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Formation of 1,1,2,3,3-Pentakis(arylthio)-1-propenes from Tris(arylthio)cyclopropenyl Cations and Their Conversion into 1,1,2,5,6,6-Hexakis(arylthio)-(3*E*)-1,3,5-hexatriene

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ABSTRACT: *The reaction of tetrachlorocyclopropene (***1***) with arenethiols (***2a–e***), followed by treatment with perchloric acid, gave tris(arylthio)cyclopropenylium perchlorates (***3a–c** *and* **e***), 1,1,2,3,3-pentakis(arylthio)-1-propenes (***4a–d***), and 2,3,3-tris(arylthio)propenals (***5a–d***). The structures of tris(phenylthio)cyclopropenylium perchlorate (***3a***), 1,1,2,3,3-pentakis(phenylthio)-1-propene (***4a***), and 2,3,3-tris(o-tolylthio)propenal (***5b***) were analyzed by single-crystal X-ray diffraction studies. The yields depended significantly on the electron-withdrawing property of the substituents of the arenethiols and the molar ratio of* **2** *to* **1***. The reaction with 2,6-dimethylbenzenethiol (***2e***) gave only tris(2,6-dimethylphenylthio)cyclopropenylium perchlorate (***3e***) without the formation of* **4e** *and* **5e***. Compounds* **5a–d** *were produced by acid hydrolysis of* **4a–d***. Pyrolysis of* **4a–d** *gave (3R,4S)-1,1,2,3,4,5,6,6-octakis(arylthio)-1,5-hexadienes (***9a–d***) and 1,1,2,5,6,6-hexakis(arylthio)-(3E)-1,3,5-hexatrienes (***10a–d***) together with diaryl disulfides (***11a–d***). Compound* **10a** *was also produced by photolysis.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:387–397, 1998

INTRODUCTION

Tris(alkylthio)cyclopropenylium perchlorates, which can be used as a three-carbon building block in organic synthesis [1], are generally synthesized by the reaction of tetrachlorocyclopropene (**1**) with alkanethiols followed by treatment with perchloric acid [1]. However, the synthesis of tris(arylthio)cyclopropenylium perchlorates is not achieved by this synthetic method using **1** and arenethiols, and the details of the reaction are uncertain. This fact led us to explore the reaction of **1** with arenethiols, such as benzenethiol (**2a**) and methyl, fluoro, and dimethyl-substituted benzenethiols (**2b–e**), and to obtain information about the reactivity of the arylthio-substituted cyclopropenyl cations. This article reveals that tris(arylthio)cyclopropenyl cations (**3a–d**), prepared from **1** and **2a–d,** react consecutively with **2a–d** to give 1,1,2,3,3-pentakis(arylthio)-1-propenes (**4a–d**) by facile ring opening (Scheme 1), al-

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Dedicated to Prof. Heinrich Nöth on the occasion of his seventieth birthday.

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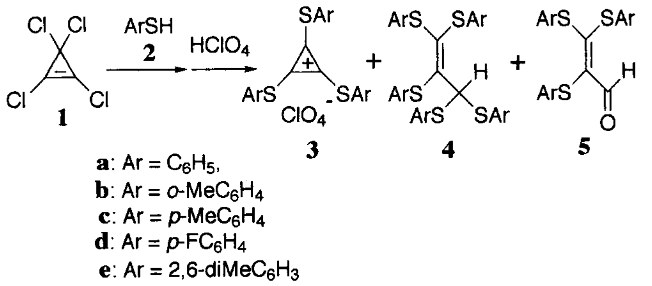
though the reaction with the bulky 2,6-dimethylbenzenethiol (**2e**) gives only the corresponding cyclopropenyl cation **3e.** In these reactions, the yields of **3a–d** and **4a–d** depend significantly on the electron-withdrawing property of the substituents of the arenethiols and the molar ratio of each **2a–d** to **1.** Furthermore, we describe that **4a–d** are converted into the corresponding (3*R*,4*S*)-1,1,2,3,4,5,6,6-octakis(arylthio)-1,5-hexadienes (**9a–d**), 1,1,2,5,6,6-hexakis(arylthio)-(3*E*)-1,3,5-hexatrienes (**10a–d**), and diaryl disulfides (**11a–d**) by pyrolysis or photolysis. A part of this study has been reported in our preliminary article [2].

RESULTS AND DISCUSSION

Reaction of 1 *with Arenethiols*

The reactions were carried out as follows. Each arenethiol **2a–e** (2–5 eq.) was added dropwise under argon to a solution of **1** in dry dichloromethane, and the solution was stirred at room temperature for 3 hours. After addition of an aqueous solution of perchloric acid, the mixture was stirred for 2 hours, and the products, **3, 4,** and **5** were isolated. The structures of **3–5** were determined by their IR, ^{1}H, and ^{13}C NMR spectra and elemental analyses. The IR spectrum of **3a** was identical to that described previously [1]. Compounds **3b, 3c,** and **3e** also exhibit IR spectra analogous to that of **3a.** The ^{13}C NMR spectrum of **3a** in $CDCl_3$ showed four signals, at δ 125.8, 130.7, 131.6, and 133.0, for the phenyl carbons and one signal, at δ 158.5, for the ring carbon of the cyclopropenyl cation. The signals due to the ring carbons of the cyclopropenyl cations of **3b, 3c,** and **3e** appeared at δ 158.1, 158.5, and 159.3, respectively. The ^{1}H and ^{13}C NMR spectra of **4a** in $CDCl_3$ showed the multiplet signals due to the allylic and phenyl protons at δ 6.56–7.56 and the signal due to the carbon of the allyl position at δ 64.5, respectively. Compounds **4b–d** also exhibited ^{1}H and ^{13}C NMR spectra analogous to those of **4a.** The ^{1}H and ^{13}C NMR spectra of **5a** showed the signals for the aldehyde proton at δ 10.30 and for the aldehyde carbon at δ 185.2, respectively. The ^{1}H and ^{13}C NMR spectra of **5b–d** were similar to those of **5a.** Furthermore, the structures of **3a, 4a,** and **5b** were confirmed by a single-crystal X-ray diffraction analysis. The ORTEP drawings and the selected bond lengths and angles of **3a, 4a,** and **5b** are shown in Figures 1–3 and Tables 1, 3, and 5, in which the X-ray diffraction pattern of **3a** is the first example of that of an arylthio-substituted cyclopropenyl cation. (Crystal data and struc-



SCHEME 1

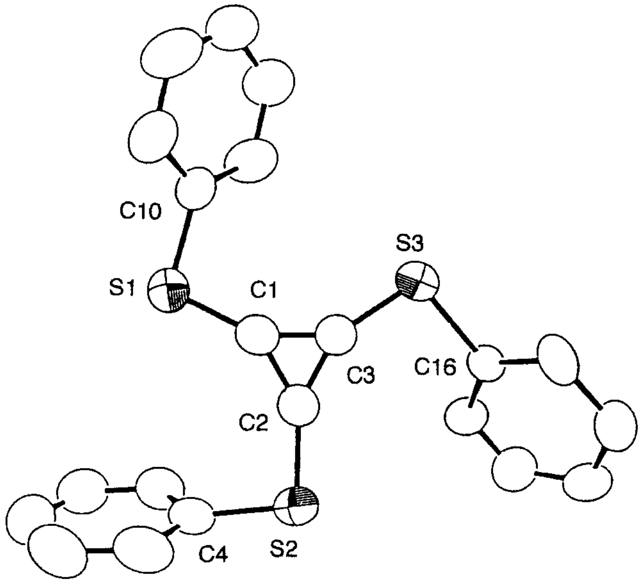


FIGURE 1 ORTEP drawing of **3a.**

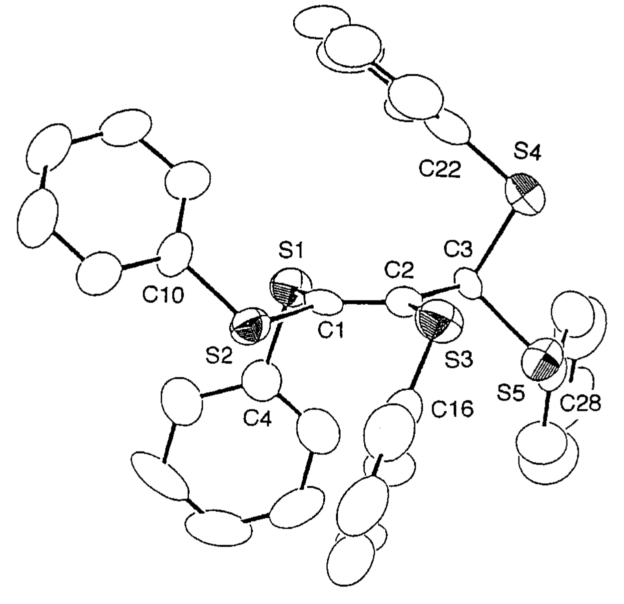


FIGURE 2 ORTEP drawing of **4a.**

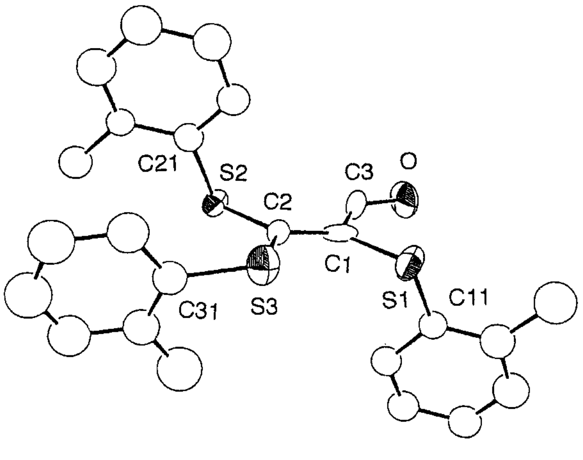


FIGURE 3 ORTEP drawing of **5b.**

TABLE 1 Selected Bond Lengths (Å) and Angles (°) of **3a**

S1-C1	1.674(2)	S3-C16	1.85(2)
S1-C10	1.781(2)	C1-C2	1.368(3)
S2-C2	1.685(2)	C1-C3	1.376(3)
S2-C4	1.789(2)	C2-C3	1.372(3)
S3-C3	1.677(2)		
C1-S1-C10	100.8(1)	S2-C2-C1	147.8(2)
C2-S2-C4	97.1(1)	S2-C2-C3	151.9(2)
C3-S3-C16	97.8(6)	C1-C2-C3	60.3(2)
S1-C1-C2	147.1(2)	S3-C3-C1	147.4(2)
S1-C1-C3	152.8(2)	S3-C3-C2	152.8(2)
C2-C1-C3	60.0(1)	C1-C3-C2	59.7(1)

TABLE 2 Crystal Data and Structure Refinement of **3a**

Empirical formula	$C_{21}H_{15}S_3O_4Cl$
Formula weight	462.98
Crystal color, habit	pale yellow, prismatic
Crystal dimensions (mm)	0.900 × 0.900 × 0.900
Crystal system	triclinic
No. reflections used for unit cell determination (2 θ range)	25(29.8–29.9°)
Lattice parameters:	
a = 10.150(1) Å	α = 103.795(9)°
b = 10.884(1) Å	β = 98.96(1)°
c = 10.016(1) Å	γ = 83.28(1)°
V = 1057.9(5) Å^3	
Space group	p1 (#2)
Z value	2
D_{calc}	1.453 g/cm^3
F_{000}	476
μ(Mo-K_α)	4.87 cm^{-1}
Diffractometer	Rigaku AFC-5R
Radiation	Mo-K_α (λ = 0.71069 Å)
Temperature	23°
Attenuators	Ni foil (factor: 3.6, 12.3, 43.8)
Take-off angle	6.0°
Detector aperture	6.0 × 6.0 mm
Crystal-to-detector distance	25.8 cm
Scan type	$2\theta - \omega$
Scan rate	16.0°/min
Scan width	(1.26 + 0.30 tan θ)°
$2\theta_{max}$	55.1°
No. of reflections measured	total 5157 unique 4876(R_{int} = 0.010)
Corrections	Lorentz-polarization effect absorp. (trans. f: 0.94–1.04)
Structure solution	Patterson method
Refinement	full-matrix least-squares
Function minimized	$\Sigma\, w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Least-squares weights	$4F_0^2/\sigma^2(F_0^2)$
p-Factor	0.05
Anomalous dispersion	all nonhydrogen
No. observations [$F_o > 2.5\ \sigma(F_0)$]	3344
No. variables	352
Reflection/parameter ratio	9.50
Residuals: R; R_w	0.034; 0.056
Goodness-of-fit indicator (GOF)	1.89
Max shift/error in final diff. map	1.16
Maximum peak in final diff. map	0.19 e^-/Å^3
Minimum peak in final diff. map	−0.31 e^-/Å^3

ture refinement of 3a, 4a, and 5a are given in Tables 2, 4, and 6.) Compound **3a** takes on a planar C_3S_3 framework with approximately C_3 symmetry, the three phenyl rings bending by 55.9° on the average, and the bond distances of S1–C1 and S1–C10 are 1.674(2) and 1.781(2) Å, respectively; thus suggesting that the S atom is conjugated with both the benzene and cyclopropenylium rings by participation of the 3d orbital. The S4–C3 bond distance [1.863(9) Å] of **4a** is longer than the other S–C bond distances.

The variation of the yields of **3a–e** and **4a–e** with the molar ratio of each **2a–e** to **1** is shown in Table 7. The yields of **4a–d** increased with increasing molar ratio of **2a–d** to **1**, whereas those of **3a–d** decreased. The formation of **4a** was observed even when the **2a/1** molar ratio was 2:1. In a separate experiment, it was also established that **3a** reacts with 2 eq. of **2a** to give **4a** in 70% yield, thus indicating that **4a** is formed by the consecutive reaction of each of the cyclopropenyl cations (**6a** and **3a**) with **2a.** The predominant formation of **3b,c** was observed when the **2b,c/1** molar ratios were 3:1. On the other hand, in the case of **2b,c/1** ratios of 5:1, **4a** and **4b** were exclusively produced. The reaction of **1** with **2d** gave only **4d,** which did not depend on the molar ratio of **2d/1.** These results indicate that the ease of formation of **4a–d** is in the order of Ar = p-FC_6H_4 >Ar = C_6H_5 >Ar = p-Me- or o-MeC_6H_4, thus depending on the electron-withdrawing property of the substitu-

TABLE 3 Selected Bond Lengths (Å) and Angles (°) of **4a**

S1-C1	1.795(9)	S4-C3	1.863(9)
S1-C4	1.78(1)	S4-C22	1.76(1)
S2-C1	1.762(8)	S5-C3	1.849(9)
S2-C10	1.78(1)	S5-C28	1.79(1)
S3-C2	1.778(9)	C1-C2	1.34(1)
S3-C16	1.77(1)	C2-C3	1.49(1)
C1-S1-C4	98.1(4)	S2-C1-C2	121.9(7)
C1-S2-C10	105.0(5)	S3-C2-C1	121.3(7)
C2-S3-C16	104.6(5)	S3-C2-C3	116.6(7)
C3-S4-C22	99.7(4)	C1-C2-C3	122.1(9)
C3-S5-C28	99.3(5)	S4-C3-S5	105.1(5)
S1-C1-S2	117.4(5)	S4-C3-C2	107.7(7)
S1-C1-C2	120.5(7)	S5-C3-C2	109.3(7)

TABLE 4 Crystal Data and Structure Refinement of **4a**

Empirical formula	$C_{33}H_{26}S_5$
Formula weight	582.90
Crystal color, habit	colorless, prismatic
Crystal dimensions (mm)	0.15 × 0.15 × 0.07
Crystal system	monoclinic
No reflections used for unit cell determination (2 θ range)	24(7.9–18.4°)
Lattice parameters:	
$a = 11.904(5)$ Å	
$b = 21.631\ (4)$ Å	$B = 103.94(3)°$
$c = 11.939\ (5)$ Å	$V = 2984(3)$Å^3
Space group	$P2_1/n$ (no. 14)
Z value	4
D_{calc}	1.295 g/cm^3
F_{000}	1212
μ (Mo-K_α)	3.93 cm^{-1}
Diffractometer	Rigaku AFC-5R
Radiation	Mo-K_α(λ = 0.71069Å)
Temperature	23°
Attenuators	Ni foil (factor: 3.6, 12.1, 43.5)
Take-off angle	6.0°
Detector aperture	6.0 × 6.0 mm
Crystal-to-detector distance	25.8 cm
Scan type	$2\theta - \omega$
Scan rate	16.0°/min
Scan width	$(1.05 + 0.30 \tan \theta)°$
$2\theta_{max}$	50.1°
No. of reflections measured	total 5741 unique 5468 ($R_{in} = 0.089$)
Corrections	Lorentz-polarization effect absorp. (trans. f:0.74–1.04)
Structure solution	direct method
Refinement	full-matrix least-squares
Function minimized	$\Sigma_W(|F_0| - |F_c|)^2$
Least-squares weights	$4F_0^2/\sigma^2(F_0^2)$
p-factor	0.01
Anomalous dispersion	all nonhydrogen
No. observations [$F_0 > 2.5\ \sigma\ (F_0)$]	1554
No. variables	343
Reflection/parameter ratio	4.53
Residuals: R; R_w	0.056; 0.042
Goodness-of-fit indicator (GOF)	1.27
Max shift error in final diff. map	0.32
Maximum peak in final diff. map	0.30 e^-/Å^3
Minimum peak in final diff. map	−0.26 e^-/Å^3

ents of the arenethiols. The reaction of **1** with **2e** gave only **3e** even when the **2e/1** molar ratio was 5:1. This is thought to be caused by the steric hindrance due to the bulky 2,6-dimethylphenyl group.

Plausible Reaction Pathway for the Formation of 4a–d *and* 5a–d

Recent studies have revealed that cyclopropenes, formed by the addition of a nucleophile to tris(alkylthio)cyclopropenyl cations, undergo ring opening to form the vinylcarbene intermediates [3]. From this fact, cyclopropenes **7a–d,** formed by the addition of **2a–d** to the cyclopropenyl cations (**6a–d** and **3a–d**), are thought to undergo ring opening to form the vinylcarbene intermediates **8a–d,** as shown in Scheme 2. This ring-opening reaction is accelerated by the presence of electron-withdrawing substituents, as described earlier. The resulting vinylcarbenes **8a–d** react easily with **2a–d** to give **4a–d.** In the reaction with **2e,** however, **4e** is not obtained. This means that the addition of **2e** to **3e** or **6e** does not occur because of steric hindrance. Compounds **5a–d** are considered to be produced by the acid hydrolysis of **4a–d,** because the treatment of **4a** with HCl in aquous dioxane leads to the formation of **5a.**

Pyrolysis of 4a–d *and Photolysis of* 4a

The pyrolysis of each **4a–d** was carried out using a bulb-to-bulb distillation apparatus under 190°C/5 mm Hg for 3 hours. The reaction mixtures were purified by column chromatography on silica gel to give (3*R*,4*S*)-1,1,2,3,4,5,6,6-octakis(arylthio)-1,5-hexadienes (**9a–d**) and 1,1,2,5,6,6-hexakis(arylthio)-(3*E*)-1,3,5-hexatrienes (**10a–d**) together with diaryl disulfides (**11a–d**) [4] (Scheme 3). The structures of the products were determined by their IR, ^{1}H and ^{13}C NMR spectra and elemental analyses. In addition, the structures of **9a** and **10b** were confirmed by single-crystal X-ray diffraction analyses. The ORTEP drawings and the selected bond lengths and angles of **9a** and **10b** are shown in Figures 4 and 5 and Tables 8 and 10. The S4–C3 bond length (1.844 Å) of **9a** is longer than the other S–C bond length (about 1.78 Å). Crystal data and structure refinement of 9a and 10b are given in Tables 9 and 11.

TABLE 5 Selected Bond Lengths (Å) and Angles (°) of **5b**

S1-C1	1.78(1)	S3-C31	1.80(1)
S1-C11	1.75(1)	C1-C2	1.36(1)
S2-C2	1.75(1)	C1-C3	1.49(2)
S2-C21	1.77(1)	C3-O	1.16(2)
S3-C2	1.75(1)	C1-H1	1.34(1)
C1-S1-C11	101.8(6)	S2-C2-S3	120.3(7)
C1-S2-C21	100.9(6)	S2-C2-C1	120.8(9)
C2-S3-C31	104.6(6)	S3-C2-C1	118.9(9)
S1-C1-C2	120.4(9)	C1-C3-O	122.1(9)
S1-C1-C3	115(1)	C1-C3-H1	110.28
C2-C1-C3	124(1)	O-C3-H1	122.42

TABLE 6 Crystal Data and Structure Refinement of **5b**

Empirical formula	$C_{24}H_{22}OS_3$
Formula weight	422.6
Crystal color, habit	colorless, rod
Crystal dimensions (mm)	0.50 × 0.10 × 0.10
Crystal system	orthorhombic
No. reflections, used for unit cell determination (2 θ range)	24(18.2–24.0°)
Lattice parameters:	
a = 16.457(3) Å	
b = 17.304(3) Å	
c = 7.519(1) Å	V = 2141.1(4) Å^3
Space group	$P2_12_12_1$ (no. 19)
Z value	4
D_{calc}	1.311 g/cm^3
F_{000}	888
μ (Mo-K_α)	3.43 cm^{-1}
Diffractometer	Rigaku AFC-5R
Radiation	Mo-K_α (λ = 0.71069 Å)
Temperature	23°
Attenuators	Ni foil (factor: 3.6, 12.3, 44.1)
Take-off angle	6.0°
Detector aperture	6.0 × 6.0 mm
Crystal-to-detector distance	25.8 cm
Scan type	$2\theta - \omega$
Scan rate	8.0°/min
Scan width	$(1.05 + 0.30 \tan \theta)°$
$2\theta_{max}$	51.3°
No. of reflections measured	unique 2208
Corrections	Lorentz-polarization effect absorp. (trans. f: 0.93–1.00)
Structure solution	Patterson method
Refinement	full-matrix least-squares
Function minimized	$\Sigma w(\lvert F_0\rvert - \lvert F_c\rvert)^2$
Least-squares weights	$4F_0^2/\sigma^2(F_0^2)$
p-Factor	0.01
Anomalous dispersion	all nonhydrogen
No. observations [$F_0 > 3.0\ \sigma(F_0)$]	878
No. variables	148
Reflection/parameter ratio	5.93
Residuals: R; R_w	0.060; 0.044
Goodness-of-fit indicator (GOF)	1.63
Max shift/error in final diff. map	0.67
Maximum peak in final diff. map	0.31e^-/Å^3
Minimum peak in final diff. map	−0.28e^-/Å^3

The yields of the products are summarized in Table 12. The pyrolyses of **4a–d** at 190°C/5 mm Hg gave **10a–d** and **11a–d** as the major products, accompanied by the formation of **9a,c.** On the other hand, the pyrolysis of **4a** at lower temperature (160°C/5 mm Hg, 10 h) gave **9a** as the major product without the formation of **10a.** In a separate experiment, it was observed that the pyrolysis of **9a** at 190°C/5 mm Hg gives **10a** and **11a** in 78 and 87% yields, respectively, thus indicating that **10a** is formed via **9a** and the conversion of **9a** into **10a** occurs at a temperature near 190°C. Furthermore, it was found that irradiation of **4a** in dry benzene under nitrogen with light of wavelength >280 nm at room temperature for 1 hour gave **10a** and **11a** in 74 and 85% yields, respectively, without any detectable formation of **9a.** Compounds **10a** and **11a** were also produced from **9a** by photolysis in 80 and 90% yields, respectively. When the photolysis of **4a** was carried out in the presence of oxygen, no reaction occurred, and **4a** was recovered in a quantitative yield. From these results, the reaction is thought to be initiated by the homolytic cleavage of the C(sp^3)–SAr bond of **4a–d.** The resulting radicals **12a–d** dimerize to form **9a–d** in the meso form that has a more stable conformation, and then the homolysis of the C(sp^3)–SAr bonds of **9a–d** leads to the formation of **10a–d** and **11a–d,** as shown in Scheme 4.

EXPERIMENTAL

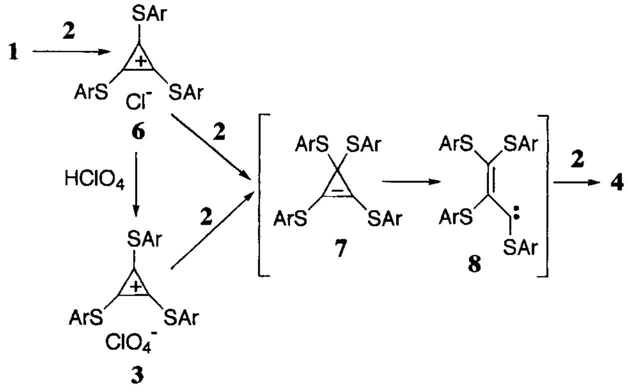
Melting points were determined on a Yanaco MP-S3 melting-point apparatus and are uncorrected. IR spectra were recorded on a Perkin–Elmer model 1600 FT spectrometer. UV spectra were obtained on a Shimadzu UV-160 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-GX 270 FT spectrometer for solutions in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded on a JEOL-DX303HF instrument. Elemental analyses were performed by a Yanaco CHN CORDER MT-3. Column chromatography was performed on silica gel (Wakogel C-300).

Reaction of **1** *with* **2a–e.** To a solution of **1** (50 mmol) in dry dichloromethane (150 mL) was added dropwise **2a–e** (150–250 mmol), and the mixture was stirred under argon at room temperature for 3 hours. Then, 70 w/w% perchloric acid (100 mmol)–H_2O was

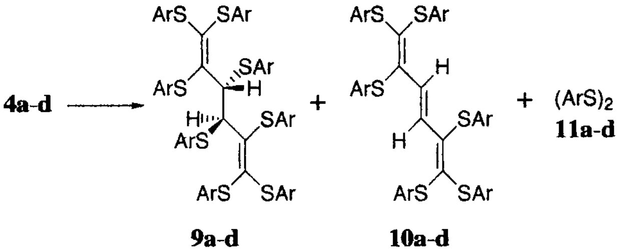
TABLE 7 The Yields of **3a–e, 4a–e,** and **5a–e** in Various Molar Ratios of **2a–e** to **1**

ArSH	*Molar Ratio* **2a–e : 1**	*Yield, %*[a] **3a–e**	**4a–e**	**5a–e**
2a (Ar = C_6H_5)	2 : 1	43	13	0
2a	3 : 1	20	35	10
2a	4 : 1	5	60	0
2a	5 : 1	0	91	0
2b (Ar = *o*-MeC_6H_4)	3 : 1	60	15	0
2b	5 : 1	0	63	27
2c (Ar = *p*-MeC_6H_4)	3 : 1	50	9	18
2c	5 : 1	0	72	10
2d (Ar = *p*-FC_6H_4)	3 : 1	0	40	12
2d	5 : 1	0	72	5
2e (Ar = 2,6-diMeC_6H_3)	3 : 1	28	0	0
2e	5 : 1	26	0	0

[a]Isolated yields based on **1.**



SCHEME 2



SCHEME 3

added under ice cooling, and the mixture was stirred at room temperature for 2 hours. After addition of water (150 mL), the mixture was stirred for 1 hour. The organic layer was separated, washed with water (100 mL × 7), dried over anhydrous sodium sulfate, and evaporated under reduced pressure. Dichloro-

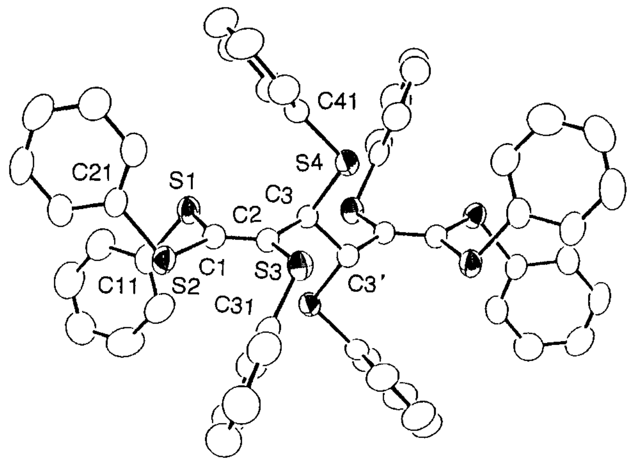


FIGURE 4 ORTEP drawing of **9a.**

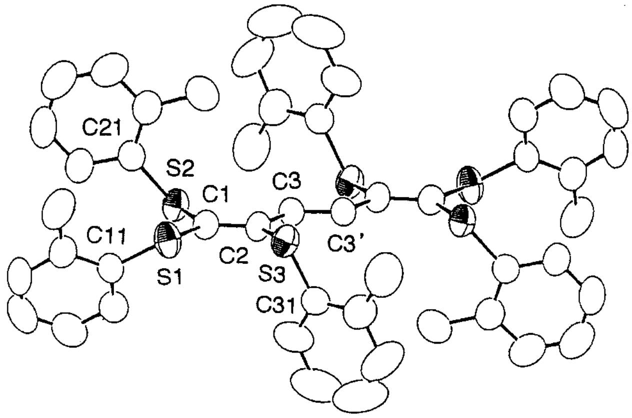


FIGURE 5 ORTEP drawing of **10b.**

TABLE 8 Selected Bond Lengths (Å) and Angles (°) of **9a**

S1-C1	1.778(3)	S4-C3	1.844(3)
S1-C11	1.771(4)	S4-C41	1.770(4)
S2-C1	1.771(3)	C1-C2	1.329(4)
S2-C21	1.779(4)	C2-C3	1.520(4)
S3-C2	1.777(3)	C3-C3′	1.564(6)
S3-C31	1.769(4)	C3-H3	0.951
C1-S1-C11	102.8(2)	S3-C2-C3	112.7(2)
C1-S2-C21	101.3(2)	C1-C2-C3	122.7(3)
C3-S3-C31	106.8(2)	S4-C3-C2	108.4(2)
C3-S4-C41	100.8(2)	S4-C3-C3′	105.1(3)
S1-C1-S2	116.3(2)	C2-C3-H3	126.2(4)
S1-C1-C2	121.5(3)	C2-C3-C3′	113.5(3)
S2-C1-C2	122.3(3)	C2-C3-H3	110.01
S3-C2-C1	124.1(3)	C3′-C3-H3	109.74

TABLE 9 Crystal Data and Structure Refinement of **9a**

Empirical formula	$C_{54}H_{42}S_8 \cdot 2CH_2Cl_2$
Formula weight	1117.29
Crystal color, habit	colorless, prismatic
Crystal dimensions (mm)	0.90 × 0.40 × 0.20
Crystal system	triclinic
No. reflections used for unit cell determination (2 θ range)	25(29.0–30.0°)
Lattice parameters:	$\alpha = 95.88(3)°$
$a = 11.820(6)$ Å	
$b = 12.266(3)$ Å	$\beta = 111.54(3)°$
$c = 10.051(4)$ Å	$\gamma = 86.44(3)°$
	$V = 1348(2)$ Å^3
Space group	$P1$ (no. 2)
Z value	1
D_{calc}	1.406 g/cm^3
F_{000}	590
μ (Mo-K_α)	5.55 cm^{-1}
Diffractometer	Rigaku AFC-5R
Radiation	Mo-K_α ($\lambda = 0.71069$ Å)
Temperature	23°
Attenuators	Ni foil (factor: 3.6, 12.3, 44.1)
Take-off angle	6.0°
Detector aperture	6.0 × 6.0 mm
Crystal-to-detector distance	25.8 cm
Scan type	$2\varepsilon - \omega$
Scan rate	16.0°/min
Scan width	$(1.31 + 0.30 \tan \theta)°$
$2\theta_{max}$	55.1°
No. of reflections measured	total 6350 unique 2208 ($R_{int} = 0.015$)
Corrections	Lorentz-polarization effect absorp. (trans. f: 0.82–1.00)
Structure solution	Patterson method
Refinement	full-matrix least-squares
Function minimized	$\Sigma w(\lvert F_0 \rvert - \lvert F_c \rvert)^2$
Least-squares weights	$4F_0^2/\sigma^2(F_0^2)$
p-Factor	0.04
Anomalous dispersion	all nonhydrogen
No observations [$F_0 > 3.0\sigma(F_0)$]	4018
No. variables	311
Reflection/parameter ratio	12.92
Residuals: R; R_w	0.045; 0.063
Goodness-of-fit indicator (GOF)	1.88
Max shift/error in final diff. map	0.58
Maximum peak in final diff. map	$0.38e^-$/Å^3
Minimum peak in final diff. map	$-0.45e^-$/Å^3

TABLE 10 Selected Bond Lengths (Å) and Angles (°) of **10b**

S1-C1	1.758(3)	S3-C31	1.770(4)
S1-C11	1.769(4)	C1-C2	1.355(4)
S2-C1	1.755(4)	C2-C3	1.445(4)
S2-C21	1.769(4)	C3-C3′	1.327(6)
S3-C2	1.770(4)	C3-H3	0.970
C1-S1-C11	105.0(2)	S3-C2-C1	118.3(3)
C1-S2-C21	103.3(2)	S3-C2-C3	118.0(3)
C2-S3-C31	103.4(2)	C1-C2-C3	118.0(3)
S1-C1-S2	119.5(2)	C2-C3-C3′	126.2(4)
S1-C1-C3	119.7(3)	C2-C3-H3	115.07
S2-C1-C2	120.8(3)	C3′-C3-H3	118.70

methane and then ether were added to the residue, and the precipitates were collected by filtration to give **3a–c** and **3e.** The filtrate was submitted to column chromatography on silica gel with dichloromethane–hexane (1:1 v/v) as eluent to give **4a–d** and **5a–d.** In these reactions, **3d, 4e,** and **5e** could not be obtained.

Tris(phenylthio)cyclopropenylium Perchlorate (**3a**) [1]. Pink crystals; mp 175–177°C (from $CHCl_3$-ether); IR (KBr) ν 3061, 1476, 1444, 1240, 1092, 757, 692, 624 cm^{-1}; UV (MeCN)λ max (nm) 282 (ε 20,600); ^{1}H NMR $\delta = 7.44$–7.57 (m, 9 H, phenyl-H), 7.70–7.76 (m, 6 H, phenyl-H); ^{13}C NMR $\delta = 125.8$, 130.7, 131.6, 133.0, 158.5. Anal. calcd for $C_{21}H_{15}ClO_4S_3$: C, 54.48; H, 3.27; S, 20.78%. Found: C, 54.17; H, 3.04; S, 20.97%.

Tris(o-tolylthio)cyclopropenylium Perchlorate (**3b**). White crystals; mp 198–201°C (from $CHCl_3$-ether); IR (KBr) ν 3049, 2921, 1474, 1456, 1259, 1245, 1096, 762, 623 cm^{-1}; UV (MeCN) λ max (nm) 276 (ε 18,264); ^{1}H NMR $\delta = 2.44$ (s, 9 H, 3 × Me), 7.24–7.41 (m, 9H, phenyl-H), 7.76–7.80 (m, 3 H, phenyl-H); ^{13}C NMR $\delta = 20.9$, 125.2, 128.4, 131.6, 132.0, 134.6, 140.8, 158.1. Anal. calcd for $C_{24}H_{21}ClO_4S_3$: C, 57.07; H, 4.20; S, 19.05%. Found: C, 56.90; H, 4.15; S, 19.27%.

Tris(p-tolylthio)cyclopropenylium Perchlorate (**3c**). Pink crystals; mp 187–189°C (from $CHCl_3$-ether); IR (KBr) ν 3050, 2921, 1492, 1244, 1087, 815, 623 cm^{-1}; UV (MeCN) λ max (nm) 277 nm (ε 21,309); ^{1}H NMR $\delta = 2.39$ (s, 9 H, 3 × Me), 7.24–7.59 (m, 12 H, phenyl-H); ^{13}C NMR $\delta = 21.4$, 122.1, 131.2, 132.9, 142.2, 158.5. Anal. calcd for $C_{24}H_{21}ClO_4S_3$: C, 57.07; H, 4.20; S, 19.05%. Found: C, 57.16; H, 4.13; S, 19.24%.

Tris(2,6-dimethylphenylthio)cyclopropenylium Perchlorate (**3e**). Pink crystals; mp 200–203°C (from $CHCl_3$-ether); IR (KBr) ν 3059, 2918, 1464, 1239, 1098, 1088, 787, 624 cm^{-1}; ^{1}H NMR $\delta = 2.42$ (s, 18 H, 6 × Me), 7.04–7.07 (m, 6H, phenyl-H), 7.18–

TABLE 11 Crystal Data and Structure Refinement of **10b**

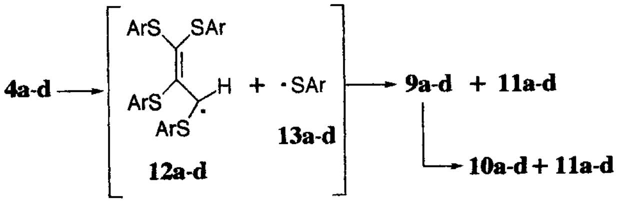
Empirical formula	$C_{48}H_{44}S_6$
Formula weight	813.24
Crystal color, habit	yellow, prismatic
Crystal dimensions (mm)	0.40 × 0.20 × 0.10
Crystal system	triclinic
No. reflections used for unit cell determination (2 θ range)	24(18.2–24.0°)
Lattice parameters:	
a = 10.568(2) Å	α = 102.74(1)°
b = 13.228(2) Å	β = 100.84(2)°
c = 7.877(2) Å	γ = 81.49(2)°
	V = 1048.4(4) Å^3
Space group	$P\bar{1}$ (No. 2)
Z value	1
D_{calc}	1.288 g/cm^3
F_{000}	428
μ (Mo-K_α)	3.45 cm^{-1}
Diffractometer	Rigaku AFC-5R
Radiation	Mo-K_α (λ = 0.71069 Å)
Temperature	23°
Attenuators	Ni foil (factor: 3.6, 12.3, 44.1)
Take-off angle	6.0°
Detector aperture	6.0 × 6.0 mm
Crystal-to-detector distance	25.8 cm
Scan type	$2\theta - \omega$
Scan rate	8.0°/min
Scan width	(1.21 + 0.30 tan θ)°
$2\theta_{max}$	55.1°
No. of reflections measured	total 5123
	unique 4861 (R_{int} = 0.030)
Corrections	Lorentz-polarization effect
	absorp. (trans. f:0.94–1.00)
Structure solution	Patterson method
Refinement	full-matrix least-squares
Function minimized	$\Sigma w(\lvert F_0\rvert - \lvert F_c\rvert)^2$
Least-squares weights	$4F_0^2/\sigma^2(F_0^2)$
p-Factor	0.01
Anomalous dispersion	all nonhydrogen
No. observations [$F_0 > 3.0\ \sigma\ (F_0)$]	2567
No. variables	244
Reflection/parameter ratio	10.52
Residuals: R; R_w	0.051; 0.043
Goodness-of-fit indicator (GOF)	2.23
Max shift/error in final diff. map	0.33
Maximum peak in final diff. map	0.25e^-/Å^3
Minimum peak in final diff. map	−0.23e^-/Å^3

TABLE 12 The Yields of the Products in the Pyrolysis of **4a–d** at 190°C/5 mm Hg for 3 Hours

	Yield, %[a]		
Compound	**9a–d**	**10a–d**	**11a–d**
4a	13	62	95
4b	—[b]	57	70
4c	22	50	81
4d	—[b]	48	63

[a]Isolated yields based on **4a–d.**

[b]Not detected.



SCHEME 4

7.26 (m, 3 H, phenyl-H); ^{13}C NMR δ = 22.0, 124.2, 129.5, 132.3, 142.6, 159.3. Anal. calcd for $C_{27}H_{27}ClO_4S_3$: C, 59.27; H, 4.97; S, 17.58%. Found: C, 59.05; H, 4.85; S, 17.30%.

1,1,2,3,3-Pentakis(phenylthio)-1-propene (**4a**). Pale yellow crystals; mp 65–66°C (from CH_2Cl_2-hexane); IR (KBr) ν 3057, 3018, 2953, 1581, 1475, 1438, 1302, 1065, 1024, 803, 737, 690 cm^{-1}; UV(CH_2Cl_2) λ max (nm) 259 (ε 86,400), 325 sh; ^{1}H NMR δ = 6.56–7.56 (m, 26 H, phenyl-H and CH); ^{13}C NMR δ = 64.5, 127.2, 127.7, 128.0, 128.3, 128.5, 129.0, 129.1, 129.5, 130.6, 132.6, 133.2, 133.7, 133.8, 134.0; MS m/z 472 (M–SPh). Anal. calcd for $C_{33}H_{26}S_5$: C, 68.00; H, 4.50%. Found: C, 68.12; H, 4.42%.

1,1,2,3,3-Pentakis(o-tolylthio)-1-propene (**4b**). Pale yellow crystals; mp 107–108°C (from CH_2Cl_2-hexane); IR (KBr) ν 3058, 3010, 2967, 2915, 1588, 1466, 1455, 1376, 1280, 1060, 1045, 797, 752, 707 cm^{-1}; UV (CH_2Cl_2) λ max (nm) 262 (ε 297,375), 311 sh; ^{1}H NMR δ = 2.38 (s, 9 H, 3 × Me), 2.52 (s, 6 H, 2 × Me), 6.43–7.65 (m, 21 H, phenyl-H and CH); ^{13}C NMR δ = 19.5, 20.0, 20.8, 21.0, 64.1, 125.4, 125.9, 126.2, 126.3, 126.5, 126.9, 128.1, 128.7, 129.6, 130.4, 130.5, 131.4, 131.6, 133.4, 135.1, 135.4, 138.3, 141.4, 141.7. Anal. calcd for $C_{38}H_{36}S_5$: C, 69.89; H, 5.56%. Found: C, 69.79; H, 5.45%.

1,1,2,3,3-Pentakis(p-tolylthio)-1-propene (**4c**). White crystals; mp 128.5–130°C (from CH_2Cl_2-hexane); IR (KBr) ν 3019, 2921, 1490, 1448, 1398, 1180, 1018, 806, 750 cm^{-1}; UV (CH_2Cl_2) λ max (nm) 252 (ε 226,777), 361 sh; ^{1}H NMR δ = 2.27 (s, 3 H, Me), 2.29 (s, 3 H, Me), 2.31 (s, 3 H, Me), 2.37 (s, 6 H, 2 × Me), 6.49–7.43 (m, 21 H, phenyl-H and CH); ^{13}C NMR δ = 21.1, 21.2, 21.3, 65.0, 128.8, 129.2, 129.7, 129.8, 130.8, 130.9, 133.4, 134.0, 137.1, 137.7, 138.4. Anal. calcd for $C_{38}H_{36}S_5$: C, 69.89; H, 5.56%. Found: C, 69.87; H, 5.36%.

1,1,2,3,3-Pentakis(p-fluorophenylthio)-1-propene (**4d**). White crystals; mp 65–66°C (from CH_2Cl_2-hexane); IR (KBr) ν 3059, 2963, 1589, 1489, 1231, 1156, 1092, 1013, 830, 754 cm^{-1}; UV (CH_2Cl_2) λ max (nm) 255 (ε 178,752), 316 sh; ^1H NMR δ = 6.52–7.60 (m, 21 H, phenyl-H and CH); ^{13}C NMR δ = 65.9, 115.3, 115.6, 115.7, 116.0, 116.1, 116.2, 116.4, 116.6, 132.3, 136.4, 136.6, 161.4, 164.6, 165.1. Anal. calcd for $C_{33}H_{21}F_5S_5$: C, 58.91; H, 3.15; S, 23.83%. Found: C, 58.86; H, 3.07; S, 23.98%.

2,3,3-Tris(phenylthio)propenal (**5a**). Yellow crystals; mp 78–80°C (from CH_2Cl_2-hexane); IR (KBr) ν 3056, 2862, 1658, 1582, 1475, 1456, 1440, 1366, 1145, 1023, 920, 741, 688 cm^{-1}; UV (CH_2Cl_2) λ max (nm) 324 (ε 12,068); ^1H NMR δ = 6.88–7.57 (m, 15 H, 3 × SC_6H_5), 10.30 (s, 1 H, CHO); ^{13}C NMR δ = 126.8, 127.8, 128.6, 129.0, 129.1, 129.2, 130.1, 132.9, 134.7, 134.9, 185.2. Anal. calcd for $C_{21}H_{16}OS_3$: C, 66.28; H, 4.24; S, 25.28%. Found: C, 66.44; H, 4.08; S, 25.03%.

2,3,3-Tris(o-tolylthio)propenal (**5b**). Yellow crystals; mp 113–114°C (from CH_2Cl_2-hexane); IR (KBr) ν 3063, 3009, 2973, 2915, 2876, 1668, 1588, 1469, 1454, 1372, 1146, 1058, 1044, 900, 747 cm^{-1}; UV (CH_2Cl_2) λ max (nm) 328 (ε 10,580); ^1H NMR δ = 1.78 (s, 3 H, Me), 2.02 (s, 3 H, Me), 2.50 (s, 3 H, Me), 6.74–7.27 (m, 12 H, 3 × SC_6H_4), 10.31 (s, 1 H, CHO); ^{13}C NMR δ = 19.7, 20.5, 20.6, 126.1, 126.5, 126.6, 126.8, 128.0, 129.0, 129.8, 130.2, 130.4, 130.5, 131.2, 135.9, 137.8, 138.8, 142.7, 185.3. Anal. calcd for $C_{24}H_{22}OS_3$: C, 68.21; H, 5.25; S, 22.76%. Found: C, 68.28; H, 5.17; S, 22.50%.

2,3,3-Tris(p-tolylthio)propenal (**5c**). Pale yellow crystals; mp 79–81°C (from CH_2Cl_2-hexane); IR (KBr) ν 3050, 2964, 2857, 1668, 1457, 1261, 1143, 805 cm^{-1}; UV (CH_2Cl_2) λ max (nm) 327 (ε 11,486); ^1H NMR δ = 2.31 (s, 3 H, Me), 2.32 (s, 3 H, Me), 2.33 (s, 3 H, Me), 6.79–7.40 (m, 12 H, 3 × SC_6H_4), 10.25 (s, 1 H, CHO); ^{13}C NMR δ = 21.1, 21.2, 21.3, 126.9, 128.9, 129.4, 129.6, 129.7, 129.8, 130.2, 131.1, 131.6, 134.9, 136.9, 138.0, 139.5, 185.5. Anal. calcd for $C_{24}H_{22}OS_3$: C, 68.21; H, 5.25; S, 22.76%. Found: C, 68.30; H, 5.10; S, 22.55%.

2,3,3-Tris(p-fluorophenylthio)propenal (**5d**). Yellow viscous liquid; IR (neat) ν 3064, 1673, 1471, 1250, 1152, 809 cm^{-1}; ^1H NMR δ = 6.85–7.52 (m, 12 H, 3 × SC_6H_4), 10.23 (s, 1H, CHO); ^{13}C NMR δ = 131.3, 131.5, 132.0, 132.1, 132.5, 132.6, 133.9, 134.0, 136.8, 136.9, 156.9, 161.6, 165.3, 185.0. Anal. calcd for $C_{21}H_{13}OS_3$: C, 58.05; H, 3.01; S, 22.14%. Found: C, 58.27; H, 3.20; S, 21.98%.

Reaction of **3a** *with* **2a.** To a solution of **3a** (1 mmol) in dry dichloromethane (10 mL) was added dropwise **2a** (2 mmol), and the mixture was stirred under argon at room temperature for 3 hours. The organic layer was washed with water (5 mL × 7), dried over anhydrous sodium sulfate, and evaporated under reduced pressure. The residue was submitted to column chromatography on silica gel with dichloromethane-hexane (1:1 v/v) as eluent to give **4a** in 70% yield.

Reaction of Tris(tert-butylthio)cyclopropenylium Perchlorate with **2a–d.** To a solution of tris(*tert*-butylthio)cyclopropenylium perchlorate (1 mmol) in dry dichloromethane (10 mL) was added dropwise **2a–d** (2 mmol), and the mixture was stirred under argon at room temperature for 3 hours. The organic layer was washed with water (5 mL × 7), dried over anhydrous sodium sulfate, and evaporated under reduced pressure. Dichloromethane and ether were added to the residue, and the precipitates were collected by filtration. Tris(*tert*-butylthio)cyclopropenylium perchlorate was recovered unchanged (93–96% recovery).

Treatment of **4a** *with HCl in Aquous Dioxane.* To a solution of **4a** (1 mmol) in dioxane (10 mL) was added conc. HCl (10 mL) and water (10 mL), and the mixture was stirred at room temperature for 24 hours. After dichloromethane (20 mL) was added to the mixture, the organic layer was separated, washed with water (5 mL × 7), dried over anhydrous sodium sulfate, and evaporated under reduced pressure. The residue was submitted to column chromatography on silica gel with dichloromethane-hexane (1:1 v/v) as eluent to give **5a** in 55% yield.

Pyrolysis of **4a–d.** Compounds **4a–d** (1 mmol) were put into a bulb-to-bulb distillation apparatus and heated at 190°C for 3 hours under reduced pressure (5 mm Hg). The reaction mixtures were submitted to column chromatography on silica gel with dichloromethane-hexane (1:1 v/v) as eluent to give the products shown in Table 12.

Pyrolysis of **4a** *at Lower Temperature.* Compound **4a** (1 mmol) was put into a bulb-to-bulb distillation apparatus and heated at 160°C for 10 hours under reduced pressure (5 mm Hg). The reaction mixtures were submitted to column chromatography on silica gel with dichloromethane-hexane (1:1 v/v) as eluent to give **9a** and **11a** in 26 and 38% yields, respectively, with 54% recovery of **4a.**

Photolysis of **4a.** The solution of **4a** (0.02 mmol) in dry benzene (10 mL) was placed in a Pyrex tube, purged with N_2 for 10 minutes, and irradiated for 1 hour with light of wavelength >280 nm at room temperature. After evaporation of the solvent under reduced pressure, the residue was submitted to column chromatography on silica gel with dichloromethane-hexane (1:1 v/v) as eluent to give **10a** and **11a** in 74 and 85% yields, respectively.

(3R,4S)-1,1,2,3,4,5,6,6-Octakis(phenylthio)-1,5-hexadiene (**9a**). Yellow crystals; mp 211–212°C (from CH_2Cl_2-ether); IR (KBr) ν 3056, 3002, 2852, 1581, 1475, 1439, 1067, 1024, 915, 738, 688 cm^{-1}; UV (CH_2Cl_2) λ max (nm) 261 (ε 33,716), 286 sh, 324 sh; ^1H NMR δ 6.17 (s, 2 H, 2 × CH), 6.59–6.62 (m, 10 H, 2 × SC_6H_5), 6.94–7.66 (m, 30 H, 6 × SC_6H_5). Anal. calcd for $C_{54}H_{42}S_8$: C, 68.46; H, 4.47%. Found: C, 68.54; H, 4.41%.

(3R,4S)-1,1,2,3,4,5,6,6-Octakis(p-tolylthio)-1,5-hexadiene (**9c**). Pale yellow crystals; mp 204–206°C (from CH_2Cl_2-ether); IR (KBr) ν 3049, 3025, 2896, 1491, 1167, 1017, 804 cm^{-1}; ^1H NMR δ = 2.24 (s, 6 H, 2 × Me), 2.26 (s, 12 H, 4 × Me), 2.39 (s, 6 H, 2 × Me), 6.08 (s, 2 H, 2 × CH), 6.50 (m, 8 H, 2 × SC_6H_4), 6.80 (m, 8 H, 2 × SC_6H_4), 7.00–7.09 (m, 8 H, 2 × SC_6H_4), 7.37 (m, 4 H, SC_6H_4), 7.56 (m, 4 H, SC_6H_4); ^{13}C NMR δ 21.0, 21.1, 21.2, 21.4, 59.5, 128.5, 128.8, 129.2, 129.4, 129.7, 129.8, 130.9, 131.2, 133.3, 133.7, 134.3, 135.5, 136.6, 137.2, 138.0. Anal. calcd for $C_{62}H_{58}S_8$: C, 70.27; H, 5.52%. Found: C, 70.45; H, 5.45%.

1,1,2,5,6,6-Hexakis(phenylthio)-(3E)-1,3,5-hexatriene (**10a**). Yellow crystals; mp 152–154°C (from CH_2Cl_2-hexane); IR (KBr) ν 3070, 3052, 3018, 3002, 1580, 1474, 1438, 1253, 1024, 944, 925, 738, 687 cm^{-1}; UV (CH_2Cl_2) λ max (nm) 411 (ε 51,124); ^1H NMR δ 6.83–7.27 (m, 30 H, 6 × SC_6H_5), 7.93 (s, 2 H, 2 × CH); ^{13}C NMR δ 126.0, 126.9, 128.0, 128.3, 128.6, 128.7, 129.0, 130.1, 132.5, 133.1, 133.9, 134.7, 135.9, 137.3, 143.7; MS 729 (M^+). Anal. calcd for $C_{42}H_{32}S_6$: C, 69.19; H, 4.42%. Found: C, 69.20; H, 4.25%.

1,1,2,5,6,6-Hexakis(o-tolylthio)-(3E)-1,3,5-hexatriene (**10b**). Yellow crystals; mp 205–206°C (from CH_2Cl_2-hexane); IR (KBr) ν 3058, 3009, 2971, 2916, 2851, 1588, 1468, 1455, 1249, 1059, 1043, 942, 742 cm^{-1}; UV (CH_2Cl_2) λ max (nm) 416 (ε 26,240); ^1H NMR δ 1.75 (s, 6 H, 2 × Me), 1.94 (s, 6 H, 2 × Me), 2.32 (s, 6H, 2 × Me), 6.78–7.15 (m, 24 H, 6 × SC_6H_4), 7.75 (s, 2H, 2 × CH); ^{13}C NMR δ 19.8, 20.4, 20.7, 125.7, 125.9, 126.0, 126.5, 127.0, 128.4, 129.7, 129.9, 130.2, 131.1, 131.5, 132.2, 133.6, 134.9, 135.1, 136.7, 137.0, 138.5, 141.7, 142.7. Anal. calcd for $C_{48}H_{44}S_6$: C, 70.89; H, 5.45%. Found: C, 70.69; H, 5.28%.

1,1,2,5,6,6-Hexakis(p-tolylthio)-(3E)-1,3,5-hexatriene (**10c**). Yellow crystals; mp 208–209°C (from CH_2Cl_2-hexane); IR (KBr) ν 3018, 2920, 2864, 1578, 1490, 1398, 1180, 1082, 1018, 948, 804 cm^{-1}; UV (CH_2Cl_2) λ max (nm) 415 (ε 37,575); ^1H NMR δ 2.29 (s, 6H, 2 × Me), 2.30 (s, 12H, 4 × Me), 6.75–7.08 (m, 24 H, 6 × SC_6H_4), 7.91 (s, 2 H, 2 × CH); ^{13}C NMR δ 21.1, 21.2, 21.3, 129.0, 129.1, 129.3, 129.7, 129.9, 130.3, 131.5, 132.5, 132.7, 134.0, 135.7, 136.7, 137.7, 138.1, 143.9. Anal. calcd for $C_{48}H_{44}S_6$: C, 70.89; H, 5.45%. Found: C, 70.81; H, 5.23%.

1,1,2,5,6,6-Hexakis(p-fluorophenylthio)-(3E)-1,3,5-hexatriene (**10d**). Yellow crystals; mp 152–154°C (from CH_2Cl_2-hexane); IR (KBr) ν 3055, 1581, 1488, 1476, 1438, 1230, 1156, 1088, 1065, 1024, 823, 736, 688 cm^{-1}; UV (CH_2Cl_2) λ max (nm) 411 (ε 43,102); ^1H NMR δ 6.75–7.18 (m, 24H, 6 × SC_6H_4), 7.81 (s, 2H, 2 × CH). Anal. calcd for $C_{42}H_{26}F_6S_6$: C, 60.27; H, 3.13%. Found: C, 59.81; H, 3.04%.

Diphenyl Disulfide (**11a**) *[4a]*. Mp 58–59°C (from CH_2Cl_2-hexane); IR (KBr) ν 3064, 1574, 1472, 1435, 1072, 1021, 996, 900, 740, 687 cm^{-1}; ^1H NMR δ 7.19–7.34 (m, 6H, phenyl-H), 7.47–7.52 (m, 4H, phenyl-H); ^{13}C NMR δ 127.2, 127.6, 129.1, 137.1; MS m/z 218 (M^+). Anal. calcd for $C_{12}H_{10}S_2$: C, 66.01; H, 4.62%. Found: C, 65.87; H, 4.55%.

Di-o-tolyl Disulfide (**11b**) *[4b]*. Mp 31–32°C (from CH_2Cl_2-hexane); IR (KBr) ν 3019, 2916, 1488, 1397, 1182, 1118, 1077, 1014, 801 cm^{-1}; ^1H NMR δ 2.42 (s, 6 H, 2 × Me), 7.09–7.16 (m, 6H, phenyl-H), 7.48–7.53 (m, 2 H, phenyl-H); ^{13}C NMR δ 20.0, 126.7, 127.4, 128.8, 130.3, 135.5, 137.4. Anal. calcd for $C_{14}H_{14}S_2$: C, 68.25; H, 5.73%. Found: C, 68.30; H, 5.80%.

Di-p-tolyl Disulfide (**11c**) *[4c]*. Mp 42–43°C (from CH_2Cl_2-hexane); IR (KBr) ν 3018, 2916, 1489, 1397, 1304, 1117, 1075, 1037, 803 cm^{-1}; ^1H NMR δ 2.31 (s, 6H, 2 × Me), 7.07–7.39 (m, 8 H, 2 × SC_6H_4); ^{13}C NMR δ 21.1, 128.6, 129.8, 133.9, 137.5. Anal. calcd for $C_{14}H_{14}S_2$: C, 68.25; H, 5.73%. Found: C, 68.23; H, 5.68%.

Di-p-fluorophenyl Disulfide (**11d**) *[4d]*. Yellow viscous liquid; IR (neat) ν 3054, 1488, 1422, 1261, 1018, 896, 750 cm^{-1}; ^{1}H NMR δ 6.95–7.04 (m, 4 H, SC_6H_4), 7.40–7.47 (m, 4H, SC_6H_4); ^{13}C NMR δ 116.1, 116.5, 131.3, 131.4, 132.2, 132.3, 161.0, 164.5. Anal. calcd for $C_{12}H_8F_2S_2$: C, 56.67; H, 3.17%. Found: C, 56.49; H, 3.09%.

Photolysis of **4a** *in Presence of Oxygen.* The solution of **4a** (0.02 mmol) in dry benzene (10 mL) was placed in a Pyrex tube, oxygen gas was bubbled into the solution for 10 minutes, and the mixture was irradiated for 1 hour with light of wavelength >280 nm at room temperature. After evaporation of the solvent under reduced pressure, the residue was submitted to column chromatography on silica gel with dichloromethane-hexane (1:1 v/v) as eluent. The starting material **4a** was recovered unchanged (97% recovery).

Pyrolysis of **9a.** Compounds **9a** (1 mmol) were put into a bulb-to-bulb distillation apparatus and heated at 190°C for 3 hours under reduced pressure (5 mm Hg). The reaction mixtures were submitted to column chromatography on silica gel with dichloromethane-hexane (1:1 v/v) as eluent to give **10a** and **11a** in 78 and 87% yields, respectively.

Photolysis of **9a.** The solution of **9a** (0.02 mmol) in dry benzene (10 mL) was placed in a Pyrex tube, purged with N_2 for 10 minutes, and irradiated for 1 hour with light of wavelength >280 nm at room temperature. After evaporation of the solvent under reduced pressure, the residue was submitted to column chromatography on silica gel with dichloromethane-hexane (1:1 v/v) as eluent to give **10a** and **11a** in 80 and 90% yields, respectively.

X-ray Crystallography. Data were collected on a Rigaku AFC-5R four-circle diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71069 Å). The structure was solved by a direct method and refined on F by full-matrix least-squares using TEXSAN [5]. Crystal data and structure refinements of **3a, 4a, 5b, 9a,** and **10b** are given in Tables 2, 4, 6, 9, and 11.

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