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Supplementary Material Available: Tables of fractional coordinates, thermal parameters, interatomic distances, and interatomic angles for 7 (5 pages). Ordering information is given on any current masthead page.

Stereoselective Synthesis of (*E*)-, (*E,Z*)-, and (*E,E*)-Conjugated Dienes via Alkylation of 3-Sulfolenes as the Key Step

Sachiko Yamada, Hideto Ohsawa, Takayoshi Suzuki, and Hiroaki Takayama*

Faculty of Pharmaceutical Sciences, Teikyo University, Sagamiko, Kanagawa 199-01, Japan

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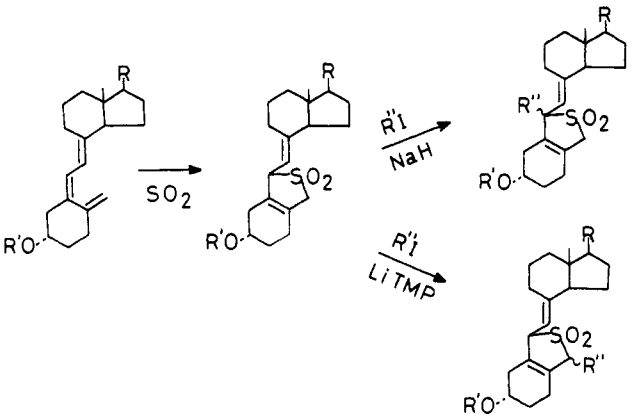
A new stereoselective method is presented for synthesizing (*E*)-, (*E,Z*)-, and (*E,E*)-conjugated dienes via alkylation of 3-sulfolenes as the key step. Direct alkylation of 3-sulfolene at the 2-position proceeds with good yields when labile sulfolene α-carbanion is generated in the presence of alkyl iodides in THF–HMPA solution at −78 °C. Alkylation of 2-alkyl-3-sulfolenes gives *trans*-2,5-dialkyl-3-sulfolenes with 100% regioselectivity and more than 90% stereoselectivity. Desulfonylation of trans-2,5-disubstituted 3-sulfolenes is examined in detail, and the conditions to give stereoselectively the corresponding (*E,Z*)- and (*E,E*)-conjugated dienes are found. Applying the method, three insect pheromones, (*E*)-9,11-dodecadien-1-yl acetate, a sex pheromone of the red bollworm moth, (*E,E*)-8,10-dodecadien-1-ol, a sex pheromone of the codling moth, and (*E,E*)-11,13-hexadecadienal, a sex pheromone of the cabbage webworm, are easily synthesized by starting with 3-sulfolene with nearly 100% stereoselectivity. Synthesis of cis-3,4,5-trisubstituted cyclohexenes using 2-substituted 3-sulfolenes as the diene synthons is also described.

Conjugated dienes are versatile building blocks in the syntheses of organic natural products, especially as a component of the Diels–Alder reaction in the synthesis of 6-membered cyclic compounds. Recent advances in the intramolecular Diels–Alder approach[1] to the synthesis of bicyclic natural products further increased the utility of conjugated dienes. A number of new methods for preparing conjugated dienes have appeared in recent years utilizing reagents such as organoaluminum,[2] -boron,[3] -cobalt,[4] -palladium,[5] -copper,[6] -nickel,[7] and -mercury.[8] The scope of many of these reactions is limited by the nature of the organometallic involved or the procedure employed. 3-Sulfolene, the 1,3-butadiene–sulfur dioxide adduct (1), and its derivatives are attractive as masked diene synthons, since they generate dienes readily by thermal desulfonylation under relatively mild conditions (120 °C) and the terminal CH bonds of the original dienes are activated by the adjacent sulfonyl group, suggesting the possibility of modifying the terminal positions of the dienes. Thus, if the introduction of variable electrophiles to the 2- or 5-position is possible, a variety of 1,4-disubstituted conjugated dienes are made available via the modification of 3-sulfolene. However, the lability of the sulfolene α-carbanion, which readily undergoes ring opening, has prohibited that possibility.[9] For that reason, no general alkylation method for 3-sulfolenes has been known except for the sulfolenes whose double bond constitutes a part of an aromatic ring.[10] Bloch et al.[11] protected the double bond of 3-sulfolene as a cyclopentadiene adduct to prevent the cycloreversion and successfully introduced electrophiles to the terminal position of the masked diene group. The method may not be suitable for compounds having a thermally labile group, because it requires high tempera-

Scheme I



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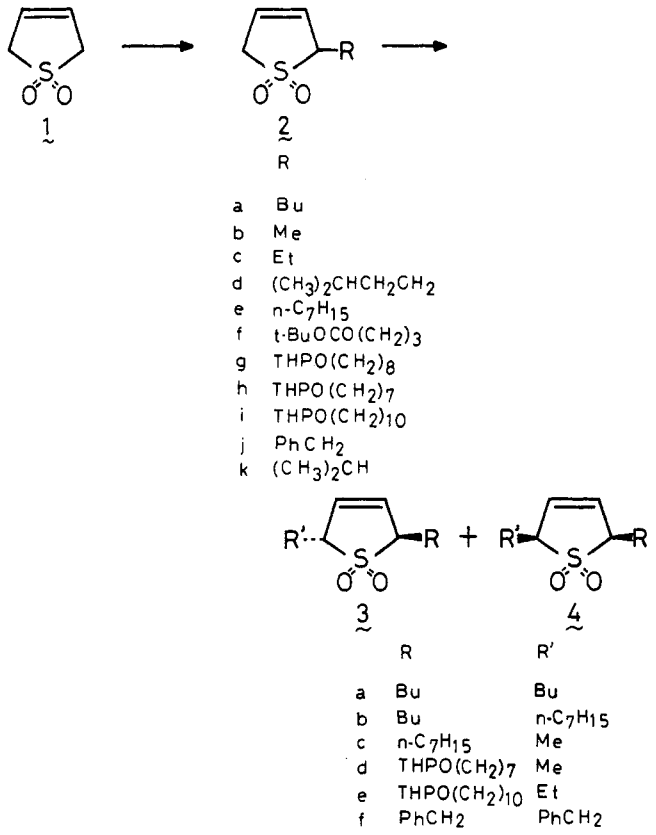
Scheme II



ture to carry out retro Diels–Alder reaction. We found that direct introduction of electrophiles to the α-position of 3-sulfolenes is possible if the sulfolene α-carbanion was generated in the presence of an electrophilic partner so that the unstable carbanion can react with the electrophile before decomposing. In the studies of the chemistry of the conjugated triene part of vitamin D, we found that vitamin D–sulfur dioxide adducts can be alkylated regioselectively at either the 6-position when the adduct is treated with sodium hydride or the 19-position when treated with lithium tetramethylpiperidide in the presence of an alkyl iodide (Scheme I).[12] We extended the reaction to parent 3-sulfolene **1** and established a general method for alkylating 3-sulfolenes.[13] Namely, a practical method for synthesizing 2-substituted and trans-2,5-disubstituted 3-sulfolenes **2** and **3** was established starting with the sulfolene **1**. We also found a novel stereoselective method for desulfonylating trans-2,5-disubstituted 3-sulfolenes **3** to (*E,E*)-conjugate dienes **10**, contrary to the selection rule for the cheletropic reaction.[14,15] Thus, the alkylation of 3-sulfolene in combination with thermal desulfonylation under controlled conditions provided a facile stereoselective route to (*E*)-, (*E,E*)-, and (*E,Z*)-conjugated dienes. Here, we report the results in detail.

Results and Discussion

Reaction of 3-Sulfolenes with Alkyl Halides (Scheme II). Treating 3-sulfolene (1) with *n*-butyl iodide as a representative of alkyl halides was examined under a variety of conditions. The results are summarized in Table I. The sulfolene **1** did not react with butyl iodide under the conditions employed for the alkylation of benzosulfolene[10b] (entry 1). Alkylation occurred when a bulky metal amide, employed as the base, was added as quickly as possible to a solution of the sulfolene and butyl iodide in THF–hexamethyl phosphoric triamide (HMPA) at low temperature (−78 °C) to yield 2-butyl-3-sulfolene (**2a**) in moderate to good yields (entries 2–6). Only a trace of the alkylation product **2a** was produced when a solution of the sulfolene **1** was first treated with the base followed by addition of the alkyl iodide. Lithium hexamethyldisilazide (LiHMDS) was the base of choice. No alkylation occurred without the addition of HMPA as the cosolvent. When about equimolar amounts of alkyl iodide and sulfolene were used, trans-2,5-dialkylated sulfolenes **3a** were obtained in appreciable yields in addition to the monoalkylation products **2a**. Formation of the dialkylation products **3a** was decreased by using an excess of sulfolene (entries 4–6). The reaction of 3-sulfolene with various alkyl halides was examined under the conditions of entry 4. The results are shown in Table II. 3-Sulfolene (1) reacted similarly with other primary alkyl iodides to give 2-alkyl-3-sulfolenes **2** in good yields. In the reaction with primary alkyl bromide, the yields of the alkylation products were somewhat lower (entries 7 and 9). Secondary alkyl iodide did not react with the sulfolene under similar

Table I. Reaction of 3-Sulfolene (1) with Butyl Iodide

		molar ratio				yield,[a] %	
entry	base	1	base	BuI	HMPA	2a	3a
1	KH	1	1.1	1.2	0	0	0
2	NaHMDS	1	1.1	1.2	2	23	tr
3	LiHMDS	1	1.1	1.2	2	35	9
4	LiHMDS	2	1.1	1.0	4	65	tr
5	LiTMP	2	1.1	1.0	4	48	tr
6	LDA	2	1.1	1.0	4	27	tr

[a] Yields are based on the butyl iodide.

Table II. Reaction of 3-Sulfolene with Alkyl Halides[a]

entry	alkyl halide	product	yield,[b] %
1	MeI	**2b**	46
2	EtI	**2c**	55
3	isoamyl iodide	**2d**	61
4	n-$C_7H_{15}I$	**2e**	65
5	t-$BuOCO(CH_2)_3I$	**2f**	40
6	$THPO(CH_2)_8I$	**2g**	50
7	$THOP(CH_2)_8Br$	**2g**	33
8	$THPO(CH_2)_7I$	**2h**	58
9	$THPO(CH_2)_{10}I$	**2i**	48
10	$PhCH_2Br$	**2j**	33
11	$PhCH_2I$	**2j**	55
12	$(CH_3)_2CHI$	**2k**	0

[a] The reaction was carried out under the conditions of entry 4 in Table I. [b] Yields are based on the alkyl halides used.

Table III. Alkylation of 2-Substituted 3-Sulfolenes[a]

entry	substrate	halide	product,[b] %	
1	**2a**	n-BuI	**3a** (58)	**4a** (1)
2	**2a**	n-$C_7H_{15}I$	**3b** (56)	**4b** (4)
3	**2e**	MeI	**3c** (71)	**4c** (9)
4	**2h**	MeI	**3d** (55)	**4d** (6)
5	**2i**	EtI	**3e** (45)	**4e** (tr)

[a] The reaction was carried out under the conditions of entry 4 in Table I except for the ratio of sulfolene **2** to alkyl iodide to LiHMDS to HMPA being 1:1.1:1.1:4. [b] Yields are based on the sulfolene **2** used.

(12) Yamada, S.; Suzuki, T.; Takayama, H. *Tetrahedron Lett.* **1981**, *22*, 3085. Yamada, S.; Suzuki, T.; Takayama, H.; Miyamoto, K.; Matsunaga, I.; Nawata, Y. *J. Org. Chem.* **1983**, *48*, 3483.
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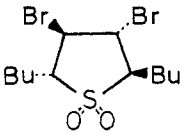
(14) (a) Mock, W. L. *J. Am. Chem. Soc.* **1966**, *88*, 2857; (b) *Ibid.* **1975**, *97*, 3666. (c) McGregor, S. D.; Lemal, D. M. *Ibid.* **1966**, *88*, 2858. (d) Isaacs, N. S.; Laila, A. A. R. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1470.
(15) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

Table IV. Desulfonylation of *trans*- and *cis*-2,5-Dibutyl-3-sulfolenes (3a and 4a)

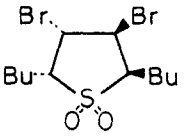
entry	substrate	conditions: additives	conditions: solvent	conditions: temp, °C	time,[b] h	product ratio (9a:10a)[c]	yield, %
1[a]	3a		octane	125	1.5	97:3	92
2[a]	3a		heptane	98	32	87:13	90
3	3a	Et_3N	95% EtOH	125	4	74:26	90
4	3a	NaOAc	95% EtOH	125	1.5	93:7	90
5	3a	$NaHCO_3$	95% EtOH	125	1	5–27:73–95	90
6	3a	$KHCO_3$	95% EtOH	125	1	2–20:80–98	90
7	3a	K_2CO_3	95% EtOH	125	0.5	1:99	96
8	3a	KOH	95% EtOH	125	0.5	0:100	90
9	3a	KOH	dioxane	125	1	95:5	93
10	3a	$LiAlH_4$	ether	35	0.5	100:0	91
11[a]	4a		octane	125	0.5	0:100	93
12	4a	$NaHCO_3$	95% EtOH	125	0.5	0:100	95
13	4a	KOH	95% EtOH	125	0.5	0:100	95

[a] Argon was bubbled during the thermolysis. [b] Time required to consume the starting sulfolene. [c] Determined by GLC analysis [5% 1,2,3-tris(2-cyanoethoxy)propane on Uniport B, 1.5 m, room temperature].

conditions (entry 11). The reactions of 2-substituted 3-sulfolenes **2** with alkyl iodide were carried out under the conditions of entry 4 in Table I except for the molar ratio of **2** to alkyl iodide being 1:1.1. The results are shown in Table III. The reactions proceeded with 100% regioselectivity and more than 90% stereoselectivity to give trans-2,5-dialkylated sulfolenes **3** in good yields, together with a trace of cis-2,5-disubstituted products **4**. It is suggested from these results that the bulky base abstracted the most acidic and less hindered proton at the 5-position situated trans to the substituent at the 2-position and the carbanion so generated reacted with iodides before inverting its stereochemistry. However, a possibility of a steric approach control of the electrophile cannot be ruled out. The stereochemistry of the dialkylated sulfolenes was determined on the basis of their spectral data and the reaction of the two 2,5-dibutyl sulfolenes **3a** and **4a** with bromine. Bromination of the major isomer **3a** of 2,5-dibutyl-3-sulfolenes gave two bromine adducts **5** and **6** while the minor isomer **4a** yielded only one adduct, **7**. Thermal desulfonylation of the dialkylated sulfolenes **3** and **4** described below supports these assignments.



5



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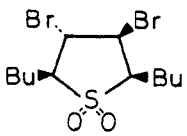


7

Desulfonylation of Substituted 3-Sulfolenes. Desulfonylation of 3-sulfolenes is a typical cheletropic reaction whose mechanism has been studied[14] extensively from the viewpoint of the Woodward–Hoffmann rule.[15] The reaction proceeds in a concerted and stereospecifically suprafacial manner with respect to the diene part. However, thermal desulfonylation of sulfolenes having substituents at the 2- and 5-positions has not been systematically studied from the synthetic point of view. We studied in detail the desulfonylation of 3-sulfolenes having substituents at the 2-position and at the 2- and 5-positions prepared in the present work.

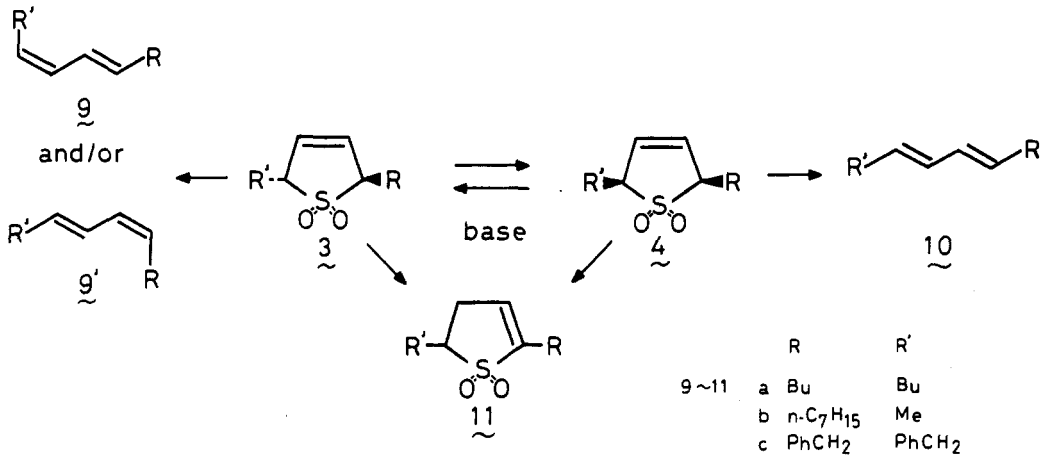
Thermolysis of 2-substituted 3-sulfolenes **2** was carried out in an ethanol solution at 125 °C in a sealed tube in the presence of $NaHCO_3$. The reaction was completed within 1 h to give (*E*)-dienes **8** with 100% selectivity in about 90% isolated yields. The stereoselective desulfonylation of 2-substituted 3-sulfolenes to (*E*)-dienes has been reported.[14d] The selectivity that the ring opens outwardly with respect to the substituent at the 2-position is closely related to the stereoselectivity observed in the electrocyclic reactions of substituted cyclobutenes.[16]

Thermal desulfonylation of *trans*-2,5-dibutyl-3-sulfolene (**3a**) was examined under a variety of conditions. The results are summarized in Table IV. Thermolysis under neutral conditions (entry 1) gave (*E,Z*)-5,7-dodecadiene (**9a**) with high selectivity in accord with the selection rule.[14] In this case, bubbling of an inert gas was necessary to eliminate from the reaction medium the sulfur dioxide evolved that catalyzes the isomerization of the (*E,Z*)-diene **9a** to the (*E,E*)-diene **10a**. The isomerization becomes significant after a long period of heating even with argon bubbling (entry 2). Addition of a weak base, specifically sodium acetate, effectively quenched sulfur dioxide and prevented the isomerization (entry 3 and 4). However, adding more basic reagents caused drastic change in the stereoselectivity. Thus, in the presence of 2 equiv of $NaHCO_3$ in 95% ethanol (entry 5), thermolysis of **3a** gave (*E,E*)-dodecadiene (**10a**) in more than 70% selectivity, contrary to the selection rule, in addition to the (*E,Z*)-diene **9a**. Potassium bicarbonate had a similar effect on the stereoselectivity (entry 6). Addition of a much stronger base such as K_2CO_3 and KOH increased the proportion of the (*E,E*)-diene **10a** to nearly 100% (entries 7 and 8). It should be noted that the addition of the strong base also enhanced the rate of the desulfonylation. The added base had no effect when the thermolysis was carried out in an aprotic solvent (entry 9).

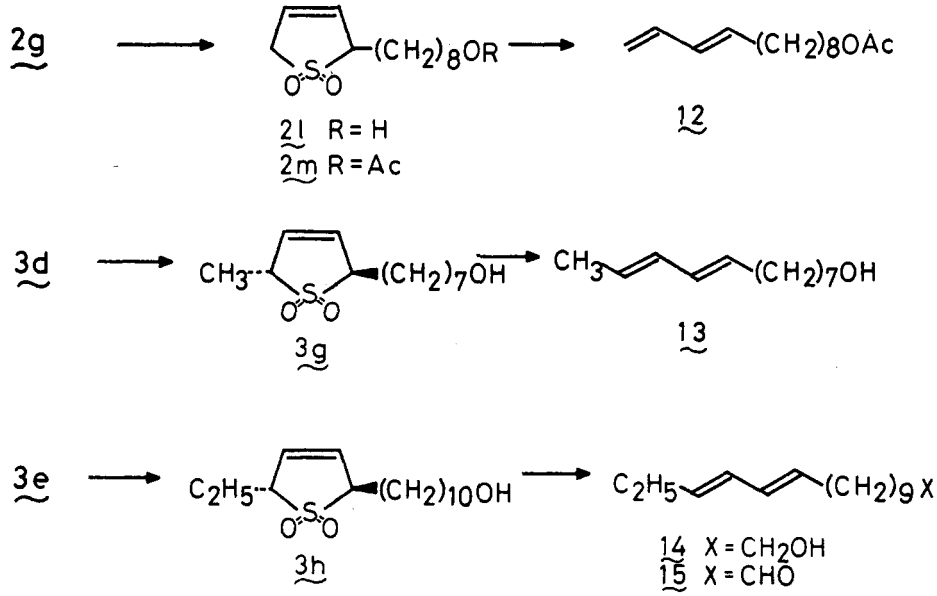
From these results, we suggest the following mechanisms for the selective formation of the (*E,E*)-diene **10a** from *trans*-2,5-dibutyl-3-sulfolene (**3a**) under basic conditions (Scheme III). In a protic solvent in the presence of a base, *trans*-2,5-dibutyl-3-sulfolene (**3a**) equilibrates with the cis isomer **4a**. It is known that *cis*-2,5-dimethyl-3-sulfolene is thermodynamically more stable than the corresponding trans isomer;[14a] however, *cis*-2,5-dimethyl-3-sulfolene undergoes thermal desulfonylation more readily than the trans isomer, giving (*E,E*)-2,4-hexadiene.[14a] The cis isomer **4a** formed under the reaction conditions, therefore, extrudes sulfur dioxide more rapidly than the trans isomer **3a**, producing the (*E,E*)-diene **10a** exclusively, in accord with the selection rule.[14] This is supported by the following experiment. Treatment of *trans*-2,5-dibutyl-3-sulfolene (**3a**) with methanolic KOH at 50 °C gave, after 30 min, a mixture of the trans **3a** and the cis **4a** isomers in 1:1.4 (45%) ratio together with the double-bond isomer 2-sulfolene **11a** (36%).[17]

(16) Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 2099.
(17) Isomerization of 3-sulfolenes to 2-sulfolenes under basic condition is known: Turk, S. D.; Cobb, R. L. In *1,4-Cycloaddition Reactions*; Hamer, J., Ed.; Academic: New York, 1967; Chapter 2.

Scheme III



Scheme IV



It is known that 3-sulfolenes undergo desulfonylation by treatment with $LiAlH_4$ in refluxing ether.[18] But it has not been known whether the reductive desulfonylation follows the selection rule. We examined the stereospecificity of the reductive desulfonylation using *trans*-2,5-dibutyl-3-sulfolene (**3a**). Treatment of **3a** with $LiAlH_4$ in refluxing ether gave (*E,Z*)-diene **9a** with 100% selectivity. It should be noted that the reductive desulfonylation gave only the thermodynamically less favorable (*E,Z*)-diene as in the case of thermal desulfonylation; so it is concluded that the reductive desulfonylation follows the symmetry rule. In this regard, it is interesting to know the role of $LiAlH_4$ in the desulfonylation.

Desulfonylation of *cis*-2,5-dibutyl-3-sulfolene (**4a**) gave only the (*E,E*)-diene **10a** regardless of the conditions employed (entries 11–13, Table IV).

Other trans-2,5-disubstituted sulfolenes, **3c** and **3f**, underwent similar (*E,Z*)- and (*E,E*)-selective desulfonylation as shown in Table V.

Thus, we have established novel (*E,E*)-selective desulfonylation of trans-2,5-disubstituted sulfolenes **3**. It is concluded, regarding the desulfonylation of trans-2,5-disubstituted 3-sulfolenes, that the thermolysis in the presence of sodium acetate or the reduction with $LiAlH_4$ in refluxing ether is the recommended method of preparing (*E,Z*)-dienes **9** and that the thermolysis in the presence of potassium carbonate in 95% ethanol is the best way to obtain (*E,E*)-dienes **10**.

Table V. Desulfonylation of Trans-2,5-disubstituted Sulfolenes 3

substrate	conditions[a]	product ratio (9 and 9':10)[b]	yield, %
3c	A	100:0	85
3c	B	0:100	85
3c	C	100:0	90
3f	A	60:40	40
3f	B	0:100	83
3f	C	100:0	94

[a] Conditions: A, entry 4; B, entry 7; C, entry 10 in Table IV. [b] Determined by GLC analysis [5% 1,2,3-tris(2-cyanoethoxy)-propane on Uniport B, 1.5 m].

Stereoselective Synthesis of Insect Pheromones (Scheme IV). The stereoselective method for synthesizing conjugated dienes developed in the present study was applied to the synthesis of insect pheromones having (*E*)- and (*E,E*)-conjugated diene structures: (*E*)-9,11-dodecadien-1-yl acetate (**12**), a sex pheromone of the red bollworm moth,[19] (*E,E*)-8,10-dodecadien-1-ol (**13**), a sex pheromone

(18) Gaoni, Y. *Tetrahedron Lett.* **1977**, 947.

(19) Nesbitt, B. F.; Beevor, P. S.; Cole, R. A.; Lester, R.; Poppi, R. G. *J. Insect Physiol.* **1975**, *21*, 1091.

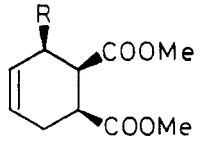
of the codling moth,[20] and (*E,E*)-11,13-hexadecadienal (**15**), a sex pheromone of the cabbage webworm[21] (Scheme IV).

(*E*)-9,11-Dodecadien-1-yl acetate (**12**),[22] a sex pheromone of the red bollworm moth, was synthesized stereoselectively in four steps in 44% overall yield starting from 8-iodo-1-octanol THP ether and 3-sulfolene (**1**). The sulfolene **2g** obtained by the reaction of sulfolene **1** with 8-iodo-1-octanol THP ether was deprotected (PPTS, MeOH–CH_2Cl_2, 40 °C) and acetylated (Ac_2O, pyridine) to give the sulfur dioxide adduct **2m** of the desired pheromone (87%). Thermal desulfonylation of **2m** ($NaHCO_3$, 95% EtOH, 125 °C) gave the desired pheromone **12** in 92% isolated yield and in 100% stereoselectivity.

(*E,E*)-8,10-Dodecadien-1-ol (**13**),[22] a sex pheromone of the codling moth, was prepared stereoselectively in four steps in 29% overall yield starting from 7-iodo-1-heptanol THP ether and 3-sulfolene (**1**). A mixture (9:1) of *trans*- and *cis*-2-methyl-5-[7-(tetrahydropyranoxy)heptyl]-3-sulfolenes (**3d, 4d**) were obtained from 3-sulfolene (**1**) by successive alkylation with 7-iodo-1-heptanol THP ether and methyl iodide in 31% total overall yield. The mixture of the isomers **3d** and **4d** was deprotected (PPTS, MeOH, 40 °C, 91%) and subjected to thermal desulfonylation in the presence of K_2CO_3 in 95% ethanol at 125 °C to give the (*E,E*)-diene **13**, the desired pheromone, in quantitative yield with nearly 100% stereoselectivity.

(*E,E*)-11,13-Hexadecadienal (**15**), a sex pheromone of the cabbage webworm, was synthesized stereoselectively starting from 10-iodo-1-decanol THP ether and 3-sulfolene (**1**) in five steps in 15% overall yield. 3-Sulfolene (**1**) was treated successively with 10-iodo-1-decanol THP ether and ethyl iodide to give *trans*-2-ethyl-5-[10-(tetrahydropyranoxy)decanyl]-3-sulfolene (**3e**) in 24% overall yield. After deprotection, the trans-2,5-disubstituted sulfolene **3h** was subjected to the thermal desulfonylation under basic conditions (K_2CO_3, 95% EtOH, 125 °C) to give exclusively the corresponding (*E,E*)-dienol **14** in 94% yield. Oxidation (PCC on alumina) of the dienol **14** gave the desired pheromone **15** in 68% yield.

Synthesis of Cyclohexane Derivatives by Diels–Alder Reaction of 2-Substituted 3-Sulfolenes. We examined the synthesis of cis-3,4,5-trisubstituted cyclohexane derivatives **16** by the Diels–Alder reaction using



16

R	
a	Bu
b	Me
c	Et
d	$n\text{-}C_7H_{15}$
e	$PhCH_2$
f	$(CH_3)_2CHCH_2CH_2$
g	$t\text{-}BuOCO(CH_2)_3$

2-substituted 3-sulfolenes **2** directly as diene synthons.[23] 2-Substituted sulfolenes were heated with maleic anhydride in toluene at 125 °C for 1 h. After methanolysis followed by esterification (CH_2N_2), the adduct esters **16** were obtained as a single product in 80–90% yields. The stereochemistries of the substituents on the cyclohexane ring were based on their ^1H NMR spectra and on the stereochemical course of the Diels–Alder reaction.

Further development of the present method for synthesizing conjugated dienes using 3-sulfolene will be reported in a successive paper.

Experimental Section

General Methods. Melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. Infrared (IR) spectra were obtained on a Hitachi 215 spectrophotometer. Proton magnetic resonance (^1H NMR) spectra were recorded with a Varian XL-100 spectrometer with tetramethylsilane as an internal standard. Carbon magnetic resonance (^{13}C NMR) spectra were recorded with a Varian XL-100 spectrometer at 25.16 MHz with tetramethylsilane as an internal standard. Mass spectra were recorded with a JEOL JMS-D300 GC-MS instrument with an interfaced computer. Ultraviolet (UV) spectra were recorded with a Hitachi 200-10 double-beam spectrophotometer. Gas–liquid chromatography (GLC) was performed on a Shimadzu GC-4CM instrument with a column packed with 5% 1,2,3-tris(2-cyanoethoxy)propane on Uniport B (Gasukuro Kogyo Inc., Tokyo, Japan).

General Method for the Reaction of 3-Sulfolene (1) with Alkyl Halides. To a solution of 3-sulfolene (**1**; 1.3 g, 10.9 mmol), alkyl halide (5.4 mmol), and HMPA (3.8 mL, 21.7 mmol) in THF (47 mL) was added a solution of LiHMDS (1.0 g, 6.0 mmol) in THF (4 mL) in one portion via a hypodermic syringe at −78 °C in argon atmosphere. The solution was stirred at that temperature for 10 min and quenched by adding saline. The mixture was extracted with $CHCl_3$ and washed with saline. The $CHCl_3$ solution was dried over Na_2SO_4 and evaporated to dryness. The residue was chromatographed on silica gel (50 g, Wako gel C-200). Elution with ethyl acetate–hexane (1:1) gave 2-alkyl-3-sulfolene (**2**) and 3-sulfolene (**1**) in this order. The result of each alkylation reaction is shown in Tables I and II in the text. **2a**: mass spectrum, *m/e* 175 ($M^+ + 1$), 110 ($M^+ - SO_2$); ^1H NMR ($CDCl_3$) δ 0.93 (3 H, t, *J* = 6 Hz), 1.12–2.20 (6 H, m), 3.67 (1 H, t, *J* = 8 Hz), 3.72 (2 H, s), 6.04 (2 H, s); ^{13}C NMR ($CDCl_3$) δ 13.96 (q), 22.48 (t), 28.34 (t), 29.02 (t), 55.64 (t), 64.40 (d), 123.19 (d), 130.37 (d); IR ($CHCl_3$) 2930, 1310, 1130 cm^{-1}. **2b**: mass spectrum, *m/e* 133 ($M^+ + 1$), 68 ($M^+ - SO_2$); ^1H NMR ($CDCl_3$) δ 0.94 (3 H, d, *J* = 7 Hz), 3.74 (2 H, s), 3.78 (1 H, q, *J* = 7 Hz), 6.03 (2 H, s); IR ($CHCl_3$) 1310, 1140, 1110 cm^{-1}. **2c**: mass spectrum, *m/e* 146 (M^+); ^1H NMR ($CDCl_3$) δ 1.10 (3 H, t, *J* = 7 Hz), 1.30–2.28 (2 H, m), 3.56 (1 H, t, *J* = 7 Hz), 3.69 (2 H, s), 5.96 (2 H, s); IR ($CHCl_3$) 1310, 1240, 1130 cm^{-1}. **2d**: mass spectrum, *m/e* 189 ($M^+ + 1$), 124 ($M^+ - SO_2$); ^1H NMR ($CDCl_3$) δ 0.92 (6 H, d, *J* = 6 Hz), 1.14–2.18 (5 H, m), 3.63 (1 H, t, *J* = 7 Hz), 3.73 (2 H, d, *J* = 2 Hz), 6.04 (2 H, s); IR ($CHCl_3$) δ 2950, 1310, 1130 cm^{-1}. **2e**: mass spectrum, *m/e* 216 (M^+), 152 ($M^+ - SO_2$); ^1H NMR ($CDCl_3$) δ 0.91 (3 H, t, *J* = 6 Hz), 1.10–2.30 (12 H, m), 3.69 (1 H, t, *J* = 7 Hz), 3.75 (2 H, s), 6.06 (2 H, s); IR ($CHCl_3$) 2920, 2850, 1310, 1130 cm^{-1}. **2f**: mass spectrum, *m/e* 261 ($M^+ + 1$); ^1H NMR ($CDCl_3$) δ 1.45 (9 H, s), 1.50–2.20 (4 H, m), 2.31 (2 H, t, *J* = 7 Hz), 3.68 (1 H, t, *J* = 6 Hz), 3.74 (2 H, d, *J* = 2 Hz), 6.06 (2 H, s); IR ($CHCl_3$) 2970, 1720, 1360, 1310, 1130 cm^{-1}. **2g**: mass spectrum, *m/e* 329 ($M^+ - 1$), 266 ($M^+ - SO_2$); ^1H NMR ($CDCl_3$) δ 0.90–2.10 (20 H, m), 3.10–4.00 (7 H, m), 4.55 (1 H, m), 5.96 (2 H, s); IR ($CHCl_3$) 2630, 1305, 1130 cm^{-1}. **2j**: mass spectrum, *m/e* 208 (M^+); ^1H NMR ($CDCl_3$) δ 2.81 (1 H, dd, *J* = 10 and 14 Hz), 3.38 (1 H, dd, *J* = 6 and 14 Hz), 3.76 (2 H, s), 3.92 (1 H, dd, *J* = 6 and 10 Hz), 5.98 (2 H, m), 6.29 (5 H, m); IR ($CHCl_3$) 3020, 2920, 1600, 1490, 1300, 1240, 1130, 1110 cm^{-1}.

Reaction of 2-Substituted 3-Sulfolenes 2 with Alkyl Iodides. Reactions were carried out under the general alkylation conditions described above except for the ratio of sulfolene **2** to alkyl iodide to LiHMDS to HMPA being 1:1.1:1.1:4. The results are shown in Table III. **3a**: mass spectrum, *m/e* 231 ($M^+ + 1$), 166 ($M^+ - SO_2$); ^1H NMR ($CDCl_3$) δ 0.93 (6 H, t, *J* = 7 Hz), 1.12–2.24 (12 H, m), 3.63 (2 H, t, *J* = 7 Hz), 6.02 (2 H, s); ^{13}C NMR ($CDCl_3$) δ 13.82 (q), 22.59 (t), 28.63 (t), 29.16 (t), 64.33 (d), 129.04 (d); IR ($CHCl_3$) 2950, 2930, 1300, 1120 cm^{-1}. **4a**: mass spectrum, *m/e* 231 ($M^+ + 1$), 166 ($M^+ - SO_2$); ^1H NMR ($CDCl_3$) δ 0.94 (6 H, t, *J* = 6 Hz), 1.14–2.20 (12 H, m), 3.70 (2 H, t, *J* = 6 Hz), 5.99 (2 H, s); ^{13}C NMR ($CDCl_3$) δ 13.79 (q), 22.54 (t), 28.62 (t), 29.25

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(t), 65.08 (d), 128.70 (d); IR ($CHCl_3$) 2950, 2930, 1300, 1120 cm^{-1}. **3b**: mass spectrum m/e 272 (M^+), 208 ($M^+ - SO_2$); ^1H NMR ($CDCl_3$) δ 0.60–2.30 (24 H, m), 3.63 (2 H, t, J = 7 Hz), 6.02 (2 H, s); IR ($CHCl_3$) 2940, 2860, 1300, 1120 cm^{-1}. **4b**: mass spectrum, m/e 272 (M^+), 208 ($M^+ - SO_2$); ^1H NMR ($CDCl_3$) δ 0.65–2.40 (24 H, m), 3.71 (2 H, t, J = 7 Hz), 6.00 (2 H, s); IR ($CHCl_3$) 2930, 2860, 1300, 1120 cm^{-1}. **3c**: mass spectrum, m/e 231 ($M^+ + 1$), 166 ($M^+ - SO_2$); ^1H NMR ($CDCl_3$) δ 0.98 (3 H, t, J = 6 Hz), 1.08–2.18 (12 H, m), 2.41 (3 H, d, J = 8 Hz), 3.62 (1 H, t, J = 7 Hz), 3.70 (1 H, q, J = 8 Hz); IR ($CHCl_3$) 2930, 2850, 1300, 1120 cm^{-1}. **4c**: mass spectrum, m/e 231 ($M^+ + 1$), 166 ($M^+ - SO_2$); ^1H NMR ($CDCl_3$) δ 0.90 (3 H, t, J = 6 Hz), 1.08–2.20 (12 H, m), 2.41 (3 H, d, J = 7 Hz), 3.69 (1 H, t, J = 6 Hz), 3.79 (1 H, q, J = 7 Hz), 5.96 (2 H, s); IR ($CHCl_3$) 2930, 2860, 1300, 1120 cm^{-1}. **3f**: mass spectrum, m/e 298 (M^+), 234 ($M^+ - SO_2$); ^1H NMR ($CDCl_3$) δ 2.82 (2 H, dd, J = 14 and 10 Hz), 3.44 (2 H, dd, J = 14 and 6 Hz), 3.96 (2 H, dd, J = 10 and 6 Hz), 5.91 (2 H, s), 7.29 (10 H, m); ^{13}C NMR ($CDCl_3$) δ 34.57 (t), 62.26 (d), 126.99 (d), 128.54 (d), 128.71 (d), 129.00 (d), 136.48 (s). **4f**: mass spectrum, m/e 298 (M^+), 234 ($M^+ - SO_2$); ^{13}C NMR ($CDCl_3$) δ 34.77 (t), 66.17 (d), 127.08 (d), 128.17 (d), 128.57 (s), 128.78 (d), 129.16 (d).

Reaction of 2,5-Dibutyl-3-sulfolenes 3a and 4a with Bromine. A solution of **3a** (50 mg) in CCl_4 was treated with an excess of bromine in CCl_4. TLC analysis of the reaction mixture exhibited the presence of two products, major (less polar) **5** and minor (more polar) **6**. The mixture was washed with 1% sodium hypochloride solution and saline, dried, and evaporated. The residue was recrystallized from hexane–ethyl acetate to afford the major bromine adducts **5**. The minor adduct **6** was isolated from the mother liquor by preparative silica gel TLC. **5**: mp 83–84 °C; ^1H NMR ($CDCl_3$) δ 0.97 (6 H, m), 1.18–2.40 (12 H, m), 3.68 (2 H, br q, J = 6 Hz), 4.93 (2 H, d, J = 6 Hz); IR (KBr) 2950, 2850, 1300, 1130, 1100 cm^{-1}. Anal. Calcd for $C_{12}H_{22}Br_2O_2S$: C, 36.94; H, 5.68. Found: C, 37.03; H, 5.66. **6**: mass spectrum, m/e 392, 390, 388 (M^+).

The isomer **4a** was similarly treated with bromine to yield a single bromine adduct **7** that was recrystallized from hexane–ethyl acetate. **7**: mp 44–46 °C; ^1H NMR ($CDCl_3$) δ 0.95 (6 H, m), 1.16–2.40 (12 H, m), 3.52 (1 H, m), 3.65 (1 H, q, J = 6 Hz), 4.52 (1 H, t, J = 4 Hz), 4.77 (1 H, dd, J = 6 and 4 Hz). Anal. Calcd for $C_{12}H_{22}Br_2O_2S$: C, 36.94; H, 5.68. Found: C, 36.94; H, 5.61.

Desulfonylation of 2-Heptyl-3-sulfolene (2e). A suspension of sulfolene **2e** (10 mg, 46 μmol) and $NaHCO_3$ (8 mg, 95 μmol) in 95% ethanol (1 mL) was heated at 125 °C for 1 h in a sealed tube. The mixture was filtered and rinsed with $CHCl_3$, and the filtrate was evaporated. The residue was chromatographed on silica gel to give (*E*)-1,3-undecadiene (**8a**; 6.5 mg, 92%) as a single product. **8a**: mass spectrum, m/e 152 (M^+); ^1H NMR ($CDCl_3$) δ 0.90 (3 H, t, J = 7 Hz), 1.10–2.70 (10 H, m), 2.07 (2 H, q, J = 7 Hz), 4.80–5.20 (2 H, m), 5.55–6.55 (3 H, m).

Desulfonylation of 2,5-Disubstituted 3-Sulfolenes. A. Desulfonylation with Continuous Argon Bubbling. Sulfolene **3** or **4** was dissolved in octane (5 mL/100 mg), and the solution was refluxed with continuous bubbling of argon gas. When the starting sulfolene was consumed (checked by TLC), the solvent was evaporated and the residue purified on a silica gel column. The ratio of the (*E,Z*)- to the (*E,E*)-diene (**9** or/and **9′**, and **10**) was determined by GLC analysis [5% 1,2,3-tris(2-cyanoethoxy)propane on Uniport B, 1.5 m, room temperature]. The results were summarized in Table IV. **9a**: mass spectrum, m/e 166 (M^+); ^1H NMR ($CDCl_3$) δ 0.90 (6 H, t, J = 6 Hz), 1.10–1.68 (8 H, m), 2.15 (4 H, m), 5.15–6.52 (4 H, m); ^{13}C NMR ($CDCl_3$) δ 14.00 (q), 22.46 (t), 27.56 (t), 31.82 (t), 32.14 (t), 32.76 (t), 125.90 (d), 128.94 (d), 129.89 (d), 134.49 (d); UV (hexane) λ_{max} 232.4 nm (21 000); IR ($CHCl_3$) 2920, 2850 cm^{-1}.

B. Thermolysis in the Presence of a Base. To a solution of sulfolene **3** or **4** (10 mg) in 95% ethanol was added one of the bases (2 equiv) described in Table IV, and the mixture was heated under argon atmosphere at 125 °C in a sealed tube until the starting sulfolene was not detected by TLC analysis. The mixture was diluted with hexane, washed with water, dried over Na_2SO_4, and evaporated. The residue was purified on a silica gel column to give the corresponding 1,3-dienes **9** or **10**. **10a**: mass spectrum, m/e 166 (M^+); ^1H NMR ($CDCl_3$) δ 0.90 (6 H, t, J = 6 Hz), 1.1–1.6 (8 H, m), 2.07 (4 H, m), 5.40–6.20 (4 H, m); ^{13}C NMR ($CDCl_3$) δ 13.95 (q), 22.28 (t), 31.65 (t), 32.31 (t), 130.44 (d), 132.28 (d); UV (hexane) λ_{max} 230.4 nm (25 800); IR ($CHCl_3$) 2930, 2860 cm^{-1}. **9b and 9b′**: mass spectrum, m/e 166 (M^+). **10b**: mp 72–74 °C; mass spectrum, m/e 166 (M^+); ^1H NMR ($CDCl_3$) δ 0.88 (3 H, t, J = 6 Hz), 1.05–1.55 (10 H, m), 1.73 (3 H, d, J = 6 Hz), 2.05 (2 H, q, J = 7 Hz), 5.45–5.75 (2 H, m), 5.85–6.20 (2 H, m). **9c**: mass spectrum, m/e 234 (M^+); ^1H NMR ($CDCl_3$) δ 3.48 (2 H, d, J = 6 Hz), 3.55 (2 H, d, J = 6 Hz), 5.40–6.80 (4 H, m), 7.25 (10 H, m); IR ($CHCl_3$) 1490, 1450, 990, 950 cm^{-1}. **10c**: mass spectrum, m/e 234 (M^+); ^1H NMR ($CDCl_3$) δ 3.39 (4 H, d, J = 6 Hz), 5.55–6.25 (4 H, m), 7.22 (10 H, m); IR ($CHCl_3$) 1490, 1450, 990 cm^{-1}.

C. Reductive Thermolysis. To a refluxing suspension of $LiAlH_4$ (equal amount by weight of the sulfolene used) in dry ether was added a solution of sulfolene **3** or **4** in ether. The mixture was refluxed for 30 min, and the excess of the reagent was decomposed by adding aqueous ether. The ether solution was dried over Na_2SO_4 and evaporated. The residue was chromatographed on silica gel to give the corresponding diene **9** or **10**.

Isomerization of *trans*-2,5-Dibutyl-3-sulfolene (3a) in Basic Protic Solvent. A solution of **3a** (50 mg, 0.22 mmol) and potassium hydroxide (17 mg, 0.44 mmol) in 95% ethanol (4.5 mL) was stirred at 50 °C under argon atmosphere for 30 min. Water was added, and the solution was extracted with ethyl acetate. The extract was dried and evaporated. The residue was chromatographed on silica gel (10 g) and eluted with ethyl acetate–hexane (1:10) to give **4a** [13 mg (26%)], **3a** [9 mg (18%)], and **11a** [18 mg (36%)]. **11a**: mass spectrum, m/e (230 (M^+); ^1H NMR ($CDCl_3$) δ 0.94 (6 H, t, J = 7 Hz), 1.10–1.80 (10 H, m), 1.90–2.55 (4 H, m), 3.10 (1 H, m), 6.22 (1 H, m).

Synthesis of (*E*)-9,11-Dodecadien-1-yl Acetate (12), a Sex Pheromone of the Red Bollworm Moth. 2-(8-Hydroxyoctyl)-3-sulfolene (21). A solution of **2g** (210 mg, 0.64 mmol) and PPTS (15 mg, 0.06 mmol) in MeOH–dichloromethane (2:1; 3 mL) was stirred at 40 °C for 2 h. Usual workup and chromatographic (SiO_2) purification gave alcohol **21**: 152 mg (91%); mass spectrum, m/e 247 ($M^+ + 1$), 182 ($M^+ - SO_2$); ^1H NMR ($CDCl_3$) δ 0.95–2.20 (14 H, m), 3.40–3.90 (5 H, m), 6.05 (2 H, s); IR ($CHCl_3$) 3500, 2930, 1300, 1130 cm^{-1}.

2-(8-Acetoxyoctyl)-3-sulfolene (2m). The alcohol **21** (137 mg, 0.56 mmol) was dissolved in acetic anhydride (1 mL) and pyridine (0.2 mL), and the mixture was stored at room temperature for 20 h. Usual workup and chromatographic (SiO_2) purification gave acetate **2m**: 127 mg (95%); mass spectrum, m/e 289 ($M^+ + 1$), 224 ($M^+ - SO_2$); ^1H NMR ($CDCl_3$) δ 1.10–2.10 (14 H, m), 2.05 (3 H, s), 3.68 (1 H, t, J = 8 Hz), 3.73 (2 H, s), 4.06 (2 H, t, J = 7 Hz), 6.03 (2 H, s); ^{13}C NMR ($CDCl_3$) δ 20.97 (q), 25.85 (t), 26.89 (t), 28. 60 (t), 29.09 (t), 29.26 (t), 55.64 (t), 64.46 (d) 64.46 (t), 123.08 (d), 130.39 (d), 171.05 (s); IR ($CHCl_3$) 2920, 1310, 1130 cm^{-1}.

(*E*)-9,11-Dodecadien-1-yl Acetate (12). To a solution of **2m** (20 mg, 69 μmol) in 95% EtOH was added $NaHCO_3$ (12 mg, 140 μmol), and the mixture was heated at 125 °C under argon in a sealed tube for 2 h. Usual workup and chromatographic (SiO_2) purification gave the pheromone **12**: 14 mg (91%); high-resolution mass spectrum for $C_{14}H_{24}O_2$, calcd m/e 224.1776, found 224.1778; ^1H NMR ($CDCl_3$) δ 0.85–1.80 (12 H, m), 2.04 (3 H, s), 2.06 (2 H, t, J = 6 Hz), 4.07 (2 H, t, J = 6 Hz), 4.97 (1 H, d, J = 10 Hz), 5.10 (1 H, d, J = 16 Hz), 5.50–6.55 (3 H, m); ^{13}C NMR ($CDCl_3$) δ 20.99 (q), 25.93 (t), 28.64 (t), 29.16 (t), 29.37 (t), 32.54 (t), 64.62 (t), 114.61 (t), 130.99 (d), 135.46 (d), 137.39 (d), 167.60 (s); IR ($CHCl_3$) 2940, 2850, 1730 cm^{-1}.

Synthesis of (*E,E*)-8,10-Dodecadien-1-ol (13), a Sex Pheromone of Codling Moth. 2-[7-(Tetrahydropyranoxy)-heptyl]-3-sulfolene (2h). A reaction of 3-sulfolene (1.28 g, 10.85 mmol) with 7-iodo-1-heptanol THP ether (1.85 g, 5.43 mmol) under the conditions described above gave, after usual workup and chromatographic (SiO_2) purification, **2h**: 991 mg (58%); mass spectrum, m/e 316 (M^+), 252 ($M^+ - SO_2$); ^1H NMR ($CDCl_3$) δ 1.15–2.20 (18 H, m), 3.2–4.05 (7 H, m), 4.60 (1 H, m), 6.06 (2 H, s); IR ($CHCl_3$) 2930, 2850, 1310, 1140 cm^{-1}.

***trans*-2-Methyl-5-[7-(tetrahydropyranoxy)heptyl]-3-sulfolene (3d).** A reaction of **2h** (223 mg, 0.71 mmol) with methyl iodide (110 mg, 0.78 mmol) under the general alkylation conditions described above gave **3d**: 107 mg (55%); mass spectrum, m/e 331 ($M^+ + 1$), 266 ($M^+ - SO_2$); ^1H NMR ($CDCl_3$) δ 1.15–2.30 (18 H, m), 1.43 (3 H, d, J = 8 Hz), 3.25–4.10 (6 H, m), 4.60 (1 H, m), 6.02 (2 H, s); IR ($CHCl_3$) 2930, 2850, 1300, 1110 cm^{-1}.

***trans*-2-Methyl-5-(7-hydroxyheptyl)-3-sulfolene (3g).** The THP ether **3d** (40 mg, 0.12 mmol) was deprotected as described above to give **3g**: 25 mg (84%); mass spectrum, *m/e* 247 (M^+ + 1), 182 ($M^+ - SO_2$); ^1H NMR ($CDCl_3$) δ 1.20–2.15 (12 H, m), 1.44 (3 H, d, *J* = 7 Hz), 3.55–3.85 (4 H, m), 6.00 (2 H, s).

(*E,E*)-8,10-Dodecadien-1-ol (13). The sulfolene **3g** (12 mg, 49 μmol) was desulfonylated under the conditions of entry 7 in Table IV to give the pheromone **13**: 9 mg, quantitative; high-resolution mass spectrum for $C_{12}H_{22}O$, calcd *m/e* 182.1671, found 182.1670; ^1H NMR ($CDCl_3$) δ 1.10–1.70 (10 H, m), 1.74 (3 H, d, *J* = 6 Hz), 2.07 (2 H, m), 3.67 (2 H, t, *J* = 7 Hz), 5.30–6.20 (4 H, m); ^{13}C NMR ($CDCl_3$) δ 17.94 (q), 25.73 (t), 29.17 (t), 29.34 (t), 32.54 (t), 32.85 (t), 63.09 (t), 126.70 (d), 130.40 (d), 131.85 (d), 132.07 (d); IR ($CHCl_3$) 2930, 990 cm^{-1}; UV (95% EtOH) λ_{max} 229.9 nm (28 000).

Synthesis of (*E,E*)-11,13-Hexadecadienal (15), a Sex Pheromone of the Cabbage Webworm. 2-[10-(Tetrahydropyranoxy)decanyl]-3-sulfolene (2i). A reaction of 3-sulfolene (2.66 g, 22.5 mmol) with 10-iodo-1-decanol THP ether (4.14 g, 11.25 mmol) under the general alkylation conditions described above gave, after usual workup and chromatographic purification, **2i**: 1.96 g (48%); mass spectrum, *m/e* 357 (M^+ - 1), 294 ($M^+ - SO_2$); ^1H NMR ($CDCl_3$) δ 1.20–2.20 (24 H, m), 3.20–4.00 (5 H, m), 3.65 (2 H, s), 4.60 (1 H, m), 6.05 (2 H, s); IR ($CHCl_3$) 2930, 2850, 1310, 1140 cm^{-1}.

***trans*-2-Ethyl-5-[10-(tetrahydropyranoxy)decanyl]-3-sulfolene (3e).** A reaction of **2i** (1.47 g, 4.10 mmol) with ethyl iodide (708 mg, 4.51 mmol) under the general alkylation condition described above gave, after usual workup and chromatographic purification, **3e**: 756 mg (50%); mass spectrum, *m/e* 387 (M^+ + 1), 322 ($M^+ - SO_2$); ^1H NMR ($CDCl_3$) δ 1.01 (3 H, t, *J* = 7 Hz), 1.15–2.20 (26 H, m), 3.20–4.05 (6 H, m), 4.62 (1 H, m), 5.98 (2 H, s); IR ($CHCl_3$) 2930, 2855, 1300, 1100 cm^{-1}.

***trans*-2-Ethyl-5-(10-hydroxydecanyl)-3-sulfolene (3h).** The THP ether **3e** (774 mg, 2 mmol) was deprotected under the conditions described above to give **3h**: 556 mg (92%); mass spectrum, *m/e* 303 (M^+ + 1), 238 ($M^+ - SO_2$); ^1H NMR ($CDCl_3$ δ 1.01 (3 H, t, *J* = 7 Hz), 1.15–2.20 (20 H, m), 3.50–3.85 (4 H, m), 4.02 (1 H, br s, disappears with adding D_2O), 5.96 (2 H, s).

(*E,E*)-11,13-Hexadecadien-1-ol (14). The sulfolene **3h** (300 mg, 1 mmol) was desulfonylated under the condition of entry 7 in Table IV to give **14** [222 mg (94%)] as a single product. **14**: mass spectrum, *m/e* 238 (M^+); ^1H NMR ($CDCl_3$) δ 1.05 (3 H, t, *J* = 7 Hz), 2.10 (2 H, m), 2.40 (2 H, td, *J* = 7 and 2 Hz), 3.65 (2 H, t, *J* = 6 Hz), 5.47 (1 H, m), 5.60 (1 H, m), 6.29 (2 H, m); ^{13}C NMR ($CDCl_3$) δ 13.67 (q), 25.61 (t), 25.86 (t), 29.28 (t), 29.56 (t), 32.67 (t), 32.78 (t), 62.71 (t), 129.55 (d), 130.44 (d), 132.36 (d), 137.73 (d); UV (95% EtOH) λ_{max} 230 nm (23 100).

(*E,E*)-11,13-Hexadecadienal (15). To a solution of **14** (344 mg, 1.45 mmol) in dichloromethane–hexane (1:1; 40 mL) was added 10% PCC on alumina (3.56 g, 2.90 mmol),[24] and the mixture was stirred at room temperature. After 5 h, additional PCC on alumina (500 mg, 0.40 mmol) was added to the reaction mixture, and it was stirred for 10 h. The oxidizing agent was filtered, and the solvent was evaporated. The residue was chromatographed on silica gel (20 g) and eluted with ethyl acetate–hexane (1:9) to give the pheromone **15**: 260 mg (68%): high-resolution mass spectrum for $C_{16}H_{28}O$, calcd *m/e* 236.2141, found 236.2141; ^1H NMR ($CDCl_3$) δ 1.00 (3 H, t, *J* = 7 Hz), 1.20–1.50 (12 H, m), 1.60 (2 H, m), 2.06 (4 H, m), 2.44 (2 H, dt, *J* = 8 and 2 Hz), 5.60 (2 H, m), 6.03 (2 H, m), 9.82 (1 H, t, *J* = 2 Hz); ^{13}C NMR ($CDCl_3$) δ 13.50 (q), 22.18 (t), 25.55 (t), 29.41 (t), 32.59 (t), 43.88 (t), 128.98 (d), 129.45 (d), 132.01 (d), 133.48 (d), 202.15 (d).

Diels–Alder Reaction of 2-Substituted 3-Sulfolenes with Maleic Anhydride. A solution of 2-substituted 3-sulfolene **3** (50 mg), hydroquinone monomethyl ether (5 mg), and maleic anhydride (10 equiv of the sulfolene) in toluene (2 mL) was stirred at 125 °C for 1 h in a sealed tube under argon. Methanol (2 mL) was added to the reaction mixture, and the whole was heated 100 °C for 30 min. The mixture was cooled to room temperature, and a solution of diazomethane in ether was added until a yellow color of the reagent persisted. The solvent was evaporated, and the residue was purified on a silica gel column to give adduct **16** as a single product in 80–90% yields. **16a**: ^1H NMR ($CDCl_3$) δ 0.91 (3 H, t, *J* = 6 Hz), 1.16–1.55 (6 H, m), 2.20–3.00 (4 H, m), 3.26 (1 H, dd, *J* = 6 and 4 Hz), 3.64 (3 H, s), 3.70 (3 H, s), 5.52 (1 H, d, *J* = 10 Hz), 5.77 (1 H, m); IR ($CHCl_3$) 2950, 2850, 1730, 1440, 1160, 1020 cm^{-1}. **16b**: ^1H NMR ($CDCl_3$) δ 1.09 (3 H, d, *J* = 7 Hz), 2.20–3.10 (4 H, m), 3.20 (1 H, dd, *J* = 6 and 4 Hz), 3.68 (3 H, s), 3.72 (3 H, s), 5.47 (1 H, d, *J* = 10 Hz), 5.80 (1 H, m); IR ($CHCl_3$) 2950, 1730, 1440, 1160 cm^{-1}. **16c**: ^1H NMR ($CDCl_3$) δ 1.00 (3 H, t, *J* = 7 Hz), 1.46 (2 H, m), 2.20–3.10 (4 H, m), 3.28 (1 H, dd, *J* = 6 and 4 Hz), 3.65 (3 H, s), 3.71 (3 H, s), 5.52 (1 H, d, *J* = 10 Hz), 5.78 (1 H, m). **16d**: ^1H NMR ($CDCl_3$) δ 0.90 (3 H, t, *J* = 6 Hz), 1.10–1.65 (12 H, m), 2.25–3.10 (4 H, m), 3.26 (1 H, dd, *J* = 6 and 4 Hz), 3.65 (3 H, s), 3.71 (3 H, s), 5.50 (1 H, d, *J* = 10 Hz), 5.78 (1 H, m); IR ($CHCl_3$) 2940, 2850, 1730, 1440, 1160 cm^{-1}. **16e**: ^1H NMR ($CDCl_3$) δ 2.30–2.68 (2 H, m), 2.70–3.05 (4 H, m), 3.24 (1 H, dd, *J* = 6 and 4 Hz), 3.69 (6 H, s), 5.53 (1 H, d, *J* = 10 Hz), 5.77 (1 H, m), 7.26 (5 H, m); IR ($CHCl_3$) 2950, 1730, 1440, 1160 cm^{-1}. **16f**: ^1H NMR ($CDCl_3$) δ 0.99 (6 H, d, *J* = 6 Hz), 1.10–1.70 (5 H, m), 2.20–3.05 (4 H, m), 3.28 (1 H, dd, *J* = 7 and 3 Hz), 3.65 (3 H, s), 3.72 (3 H, s), 5.53 (1 H, d, *J* = 10 Hz), 5.78 (1 H, m); IR ($CHCl_3$) 2950, 1730, 1440, 1160 cm^{-1}. **16g**: ^1H NMR ($CDCl_3$) δ 1.25–1.95 (4 H, m), 2.25–3.05 (4 H, m), 2.36 (2 H, t, *J* = 7 Hz), 3.29 (1 H, dd, *J* = 6 and 3 Hz), 3.66 (3 H, s), 3.70 (3 H, s), 3.72 (3 H, s), 5.52 (1 H, d, *J* = 10 Hz), 5.82 (1 H, m); IR ($CHCl_3$) 2950, 1730, 1440, 1160 cm^{-1}.

Registry No. 1, 77-79-2; **2a**, 87240-86-6; **2b**, 6007-71-2; **2c**, 87240-87-7; **2d**, 87240-89-9; **2e**, 87240-88-8; **2f**, 87240-90-2; **2g**, 87240-91-3; **2h**, 87240-92-4; **2i**, 103627-50-5; **2j**, 73617-44-4; **2k**, 105230-91-9; **2l**, 105230-92-0; **2m**, 51760-36-2; **3a**, 87240-93-5; **3b**, 87240-94-6; **3c**, 87240-95-7; **3d**, 87240-96-8; **3e**, 103627-51-6; **3f**, 105230-93-1; **3g**, 87241-02-9; **3h**, 103654-18-8; **4a**, 87240-97-9; **4b**, 87240-98-0; **4c**, 87240-99-1; **4d**, 87303-98-8; **4f**, 105230-94-2; **5**, 105230-95-3; **6**, 105230-96-4; **7**, 105230-97-5; **8a**, 79309-74-3; **9a**, 21293-04-9; **9b**, 87241-00-7; **9b′**, 74685-27-1; **9c**, 105230-98-6; **10a**, 30651-68-4; **10b**, 87241-01-8; **10c**, 105230-99-7; **11a**, 105231-00-3; **12**, 50767-78-7; **13**, 33956-49-9; **14**, 98010-23-2; **15**, 73264-91-2; **16a**, 105231-01-4; **16b**, 54795-49-2; **16c**, 105231-02-5; **16d**, 105231-03-6; **16e**, 105231-04-7; **16f**, 105231-05-8; **16g**, 105231-06-9; BuI, 542-69-8; MeI, 74-88-4; EtI, 75-03-6; $C_7H_{15}I$, 4282-40-0; $I(CH_3)_2COOBu$-*t*, 6182-78-1; $I(CH_2)_8OTHP$, 53596-83-1; $Br(CH_2)_8OTHP$, 50816-20-1; $I(CH_2)_7OTHP$, 65785-43-5; $I(CH_2)_{10}OTHP$, 80863-16-7; $PhCH_2Br$, 100-39-0; $PhCH_2I$, 620-05-3; $ICH(CH_3)_2$, 75-30-9; isoamyl iodide, 541-28-6; maleic anhydride, 108-31-6.

(24) Cheng, Y.-S.; Liu, W.-L.; Chen, S.-h. *Synthesis* **1980**, 223.