mixture was stirred at 25 °C for 12–24 h, concentrated under diminished pressure to $^{1}/_{2}$ volume, and filtered to provide the requisite 1,2-di-*O*-acetyl-3,4-di-*O*-benzyl-β-D-glucodialdehydo-1,5-pyranose 6-acylhydrazone derivative. Concentration of the filtrate provided additional product; purification was achieved by crystallization from methanol–ether.

General Procedure for Preparation of *N*-Acylhydrazones 37–39. A suspension of 1,2-di-*O*-acetyl-3,4-di-*O*-benzyl-β-D-glucodialdehydo-1,5-pyranose 6-acylhydrazone (0.2 mmol) (**33–35**) in 10 mL of methanol was treated with 20 μL of 1.0 M sodium methoxide in CH_3OH at 25 °C for 1–2 h. The reaction mixture was concentrated and the desired 3,4-di-*O*-benzyl-β-D-glucodialdehydo-1,5-pyranose 6-acylhydrazone was purified by preparative silica gel TLC, development with 5–8% methanol in dichloromethane.

3,4-Di-*O*-benzyl-1,6-dideoxy-1,6-(1-hydrazinyl-2-ylidene)-β-D-glucodialdehydo-1,5-pyranose (28). Hydrazinoglucodialdehyde derivative **39** (80 mg, 0.14 mmol) in 0.85 mL of THF was treated with 90 mg of freshly activated (HCl washed) Zn dust suspended in 0.17 mL of 0.1 M potassium phosphate buffer, pH 4.6. The reaction mixture was stirred at 25 °C for 48 h, then diluted with ether (20 mL), and filtered. The filtrate was concentrated, and the residue was partitioned between ether (20 mL) and saturated brine (10 mL). The organic layer was dried (Na_2SO_4) and concentrated to give 43 mg of a yellow oil, which was purified by preparative silica gel TLC, development with 25% hexane in ethyl acetate. 3,4-Di-*O*-benzyl-1,6-(1-hydrazinyl-2-ylidene)-β-D-glucodialdehydo-1,5-pyranose (**28**) was obtained as a colorless syrup, yield 24 mg (50%): ^1H NMR ($CDCl_3$, $(CH_3)_4Si$) δ 2.20–2.68 (m, 2), 3.5–3.65 (m, 3), 4.5–4.85 (m, 5), 5.15 (m, 1), 6.7–6.8 (br s, 1), 7.25 (s, 10); mass spectrum (chemical ionization, CH_4), *m/z* 395 [$(M + 41)^+$], 383 [$(M + 29)^+$], 335 [$(M + 1)^+$].

Acetylation (acetic anhydride, pyridine) provided a diacetate that was purified by preparative TLC on silica gel (development with 40% ethyl acetate in hexane) and obtained as a colorless syrup: ^1H NMR ($CDCl_3$, $(CH_3)_4Si$) δ 1.85 (s, 3), 2.25 (s, 3), 3.60–4.05 (m, 2), 4.4–4.8 (m, 4), 5.00 (m, 1), 5.25 (m, 1), 5.55 (m, 1), 6.75 (br s, 1), 7.25 (m, 10); mass spectrum (chemical ionization, CH_4), *m/z* 438 (M^+), 396.

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Synthesis of 1,5-Dienes via [2 + 2] Photocycloaddition between 2,5-Dihydrothiophene 1,1-Dioxides (Sulfolenes) and α,β-Unsaturated Cyclic Ketones and Anhydrides. Synthesis of 10-Hydroxygeraniol[1a]

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Photocycloaddition between 2,5-dihydrothiophene 1,1-dioxide (**1a**) and 2-cyclohexenones **2a,b** afforded cis-anti-cis and cis-trans photoadducts **3a,b** and **4a** in low yield. Photocycloaddition between sulfolene **1a** and 2-cyclopentenones **8a,b** yielded cis-anti-cis photoadducts **9a,b**. The α-methyl derivative **9b** underwent α-cleavage to yield the unsaturated aldehyde **10**. Flash vacuum pyrolysis of photoadduct **3b** yielded the *trans*- and *cis*-2,3-divinylcyclohexanones **11** and **12**, respectively, together with the diunsaturated *trans*-decalin **13**. Photocycloaddition between sulfolenes **1a,b** and the α,β-unsaturated cyclic anhydrides **15a,b** afforded photoadducts **16a,b** in good yields. Esterification of **16a** and **16b** yielded the *cis*-diesters **17** and **23**, respectively. Flash vacuum pyrolysis of **17** gave the disubstituted (*E,Z*)-1,5-diene **18** stereoselectively, whereas **23** afforded the trisubstituted (*E,-Z*)-1,5-dienes **25** and **26** less stereoselectively. Flash vacuum pyrolysis of the *trans*-diester **21** yielded the (*E,E*)-1,5-diene **19** stereoselectively, whereas the *trans*-diester **28** yielded both the (*E,E*)- and (*Z,Z*)-1,5-dienes **24a** and **27** as the major products. Reduction of the (*E,E*)-diene **24a** afforded 10-hydroxygeraniol **24b**. The 1,5-dienes were generated by thermal extrusion of sulfur dioxide from the cyclic sulfone diesters followed by a Cope rearrangement of the resulting 1,2-divinyl intermediates.

The [2 + 2] photocycloaddition between substituted cyclobutenes and chiral cyclohexanones has afforded a convenient entry into the stereospecific synthesis of elemane (E), germacrane (G), and cadinane (C) sesquiterpene skeletons,[2] containing a 1,5-diene system (Scheme I). In these reactions the cyclobutene is acting as a 1,2-divinyl synthon. Since cyclobutene and methylcyclobutene are expensive, we sought a cheaper and more readily available 1,2-divinyl synthon. As a solution to this problem, we wish to report the use of 2,5-dihydrothiophene 1,1-dioxides (sulfolenes) as 1,2-divinyl synthons. Secondly, we report the application of this method to the stereoselective synthesis of acyclic 1,5-dienes and have applied it to the synthesis of the monoterpene, 10-hydroxygeraniol.[3]

Results and Discussion

The photocycloaddition reaction between sulfolene **1a** and 2-cyclohexenone **2a** afforded photoadduct **3a** in a low yield (23%) together with the previously reported[4] head-

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(1) (a) For the previous paper in this series, see: Williams, J. R.; Callahan, J. F.; Lin, C. *J. Org. Chem.* **1983**, *48*, 3162. (b) Temple University. (c) Smith Kline and French Laboratories.

(2) For 1,2-bis(trimethylsiloxy)cyclobutene, see: (a) Van Audenhove, M.; De Keukeleire, D.; Vandewalle, M. *Tetrahedron Lett.* **1980**, *21*, 1979. (b) Williams, J. R.; Caggiano, T. J. *Synthesis* **1980**, 1024. For 1-methylcyclobutene, see: (c) Williams, J. R.; Callahan, J. F. *J. Org. Chem.* **1980**, *45*, 4475. For methyl 1-cyclobutenecarboxylate, see: (d) Wender, P. A.; Lechleiter, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 267; (e) Wilson, S. R.; Phillips, L. R.; Pelister, Y.; Huffman, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 7373. (f) Williams, J. R.; Callahan, J. F. *J. Org. Chem.* **1980**, *45*, 4479 and references cited therein. For cyclobutenecarboxylic acid, see: (g) Lange, G. L.; McCarthy, F. C. *Tetrahedron Lett.* **1978**, 4749. For dimethyl cyclobutene-1,2-dicarboxylate, see: Lange, G. L.; Huggins, M. A.; Neidert, E. *Tetrahedron Lett.* **1976**, 4409.

(3) The preliminary results reported by Williams and Lin (Williams, J. R.; Lin, C. *J. Chem. Soc., Chem. Commun.* **1981**, 752) should be revised in light of the complete experimental data reported herein.

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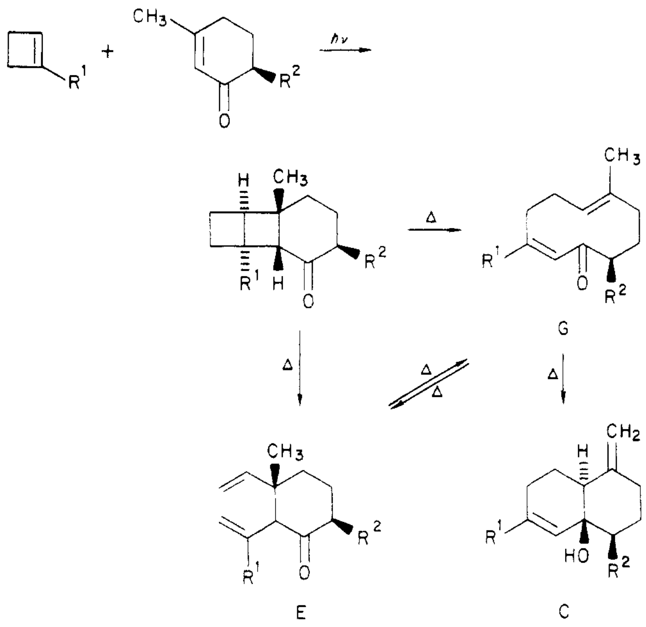
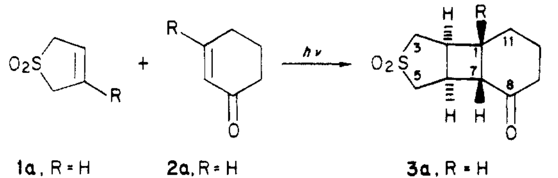
Table I. Carbon-13 NMR Spectra of the Sulfolene Photoadducts

C atom	δ 3a	 3b	 4a	 4b	 7	 9a	 9b	 10
1	35.1	39.9	45.7	40.3	38.6	48.2	48.0	140.3
2	36.6	32.6	33.9	31.6	35.9	39.6	46.5	39.6
3	54.4	50.3	49.5	50.0	48.5	55.1	49.8	50.5
5	54.5	54.0	54.5	50.2	53.8	54.6	54.3	50.8
6	39.3	41.5	46.3	41.9	47.2	38.0	37.4	40.5
7	46.8	54.6	57.2	50.6	50.8	34.6	34.8	141.1
8	211.6	210.7	204.3	211.5	65.2	27.2	24.7	19.4
9	39.2	37.6	38.9	38.7	33.7	36.8	35.5	41.1
10	20.9	19.9	23.5	18.7	17.5	218.5	221.0	201.0
11	26.7	35.9	31.9	29.1	33.1		14.1	12.0
12		22.4	20.9	29.7	23.0			

Scheme I



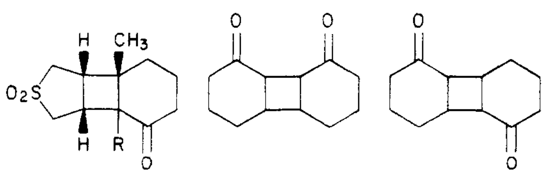
to-head and head-to-tail photodimers of 2-cyclohexenone **5** and **6**, respectively. The cis-anti-cis stereochemistry of photoadduct **3a** was established from the ^{13}C NMR spectra (see Table I and the following discussion).



1a, R = H
b, R = CH3

2a, R = H
b, R = CH3

3a, R = H
b, R = CH3



4a, R = αH
b, R = βH

5

6

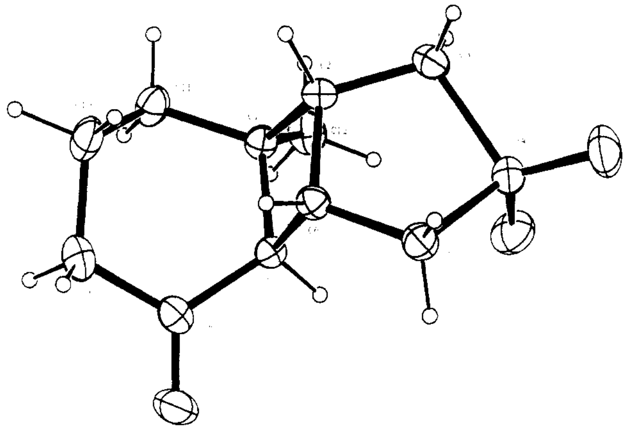


Figure 1. ORTEP structure of **3b**.

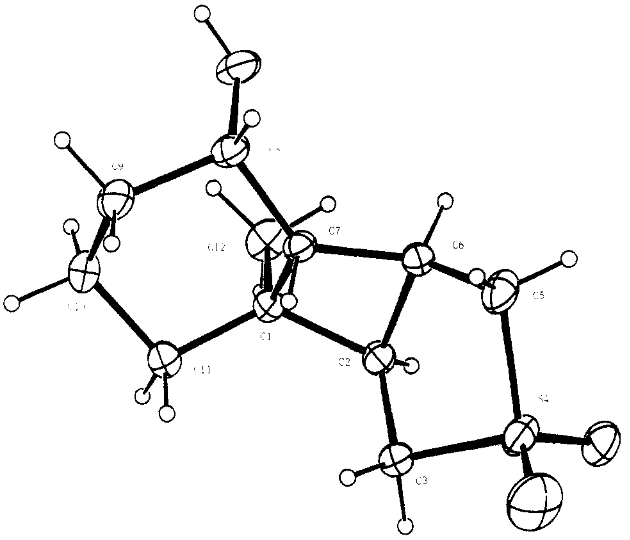
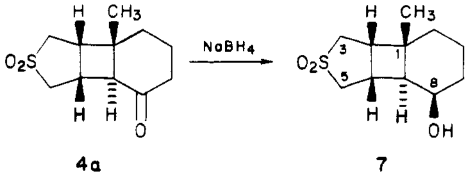


Figure 2. ORTEP structure of **7**.

The photocycloaddition reaction between sulfolene **1a** and 3-methyl-2-cyclohexenone (**2b**) yielded cis-anti-cis photoadduct **3b** and the cis-trans photoadduct **4a** in 27% and 9% yields, respectively. The structures and stereochemistries of **3b** and **4a** were proven by single-crystal X-ray analyses. In the case of **4a**, the crystals were unsuitable for X-ray analysis due to twinning, so the carbonyl group was reduced to the alcohol **7** with sodium borohydride. Crystal data for **3b** and **7** are given in the Experimental Section. Figure 1 shows the cis-anti-cis photoadduct **3b** and Figure 2 the cis-trans alcohol **7**. Treatment of **4a** with sodium methoxide caused epimerization of the trans ring junction to the more stable cis ring junction in **4b**. ^{13}C NMR spectra of the sulfone photoadducts **3a**,**b**,**4a**,**b**, and **7** were assigned as shown in Table I. Based on the known structures **3b** and **4a**,**b** it was



4a

7

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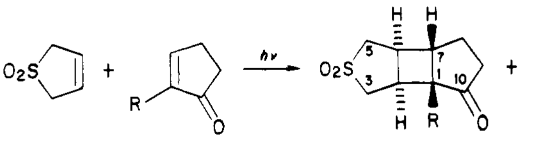
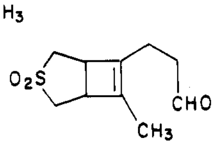
(4) (a) Valentine, D.; Turro, N. J.; Hammond, G. S. *J. Am. Chem. Soc.* **1964**, *86*, 5202. (b) Ziffer, H.; Fales, H. M.; Milne, G. W. A.; Field, F. H. *J. Am. Chem. Soc.* **1970**, *92*, 1597.

observed that a γ-gauche interaction between the C-3 and C-5 carbons and the cyclohexanone ring in the cis-syn-cis adduct **4b** caused these carbons to be shifted upfield about 4.3 ppm relative to cis-anti-cis adduct **3a**.[5] The chemical shifts of C-3 and C-5 in **3a** are at δ 54.5, exhibiting no γ-gauche interactions from the neighboring six-membered ring; thus, the stereochemistry about the cyclobutane ring is anti.

The photocycloaddition reaction between sulfolene **1a** and 2-cyclopentenone (**8a**) also yielded a cis-anti-cis photoadduct, **9a**, in 25% yield. 2-Methyl-2-cyclopentenone (**8b**) yielded the cis-anti-cis photoadduct **9b** (3%) together with an aldehyde **10** as the major product (9%). The cis-anti-cis stereochemistry of the photoadducts was established via carbon-13 NMR (see Table I). The structure of the aldehyde **10** was proven by spectral data and its preparation via irradiation of pure **9b**.

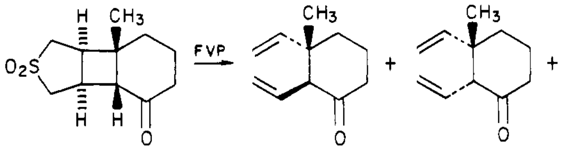


1a **8a**, R = H **b**, R = CH$_3$ **9a**, R = H **b**, R = CH$_3$

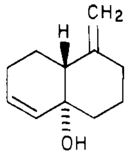


10

Since sulfolene **1a** underwent photocycloaddition with 2-cyclopentenones and 2-cyclohexenones in low yield, only the photoadduct obtained in the highest yield was thermolyzed. Flash vacuum pyrolysis of 3-methylcyclohexenone photoadduct **3b** at 500 °C yielded the *trans*- and *cis*-2,3-divinyl ketones **11** and **12**, respectively, together with *trans*-decalin **13**. The divinyl ketones were obtained in 73% yield with the ratio of trans to cis, i.e., **11**:**12** = 27:73 and the *trans*-decalin **13** in 25% yield based on recovered starting material. The structures of **11** and **12** were proven by comparison of their spectral data with those of the elemane isomers.[6] Furthermore, it is known that upon heating, a *cis*-2,3-divinylcyclohexanone undergoes a Cope reaction to yield a *cis,trans*-cyclodecadienone, which can undergo a transannular ene reaction to yield a *trans*-decalin containing a ring junction hydroxyl.[6] Thus, if the mixture of **11** and **12** is heated the *cis*-divinyl ketone **12** should be converted to *trans*-decalin **13** via the *cis,trans*-cyclodecadienone **14** leading to a reduction of the amount of **12** present. This is what is observed. If the 27:73 mixture of **11** and **12** is again flash vacuum pyrolyzed at 500 °C, the ratio changes to 37:63 and **13** is also formed. When the 37:63 mixture of **11** and **12** is thermolyzed in dry benzene (silanized Pyrex tube) for 1 h at 250 °C, all the cis isomer **12** is converted to the *trans*-decalin **13** (67% yield), whereas **11** is unchanged (18% yield).



3b **11** **12**



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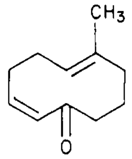
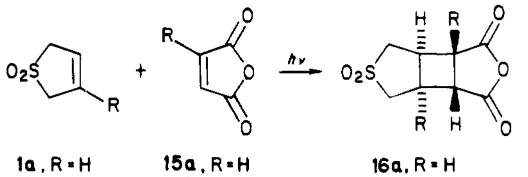


14

The photolyses of 3-methylsulfolene and piperitone failed to yield any photoadduct. This lack of reactivity with piperitone is due to the increased steric hindrance caused by the C-3 methyl and C-6 isopropyl groups.

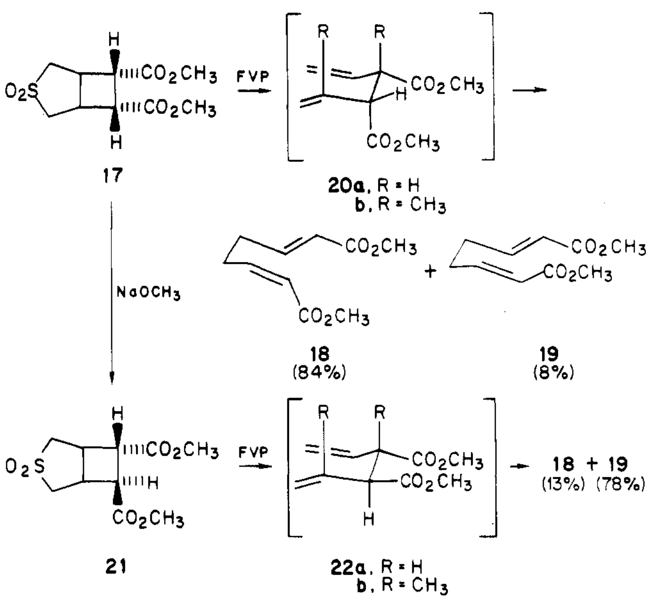
In summary, even though the photocycloaddition of sulfolene to cyclic enones does not proceed in good yield, the starting materials are cheap and readily available, thereby making it a useful reaction.

Photocycloaddition between sulfolene **1a** and maleic anhydride **15a** either directly or via photosensitization using acetone afforded the photoadduct **16a** in good yield (85%).[7,8] Photoadduct **16a** probably has the cis-anti-cis structure[9] rather than cis-syn-cis, but this was not proven. Furthermore, it is not important since this stereochemistry is lost in latter transformations. Esterification of **16a** with refluxing methanol containing *p*-toluenesulfonic acid afforded the *cis*-diester **17**. The proton decoupled ^{13}C NMR of **17** showed only five lines, proving that there was a plane of symmetry through the molecule.[10]



1a, R = H **b**, R = CH$_3$ **15a**, R = H **b**, R = CH$_3$ **16a**, R = H **b**, R = CH$_3$

Flash vacuum pyrolysis of the *cis*-diester **17** at 500 °C afforded the known acyclic 1,5-dienyl diesters:[10–12] (*E*,*Z*)-dimethyl 2,6-octadiene-1,8-dioate, (**18**) in 84% yield together with the *E*,*E* isomer **19** in 8% yield. Under the



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[5] Levy, G.; Lichter, R. L.; Nelson, G. L. "C-13 NMR for Organic Chemists" Wiley: New York, 1980; 55.

[6] Williams, J. R.; Callahan, J. F. *J. Org. Chem.* **1980**, *45*, 4479.

[7] Shaikhrazieva, V. Sh.; Enikeev, R. S.; Tolstokov, G. A. *Zh. Org. Khim.* **1972**, *8*, 377.

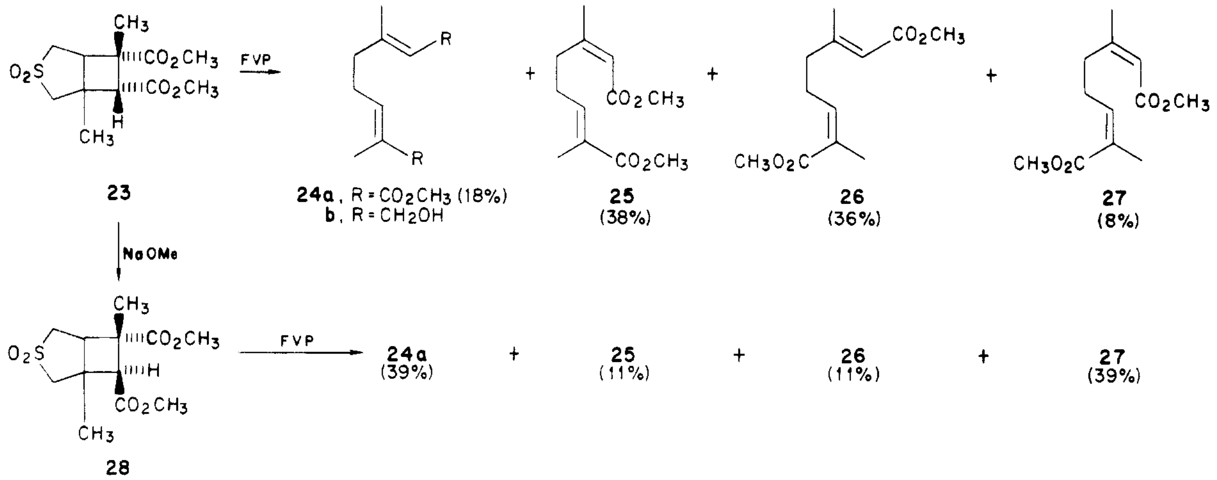
[8] (a) Cadogan, J. I. G.; Gosney, I.; McLaughlin, L. M.; Hamill, B. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1242. (b) Cadogan, J. I. G.; Aitken, R. A.; Gosney, I.; Hamill, B. J.; McLaughlin, L. M. *J. Chem. Soc., Chem. Commun.* **1982**, 1164. (c) Cadogan, J. I. G.; Buchan, C. M.; Gosney, I.; Hamill, B. J.; Newlands, S. F.; Wham, D. A. *J. Chem. Soc., Chem. Commun.* **1983**, 725.

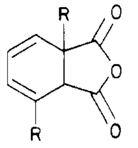
[9] Ziffer, H.; Williams, J. R. *J. Org. Chem.* **1968**, *33*, 920.

[10] Cadogan, J. I. G.; Buchan, C. M.; Gosney, I.; Hamill, B. J.; McLaughlin, L. M. *J. Chem. Soc., Chem. Commun.* **1982**, 325.

[11] Paquette, L. A.; Schwartz, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 3215.

[12] Scheffer, J. R.; Wostradowski, R. A. *J. Org. Chem.* **1972**, *37*, 4317.





29a R = H
b R = CH$_3$

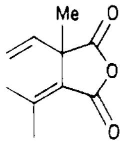


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Table II. Product Compositions from the Pyrolysis of the Cyclic Sulfone Diesters

diester	composition,[a] %			
	(2*E*,6*E*)-**24a**	(2*E*,6*Z*)-**25**	(2*Z*,6*E*)-**26**	(2*Z*,6*Z*)-**27**
cis-**23**	18	38	36	8
trans-**28**	39	11	11	39

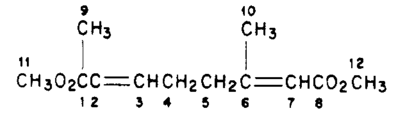
[a] Analyzed by HPLC as described in the Experimental Section.

reaction conditions, thermal extrusion of sulfur dioxide from **17** should yield the meso-1,2-divinyl compound **20a**, which would undergo a Cope rearrangement via the usual chairlike transition state to yield **18**.[13]

However, if the *cis*-diester **17** is first epimerized to the *trans*-diester **21**, then flash vacuum pyrolysis of the latter affords the *E*,*E*-diester **19** as the major product (78% yield) together with **18** (13%). The *E*,*E*-diester **19** resulted from a similar Cope rearrangement of the *dl*-1,2-divinyl system **22a**.[13] The *Z*,*Z* isomer was not produced since the chair conformation of the transition state for the Cope rearrangement required both of the esters to be axial. Thus, it is possible to use the *cis*-diester **17** as a common intermediate for the stereoselective preparation of both (*E*,*Z*)- and (*E*,*E*)-1,5-dienes.

We then applied this procedure to the synthesis of 10-hydroxygeraniol (**24b**), the biosynthetic precursor of loganin and the indole alkaloids.[14] 10-Hydroxygeraniol (**24b**) contains an *E*,*E* 1,5-trisubstituted diene with methyl substituents on the double bonds. Using the same approach as before, photocycloaddition between 2,5-dihydro-3-methylthiophene 1,1-dioxide (**1b**) and citraconic anhydride (**15b**) afforded photoadduct **16b** (80% yield). Cleavage of the anhydride ring with methanolic hydrochloric acid and flash vacuum pyrolysis of the dimethyl *cis*-diester **23** at 500 °C afforded a mixture of the four acyclic 1,5-dienyl diesters **24a**, **25**, **26**, and **27** in 77% yield together with unreacted starting material (20%). In order to obtain an increased yield of the desired *E*,*E* isomer **24a**, the *cis*-diester **23** was epimerized to the *trans*-diester **28** by treatment with sodium methoxide in methanol. Flash vacuum pyrolysis of the *trans*-diester **28** afforded a mixture of the same four acyclic-1,5-dienyl diesters now greatly increased in the *E*,*E* isomer **24a**. The product compositions were quantitatively analyzed by high-pressure liquid chromatography, and the individual components were isolated in pure form by flash silica gel chromatography. The results are summarized in Table II.

Table III. Carbon-13 NMR Spectra of 2,6-Tetramethylocta-2,6-diene-1,8-dioates



$CH_3O_2C\overset{CH_3}{C}{=}CHCH_2CH_2\overset{CH_3}{C}{=}CHCO_2CH_3$

C atom	δ			
	24a	**25**	**26**	**27**
1	167.9[a]	167.4[a]	166.0[a]	165.6[a]
2	128.2	127.7	127.4	126.5
3	140.0	140.2	140.4	141.0
4	26.0	26.7	26.8	27.0
5	39.0	31.5	39.5	31.7
6	158.0	157.9	158.0	158.4
7	115.6	116.2	115.1	115.3
8	166.6[a]	165.6[a]	167.0[a]	167.2[a]
9	12.1	11.5	17.8	19.5
10	18.4	24.3	19.7	23.9
11	51.4[b]	50.7[b]	49.7[b]	49.6[b]
12	50.5[b]	49.8[b]	50.3[b]	50.0[b]

[a,b] Assignments may be reversed.

Assignment of stereochemistry (*E* and *Z*) to the various geometric isomers was based on their spectral data especially proton and carbon-13 NMR spectra (see Table III). In unsubstituted and β-substituted α,β-unsaturated esters, the hydrogen or β-group cis to the carbonyl experiences a larger deshielding effect than the trans group[15] (0.78 ± 0.04 ppm for hydrogen; 0.27 ± 0.01 ppm for methyl). Furthermore, in β-substituted α,β-unsaturated esters, the hydrogen occurred at 5.73 ± 0.01 ppm as a broad singlet

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[13] Rhoads, S. J.; Raulins, N. R. *Org. React.* (*N.Y.*) **1975**, *22*, 1.

[14] (a) Escher, S.; Loew, P.; Arigoni, D. *J. Chem. Soc., Chem. Commun.* **1970**, 823. (b) Battersby, A. R.; Brown, S. H.; Payne, T. G. *J. Chem. Soc., Chem. Commun.* **1970**, 827. (c) Inouye, H.; Ueda, S.; Uesato, S.; Kobayashi, K. *Chem. Pharm. Bull.* **1978**, *26*, 3384.

[15] Jackman, L. M.; Sternhill, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry"; Pergamon Press: Oxford, 1969; pp 171.

irrespective of the *E* or *Z* nature of the olefin. β-Hydrogens of α-substituted α,β-unsaturated esters appeared as approximate triplets ($J = 7.5$ Hz) due to coupling with the neighboring methylene group. In the ^{13}C NMR spectra of α,β-unsaturated esters, the chemical shift of the β-group cis to the carbonyl experiences a shielding effect. For example, C-5 in **25** and **27** and C-10 in **24a** and **26** are shifted upfield by 7.6 ± 0.1 and 5.1 ± 0.9 ppm, respectively, indicating a 6*Z* configuration. The shielding effect of the C-4 methylene causes the C-9 methyl group in **24a** and **25** to be shifted upfield by 6.9 ± 1.1 ppm, indicating a 2*E* configuration.

Aluminum hydride reduction of the 2*E*,6*E* diester **24a** afforded 10-hydroxygeraniol (**24b**)[14] in 97% yield.

Examination of Table II shows that the *cis*-diester **23** yields the two different (2*E*,6*Z*)- and (2*Z*,6*E*)-dienes **25** and **26** as the major products. This is because the methylated 1,2-divinyl intermediate **20b** can undergo a Cope rearrangement via two different chairlike transition states yielding **25** and **26**. The *trans*-diester **28** similarly yields the (2*E*,6*E*)- and (2*Z*,6*Z*)-dienes **24a** and **27** as major products, again via a Cope rearrangement involving two different chairlike transition states of the intermediate **22b**.

When the cyclic sulfone anhydride **16a** was flash vacuum pyrolyzed at 500 °C, sulfur dioxide was extruded, but the resulting *cis*-3,4-divinyl anhydride **29a** did not undergo a Cope rearrangement.[8a] Flash vacuum pyrolysis of the dimethyl analogue **16b** afforded a mixture of divinyl anhydride **29b** and the conjugated isomer **30**. Only **30** was obtained when **16b** was thermolyzed in toluene at 290 °C for 5 h in a sealed tube.

In conclusion, sulfolenes undergo photocycloaddtion to α,β-unsaturated cyclic ketones in low yields and to α,β-unsaturated cyclic anhydrides in good yields. Secondly, it has been demonstrated in previous work that the photocycloaddition method can be used to add a C_5 isoprene synthon onto a C_{10} monoterpene to generate C_{15} sesquiterpenes. The present work extends this idea to the use of two C_5 units for the synthesis of a C_{10} monoterpene.

Experimental Section

Melting points were taken on a Thomas-Hoover apparatus and are uncorrected. IR spectra were taken with a Perkin-Elmer 137 infracord spectrophotometer. ^{13}C NMR spectra were recorded at 25.16 MHz on a Varian XL-100 spectrometer fitted with a Nicolet 1180 pulse system, and ^{1}H NMR spectra were recorded at 90 MHz on a Perkin Elmer R-32 spectrometer. Chemical shifts are recorded in δ units from the internal standard Me_4Si in $CDCl_3$ unless otherwise noted. Low-resolution mass spectra were taken with a Hitachi Perkin-Elmer RMU-6H instrument. High-resolution mass spectra were taken with a VG U-Mass 7070-H instrument. TLC was carried out on Analtech silica gel GF plates and flash chromatography performed by using Merck silica gel 60 (230–400 mesh). High-performance liquid chromatography was carried out using a Waters Associates Model 6000 series pump, U6K injector, Model 440 UV detector, refractive index detector, and a μ-Porasil silica gel column. Solvents used for HPLC were Burdick & Jackson HPLC grade and were filtered twice through Rainin 0.45-μm membranes. HPLC mobile phases were degassed by sparging with helium.

4-Thiatricyclo[5.4.0.0^{2,6}]undecan-8-one 4,4-Dioxide (3a). Enone **2a** (4.00 g, 41.6 mmol) and sulfolene **1a** (10.0 g, 84.6 mmol) were dissolved in CH_3CN (15 mL) and degassed with N_2 in a Vycor tube. The mixture was irradiated while being cooled with an ice–water bath until enone **2a** was no longer evident by TLC (15 h). Evaporation of the solvent afforded a crude oil, which was flash chromatographed over silica gel (200 g) eluted with 40% EtOAc/hexane to afford (head to head) enone dimer **5**,[4] 1.11 g (28%): mp 74–75 °C (crystallized from hexane); IR (neat) 1701 cm^{-1}; ^{13}C NMR 211.7 (s), 46.9 (d), 40.3 (t), 39.4 (d), 24.5 (t), 22.2 (t); MS, *m/e* (relative intensity) 192 (M$^+$, 33), 164 (16), 136 (25), 97 (33), 96 (50), 79 (25), 68 (100), 55 (27). Next was eluted (head to tail) enone dimer **6**,[4] 1.08 g (27%): mp 49–50 °C (crystallized from hexane); IR (neat) 1701 cm^{-1}; ^{13}C NMR 210.4 (s), 46.0 (d), 38.4 (t), 36.8 (d), 25.5 (t), 20.0 (t); MS, *m/e*, (relative intensity) 192 (M$^+$, 69), 163 (20), 150 (37), 136 (26), 119 (14), 97 (28), 96 (37), 68 (100). Sulfolene **1a**, 8.88 g, was also recovered. Further elution afforded photoadduct **3a** contaminated with a small amount of another unidentified photoadduct. Careful crystallization from EtOAc/hexane afforded pure **3a**, 2.03 g (23%): mp 84–85 °C; IR (neat) 1700, 1300, 1130 cm^{-1}; ^{1}H NMR 3.70–1.40 (m, 14 H); ^{13}C NMR 211.6 (s), 54.5 (t), 54.4 (t), 46.8 (d), 39.3 (d), 39.2 (t), 36.6 (d), 35.1 (d), 26.7 (t), 20.9 (t); MS *m/e* (relative intensity) 214 (M$^+$, 3), 150 (55), 135 (24), 122 (27), 97 (30), 94(58), 91 (55), 79 (100), 68 (91). Anal. Calcd for $C_{10}H_{14}O_3S$: C, 56.05; H, 6.59; S, 14.96. Found: C, 56.22; H, 6.65; S, 14.85.

1-Methyl-4-thiatricyclo[5.4.0.0^{2,6}]undecan-8-one 4,4-Dioxide Photoadducts 3b and 4a. Enone **2b** (7.17 g, 65.1 mmol) and sulfolene **1a** (15.4 g, 130 mmol) were dissolved in CH_3CN (10 mL) and degassed with N_2 in a Vycor tube which was jacketed to allow for water cooling. The mixture was irradiated until **2b** was no longer evident by TLC (48 h). Evaporation of the solvent afforded a crude oil, which was flash chromatographed over silica gel (40% EtOAc/hexane) to yield 9.2 g recovered sulfolene **1a**, followed by cis-trans photoadduct **4a**, 1.36 g (9.1%): mp 176–177 °C (crystallized from EtOAc/hexane); IR (KBr) 1720, 1310, 1135 cm^{-1}; ^{1}H NMR 4.00–2.70 (m, 7 H), 2.60–1.30 (m, 6 H), 1.22 (s, 3 H); ^{13}C NMR 204.3 (s), 57.2 (d), 54.5 (t), 49.5 (t), 46.3 (d), 45.7 (s), 38.9 (t), 33.9 (d), 31.9 (t), 23.5 (t), 20.9 (q); MS, *m/e* (relative intensity) 228 (M$^+$, 1), 213 (3), 164 (9), 149 (24), 110 (40), 93 (39), 82 (100), 81 (69), 79 (55). Anal. Calcd for $C_{11}H_{16}O_3S$: C, 57.87; H, 7.06; S, 14.04. Found: C, 57.91; H, 7.01; S, 14.10.

Next was eluted cis-anti-cis photoadduct **3b**, 4.05 g (27%): mp 97–98 °C (crystallized from EtOAc/hexane); IR (KBr) 1680, 1300, 1230 cm^{-1}; ^{1}H NMR 3.50–2.74 (m, 7 H), 2.60–2.27 (m, 2 H), 2.25–1.61 (m, 4 H), 1.23 (s, 3 H); ^{13}C NMR 210.7 (s), 54.6 (d), 54.0 (t), 50.3 (t), 41.5 (d), 39.9 (s), 37.6 (t), 35.9 (t), 32.6 (d), 22.4 (q), 19.9 (t); MS, *m/e* 228 (M$^+$, 0.5), 149 (3), 110 (46), 92 (10), 91 (11), 82 (100), 81 (19), 79 (21). Anal. Calcd for $C_{11}H_{16}O_3S$: C, 57.87; H, 7.06; S, 14.04. Found: C, 58.01; H, 7.03; S, 14.07.

1-Methyl-4-thiatricyclo[5.4.0.0^{2,6}]undecan-8-one 4,4-Dioxide (4b). Cis-trans photoadduct **4a** (400 mg, 1.75 mmol) and sodium metal (46 mg, 2.0 mmol) were dissolved in MeOH (40 mL) and stirred at room temperature for 2 h. The MeOH was evaporated to afford a gum, which was dissolved in EtOAc (100 mL), extracted with a saturated aqueous $NaHCO_3$ solution (75 mL × 2), and dried with $MgSO_4$. Evaporation of the EtOAc afforded an oil, which crystallized from MeOH to yield cis-syn-cis photoadduct **4b**, 320 mg (80%): mp 96–97 °C; IR (KBr) 1680, 1295, 1130 cm^{-1}; ^{1}H NMR 3.80–1.65 (complex, 13 H), 1.41 (s, 3 H); ^{13}C NMR 211.5 (s), 50.6 (d), 50.2 (t), 50.0 (t), 41.9 (d), 40.3 (s), 38.7 (t), 31.6 (d), 29.7 (q), 29.1 (t), 18.7 (t); MS, *m/e* (relative intensity) 228 (M$^+$, 6), 111 (33), 110 (79), 95 (8), 82 (100), 81 (21), 68 (10), 55 (13). Anal. Calcd for $C_{11}H_{16}O_3S$: C, 57.87; H, 7.06; S, 14.04. Found: C, 58.04; H, 7.02; S, 14.02.

1-Methyl-4-thiatricyclo[5.4.0.0^{2,6}]undecan-8-ol 4,4-Dioxide (7). Trans photoadduct **4a** (350 mg, 1.53 mmol) and $NaBH_4$ (290 mg, 7.66 mmol) were dissolved in dry MeOH (40 mL) under a N_2 blanket and stirred at 0 °C for 5 h. The reaction was allowed to warm to room temperature and was quenched with acetone (5 mL). Evaporation of the solvents afforded a slurry, which was dissolved in EtOAc (100 mL), extracted with a saturated aqueous $NaHCO_3$ solution (60 mL × 2), and dried with $MgSO_4$. Evaporation of the EtOAc afforded an oil, which crystallized from EtOAc/hexane to afford trans alcohol **7**, 270 mg (76%): mp 178–179 °C; IR (KBr) 3500, 1300, 1130 cm^{-1}; ^{1}H NMR 4.18 (s, 1 H), 3.65–2.62 (m, 6 H), 2.30–1.31 (m, 8 H), 1.49 (s, 3 H); ^{13}C NMR (Me_2SO-d_6) 65.2 (d), 53.8 (t), 50.8 (d), 48.5 (t), 47.2 (d), 38.6 (s), 35.9 (d), 33.7 (t), 33.1 (t), 23.0 (q), 17.5 (t); MS *m/e* (relative intensity) (M$^+$, not observed), 212 (1), 166 (3), 112 (28), 97 (100), 81 (98), 80 (94), 67 (48). Anal. Calcd for $C_{11}H_{18}O_3S$: C, 57.36; H, 7.88; S, 13.92. Found: C, 57.47; H, 7.95; S, 13.94.

4-Thiatricyclo[5.3.0.0^{2,6}]decan-8-one 4,4-Dioxide (9a). Enone **8a** (1.00 g, 12.2 mmol) and sulfolene **1a** (3.60 g, 30.5 mmol) were dissolved in CH_2Cl_2 (10 mL) and degassed with N_2 in a quartz tube. The mixture was irradiated while being cooled with an ice–water/NaCl bath until enone **8a** was no longer evident by TLC (8.5 h). Evaporation of the solvent afforded a crude oil, which was flash chromatographed over silica gel (150 g) eluted with 40% EtOAc/hexane to yield recovered sulfolene **1a**, 1.50 g. Further elution afforded cis-anti-cis photoadduct **9a**, 620 mg, (25%): mp 129–130 °C (crystallized from $CHCl_3$/hexane); IR (KBr) 1715, 1281 cm^{-1}; ^1H NMR 3.36–1.91 (m, 12 H); ^{13}C NMR 218.5 (s), 55.1 (t), 54.6 (t), 48.2 (d), 39.6 (d), 38.0 (d), 36.8 (t), 34.6 (d), 27.2 (t); MS, *m/e* (relative intensity) 200 (M$^+$, 22), 136 (24), 121 (14), 108(14), 94 (53), 93 (36), 82 (31), 80 (44), 79 (100), 68 (42). Anal. Calcd for $C_9H_{12}O_3S$: C, 53.98; H, 6.04; S, 16.01. Found: C, 53.89; H, 6.13; S, 15.95.

7-Methyl-4-thiatricyclo[5.3.0.0^{2,6}]decan-8-one 4,4-Dioxide (9b). Enone **8b** (1.00 g, 10.4 mmol) and sulfolene **1a** (3.07 g, 26.0 mmol) were dissolved in CH_2Cl_2 (10 mL) and degassed with N_2 in a quartz tube. The mixture was irradiated while being cooled with an ice–water/NaCl bath until enone **8b** was no longer evident by TLC (6.5 h). The solvent was evaporated to afford a crude oil, which was flash chromatographed over silica gel (150 g) eluted with 30% EtOAc/hexane to yield recovered sulfolene **1a**, 1.57 g. Further elution afforded aldehyde **10**, 194 mg (9.0%): IR (neat) 2830, 2725, 1730, 1300 cm^{-1}; ^1H NMR 9.78 (s, 1 H), 1.68 (s, 3 H); ^{13}C NMR 201.0 (d), 141.1 (s), 140.3 (s), 50.8 (t), 50.5 (t), 41.1 (t), 40.5 (d), 39.6 (d), 19.4 (t), 12.0 (q); MS, *m/e* (relative intensity) 214 (M$^+$, 1), 122 (12), 107 (44), 105 (27), 93 (84), 91 (100), 79 (85); exact mass calcd for $C_{10}H_{14}O_3S$ 214.0664; found 214.0665.

Next was eluted cis-anti-cis photoadduct **9b**, 74 mg (3.4%): mp 125 °C (crystallized from EtOAc/hexane); IR (KBr) 1725, 1390, 1315 cm^{-1}; ^1H NMR 3.60–1.75 (m, 11 H), 1.18 (s, 3 H); ^{13}C NMR 221.0 (s), 54.3 (t), 49.8 (t), 48.0 (s), 46.5 (d), 37.4 (d), 35.5 (t), 34.8 (d), 24.7 (t), 14.7 (q); MS, *m/e* (relative intensity) 214 (M$^+$, 45), 150 (15), 135 (23), 122 (21), 107 (59), 93 (87), 79 (100), 67 (41). Anal. Calcd for $C_{10}H_{14}O_3S$: C, 56.05; H, 6.58; S, 14.96. Found: C, 56.25; H, 6.75; S, 14.97.

Flash Vacuum Pyrolysis of Cis-Anti-Cis Photoadduct 3b. Photoadduct **3b** (688 mg, 3.01 mmol) was placed at the closed end of a Vycor thermolysis tube (50 cm × 22 mm i.d.) which was connected to a vacuum trap cooled with liquid N_2. The middle section of the tube was heated to 500 °C (0.5 mmHg) in a Lindberg tube furnace. The closed end of the tube protruded out so that **3b** could be melted with a heat gun before pulling the tube completely into the furnace. After pyrolysis, the Vycor tube and vacuum trap were washed with EtOAc. Evaporation of the EtOAc afforded an oil, which was flash chromatographed over silica gel (100 g, deactivated with H_2O, 5% w/w) eluted with 5% EtOAc/hexane to give 247 mg (50%) of a mixture of *trans*- and *cis*-2,3-divinyl-3-methyl-cyclohexanones (*11* and *12*) (27:73 by integration of the C-3 methyl groups in their ^1H NMR spectra): IR (neat) 1710, 1640 cm^{-1}; ^1H NMR 6.18–5.60 (m), 5.30–4.85 (m), 2.96 (d, 1 H, *J* = 9 Hz **11**), 2.83 (d, 1 H, *J* = 9 Hz **12**), 1.09 (s, 3 H, **12**), 0.96 (s, 3 H, **11**); MS, *m/e* (relative intensity) 164 (M$^+$, 13), 149 (11), 131 (9), 94 (27), 86 (5), 84 (9), 81 (100), 79 (30); exact mass calcd for $C_{11}H_{16}O$ 164.1201, found 164.1200.

Next was eluted *trans*-decalin **13** 85 mg (17%): IR (neat) 3500, 1649 cm^{-1}; ^1H NMR (5.81 (m, 2 H), 4.98 (m, 1 H), 4.72 (m, 1 H); ^{13}C NMR 149.4 (s), 133.1 (d), 129.7 (d), 107.6 (t), 69.3 (s), 48.0 (d), 38.1 (t), 36.1 (t), 26.1 (t), 23.3 (t), 19.9 (t); MS *m/e* (relative intensity) 164 (M$^+$, 7), 146 (29), 131 (50), 117 (36), 91 (100), 81 (79), 79 (93); exact mass calcd for $C_{11}H_{16}O$ 164.1201, found 164.1195.

Further elution with 60% EtOAc/hexane afforded (230 mg, 0.960 mmol) recovered starting material (**3b**).

Thermolysis of 2,3-Divinyl-3-methylcyclohexanones 11 and 12. The mixture of divinyl cyclohexanones **11** and **12** (37:63 ratio by ^1H NMR) (90 mg, 0.55 mmol) and dry benzene (5 mL) were degassed with N_2 in a Pyrex tube. The lower part of the tube containing the benzene solution was cooled to −78 °C, and then the N_2 stream was removed and the tube sealed under vacuum (0.25 mmHg). The tube was heated at 250 °C for 1 h. Evaporation of the solvent afforded a crude oil, which was flash chromatographed over silica gel (30 g, deactivated with H_2O, 5% w/w) eluted with 5% ether/hexane to yield recovered **11**, 16 mg (18%): IR (neat) 1710, 1640 cm^{-1}; ^1H NMR 6.12–5.62 (m, 2 H), 5.30–4.88 (m, 4 H), 2.96 (d, 1 H, *J* = 9 Hz), 0.97 (s, 3 H); MS, *m/e* 164 (M$^+$, 15), 149 (12), 131 (9), 94 (30), 86 (53), 84 (77), 81 (100), 79 (28); exact mass calcd for $C_{11}H_{16}O$ 164.1201, found 164.1200.

Next was eluted *trans*-decalin **13**, 60 mg (67%), which exhibited identical spectral data as before.

3,3-Dioxo-3-thiatricyclo[3.2.0]heptane-6,7-dicarboxylic Anhydride (16a). Sulfolene **1a** (2.00 g, 16.9 mmol) and maleic anhydride (**15a**) (1.66 g, 16.9 mmol) were dissolved in CH_2Cl_2 (30 mL), degassed with argon, and photolyzed via quartz filtered light at −78 °C (dry ice/propanol) for 29 h. The photoadduct **16a** was filtered off, and concentration of the filtrate afforded another crop of **16a**. The mother liquors were concentrated and flash chromatographed over silica gel (150 g) eluted with 60% EtOAc/hexane to afford recovered sulfolene **1a**, 0.651 g, and anhydride **15a**, 0.304 g. Recrystallization of photoadduct **16a** from acetone yielded 2.10 g (85% based on recovered **1a**: mp 289–290 °C (lit.[7] mp 292–293 °C); IR (KBr) 1870, 1295, 1255, 1140 cm^{-1}; ^1H NMR (Me_2SO-d_6) 3.60–3.20 (m); ^{13}C NMR (Me_2SO-d_6) 172.6 (s), 52.4 (t), 43.1 (d), 34.8 (d).

***cis*-3,3-Dioxo-3-thiabicyclo[3.2.0]heptane-6,7-dicarboxylic Acid Dimethyl Ester (17).** A solution of photoadduct **16a** (2.50 g, 11.6 mmol) and *p*-TSA (0.40 g) in dry MeOH (600 mL) was refluxed for 24 h. Evaporation of the solvent and crystallization from MeOH afforded 2.80 g (92%) of *cis*-diester **17**: mp 126 °C (lit.[7] mp 126–127 °C); IR (KBr) 1749, 1730, 1318, 1280 cm^{-1}; ^1H NMR 3.73 (s, 6 H), 3.80–3.50 (m, 2 H), 3.27–3.12 (m, 6 H); ^{13}C NMR 171.9 (s), 54.2 (t), 52.2 (q), 43.1 (d), 33.6 (d).

Flash Vacuum Pyrolysis of *cis*-Diester 17. Sulfone *cis*-diester **17** (0.580 g, 2.21 mmol) was flash vacuum pyrolyzed [500 °C (0.5 mmHg)] as before. The crude reaction mixture was flash chromatographed over silica gel (40 g) eluted with 10% EtOAc/hexane to yield (*E,Z*)-dimethyl-2,6-octadiene-1,8-dioate (**18**), 369 mg (84%): IR (neat) 1730, 1650, 1430 cm^{-1}; ^1H NMR 6.97 (d of t, 1 H, *J* = 16, 7.5 Hz), 6.23 (d of t, 1H, *J* = 11, 7.5 Hz), 5.89 (d, 1 H, *J* = 16 Hz), 5.86 (d, 1 H, *J* = 11 Hz), 3.68 (s, 6 H), 2.81 (m, 2 H), 2.40 (m, 2 H); ^{13}C NMR 166.4 (s), 166.1 (s), 147.6 (d), 147.3 (d), 121.5 (d), 120.3 (d), 51.0 (q), 50.7 (q), 31.1 (t), 27.0 (t).

Further elution yielded (*E,E*)-dimethyl-2,6-octadiene-1,8-dioate (**19**), 36 mg (8%): IR (neat) 1735, 1660, 1439 cm^{-1}; ^1H NMR 6.96 (d of t, 2 H, *J* = 16, 7.5 Hz), 5.89 (d, 2 H, *J* = 16 Hz), 3.70 (s, 6 H), 2.40 (m, 4 H); ^{13}C NMR 165.7 (s), 146.5 (d), 121.4 (d), 50.5 (q), 29.9 (t).

The column was then eluted with 60% EtOAc/hexane to afford 45 mg recovered **17**.

The sulfone *trans*-diester **21** (220 mg, 0.838 mmol) was pyrolyzed as above to yield 21 mg (13%) of *E,Z* diester **18** and 130 mg (78%) of the *E,E* diester **19**.

***trans*-3,3-Dioxo-3-thiabicyclo[3.2.0]heptane-6,7-dicarboxylic Acid Dimethyl Ester (21).** Sodium metal (46 mg, 2.0 mmol) was added to MeOH (100 mL) followed by *cis*-diester **17** (500 mg, 1.91 mmol) and the solution refluxed for 20 h. The solution was acidified with HCl gas and evaporated to a slurry (~10 mL), and $CHCl_3$ (150 mL) and H_2O (100 mL) were added. The $CHCl_3$ was extracted with aqueous saturated $NaHCO_3$, dried with $MgSO_4$, and evaporated to a crude oil, which crystallized from ether/hexane to yield 188 mg (0.717 mmol) of *trans*-diester **21**: mp 119–120 °C; IR (KBr) 1720, 1370, 1295, 1145 cm^{-1}; ^1H NMR 3.78 (s, 6 H), 3.85–3.05 (m, 8 H); ^{13}C NMR 172.0 (s), 170.5 (s), 53.8 (t), 52.1 (q), 51.9 (q), 50.0 (t), 44.0 (d), 39.8 (d), 33.2 (d); MS, *m/e* (relative intensity) 262 (M$^+$, 1), 231 (29), 145 (19), 138 (43), 99 (100), 79 (71). Anal. Calcd for $C_{10}H_{14}O_6S$: C, 45.79; H, 5.38; S, 12.22. Found: C, 46.00; H, 5.42; S, 12.06.

Concentration of the mother liquors gave two additional crops, 293 mg (1.11 mmol), of a mixture of **17** and **21**.

1,6-Dimethyl-3,3-dioxo-3-thiabicyclo[3.2.0]heptane-6,7-dicarboxylic Anhydride (16b). 3-Methyl-2,5-dihydrothiophene 1,1-dioxide (**1b**) (3.0 g, 22.7 mmol), citraconic anhydride (**15b**) (2.55 g, 22.7 mmol), and CH_2Cl_2 (25 mL) were degassed with argon in a quartz tube. The solution was photolyzed as before at −78 °C. The precipitate, photoadduct **16b**, was filtered off periodically during the photolysis (30 h). Concentration of the filtrate afforded a further crop of photoadduct **16b**. Flash chromatography of the mother liquors with 60% EtOAc/hexane yielded recovered starting materials: 1.32 g of **1b** and 0.8 g of **15b**. Further elution afforded 110 mg of photoadduct **16b**. Recrystallization of the precipitate from acetone yielded 2.5 g (80% yield based on recovered **1b**) of photoadduct **16b** as two crystalline forms: mp 194–196 and 210–211 °C; IR (KBr) 1860, 1780, 1310, 1012 cm^{-1}; ^1H NMR (Me_2SO-d_6) 3.80–2.90 (m, 6 H), 1.46 (s, 3 H), 1.32 (s, 3 H); MS, *m/e* (relative intensity) 244 (M$^+$, 0.1), 172 (11), 136 (5), 108 (39), 93 (100), 82 (11), 77 (18), 68 (25). Anal. Calcd for

$C_{10}H_{12}O_5S$: C, 49.17; H, 4.95; S, 13.13. Found: C, 49.35; H, 5.08; S, 13.04.

***cis*-1,6-Dimethyl-3,3-dioxo-3-thiabicyclo[3.2.0]heptane-6,7-dicarboxylic Acid Dimethyl Ester (23).** Photoadduct **16b** (1.00 g, 4.10 mmol) was dissolved in MeOH (700 mL) saturated with HCl gas and the solution refluxed for 20 h. Concentration of the solvent to ~30 mL was followed by the addition of $CHCl_3$ (125 mL) and H_2O (100 mL). The $CHCl_3$ layer was extracted several times with a saturated aqueous $NaHCO_3$ solution, dried with $MgSO_4$, and evaporated to yield 0.748 g (62%) of the *cis*-diester **23** when crystallized from $CHCl_3$/ether (1:10): mp 138–139 °C; IR (KBr) 1745, 1725, 1315, 1260 cm^{-1}; ^1H NMR 3.74 (s, 3 H), 3.74–2.80 (m, 6 H), 3.66 (s, 3H), 1.55 (s, 3 H), 1.52 (s, 3 H); exact mass calcd for $C_{12}H_{18}O_6S$ 290.0824, found 290.0874. Anal. Calcd for $C_{12}H_{18}O_6S$: C, 49.64; H, 6.25. Found: C, 49.55; H, 6.32.

***trans*-1,6-Dimethyl-3,3-dioxo-3-thiabicyclo[3.2.0]heptane-6,7-dicarboxylic Acid Dimethyl Ester (28).** To MeOH (100 mL) was added sodium metal (44 mg, 1.9 mmol) followed by *cis*-diester **23** (500 mg, 1.91 mmol) and the solution refluxed for 24 h. The solution was acidified with HCl gas and evaporated to a slurry (~10 mL), and $CHCl_3$ (150 mL) and H_2O (100 mL) were added. The $CHCl_3$ was extracted with aqueous saturated $NaHCO_3$, dried with $MgSO_4$, and evaporated to yield a crude oil. HPLC analysis of the crude oil revealed that it was a mixture of *trans*-diester **28** and *cis*-diester **23** (7:3). Flash chromatography over silica gel (60 g) and elution with 5% EtOAc/$CHCl_3$ gave 198 mg (35%) of **28**: mp 125–126 °C; IR (neat) 1735, 1310, 1135 cm^{-1}; ^1H NMR 3.78 (s, 3 H), 3.73 (s, 3 H), 3.73–2.90 (m, 6 H), 1.58 (s, 3 H), 1.46 (s, 3 H); MS, *m/e* 290 (M^+, 0.2), 259 (11), 231 (7), 166 (29), 135 (11), 127 (18), 113 (100), 107 (54). Anal. Calcd for $C_{12}H_{18}O_6S$: C, 49.64; H, 6.25; S, 11.04. Found: C, 49.94; H, 6.35; S, 10.93.

Further elution afforded 180 mg (32%) of starting material **23**.

HPLC data: column, Waters 5-μm silica gel; mobile phase, 4% $CHCl_3$/hexane; flow rate, 2 mL/min; detector, refractive index.

(*Z*,*Z*)-, (*Z*,*E*)-, (*E*,*Z*)- and (*E*,*E*)-Dimethyl 2,6-Dimethylocta-2,6-diene-1,8-dioate (27, 26, 25, and 24a). The sulfone *cis*-diester **23** (3.00 g, 10.3 mmol) was flash vacuum pyrolyzed [500 °C (0.5 mmHg)] as before. HPLC analysis of the crude product mixture revealed a mixture of **27**, **26**, **25**, and **24a** in the following ratio: 8:36:38:18. The crude residue was flash chromatographed on a silica gel column (80 g) eluted with 3% EtOAc/hexane. The composition of each fraction was determined by HPLC, and the pure fractions and "mixture" fractions were grouped accordingly. Evaporation of the solvent from the pure fractions afforded the following: 12 mg (5%) of the 2*Z*,6*Z* diester **27** 255 mg (11%) of the 2*Z*,6*E* diester **26**, 304 mg (13%) of the 2*E*,6*Z* diester **25**, and 247 mg (11%) of the 2*E*,6*E* diester **24a**. Evaporation of the solvent from the mixed fractions afforded 973 mg of a mixture of **27**, **26**, **25**, and **24a**. The combined isolated yields of the mixed and pure fractions was 77%. Further elution with 60% EtOAc/hexane afforded 610 mg (20%) of starting material (**23**).

HPLC data: column, Waters 5-μm silica gel; mobile phase, 5% EtOAc/hexane; flow rate, 2 mL/min; detector, UV at 254 nm.

2*Z*,6*Z* Diester **27**: IR (neat) 1720, 1649, 1430 cm^{-1}; ^1H NMR 6.03 (t, 1 H, J = 7.5 Hz), 5.73 (s, 1 H), 3.75 (s, 3 H), 3.69 (s, 3 H), 2.77 (m, 4 H), 1.91 (s, 6 H); ^{13}C NMR 167.2 (s), 165.6 (s), 158.4 (s), 141.0 (d), 126.5 (s), 115.3 (d), 50.0 (q), 49.6 (q), 31.7 (t), 27.0 (t), 23.9 (q), 19.5 (q); MS m/e 226 (M^+,2), 195 (18), 194 (44), 166 (26), 162 (71), 134 (100), 113 (32), 107 (88), 91 (32). Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.54; H, 8.01.

2*Z*,6*E* Diester **26**: IR (neat) 1720, 1650, 1430 cm^{-1}; ^1H NMR 5.94 (t, 1 H, J = 7.5 Hz), 5.73 (s, 1 H), 3.74 (s, 3 H), 3.68 (s, 3 H), 2.90–2.49 (m, 2 H), 2.40–2.10 (m, 2 H), 2.18 (s, 3 H), 1.91 (s, 3 H); ^{13}C NMR 167.0 (s), 166.0 (s), 158.0 (s), 140.4 (d), 127.4 (s), 115.1 (d), 50.3 (q), 49.7 (q), 39.5 (t), 26.8 (t), 19.7 (q), 17.8 (q); MS, *m/e* (relative intensity) 226 (M^+, 3), 195 (17), 194 (38), 166 (38), 162 (38), 135 (45), 134 (66), 107 (100), 91 (31). Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.54; H, 8.18.

2*E*,6*Z* Diester **25**: IR (neat) 1725, 1650, 1435 cm^{-1}; ^1H NMR 6.82 (t, 1 H, J = 7.5 Hz), 5.74 (s, 1 H), 3.73 (s, 3 H), 3.68 (s, 3 H), 2.95–2.65 (m, 2 H), 2.55–2.15 (m, 2 H), 1.93 (s, 3 H), 1.87 (s, 3 H); ^{13}C NMR 167.4 (s), 165.6 (s), 157.9 (s), 140.2 (d), 127.7 (s), 116.2 (d), 50.7 (q), 49.8 (q), 31.5 (t), 26.7 (t), 24.3 (q), 11.5 (q); MS *m/e* 226 (M^+, 2), 195 (15), 194 (49), 166 (31), 162 (54), 134 (74), 113 (36), 107 (100), 91 (28). Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.53; H, 8.00.

2*E*,6*E* Diester **24a**: IR (neat) 1720, 1640, 1428 cm^{-1}; ^1H NMR 6.74 (t, 1 H, J = 7.5 Hz), 5.73 (s, 1 H), 3.73 (s, 3 H), 3.68 (s, 3 H), 2.80–2.25 (m, 4 H), 2.19 (s, 3 H), 1.76 (s, 3 H); ^{13}C NMR 167.9 (s), 166.6 (s), 158.0 (s), 140.0 (d), 128.2 (s), 115.6 (d), 51.4 (q), 50.5 (q), 39.0 (t), 26.0 (t), 18.4 (q), 12.1 (q); MS, *m/e* 226 (M^+, 1) 195 (33), 194 (67), 166 (60), 162 (53), 134 (67), 113 (53), 107 (100), 82 (67). Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.54; H, 8.01.

The *trans*-sulfone diester **28** (554 mg, 1.91 mmol) was flash vacuum pyrolyzed as above. HPLC analysis of the crude product mixture showed a mixture of **27**, **26**, **25**, and **24** in the following ratio: 39:11:11:39. Flash chromatography as above afforded 45 mg (10%) of the 2*Z*,6*Z* diester **27**, 7 mg (2%) of the 2*Z*,6*E* diester **26**, 10 mg (2%) of the 2*E*,6*Z* diester **25**, 77 mg (18%) of the 2*E*,6*E* diester **24a** and recovered starting material **28**, 365 mg (65%).

10-Hydroxygeraniol (24b). To a suspension of $LiAlH_4$ (0.626 g, 16.5 mmol) and $AlCl_3$ (0.753 mg, 5.65 mmol) in ether (50 mL) at 0 °C was added 2,6*E* diester **24a** (220 mg, 0.973 mmol) in ether (15 mL). The mixture was stirred for 15 min, then quenched with H_2O under a N_2 stream. Ether (50 mL) and H_2O (50 mL) were added. The aqueous layer was separated and extracted with ether (100 mL × 3). The combined ether layers were dried with $MgSO_4$ and evaporated to afford 10-hydroxygeraniol, 161 mg (97%), exhibiting identical spectral data with the reported literature data:[14c] IR (neat) 3600, 1670, 1010 cm^{-1}; ^1H NMR 5.56–5.23 (m, 2 H), 4.13 (d, 2 H, J = 7 Hz), 3.97 (s, 2 H), 3.74–3.49 (brs, 2H), 2.40–1.96 (m, 4 H), 1.65 (m, 6 H); MS, *m/e* 170 (M^+, 1), 152 (3), 137 (8), 134 (5), 121 (19), 84 (48), 68 (100), 67 (50); ^{13}C NMR 137.8 (s), 134.8 (s), 124.7 (d), 123.8 (d), 67.9 (t), 58.6 (t), 38.9 (t), 25.5 (t), 15.9 (q), 13.4 (q).

***cis*-Hexa-1,5-diene-3,4-dicarboxylic Anhydride (29a).** The photoadduct **16a** (1.60 g, 7.40 mmol) was flash vacuum pyrolyzed [700 °C (0.5 mmHg)] as before. The residue was distilled [60–68 °C (0.5 mmHg)] to give **29a**, 0.910 g (81%), as a colorless oil: IR (neat) 1865, 1780, 1650, 1420 cm^{-1}; ^1H NMR 6.25–5.23 (m, 2 H), 5.43 (d, 2 H, J = 10 Hz), 5.40 (d, 2 H, J = 17 Hz), 4.07 (d of d, 2 H, J = 5, 3 Hz); MS, *m/e* 152 (M^+, 40), 137 (10), 124 (15), 108 (15), 80 (42), 79 (100), 77 (35), 59 (48).

2,4-Dimethylhexa-2,5-diene-3,4-dicarboxylic Anhydride (30b). Photoadduct **16b** (100 mg, 0.410 mmol) and dry toluene (3 mL) was sealed under vacuum in a Pyrex thermolysis tube and heated at 290 °C for 5 h. The solvent was removed under reduced pressure and the crude oil flash chromatographed on a silica gel column (30 g) eluted with 10% EtOAc/hexane to afford 64 mg of anhydride **30** (97% based on recovered **16b**): IR (neat) 1840, 1770, 1650, 1235 cm^{-1}; ^1H NMR 5.95 (dd, 1 H, J = 17, 10 Hz), 5.38 (d, 1 H, J = 10 Hz), 5.28 (d, 1 H, J = 17 Hz), 2.40 (s, 3 H), 1.98 (s, 3 H), 1.66 (s, 3 H); MS, *m/e* 180 (M^+, 0.1), 136 (34), 120 (5), 108 (23), 107 (13), 94 (100), 91 (29), 77 (29); ^{13}C NMR 173.1 (s), 162.7 (s), 160.2 (s), 135.0 (d), 122.3 (s), 117.0 (t), 50.7 (s), 23.3 (q), 22.4 (q), 21.0 (q). Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65% H, 6.71. Found C, 66.85; H, 6.79.

Further elution with 60% EtOAc/hexane afforded 11 mg of recovered starting material (**16b**).

Single-Crystal X-ray Structure Determination of 3b. Crystals suitable for X-ray diffraction analysis were grown from ethyl acetate/hexane. The crystals were monoclinic, space group $P2_1/n$, with a = 8.874 (5) Å, b = 13.034 (5) Å, c = 9.378 (4) Å, β = 96.33 (4)°, V = 1078.0 Å^3, and d_c = 1.407 g cm^{-3} for Z = 4 ($C_{11}H_{16}O_3S$, M_r 228.31). The sample was submitted as a colorless crystalline block measuring 0.55 × 0.35 × 0.35 mm. Intensity data were collected at 273 K (ω–θ scan technique, radiation—Mo Kα λ = 0.71073 Å) using an Enraf-Nonius diffractometer. The data were reduced and corrected for Lorentz-polarization effects. A plot of standard intensities showed a maximum loss in intensity of 0.3% during data collection; therefore, no correction for crystal decay was deemed necessary. After rejection of systematic absences and averaging Freidel pairs, 3128 unique observations remained of which 2797 with $I > 3\sigma(I)$ were used in the subsequent least-squares treatments. The data were not corrected for absorption effects. The data were converted to normalized structure factor amplitudes (E) and the structure solved by direct methods. Phase sets were prepared by using 231 reflections (E_{min} = 1.768) and 2413 phase relationships. The positions of the sulfur atom and its oxygen atom substituents were located in the E map prepared from the phase set with the highest figure of merit. The positions of these three atoms were refined, with isotropic temperature factors, by full-matrix least-squares (based on F) to give values of the standard agreement factors where the weights, w, were initially assigned as unity.

$$R = \sum(|F_o| - |F_c||)/\sum|F_o| = 52.0\%$$

$$R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2} = 57.6\%$$

The function minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$. A difference Fourier calculation next revealed the positions for all remaining non-hydrogen atoms. Refinement of these positions with isotropic temperature factors yielded the residuals R and R_w, 10.5% and 11.4%, respectively. Further refinement of all non-hydrogen atoms with anisotropic librational parameters afforded the residuals $R = 7.1\%$ and $R_w = 14.4\%$ where the weights are now defined as $w = 1/\sigma(R_o)^2$ with $\sigma(F_o)^2$ given by the expression$[(\sigma(I)^2 + (pF_o)^2]^{1/2}$ and $p = 0.05$. A difference Fourier map next revealed the positions of all 16 hydrogen atoms. All hydrogen atoms were assigned isotropic thermal parameters (4.0) which remained fixed during the remainder of the structure refinement. Least-squares treatment of the 15 non-hydrogen atoms (anisotropic liberational parameters) along with the 16 hydrogen atom positions gave residuals $R = 3.9\%$ and $R_w = 7.8\%$. At this stage of the refinement three reflections with asymmetric backgrounds and five strong reflections suspected of counter flooding were rejected. Of the remaining 3120 reflections, 2790 reflections ($I > 3*(I)$) were used in the final least-squares treatment. After a statistical analysis of the weighting scheme the ignorance factor, p, was reset to 0.02. The final least-squares refinement (184 variables, 2790 observations) converged to $R = 3.6\%$ and $R_w = 5.6\%$ with no parameter shifting by more than 0.05 times its estimated standard deviation in the final cycle. Examination of values F_o and F_c for several low order reflections showed no evidence of secondary extinction effects. The goodness of fit was 3.651. A final difference Fourier calculation was featureless showing only one significant peak (0.4 eA^{-3}) near the sulfur atom. A plot of the function minimized vs. sin $\theta\lambda^{-1}$ showed no significant trends. Values of the neutral atom scattering factors were taken from the "International Tables for X-Ray Crystallography". Effects of anomalous dispersion for all atoms were included with values of f' and f'' taken from the "International Tables". Hydrogen atoms scattering factors were those of Stewart, Davidson, and Simpson. All programs used for structure solution and refinement were from the Enraf-Nonius Structure Determination Package.

Single-Crystal X-ray Structure Determination of 7. Crystals suitable for X-ray diffraction were grown from ethyl acetate/hexane. The crystal were monoclinic space group $P2_1/n$, with a = 6.643 (1) Å, b = 22.695 (5) Å, c = 7.449 (2) Å, β = 99.99 (2)°, and $d_c = 1.383$ g cm^{-3} for $Z = 4$ ($C_{11}H_{18}O_3S$, M_r 230.33). The crystal used for data collection was a colorless, transparent block measuring 0.40 × 0.35 × 0.35 mm. Excluding standards a total of 3564 measurements were obtained and the data analyzed as previously described. A plot of standard intensities showed a significant decay in the crystal during data collection, the maximum loss in intensity was 6.7%. The data were corrected for this decay. After rejection of 91 systematically absent reflections and averaging Friedel pairs, 3225 unique observations remained of which 2374 with $I > 3\sigma(I)$ were used in the subsequent least-squares treatments. In the final cycle of refinement, 15 non-hydrogen atoms (anisotropic), 18 hydrogen atoms (isotropic), 209 variable, 2374 observations, converged to $R = 3.6\%$ and $R_w = 4.9\%$ with no parameter shifting by more than 0.01 times its estimated standard deviation. The goodness of fit was 1.323. A final difference Fourier synthesis was featureless. A plot of the function minimized vs. sin $\theta\lambda^{-1}$ showed no significant trends.

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Supplementary Material Available: Tables of positional parameters and their esd's for **3b** and **7** (22 pages). Ordering information is given on any current masthead page.

Conformations and Internal Mobility of Side Chains in Heterosubstituted Hexaalkylbenzenes. Isopropyl/Ethyl and Isopropyl/Cyclopropyl Systems

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Variable-temperature NMR spectra of hexaalkylbenzenes containing both isopropyl and ethyl or cyclopropyl groups, in conjunction with empirical force-field calculations, have shown that the alkyl groups in these heterosubstituted benzenes retain the conformation they individually adopt in the homosubstituted analogues: isopropyl groups maintain a bisected conformation, whereas ethyl or cyclopropyl groups adopt a perpendicular one. Two site-exchange processes have been observed in heterosubstituted benzenes containing vicinal isopropyl groups: a low-energy process, which leads to fast rotation of all alkyl groups *except* for the isopropyl groups, and a high-energy process that corresponds to the unfreezing of the gear-locked isopropyl groups. The magnitude of the barriers for both processes has been determined for 1,2-diethyl- and 1,2-dicyclopropyl-3,4,5,6-tetraisopropylbenzene and for 1,2-diisopropyl-3,4,5,6-tetracyclopropylbenzene.

Homosubstituted hexaalkylbenzenes of the type $C_6(Cab_2)_6$ are found to follow two conformational patterns, conveniently characterized by the values of the a–C–C_{ar}–C_{ar} torsion angles (θ) as *perpendicular* (θ = 90 ± 30°) or *eclipsed* (θ = 0 ± 30°); the latter is also called *bisected* with reference to the bCb angles (Figure 1).[2] In the perpendicular conformation, exemplified by hexaethylbenzene (**1**)[3] and hexacyclopropylbenzene (**2**),[4] the Cab_2 groups are arranged so that the a's (atoms or groups) extend alternately above and below the plane of the benzene ring, and

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[1] (a) Max Kade Postdoctoral Research Fellow, on leave from the Universität Wien. (b) Government of India Scholar, on leave from Manipur University.

[2] The descriptors in Figure 1 are adapted from the analogous scheme for ethane skeletons. See: Hounshell, W. D.; Dougherty, D. A.; Mislow, K. *J. Am. Chem. Soc.* **1978**, *100*, 3149.

[3] Iverson, D. J.; Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 6073.

[4] Bar, I.; Bernstein, J.; Christensen, A. *Tetrahedron* **1977**, *33*, 3177.

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