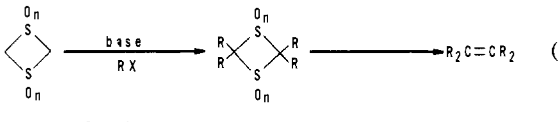
Abstract: Syntheses of 1,3-dithietane (**1**), 1,3-dithietane 1-oxide (**2**), 1,3-dithietane 1,1-dioxide (**3**), *cis*-1,3-dithietane 1,3-dioxide (**4**), *trans*-1,3-dithietane 1,3-dioxide (**5**), and 1,3-dithietane 1,1,3-trioxide (**6**) are reported for the first time. These compounds are converted in high yield to the previously described sulfene dimer 1,3-dithietane 1,1,3,3-tetraoxide (**7**). The structures of **2** and **7** are found to be respectively puckered (by microwave spectroscopy) and planar (by X-ray crystallography). Spectroscopic and physical data are discussed (photoelectron (PE) and NMR spectroscopy, pK_a values, oxidation potentials) along with some data on base-catalyzed H/D exchange. The PE spectra are assigned using MO models on different levels, including PNO/CEPA for thioformaldehyde (CH_2S). Thermal decomposition is investigated using three independent methods: mass, microwave, and PE spectroscopy. Two types of decomposition channels are observed: retro 2 + 2 and retro 3 + 1. Among others, species like thioformaldehyde and sulfine (CH_2SO, thioformaldehyde *S*-oxide) are produced. They are characterized by their microwave structure as well as by their PE ionization patterns and IR spectra.

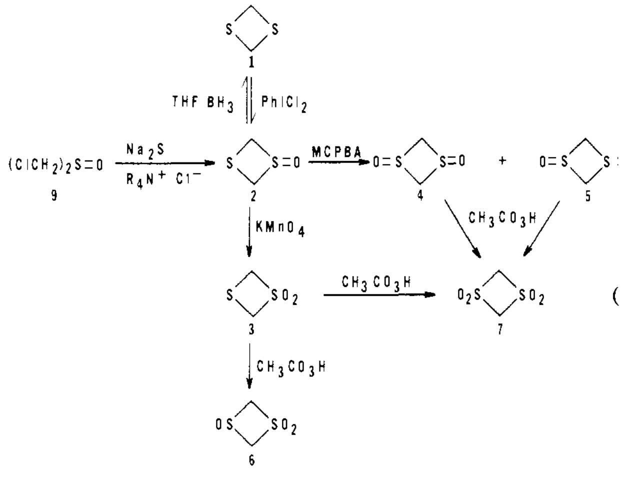
I. Introduction

The search for a new olefin synthesis based on the tetraalkylation–two-fold extrusion sequence depicted in eq 1[6] led us to the



(1)

development of a simple synthesis of the hitherto unknown 1,3-dithietane (**1**) and its several *S*-oxides **2**–**7**, utilizing the phase-transfer-catalyzed ring-closure reaction of bis(chloromethyl) sulfoxide with sodium sulfide followed either by reduction or oxidation (eq 2).[7] The synthesis of the novel diheterocyclobutanes



(2)

prompted physical measurements to determine their molecular properties. Thus structures of several of them have determined:

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(1) Part 9 of Flash Vacuum Pyrolysis Studies;[2] Part 101 of Photoelectron Spectra and Molecular Properties.[3]

(2) Part 8: Powers, D. E.; Arrington, C. A.; Harris, W. C.; Block, E.; Kalasinsky, V. F. *J. Phys. Chem.* **1979**, *83*, 1890–1892.

(3) Part 100: Bock, H.; Solouki, B. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 427–444.

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(5) National Science Foundation Undergraduate Research Participant, 1975.

(6) For a related "twofold extrusion" approach to the synthesis of olefins, see: (a) Barton, D. H. R.; Willis, B. J. *J. Chem. Soc., Perkin Trans. 1* **1972**, 305–310. (b) Also see: Block, E. "Reactions of Organosulfur Compounds"; Academic Press: New York, 1978; pp 99–100. (c) Note also: Seelinger, R.; Sundermeyer, W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 203–204.

(7) Preliminary communication: Block, E.; Corey, E. R.; Penn, R. E.; Renken, T. L.; Sherwin, P. F. *J. Am. Chem. Soc.* **1976**, *98*, 5715–5717.

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