Reactions of (2,4,6-Tri-*t*-butyl)thiobenzaldehyde with Diazo Compounds. Synthesis and Reactions of Sterically Congested Thiiranes

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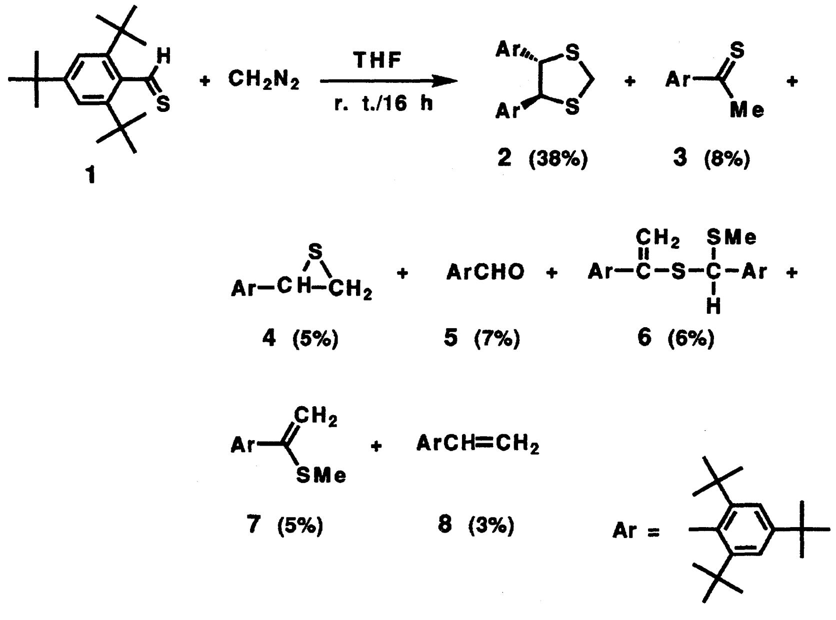
Sterically congested thiiranes having a 2,4,6-tri-*t*-butylphenyl group were synthesized by the reactions of (2,4,6-tri-*t*-butyl)thiobenzaldehyde with sterically hindered diazo compounds. Thermal desulfurization of the most congested thiirane, 2,2-di-*t*-butyl-3-(2,4,6-tri-*t*-butylphenyl)thiirane (**15c**), did not proceed even upon using highly reactive reagents, such as hexamethylphosphorous triamide or organolithiums. The photoreaction of **15c** did not give the corresponding styrene, but afforded several products containing 2,4,6-tri-*t*-butylbenzo[*b*]thiophene and Dewar benzenes, 2,2-di-*t*-butyl-3-(3,4,6-tri-*t*-butylbicyclo[2.2.0]hexa-2,5-dien-2-yl)thiirane and 2-*t*-butyl-3,3-dimethyl-1-(1,3,5-tri-*t*-butylbicyclo[2.2.0]hexa-2,5-diene-2-yl)-1-butene (**24**), the latter of which is the first example for a vinyl-substituted Dewar benzene. Compound **24** has a unique reactivity, giving a rearrangement product, 2-*t*-butyl-3,3-dimethyl-1-(1,3,5-tri-*t*-butylbicyclo[2.2.0]hexa-2,5-diene-2-yl)-1-butene on thermolysis.

Recently, much attention has been paid to sterically congested molecules, because of their unique and interesting properties$^{1)}$ as well as of their utility for kinetic stabilization of highly reactive molecules, such as multiple-bond compounds of heavier main-group elements.$^{2)}$ We previously reported on the synthesis and isolation of (2,4,6-tri-*t*-butyl)thiobenzaldehyde (**1**) kinetically stabilized by a sterically bulky group.$^{3)}$ It is interesting to investigate the reactivity of **1** because it is considered to have the properties of a genuine thioformyl group in contrast with well studied thermodynamically stabilized thioaldehydes that are perturbed by a neighboring heteroatom. As an extension of our interest in sterically congested molecules having the 2,4,6-tri-*t*-butylphenyl group,$^{4)}$ we now report on the synthesis and reactivity of highly congested 2-(2,4,6-tri-*t*-butyphenyl)thiiranes **15**.$^{5)}$

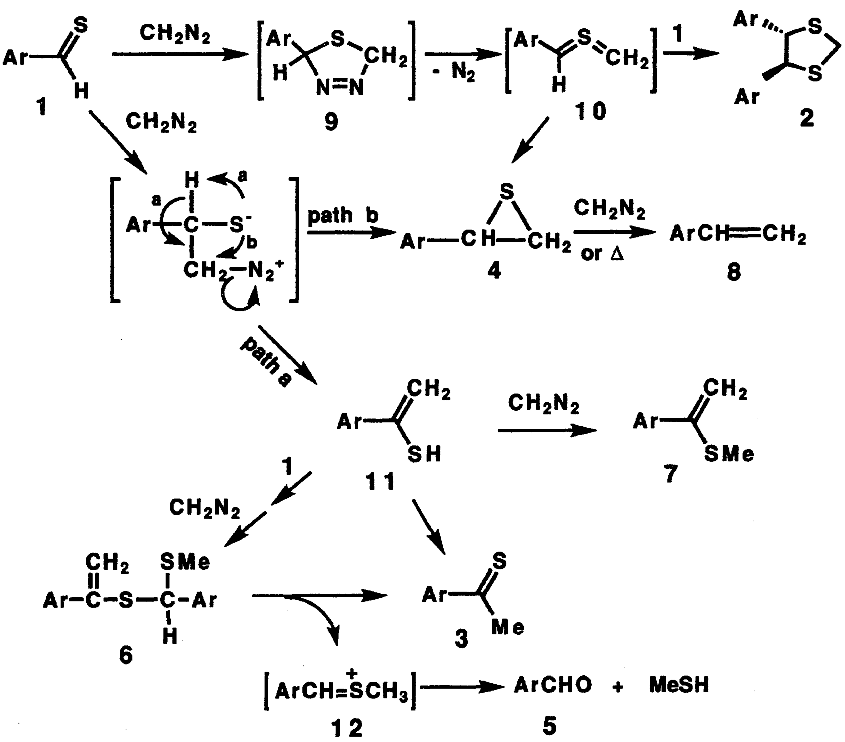
Results and Discussion

The reaction of (2,4,6-tri-*t*-butyl)thiobenzaldehyde (**1**) with diazomethane was carried out at −78 °C and at room temperature. Although no reaction took place at −78 °C, products **2**—**8** were obtained when the reaction was carried out at room temperature. The results are summarized in Scheme 1. Although ^{1}H NMR of the reaction mixture indicated the presence of an enethiol Ar(SH)C=CH$_2$ (**11**),$^{6)}$ it was not found in the isolated products, indicating that **11** most likely underwent tautomerization to thioacetophenone **3** on silica gel during the work-up procedure.

In the ^{1}H NMR spectrum of dithiolane **2**, the signal due to methylene protons was observed as a singlet, indicating that **2** was a *trans*-isomer. Achiwa et al. reported that a thiocarbonyl ylide generated from a thioketone underwent a 1,3-dipolar cycloaddition reaction with a thioketone to give a dithiolane.$^{7)}$ In the present reaction, **2** is considered to have been formed similarly in the reaction of thiocarbonyl ylide **10** with **1** in preference to the corresponding *cis*-isomer for a steric reason (Scheme 2). Enethiol **11** and thiirane **4** seem to be formed by an attack of the carbanion center of diazomethane on the carbon of the thioformyl group followed by the elimination of nitrogen. Thioacetophenone **3** is a violet crystalline compound and is stable in deuteriochloroform. The signals due to the methyl protons and the thiocarbonyl carbon of **3** appeared at $\delta=3.30$ and 262.2 in the ^{1}H and ^{13}C NMR spectra, respectively. Enethiol **11** is also a key intermediate for the formation of **6** and **7**. A nucleophilic attack of **11** on the thiocarbonyl carbon of **1**, followed by methylation, afforded dithioacetal **6**, while methylation of the S–H group of **11** with diazomethane gave **7**. Dithioacetal **6** is considered to undergo an acid-catalyzed reaction to give **3** and **12**, the latter of which is hydrolyzed to provide **5** along with methanethiol. In fact, **6** was spontaneously changed to a 1 : 1 mixture of **3** and **5** in deuteriochloroform, as observed by ^{1}H NMR. Benzaldehyde **5** is considered to also be obtained by the oxidation of unreacted **1** during the work-up. Styrene **8** seems to be formed from **4** by thermal desulfurization



Scheme 1.

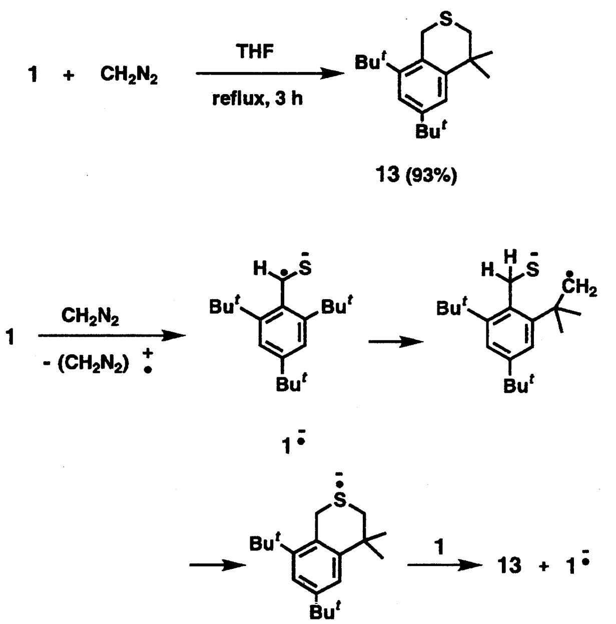


Scheme 2.

or a reaction promoted by diazomethane.[8)]

The reaction of **1** with diazomethane in refluxing THF gave 3,4-dihydro-1*H*-2-benzothiin **13** in high yield. We previously observed that **13** was obtained from the thermolysis of **1** at around 200 °C.[9)] It was also found that **1** readily underwent intramolecular cyclization to give **13** by reactions with radicals[9)] or a trivalent phosphorus compound,[10)] the latter reaction proceeding probably via an anion radical of **1** generated by a single-electron transfer (SET). Although a mechanism involving some radical generated from hydrogen abstraction by triplet methylene is also conceivable, **13** is considered to be formed by the SET mechanism, probably from diazomethane, not by simple thermolysis (Scheme 3).

In order to simplify a reaction by preventing the carbon atom of diazomethanes from attacking at the thioformyl carbon atom, diazomethanes **14a**—**d** having a bulky group were used. Expectedly, the reactions gave only triiranes **15** (10—20%), **13**, and **5**, together with the some recovery of **1** (Scheme 4). No thiadiazoline was also obtained in these reactions. This is in contrast to the reactions of bulky thiones, which give thiadiazo-



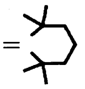
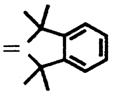
Scheme 3.

lines.[11] The thiadiazolines derived from **1** are considered to be unstable under the present reaction conditions, or to decompose on silica gel. For the purpose of increasing the yield of thiirane **15**, reactions of **1** with carbenes or carbenoids generated from diazo compounds in the presence of copper(I) chloride were carried out. The results obtained for the reactions of **14c** in three solvents (THF, CH_2Cl_2, pentane) are shown in Scheme 5. Since THF gave the best result, it was selected as a solvent for subsequent experiments, the results of which are summarized in Table 1. The use of copper(I) chloride shortened the reaction time and increased the yield of thiiranes **15a**—**d**.

Since thiiranes **15a**—**d** have two bulky groups in addition to the 2,4,6-tri-*t*-butylphenyl group, it is interesting to investigate the influence of the bulky substituents on the reactivities of the thiiranes.

First, desulfurization with trivalent phosphorus compounds was studied. The reactions of **15a** (room temperature) and **15d** (reflux) with hexamethylphosphorous triamide in THF gave the corresponding styrenes, **16a** and **16d**, in 90 and 33% yields, respectively, while those of **15b** and **15c** did not afford styrenes, **16b** and **16c**. Attempted desulfurization of **15b** and **15c** with organolithium reagents, such as methyllithium, butyllithium, and phenyllithium, did not proceed either because of extremely great congestion of **15b** and **15c** (Scheme 6).

Table 1. Reactions of Thiobenzaldehyde **1** with Diazo Compounds **14**

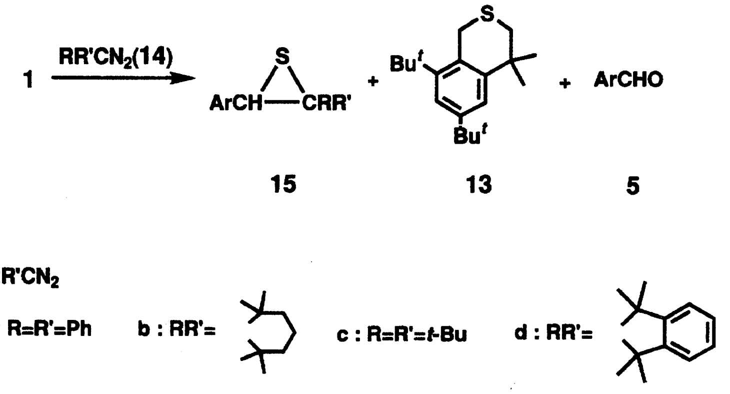
14	Yield/%		
	15	**13**	**5**
a: R=R′=Ph	20	55	13[a)]
	78	—	12[b,c)]
b: RR′= 	10	—	23[b)]
	47	—	12[b,c)]
c: R=R′=*t*-Bu	13	—	9[a)]
	54	—	21[b,c)]
d: RR′= 	48	—	15[b,c)]

a) Reflux. b) Room temperature. c) Cat. CuCl.

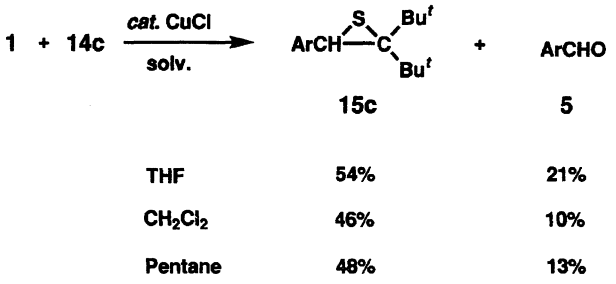
Thermolysis of the thiiranes was next studied. The reactions of **15a**—**c** in toluene at 180 °C in a sealed tube gave styrene **16a** and benzo[*b*]thiophene derivatives, **17** and **18**, respectively (Scheme 7). A plausible mechanism for the formation of benzo[*b*]thiophenes **17** and **18** is shown in Scheme 8.

Biradical **19** formed by C–S bond cleavage does not undergo extrusion of sulfur to afford the corresponding styrene, but instead cyclizes at the *ortho*-position of the benzene ring to give the benzo[*b*]thiophene derivative, probably via 2,7a-dihydrobenzo[*b*]thiophene intermediate **20**. It is interesting that cyclization of the biradical takes place in the cases of **15b** and **15c**, since the process **15**→**20** accompanies a loss of aromaticity.

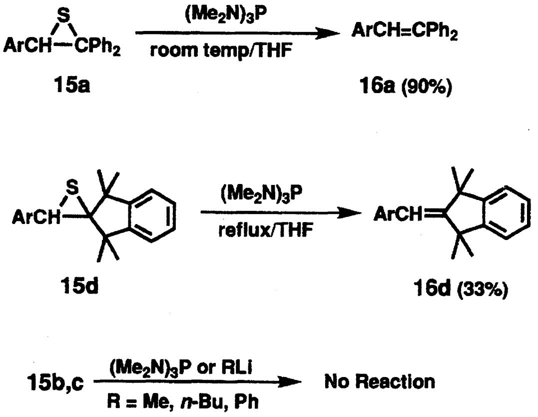
Finally, the photolysis of the thiiranes was studied. When **15a** was photolyzed with a 400-W medium-pressure mercury lamp in THF at room temperature for 4



Scheme 4.



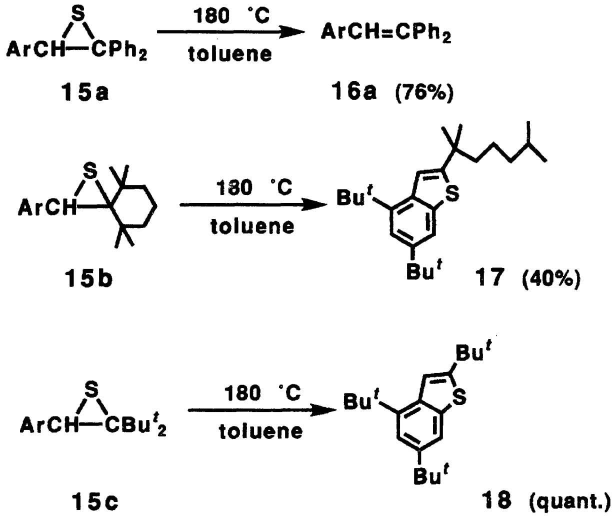
Scheme 5.



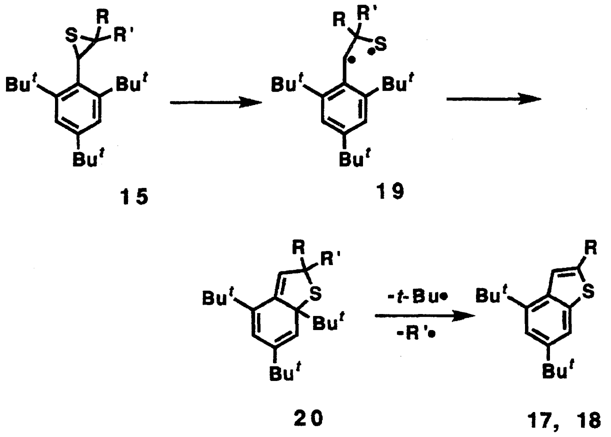
Scheme 6.

d, **16a** and a phenanthrene derivative **21** were obtained in 21 and 66% yields, respectively. Since the photolysis (THF, 2 d) of **16a** gave **21** (28%), **21** is considered to be formed via **16a**. A plausible reaction mechanism is shown in Scheme 9. Photocyclization of stilbenes to dihydrophenanthrenes is well known.[12)]

The photolysis of **15c** under similar conditions afforded a variety of products, i.e., benzo[*b*]thiophene **18** (9%), thiirane **22** (13%), Dewar benzenes **23** (10%) and **24** (12%), and styrene **25** (10%) (Scheme 10).[13)] As far as we are aware, **24** is the first example of a vinyl substituted Dewar benzene. Interestingly, styrene **16c** ($\mathrm{ArCH{=}CBu^t{}_2}$), an expected product of the photolysis of thiirane,[14)] was not obtained in this reaction.

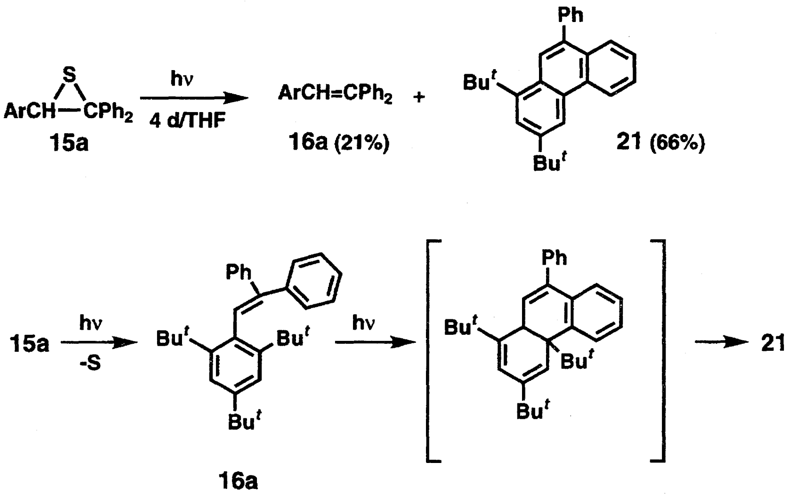


Scheme 7.

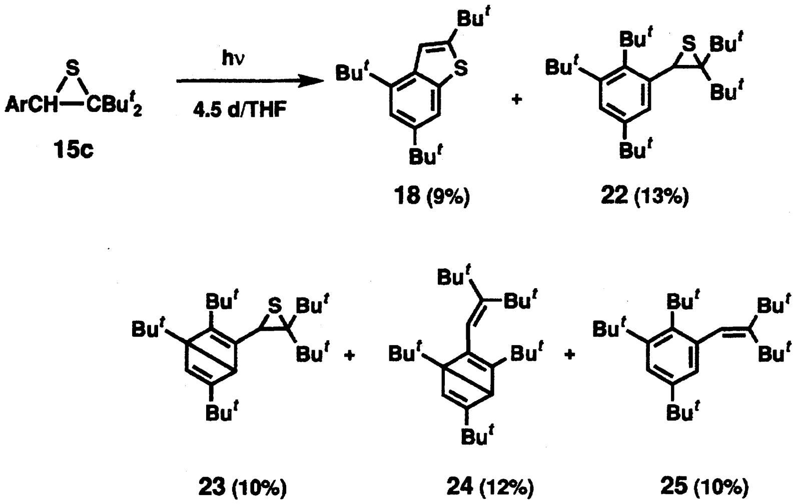


Scheme 8.

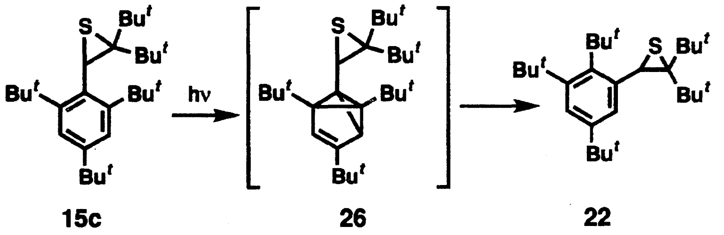
The structure of **25** resulting from the rearrangement of a *t*-butyl group was determined by a crystallographic analysis (Table 2); its ORTEP drawing is shown in Fig. 1. The atomic coordinates and isotropic displacement, bond lengths, and bond angles of **25** are listed in Tables 3, 4, and 5, respectively.[15)] The styrene **25** has a



Scheme 9.



Scheme 10.



Scheme 11.

unique structure due to its steric congestion. The dihedral angle formed by the benzene ring and olefin plane is almost perpendicular (91.7°), indicating that the conjugation between the benzene ring and olefin moiety is negligible.

Table 2. Crystal and Intensity Collection Data for **25**

Mol formula	$C_{28}H_{48}$
Mol wt	384.69
Crystal syst	Monoclinic
Space group	$P2_1/n$
a/Å	12.438(9)
b/Å	12.847(7)
c/Å	16.352(6)
β/deg	95.07(4)
V/Å^3	2603(2)
Z	4
D_{calcd}/g cm^{-3}	0.982
Cryst dimens/mm	0.60×0.40×0.05
Linear abs coeff/cm^{-1}	0.5
Radiation	Mo $K\alpha$ (λ=0.71069 Å)
2θ range/deg	<50.1
Scan type	ω–2θ
Total no. of rflns scanned	4825
No. of unique rflns	4592
No. of obsd rflns	1209 [I>2.50σ(I)]
No. of variables	253
R	0.069
R_w	0.065
Residual electron density/e Å^{-3}	+0.18/−0.17

The benzo[*b*]thiophene **18** is formed by a mechanism similar to that shown in Scheme 8; in this reaction, however, the C–S bond cleavage occurs under irradiation. The thiirane **22** is formed via a benzvalene intermediate **26** (Scheme 11). Similar photochemical valence isomerizations are well known.[16)] Since **22** gave **23**, **24**, and **25**, and both of **23** and **25** gave **24** (Scheme 12) under reaction conditions similar to those for **15c**, **23**—**25** are considered to be secondary photoproducts of **22**. Benzo[*b*]thiophene **18** was not photoreactive under identical conditions. A possibility that **25**

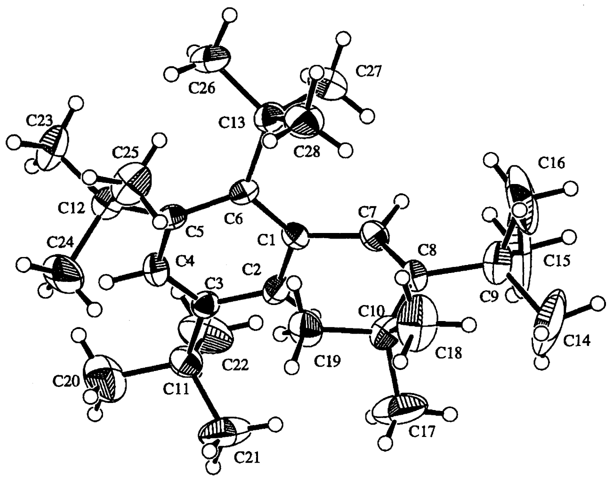
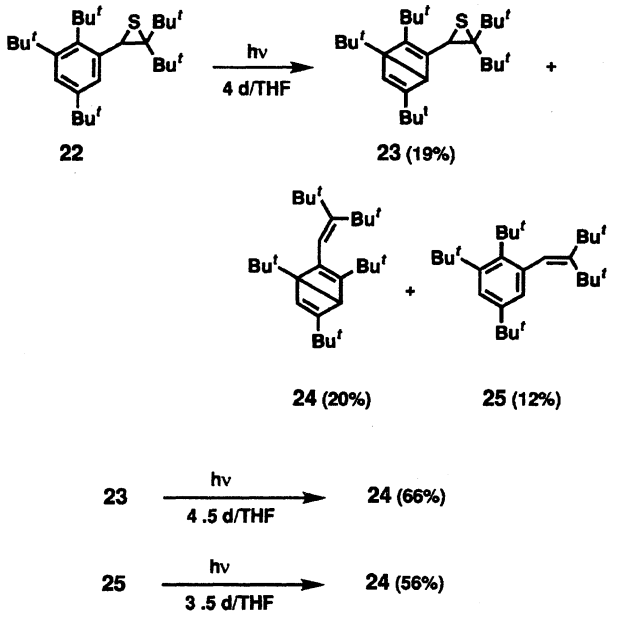


Fig. 1. ORTEP drawing of styrene **25** with thermal ellipsoid plot (30% probability).



Scheme 12.

Table 3. Atomic Coordinates and Isotropic Displacement of **25**

Atom	x/a	y/b	z/c	B
C(1)	0.8396(6)	0.1064(5)	0.2472(5)	3.2(4)
C(2)	0.8075(6)	0.1077(6)	0.3260(5)	3.9(4)
C(3)	0.7015(7)	0.1218(6)	0.3405(5)	3.6(4)
C(4)	0.6340(6)	0.1462(6)	0.2740(6)	4.1(4)
C(5)	0.6616(6)	0.1510(5)	0.1928(5)	3.3(4)
C(6)	0.7654(6)	0.1142(6)	0.1779(4)	3.3(4)
C(7)	0.9599(7)	0.1024(6)	0.2477(5)	4.1(4)
C(8)	1.0340(6)	0.1772(6)	0.2564(5)	3.8(4)
C(9)	1.1515(7)	0.1364(8)	0.2619(6)	6.2(6)
C(10)	1.0104(6)	0.2933(7)	0.2634(5)	4.5(5)
C(11)	0.6677(7)	0.1166(7)	0.4283(5)	4.7(5)
C(12)	0.5771(6)	0.2096(6)	0.1343(5)	4.4(4)
C(13)	0.8004(6)	0.0718(7)	0.0956(5)	4.6(5)
C(14)	1.2385(8)	0.200(1)	0.306(1)	17(1)
C(15)	1.1644(8)	0.040(1)	0.308(1)	19(1)
C(16)	1.188(1)	0.117(2)	0.1808(8)	23(2)
C(17)	1.0344(9)	0.3299(7)	0.3515(6)	10.2(7)
C(18)	1.0726(7)	0.3590(7)	0.2052(6)	9.0(7)
C(19)	0.8940(7)	0.3237(5)	0.2393(5)	5.6(5)
C(20)	0.5505(9)	0.151(1)	0.4324(5)	9.4(7)
C(21)	0.7372(8)	0.1886(8)	0.4842(6)	9.2(7)
C(22)	0.6768(8)	0.0073(8)	0.4597(5)	8.8(7)
C(23)	0.4833(6)	0.1403(7)	0.1001(5)	6.9(5)
C(24)	0.5249(7)	0.2979(8)	0.1816(6)	8.0(6)
C(25)	0.6268(7)	0.2687(6)	0.0662(5)	6.6(5)
C(26)	0.7052(7)	0.0314(7)	0.0381(5)	6.8(5)
C(27)	0.8709(7)	−0.0261(7)	0.1103(6)	7.3(6)
C(28)	0.8680(7)	0.1485(7)	0.0491(5)	6.8(5)

Table 4. Bond Lengths of **25** (Å)

C1–C2	1.383(9)	C9–C15	1.45(1)
C1–C6	1.401(9)	C9–C16	1.46(1)
C1–C7	1.50(1)	C10–C17	1.52(1)
C2–C3	1.372(9)	C10–C18	1.53(1)
C3–C4	1.351(9)	C10–C19	1.518(9)
C3–C11	1.53(1)	C11–C20	1.53(1)
C4–C5	1.403(9)	C11–C21	1.52(1)
C5–C6	1.415(9)	C11–C22	1.50(1)
C5–C12	1.552(9)	C12–C23	1.53(1)
C6–C13	1.55(1)	C12–C24	1.55(1)
C7–C8	1.330(9)	C12–C25	1.52(1)
C8–C9	1.55(1)	C13–C26	1.54(1)
C8–C10	1.53(1)	C13–C27	1.54(1)
C9–C14	1.49(1)	C13–C28	1.54(1)

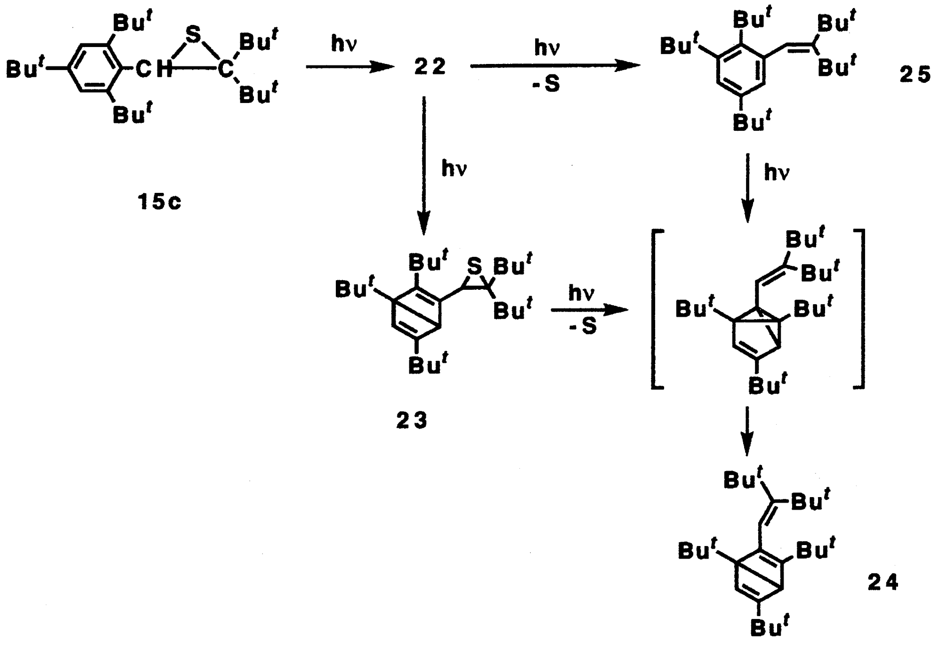
Table 5. Bond Angles of **25** (deg)

C2–C1–C6	122.0(7)	C8–C10–C17	110.5(7)
C2–C1–C7	111.4(7)	C8–C10–C18	112.4(7)
C6–C1–C7	126.5(7)	C8–C10–C19	114.7(7)
C1–C2–C3	121.6(7)	C17–C10–C18	110.5(8)
C2–C3–C4	115.5(7)	C17–C10–C19	105.6(7)
C2–C3–C11	120.3(8)	C18–C10–C19	102.7(7)
C4–C3–C11	124.1(8)	C3–C11–C20	111.8(7)
C3–C4–C5	125.9(7)	C3–C11–C21	110.4(7)
C4–C5–C6	116.9(7)	C3–C11–C22	110.1(7)
C4–C5–C12	113.3(7)	C20–C11–C21	107.1(8)
C6–C5–C12	129.4(7)	C20–C11–C22	107.3(8)
C1–C6–C5	115.5(7)	C21–C11–C22	110.1(8)
C1–C6–C13	117.5(7)	C5–C12–C23	113.3(6)
C5–C6–C13	126.7(7)	C5–C12–C24	109.8(6)
C1–C7–C8	131.2(7)	C5–C12–C25	113.3(7)
C7–C8–C9	113.8(7)	C23–C12–C24	105.6(7)
C7–C8–C10	125.3(7)	C23–C12–C25	111.5(7)
C9–C8–C10	120.9(7)	C24–C12–C25	102.4(7)
C8–C9–C14	118.9(9)	C6–C13–C26	112.9(7)
C8–C9–C15	112.4(8)	C6–C13–C27	110.6(7)
C8–C9–C16	111.7(9)	C6–C13–C28	114.3(7)
C14–C9–C15	100(1)	C26–C13–C27	102.6(7)
C14–C9–C16	105(1)	C26–C13–C28	109.9(7)
C15–C9–C16	107(1)	C27–C13–C28	105.8(7)

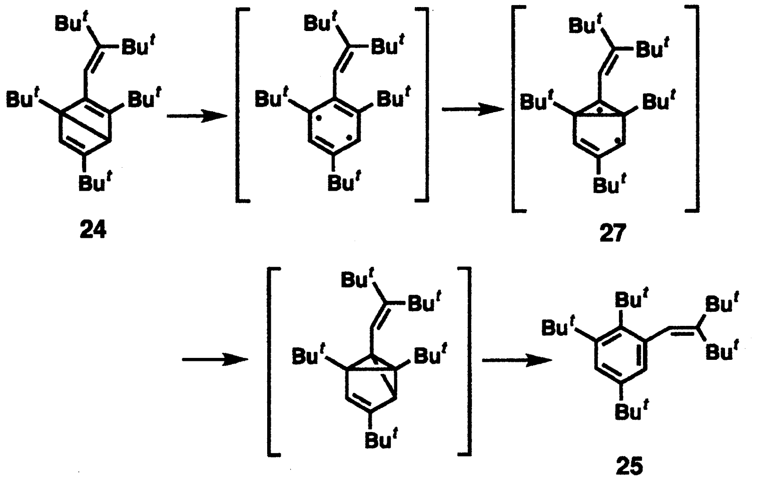
is formed via styrene **16c** can be eliminated by the fact that **16c** is stable under irradiation. A plausible reaction mechanism for the formation of **23**—**25** is shown in Scheme 13. These results indicate that steric congestion around the sp^3 benzylic carbon caused by two bulky *o*-*t*-butyl groups is an important factor for rearrangement to the Dewar benzene derivative.

Desulfurization of **15c** by hexamethylphosphorous triamide does not take place as described above, whereas that of **22** occurs to give **25**, suggesting less severe steric congestion around the thiirane ring in **22**. While the thiirane ring of **15** is protected by *t*-butyl groups at both *ortho*-positions, that of **22** is flanked by only one *t*-butyl group.

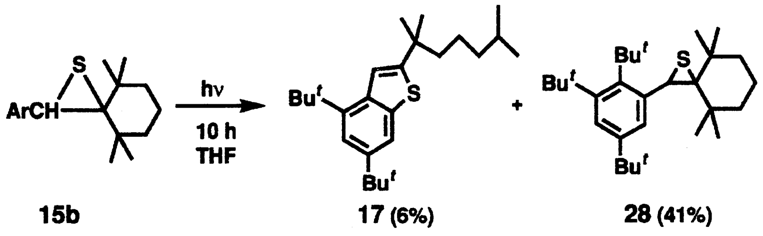
Thermolysis of **23** at 180 °C in toluene-d_8 in a sealed tube afforded **25**. The formation of **25** is most likely explained by desulfurization followed by aromatization, which is usually observed for Dewar benzenes.[16)] Interestingly, thermolysis of **24** under identical conditions gave also **25**. To our knowledge, this is the first thermal skeletal rearrangement from a Dewar benzene to a Kekulé benzene, and probably proceeds via a radical intermediate **27** stabilized by conjugation with a vinyl



Scheme 13.



Scheme 14.



Scheme 15.

group, as shown in Scheme 14.

The photolysis of thiirane **15b** gave benzo[*b*]thiophene **17** (6%) and a valence isomer **28** (41%) along with **15b** unreacted (27%) (Scheme 15), suggesting that the photochemical behavior of **15b** is similar to that of **15c** and that the formation of benzo[*b*]thiophene derivatives and valence isomers is common for the photolysis of highly congested thiiranes.

Experimental

All of the reactions were carried out under an argon atmosphere. Tetrahydrofuran (THF) was freshly distilled from sodium diphenylketyl under an argon atmosphere before use. The ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ with a Bruker AM-500 spectrometer using tetramethylsilane as an internal standard. High-resolution mass spectra (HRMS) were taken with a JEOL JMX-SX102 mass spectrometer.

UV-vis and infrared spectra were recorded on JASCO Ubest-50 and Horiba FT-200 spectrophotometers, respectively. All of the melting points were determined on a Yanaco micro melting-point apparatus and were uncorrected. Preparative high-performance liquid chromatography (HPLC) was carried out with LC-08 or LC-908 (column: Japan Analytical Industry, JAIGEL 1H+2H, styrene–divinylbenzene copolymer, pore size 25 Å) using chloroform as a solvent. Dry column chromatography (DCC), flash column chromatography (FCC), and preparative thin-layer chromatography (PTLC) were carried out using ICN silica DCC60A, silica gel BW-300 (Fuji Davison Chemical Co.), and Merck Kieselgel 60 PF254 Art. 7747, respectively. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, The University of Tokyo.

Reaction of (2,4,6-Tri-*t*-butyl)thiobenzaldehyde (1) with Diazomethane. To a solution of **1** (511 mg, 1.75 mmol) in THF (35 ml) was added an ether solution of diazomethane (10 molar amounts) via a dropping funnel over 1.5 h at room temperature; the mixture was stirred for 16 h. After nitrogen was bubbled through the solution, the solvent was evaporated under reduced pressure. The residue was separated by DCC (SiO_2/hexane) to give *trans*-4,5-bis-(2,4,6-tri-*t*-butylphenyl)-1,3-dithiolane (**2**) (195 mg, 38%), (2,4,6-tri-*t*-butyl)thioacetophenone (**3**) (44.5 mg, 8%), 2,4,6-tri-*t*-butylphenylthiirane (**4**) (26.4 mg, 5%), and 2,4,6-tri-*t*-butylbenzaldehyde (**5**) (34.4 mg, 7%),[17] 2,4-bis(2,4,6-tri-*t*-butylphenyl)-3,5-dithiahex-1-ene (**6**) (33.4 mg, 6%), 2,4,6-tri-*t*-butyl-α-methylthiostyrene (**7**) (27.1 mg, 5%), 2,4,6-tri-*t*-butylstyrene (**8**) (14.5 mg, 3%).

2: White crystals; mp 207.8—209.5 °C; ^{1}H NMR δ=1.16 (s, 18H), 1.20 (s, 18H), 1.64 (s, 18H), 4.31 (s, 2H), 5.27 (s, 2H), 6.78 (d, J=2.2 Hz, 2H), and 7.24 (d, J=2.2 Hz, 2H); ^{13}C NMR δ=31.27 (q), 34.21 (q), 34.41 (q), 37.45 (t), 38.23 (s), 40.16 (s×2), 65.46 (d), 121.92 (d), 124.15 (d), 132.00 (s), 148.12 (s), 149.13 (s), and 153.50 (s). HRMS (70 eV) Found: m/z 594.4313. Calcd for $C_{39}H_{62}{}^{32}S_2$: M, 594.4293. Found: C, 78.85; H, 10.45; S, 10.89%. Calcd for $C_{39}H_{62}S_2$: C, 78.72; H, 10.50; S, 10.78%.

3: Violet crystals; mp 121.0—123.0 °C; ^{1}H NMR δ= 1.31 (s, 9H), 1.43 (s, 18H), 3.30 (s, 3H), and 7.45 (s, 2H); ^{13}C NMR δ=31.30 (q), 33.66 (q), 34.81 (s), 38.19 (s), 49.83 (q), 123.39 (d), 143.09 (s), 147.23 (s), 148.58 (s), and 282.24 (s); UV-vis (hexane) 210 (ε 19900), 320 (800), and 561 (16). HRMS (70 eV) Found: m/z 304.2215. Calcd for $C_{20}H_{32}{}^{32}S$: M, 304.2223.

4: White crystals; mp 90.0—91.9 °C; ^{1}H NMR δ=1.26 (s, 9H), 1.52 (s, 18H), 2.53 (d, J=5.7 Hz, 1H), 2.87 (d, J=5.7 Hz, 1H), 4.30 (t, J=5.7 Hz, 1H), and 7.18 (s, 2H); ^{13}C NMR δ=31.30 (q), 31.68 (t), 33.66 (q), 38.05 (s×2), 39.71 (d), 122.70 (d), 134.59 (s), 147.02 (s), and 151.32 (s). HRMS (70 eV) Found: m/z 304.2213. Calcd for $C_{20}H_{32}{}^{32}S$: M, 304.2225. Found: C, 78.71; H, 10.49; S, 10.64%. Calcd for $C_{20}H_{32}S$: C, 78.88; H, 10.59; S, 10.53%.

6: White crystals; mp 154.5—156.0 °C (decomp); ^{1}H NMR δ=1.297 (s, 9H), 1.303 (s, 9H), 1.41 (s, 9H), 1.61 (s, 9H), 1.62 (s, 9H), 1.65 (s, 9H), 1.80 (s, 3H), 5.40 (brs, 1H), 5.45 (brs, 1H), 6.37 (s, 1H), and 7.35—7.51 (m, 4H); ^{13}C NMR δ=16.29 (q), 31.21 (q), 31.29 (q), 34.10 (q), 34.23 (q), 34.51 (q), 34.76 (s), 34.84 (s), 35.14 (q), 38.07 (s), 38.66 (s), 39.05 (s), 39.32 (s), 51.50 (d), 114.45 (t), 121.95 (d), 123.37 (d), 123.89 (d), 125.95 (d), 133.50 (s), 134.06 (s), 145.23 (s), 148.26 (s), 148.67 (s), 148.72 (s), 149.14 (s), 149.64 (s), and 151.80 (s). HRMS (70 eV) Found: m/z 608.4465. Calcd for $C_{40}H_{64}{}^{32}S_2$: M, 608.4449. Found: C, 78.86; H, 10.47; S, 10.43%. Calcd for $C_{40}H_{64}S_2$: C, 78.88; H, 10.59; S, 10.53%.

7: Colorless viscous oil; ^{1}H NMR δ=1.31 (s, 9H), 1.50 (s, 18H), 2.21 (s, 3H), 5.13 (brs, 1H), 5.36 (brs, 1H), and 7.43 (s, 2H); ^{13}C NMR δ=15.71 (q), 31.32 (q), 33.71 (q), 33.90 (s), 34.84 (s), 112.60 (t), 123.45 (d), 134.27 (s), 147.40 (s), 148.01 (s), and 148.67 (s). HRMS (70 eV) Found: m/z 318.2384. Calcd for $C_{21}H_{34}{}^{32}S$: M, 318.2381.

8: White crystals; mp 107.0—109.0 °C; ^{1}H NMR δ=1.33 (s, 9H), 1.41 (s, 18H), 5.04 (dd, J=18, 2.4 Hz, 1H), 5.43 (dd, J=11, 2.4 Hz, 1H), 7.20 (dd, J=18, 11 Hz, 1H), and 7.39 (s, 2H); ^{13}C NMR δ=31.5 (q), 32.4 (q), 34.9 (s), 37.1 (s), 119.3 (t), 121.3 (d), 136.5 (s), 140.8 (d), 147.9 (s), and 148.1 (s). HRMS (70 eV) Found: m/z 272.2527. Calcd for $C_{20}H_{32}$: M, 272.2504.

Reaction of Thiobenzaldehyde 1 with Diphenyldiazomethane (14a). To a solution of **1** (232 mg, 0.80 mmol) and diphenyldiazomethane (**14a**)[18] (263 mg, 1.36 mmol) in THF (15 ml) was added a catalytic amount of copper(I) chloride at 0 °C. The reaction mixture was warmed to room temperature and stirred for 4.5 h. The reaction mixture was filtered through cotton, and the solvent was evaporated under reduced pressure. The residue was separated by DCC (SiO_2/hexane : CH_2Cl_2=2 : 1) and HPLC to give 2,2-diphenyl-3-(2,4,6-tri-*t*-butylphenyl)thiirane (**15a**) (284 mg, 78%) and 2,4,6-tri-*t*-butylbenzaldehyde (**5**) (25 mg, 12%). The reaction of **1** with **14a** (5 molar amounts) in refluxing THF for 6 d without the catalyst gave **15a** (20%), 6, 8-di-*t*-butyl-3,4-dihydro-4,4-dimethyl-1*H*-2-benzothiopyran (**13**) (55%)[9] and **5** (13%).

15a: White crystals; mp 144.2—145.2 °C; ^{1}H NMR δ=1.03 (s, 9H), 1.28 (s, 9H), 1.58 (s, 9H), 5.50 (s, 1H), and 6.49—7.54 (m, 12H); ^{13}C NMR δ=31.43 (q), 33.54 (q), 33.74 (q), 34.16 (s), 37.97 (s), 39.06 (s), 52.66 (d), 56.47 (s), 120.74 (d), 122.64 (d), 126.38 (d), 126.43 (d), 126.71 (d), 128.13 (d), 128.94 (d), 129.92 (s), 131.08 (d), 138.72 (s), 144.75 (s), 146.90 (s), 150.83 (s), and 155.06 (s); UV-vis (hexane) 239 (ε 9200) and 293 (750) nm. HRMS (70 eV) Found: m/z 456.2847. Calcd for $C_{32}H_{40}{}^{32}S$: M, 456.2849. Found: C, 84.22; H, 8.70; S, 6.98%. Calcd for $C_{32}H_{40}S$: C, 84.15; H, 8.83; S, 7.02%.

Reaction of Thiobenzaldehyde 1 with Diazo-2,2,6,6-tetramethylcyclohexane (14b). To a solution of **1** (595 mg, 2.05 mmol) and diazo-2,2,6,6-tetramethylcyclohexane (**14b**)[19] (404 mg, 2.44 mmol) in THF (40 ml) was added a catalytic amount of copper(I) chloride at −78 °C. The reaction mixture was warmed to room temperature and stirred for 12 h. After insoluble substances were filtered through cotton, the solvent was evaporated under reduced pressure. The residue was separated by DCC (SiO_2/hexane) and HPLC to give 3′-(2,4,6-tri-*t*-butylphenyl)-2,2,6,6-tetramethylspiro[cyclohexane-1,2′-thiirane] (**15b**) (408 mg, 47%) and benzaldehyde **5** (64 mg, 12%) with recovery of **1** (20%). The reaction of **1** with **14b** (2 molar amounts) at room temperature for 5 d without the catalyst gave **15b** (10%) and **5** (23%) with recovery of **1** (21%).

15b: White crystals; mp 98.8—99.9 °C; ^{1}H NMR δ= −0.17 (s, 3H), 0.67 (s, 3H), 1.18 (s, 3H), 1.23 (s, 9H), 1.43

(s, 3H), 1.46 (s, 9H), 1.49 (s, 9H), 1.16—1.70 (m, 6H), 4.78 (s, 1H), 7.01 (d, J=2.3 Hz, 1H), and 7.05 (d, J=2.3 Hz, 1H); ^{13}C NMR δ=19.47 (t), 25.80 (q), 27.50 (q), 30.18 (q), 31.39 (q), 31.85 (q), 33.67 (q), 33.98 (s), 34.36 (q), 38.04 (s), 38.95 (s), 39.12 (s), 39.26 (s), 41.68 (t), 43.77 (t), 50.51 (d), 67.07 (s), 120.69 (d), 122.97 (d), 132.16 (s), 146.28 (s), 151.17 (s), and 154.18 (s); UV-vis (hexane) 301 (ε 280), 251 (5000), and 221 (18000) nm. HRMS (70 eV) Found: m/z 428.3477. Calcd for $C_{29}H_{48}{}^{32}S$: M, 428.3476. Found: C, 81.15; H, 11.18; S, 7.47%. Calcd for $C_{29}H_{48}S$: C, 81.24; H, 11.28; S, 7.48%.

Reaction of Thiobenzaldehyde 1 with 3-Diazo-2,2,4,4-tetramethylpentane (14c). To a solution of **1** (62.6 mg, 0.21 mmol) and a catalytic amount of copper(I) chloride in THF (5 ml) was added 3-diazo-2,2,4,4-tetramethylpentane (**14c**)[11] (171 mg, 1.1 mmol) at −40 °C. The reaction mixture was gradually warmed to room temperature and stirred for 12 h. After insoluble substances were filtered off through cotton, the solvent was evaporated under reduced pressure. The residue was separated by PTLC (SiO_2/hexane) and HPLC to give 2,2-di-*t*-butyl-3-(2,4,6-tri-*t*-butylphenyl)thiirane (**15c**) (47.5 mg, 54%) and benzaldehyde **5** (12.4 mg, 21%). When CH_2Cl_2 or pentane was used as solvent, the yields of **15c** and **5** were 46 and 10% or 48 and 13%, respectively. The reaction of **1** with **14c** (1.2 molar amounts) in refluxing THF for 4 d without the catalyst gave **15c** (13%) and **5** (9%) with recovery of **1** (74%).

15c: White crystals; mp 104.2—106.0 °C; ^{1}H NMR δ=0.56 (s, 9H), 1.23 (s, 9H), 1.30 (s, 9H), 1.42 (s, 9H), 1.50 (s, 9H), 4.64 (s, 1H), 6.99 (d, J=2.7 Hz, 1H), and 7.08 (d, J=2.7 Hz, 1H); ^{13}C NMR δ=31.37 (q), 31.56 (q), 33.62 (q), 34.09 (q×2), 34.06 (s), 38.96 (s), 39.30 (s×2), 40.22 (s), 52.14 (d), 66.38 (s), 119.26 (d), 123.05 (d), 132.87 (s), 146.52 (s), 151.41 (s), and 154.55 (s); UV-vis (hexane) 221 (ε 26000), 252 (7800), and 303 (240) nm. HRMS (70 eV) Found: m/z 416.3486. Calcd for $C_{28}H_{48}{}^{32}S$: M, 416.3477. Found: C, 80.59; H, 11.68; S, 7.79%. Calcd for $C_{28}H_{48}S$: C, 80.70; H, 11.61; S, 7.69%.

Reaction of Thiobenzaldehyde 1 with 2-Diazo-1,1,3,3-tetramethylindan (14d). To a solution of **1** (53.4 mg, 0.18 mmol) and 2-diazo-1,1,3,3-tetramethylindan (**14d**) (186.7 mg, 0.93 mmol)[19] in THF (4 ml) was added a catalytic amount of copper(I) chloride at −78 °C. The reaction mixture was gradually warmed to room temperature and stirred for 13.5 h. After insoluble substances were filtered off through cotton, the solvent was evaporated under reduced pressure. The residue was separated by DCC (SiO_2/hexane) and HPLC to give 3′-(2,4,6-tri-*t*-butylphenyl)-1,1,3,3-tetramethylspiro[indan-2,2′-thiirane] (**15d**) (40.0 mg, 48%) and benzaldehyde **5** (7.4 mg, 15%).

15d: White crystals; mp 197.1—198.2 °C; ^{1}H NMR δ=−0.01 (s, 3H), 1.07 (s, 9H), 1.20 (s, 3H), 1.25 (s, 9H), 1.41 (s, 3H), 1.45 (s, 3H), 1.55 (s, 9H), 4.74 (s, 1H), 6.85 (d, J=2.2 Hz, 1H), 6.90—6.91 (m, 1H), 7.10—7.17 (m, 3H), and 7.21 (d, J=2.2 Hz, 1H); ^{13}C NMR δ=21.44 (q), 23.53 (q), 31.42 (q), 31.79 (q), 34.11 (q), 34.18 (s), 35.65 (q), 37.29 (q), 37.31 (s), 39.45 (s), 46.29 (s), 47.68 (s), 50.04 (d), 72.04 (s), 119.21 (d), 121.66 (d), 121.92 (d), 123.78 (d), 126.53 (d), 126.68 (d), 134.97 (s), 146.66 (s), 148.81 (s), 149.97 (s), 151.28 (s), and 154.56 (s). HRMS (70 eV) Found: m/z 462.3329. Calcd for $C_{32}H_{46}{}^{32}S$: M, 462.3320. Found: C, 82.76; H, 9.83; S, 6.87%. Calcd for $C_{32}H_{46}S$: C, 83.05; H, 10.02; S, 6.93%.

Reaction of Thiobenzaldehyde 1 with Diazo Compounds 14a, 14b, and 14c. To a solution of **1** (205.8 mg, 0.71 mmol) in THF (14 ml) was added a solution of **14a** (735.0 mg, 3.8 mmol) in THF (5 ml) at room temperature. The reaction mixture was warmed to reflux and stirred for 6 d. The solvent was evaporated under reduced pressure, and the residue was separated by DCC (SiO_2/hexane : CH_2Cl_2=5 : 1) to give **15a** (64.2 mg, 20%), **13** (112.6 mg, 55%), and **5** (25.3 mg, 13%). The reaction of **1** (154.3 mg, 0.53 mmol) with **14c** (99.5 mg, 0.65 mmol) was similarly carried out to give **15c** (28.6 mg, 13%) and **5** (12.9 mg, 9%) with recovery of **1** (113.8 mg, 74%). The reaction of **1** (101.2 mg, 0.35 mmol) with **14b** (132.3 mg, 0.80 mmol) was also carried out at room temperature to give **15b** (14.8 mg, 10%) and **5** (22.3 mg, 23%) with recovery of **1** (21.1 mg, 21%).

Desulfurization of Thiirane 15a. To a solution of **15a** (98.4 mg, 0.22 mmol) in THF (4 ml) was added hexamethylphosphorous triamide (140 µl, 0.66 mmol) at −78 °C. The reaction mixture was warmed to room temperature and stirred overnight. The solvent was evaporated under reduced pressure, and the residue was separated by HPLC to give 1,1-diphenyl-2-(2,4,6-tri-*t*-butylphenyl)ethene (**16a**) (83.6 mg, 90%).

16a: White crystals; mp 123.5—124.8 °C; ^{1}H NMR δ=1.31 (s, 18H), 1.36 (s, 9H), 6.54—6.56 (m, 2H), 6.91—6.94 (m, 2H), 6.97—7.02 (m, 1H), 7.32—7.35 (m, 1H), 7.35 (s, 1H), 7.36 (s, 2H), and 7.38—7.43 (m, 4H); ^{13}C NMR δ=31.54 (q), 32.14 (q), 34.66 (s), 37.15 (s), 121.99 (d), 126.51 (d), 126.68 (d), 127.07 (d), 128.33 (d), 128.40 (d), 130.10 (d), 133.52 (s), 134.20 (d), 139.43 (s), 139.83 (s), 145.12 (s), 147.96 (s), and 146.57 (s); UV-vis (hexane) 247 (ε 11000) nm. HRMS (70 eV) Found: m/z 424.3139. Calcd for $C_{32}H_{40}$: M, 424.3129. Found: C, 90.61; H, 9.50%. Calcd for $C_{32}H_{40}$: C, 90.51; H, 9.49%.

Desulfurization of Thiirane 15d. To a solution of **15d** (50.9 mg, 0.11 mmol) in THF (2 ml) was added hexamethylphosphorous triamide (250 µl, 1.1 mmol) at room temperature. The reaction mixture was stirred under reflux for 10 d. It was then evaporated under reduced pressure, and the residue was separated by PTLC (SiO_2/hexane) to give 2-(2,4,6-tri-*t*-butylbenzylidene)-1,1,3,3-tetramethylindan (**16d**) (15.4 mg, 33%) with recovery of **15d** (22.9 mg, 45%).

16d: White crystals; mp 132.0—133.0 °C; ^{1}H NMR δ=0.93 (s, 6H), 1.33 (s, 9H), 1.36 (s, 18H), 1.55 (s, 6H), 6.98 (m, 1H), 7.11 (s, 1H), 7.15—7.20 (m, 3H), and 7.26 (s, 2H); ^{13}C NMR δ=30.62 (q), 31.30 (q), 31.52 (q), 33.85 (q), 34.57 (s), 38.17 (s), 46.72 (s), 48.01 (s), 121.16 (d), 121.92 (d), 122.38 (d), 125.57 (d), 126.64 (d), 126.93 (d), 131.49 (s), 147.50 (s), 148.54 (s), 148.77 (s), 150.81 (s), and 152.67 (s). HRMS (70 eV) Found: m/z 430.3591. Calcd for $C_{32}H_{46}$: M, 430.3599. Found: C, 89.27; H, 10.83%. Calcd for $C_{32}H_{46}$: C, 89.24; H, 10.76%.

Thermolysis of Thiiranes 15a, 15b, and 15c. After a solution of **15a** (37.4 mg, 0.082 mmol) in dry toluene (0.5 ml) was heated at 180 °C for 2 d in a degassed sealed tube, the solvent was evaporated under reduced pressure. The residue was separated by PTLC (SiO_2/hexane) to give olefin **16a** (26.5 mg, 76%) and elemental sulfur (2.2 mg, 84%). Thermolysis of **15b** (75.2 mg, 0.18 mmol) and **15c** (43.1

mg, 0.10 mmol) was similarly carried out to give 4,6-di-*t*-butyl-2-(1,1,5-trimethylhexyl)benzo[*b*]thiophene (**17**) (26.0 mg, 40%) and 2,4,6-tri-*t*-butylbenzo[*b*]thiophene (**18**) (31.4 mg, 100%), respectively.

17: Colorless oil; ^{1}H NMR δ=0.81 (d, J=6.6 Hz, 6H), 1.37 (s, 9H), 1.41 (s, 6H), 1.51 (s, 9H), 1.12—1.66 (m, 7H), 7.28 (s, 1H), 7.33 (d, J=1.6 Hz, 1H), and 7.64 (d, J=1.6 Hz, 1H); ^{13}C NMR δ=22.53 (t), 22.65 (q), 27.85 (d), 30.04 (q), 30.92 (q), 31.58 (q), 34.96 (s), 36.13 (s), 38.00 (s), 39.57 (t), 45.34 (t), 116.26 (d), 118.88 (d), 119.04 (d), 134.81 (s), 140.60 (s), 144.11 (s), 146.07 (s), and 154.24 (s). HRMS (70 eV) Found: m/z 372.2841. Calcd for $C_{25}H_{40}{}^{32}S$: M, 372.2851.

18: White crystals; mp 140.8—141.3 °C; ^{1}H NMR δ= 1.36 (s, 9H), 1.44 (s, 9H), 1.51 (s, 9H), 7.32 (s, 1H), 7.32 (d, J=1.4 Hz, 1H), and 7.63 (d, J=1.4 Hz, 1H); ^{13}C NMR δ=30.92 (q), 31.57 (q), 32.24 (q), 34.81 (s), 34.95 (s), 36.13 (s), 116.26 (d), 118.10 (d), 118.93 (d), 134.76 (s), 140.48 (s), 144.19 (s), 146.19 (s), and 155.41 (s); UV-vis (hexane) 206 (ε 20000), 229 (30000), 263 (12000), 269 (12000), 289 (2800), and 300 (2100) nm. HRMS (70 eV) Found: m/z 302.2061. Calcd for $C_{20}H_{30}{}^{32}S$: M, 302.2068. Found: C, 79.26; H, 10.01; S, 10.74%. Calcd for $C_{20}H_{30}S$: C, 79.41; H, 10.00; S, 10.60%.

Photochemical Reactions of Thiirane 15a and Olefin 16a. A THF solution (8 ml) of **15a** (202 mg, 0.44 mmol) in a Pyrex flask was irradiated with a 400-W medium-pressure mercury lamp at room temperature for 4 d; the solvent was then evaporated under reduced pressure. The residue was separated by DCC (SiO_2/hexane) to give 1,1-diphenyl-2-(2,4,6-tri-*t*-butylphenyl)ethene (**16a**) (39 mg, 21%) and 1,3-di-*t*-butyl-9-phenylphenanthrene (**21**) (106 mg, 66%). Photoreaction (2 d, in 1 ml THF) of **16a** (15.6 mg, 0.037 mmol) was similarly carried out to give phenanthrene **21** (3.8 mg, 28%) with recovery of **16a** (6.4 mg, 41%).

21: White crystals; mp 176.2—178.0 °C; ^{1}H NMR δ=1.51 (s, 9H), 1.67 (s, 9H), and 7.43—8.82 (m, 12H); ^{13}C NMR δ=31.53 (q), 32.25 (q), 35.43 (s), 36.35 (s), 116.89 (d), 122.80 (d), 123.27 (d), 126.05 (d), 126.12 (d), 126.16 (d), 126.56 (d), 127.15 (d), 127.51 (s), 128.32 (d), 130.13 (s), 130.17 (d), 131.05 (s), 131.67 (s), 136.26 (s), 141.80 (s), 146.29 (s), and 148.04 (s). HRMS (70 eV) Found: m/z 366.2326. Calcd for $C_{28}H_{30}$: M, 366.2348. Found: C, 91.68; H, 8.38%. Calcd for $C_{28}H_{30}$: C, 91.75; H, 8.25%.

Photochemical Reaction of Thiirane 15c. A solution of **15c** (181 mg, 0.44 mmol) in THF (8 ml) was irradiated for 4.5 d in a manner similar to **15a**. After removing the solvent under reduced pressure, the residue was separated by DCC (SiO_2/hexane) and HPLC to give benzo[*b*]thiophene **18** (11.6 mg, 9%), 2,2-di-*t*-butyl-3-(2,3,5-tri-*t*-butylphenyl)thiirane (**22**) (22.9 mg, 13%), 2,2-di-*t*-butyl-3-(3,4,6-tri-*t*-butylbicyclo[2.2.0]hexa-2,5-dien-2-yl)thiirane (**23**) (18.6 mg, 10%), 2-*t*-butyl-3,3-dimethyl-1-(1,3,5-tri-*t*-butylbicylco[2.2.0]hexa-2,5-diene-2-yl)-1-butene (**24**) (20.2 mg, 12%), and 1,2,4-tri-*t*-butyl-6-(2-*t*-butyl-3,3-dimethyl-1-butenyl)benzene (**25**) (18.4 mg, 10%).

22: Colorless oil; ^{1}H NMR δ=0.76 (brs, 9H), 1.26 (s, 9H), 1.34 (s, 9H), 1.38 (s, 9H), 1.56 (s, 9H), 4.53 (s, 1H), 7.14 (d, J=2.2 Hz, 1H), and 7.25 (d, J=2.2 Hz, 1H); ^{13}C NMR δ=31.24 (q), 32.12 (q), 33.74 (s), 34.58 (q), 34.96 (q×2), 38.77 (s), 39.69 (s), 39.76 (s), 40.08 (s), 54.27 (d), 67.92 (s), 124.66 (d), 125.85 (d), 139.14 (s), 142.93 (s), 146.28 (s), and 152.15 (s). HRMS (70 eV) Found: m/z 416.3495. Calcd for $C_{28}H_{48}{}^{32}S$: M, 416.3477.

23: Colorless oil; ^{1}H NMR δ=0.97 (s, 9H), 1.08 (s, 9H), 1.19 (s, 9H), 1.20 (s, 9H), 1.33 (s, 9H), 3.35 (d, J=1.4 Hz, 1H), 3.48 (s, 1H), and 6.09 (d, J=1.4 H, 1H); ^{13}C NMR δ=28.44 (q), 28.86 (q), 29.68 (q), 31.54 (q), 33.05 (s), 33.11 (s), 33.25 (q), 34.45 (s), 38.54 (s), 39.61 (s), 45.61 (d), 49.67 (d), 63.16 (s), 68.14 (s), 131.01 (d), 143.16 (s), 158.52 (s), and 165.27 (s). HRMS (70 eV) Found: m/z 416.3494. Calcd for $C_{28}H_{48}{}^{32}S$: M, 416.3477.

24: Colorless oil; ^{1}H NMR δ=1.00 (s, 18H), 1.07 (s, 9H), 1.18 (s, 9H), 1.35 (s, 9H), 3.33 (d, J=1.3 Hz 1H), 5.97 (s, 1H), and 6.04 (d, J=1.3 Hz, 1H); ^{13}C NMR δ=27.84 (q), 28.68 (q), 28.88 (q), 32.27 (q), 32.87 (s), 32.97 (s), 33.46 (q), 34.65 (s), 37.74 (s), 38.83 (s), 49.94 (d), 63.29 (s), 123.95 (d), 130.96 (d), 145.80 (s), 152.55 (s), 153.16 (s), and 164.74 (s). HRMS (70 eV) Found: m/z 384.3754. Calcd for $C_{28}H_{48}$: M, 384.3756.

25: White crystals; mp 72.5—75.0 °C; ^{1}H NMR δ=0.89 (s, 9H), 1.26 (s, 9H), 1.35 (s, 9H), 1.45 (s, 9H), 1.50 (s, 9H), 6.62 (d, J=2.5 Hz, 1H), 7.15 (s, 1H), and 7.30 (d, J=2.5 Hz, 1H), ^{13}C NMR δ=31.26 (q), 33.11 (q), 33.27 (q), 34.14 (q), 34.94 (q), 37.51 (s), 38.05 (s), 38.39 (s), 39.35 (s), 39.50 (s), 124.67 (d), 124.99 (d), 130.28 (d), 141.86 (s), 143.49 (s), 145.49 (s), 149.22 (s), and 149.62 (s). HRMS (70 eV) Found: m/z 384.3760. Calcd for $C_{28}H_{48}$: M, 384.3756.

Photochemical Reaction of Thiiranes 22 and 23. Thiiranes **22** (76.2 mg, 0.18 mmol) and **23** (14.5 mg, 0.035 mmol) in THF (5 ml and 1 ml, respectively) were similarly irradiated for 4 d. After separation by PTLC (SiO_2/hexane), **22** gave **23** (14.2 mg, 19%), **24** (13.7 mg, 20%), and **25** (7.4 mg, 12%) with the recovery of **22** (8.6 mg, 12%), while **23** gave **24** (8.9 mg, 66%).

Photochemical Reaction of Olefins 25 and 16c. Olefins **25** (10.0 mg, 0.026 mmol) and **16c** (3.6 mg, 0.0094 mmol) in THF were similarly irradiated for 4 d. After purification by PTLC (SiO_2/hexane), **25** gave **24** (5.6 mg, 56%), while **16c** was recovered quantitatively.

Desulfurization of Thiirane 22. To a solution of **22** (7.5 mg, 0.018 mmol) in deuteriochloroform (0.5 ml) was added hexamethylphosphorous triamide (94 µl, 0.43 mmol) at room temperature. The reaction mixture was warmed to 80 °C and kept at the same temperature for 15 d. The ^{1}H NMR spectrum showed a quantitative formation of the corresponding olefin **25**.

Thermolysis of Thiirane 23 and Dewar Benzene 24. A solution of **23** (8.7 mg, 0.021 mmol) in toluene-d_8 (0.5 ml) was placed in an NMR tube, degassed and sealed. After the mixture was heated at 180 °C for 7 d, a quantitative formation of the corresponding benzene derivative **25** was confirmed by ^{1}H NMR. Similarly, ^{1}H NMR monitoring of the thermolysis of **24** (180 °C, 11 d) showed a quantitative formation of **25**.

Photochemical Reaction of Thiirane 15b. A solution of **15b** (101.1 mg, 0.24 mmol) in THF (8 ml) was irradiated with a 400-W medium-pressure mercury lamp at room temperature for 10 h. After removing the solvent under reduced pressure, the residue was subjected to PTLC (SiO_2/hexane) and HPLC to give 4,6-di-*t*-butyl-2-(1,1,5-trimethylhexyl)benzo[*b*]thiophene (**17**) (5.3 mg, 6%) and 2,2,6,6-tetramethyl-3′-(2,3,5-tri-*t*-butylphenyl)spiro[cyclohexane-1,2′-thiirane] (**28**) (42.0 mg, 41%) with recovery of **15b**

(27.5 mg, 27%).

28: White crystals; mp 124.8—126.0 °C; ^{1}H NMR δ= 0.43 (s, 3H), 0.66 (s, 3H), 1.16 (s, 3H), 1.28 (s, 9H), 1.37 (s, 3H), 1.39 (s, 9H), 1.57 (s, 9H), 1.20—1.77 (m, 6H), 4.66 (s, 1H), 7.03 (d, J=2.5 Hz, 1H), and 7.25 (d, J=2.5 Hz, 1H); ^{13}C NMR δ=19.41 (t), 26.82 (q), 29.00 (q), 30.30 (q), 31.14 (q), 32.49 (q), 33.59 (s), 34.55 (q), 34.82 (q), 38.20 (s), 38.30 (s), 38.62 (s), 39.96 (s), 39.96 (t), 40.74 (t), 52.42 (d), 67.95 (s), 125.02 (d), 125.71 (d), 138.45 (s), 141.45 (s), 147.96 (s), and 151.87 (s). HRMS (70 eV) Found: m/z 428.3462. Calcd for $C_{29}H_{48}{}^{32}S$: M, 428.3477. Found: C, 81.03; H, 11.06; S, 7.40%. Calcd for $C_{29}H_{48}S$: C, 81.24; H, 11.28; S, 7.48%.

Single-Crystal X-Ray Diffraction Analysis of 25. Single crystals of **25** suitable for X-ray diffraction analysis were grown by recrystallization from EtOH. A measurement was made on a Rigaku AFC5R diffractometer with graphite-monochromated Mo $K\alpha$ (λ=0.71069 Å) radiation and a 12-kW rotating anode generator. Initial lattice parameters were determined from 23 accurately centered reflections with 2θ values in the range from 12.7 to 23.4°. Cell constants and other pertinent data were collected, and are listed in Table 2. The data were collected at 23±1 °C using the ω–2θ scan technique to a maximum 2θ value of 50.1°. Of the 4825 reflections which were collected, 4592 were unique (R_{int}=0.060). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied). The linear absorption coefficient for Mo $K\alpha$ is 0.5 cm^{-1}. An empirical absorption correction, based on azimuthal scans of several reflections, was applied and resulted in transmission factors ranging from 0.96 to 1.00. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were located in the calculated positions. The final cycle of full-matrix least-squares refinement was based on 1209 observed reflections [$I>2.50\sigma(I)$] and 253 variable parameters and converged (the largest parameter shift was 0.05-times its esd) with unweighted and weighted agreement factor of R=0.069 and R_{w}=0.065. The final values of selected bond distances and angles are listed in Tables 4 and 5. All calculations were performed using the TEXSAN crystallographic software package of the Molecular Structure Corp.

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