2-Acetyl-3-(phenylthio)-1,3-butadiene: A Novel Diels–Alder Diene and Dienophile

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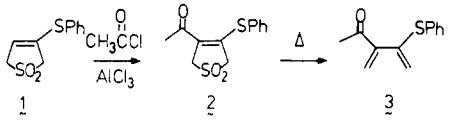
The title compound **3** was readily obtained by the thermolysis of 3-acetyl-4-(phenylthio)-3-sulfolene (**2**), which was prepared from 3-(phenylthio)-3-sulfolene (**1**) by Friedel–Crafts acylation. Compound **3**, bearing an electron-donating phenylthio group and an electron-withdrawing acetyl group, reacted as both a diene and a dienophile in the Diels–Alder reaction. In many cases it was more convenient to use the sulfolene precursor **2** directly in these reactions. In the reaction with electron-deficient dienophiles, the regiochemistry was dominated by the phenylthio group. On the other hand, a hetero Diels–Alder reaction was observed when an electron-rich dienophile, ethyl vinyl ether, was used. In the presence of an electron-rich diene such as 2-(trimethylsiloxy)-1,3-butadiene or cyclopentadiene, the diene **3** reacted as a dienophile with complete chemoselectivity and high stereoselectivity.

Sulfur-substituted dienes have been widely used in the Diels–Alder reaction.[1] The sulfur atom not only increases the reactivity of the diene but also adds control to the regioselectivity of this reaction. Furthermore, the richness of synthetic transformations involving sulfur functionality should make the cycloaddition products very useful in organic synthesis.[2] Using 3-sulfolenes as diene precursors, we have recently developed two general methods for the stereoselective synthesis of phenylthio-substituted dienes[3] and have studied their Diels–Alder reactions.[4]

We now report a convenient synthesis of 2-acetyl-3-(phenylthio)-1,3-butadiene (**3**) from 3-(phenylthio)-3-sulfolene (**1**). The diene **3** has an interesting feature in that it bears both an electron-donating phenylthio group and an electron-withdrawing acetyl group. In this paper we describe the relative ability of these two groups in determining the regiochemistry of the Diels–Alder reaction, and the different reaction modes in the presence of unsaturated substrates. To our knowledge, this is the first example of a thio-substituted diene that also has an electron-withdrawing group attached to it.

Results and Discussion

2-Acetyl-3-(phenylthio)-1,3-butadiene (**3**) was readily prepared in two steps, Acylation of 3-(phenylthio)-3-sulfolene (**1**) with acetyl chloride in refluxing carbon disulfide in the presence of aluminum chloride gave 3-acetyl-4-(phenylthio)-3-sulfolene (**2**) (70%); subsequent vacuum pyrolysis of **2** at 170 °C (3 mmHg) provided the diene **3** (80%). Sulfolene **2** was quite stable in refluxing *p*-xylene, the usual condition for the thermal removal of sulfur dioxide from 3-sulfolenes.



1 2 3

Table I. The Diels–Alder Reaction of Diene 3 or the Sulfolene Precursor 2

entry	reactant	dienophile/diene	product[a]	% yield[b]
1	2	$HC{\equiv}CCO_2CH_3$	**5** + **6** (74:26)	86 (A)
2	2	$H_2C{=}CHCO_2CH_3$	**10** + **11** (78:22)	98 (A)
3	3	$H_2C{=}CHCOCH_3$	**12**	20 (D), 50 (F)
4	2	*N*-phenylmaleimide	**13**	99 (B)
5	2	$H_2C{=}CHOEt$	**14**	20 (A), 74 (C)
6	2	$H_2C{=}C(CH_3)OAc$	**16**	52 (A)
7	2	$H_2C{=}CHC(OSiMe_3){=}CH_2$	**17**	48 (C)
8	3	cyclopentadiene	**18** + **19** (89:11)	55 (E)

[a] The isomer ratio given in parentheses was determined either by HPLC or ^1H NMR of the purified product(s). [b] The reaction conditions shown in parentheses were as follows: A, neat, sealed tube, 200 °C, 4 h; B, in benzene, sealed tube, 200 °C, 4 h; C, neat, sealed tube, Et_3N (1 equiv), 200 °C, 4 h; D, reflux in toluene, 24 h; E, reflux in benzene, 24 h; F, in Et_2O/CH_2Cl_2, $ZnCl_2$, room temperature, 2 days.

The exact reaction conditions for the Friedel–Crafts acylation of compound **1** were quite critical. It was necessary to add the sulfolene **1** in one portion to a well-stirred mixture of acetyl chloride and aluminum chloride in refluxing carbon disulfide at 50 °C. If the reaction was carried out in other solvents such as hexane, heptane, or dichloromethane at reflux, or in carbon disulfide at room temperature (20–28 °C), 3-(phenylthio)-2-sulfolene (**4**) was obtained as the major product. It was also found that sulfolene **1** and aluminum chloride alone did not yield the 2-sulfolene **4** after the same aqueous workup.

It should also be pointed out that the phenylthio group in **1** was necessary for the success of the Friedel–Crafts acylation. 3-Sulfolene itself failed to acylate under similar conditions, presumably because the strong electron-withdrawing sulfone group made the double bond less nucleophilic.

Although the diene **3** could be easily prepared in high purity, it polymerized readily even at room temperature in the neat form. However, it could be stored indefinitely in the refrigerator as a 0.05 M solution in ethyl acetate. For synthetic purpose it was more convenient to use the sulfolene precursor **2** directly in the Diels–Alder reaction. The reactions of sulfolene **2** with several dienophiles are shown in Table I. Heating a mixture of sulfolene **2** and excess methyl propiolate in a sealed tube at 200 °C, together with a catalytic amount of hydroquinone as a polymerization inhibitor, gave the cycloaddition products **5** and **6** in a ratio of 74:26 (entry 1). This indicates that the phenylthio group has greater influence than the acetyl group on the regiochemistry of the Diels–Alder reaction.

(1) (a) Petrzilka, M.; Grayson, J. L. *Synthesis* **1981**, 753. (b) Kozikowski, A. P.; Huie, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 2923. (c) Cohen, T.; Kosarych, A. *J. Org. Chem.* **1982**, *47*, 4005. (d) Bridges, A. J.; Fischer, J. W. *Tetrahedron Lett.* **1983**, *24*, 445, 447. (e) Trost, B. M.; Lavoie, A. C. *J. Am. Chem. Soc.* **1983**, *105*, 5075. (f) Overman, L. E.; Petty, C. B.; Ban, T.; Huang, G. T. *J. Am. Chem. Soc.* **1983**, *105*, 6335. (g) Liotta, C. L.; Verbicky, J. W., Jr. *Tetrahedron Lett.* **1985**, *26*, 1395. (h) Proteau, P. J.; Hopkins, P. B. *J. Org. Chem.* **1985**, *50*, 141. (i) Cuvigny, T.; Herve du Penhoat, C.; Julia, M. *Tetrahedron* **1986**, *42*, 5321, 5329. (j) Backvall, J. E.; Juntunen, S. K. *J. Am. Chem. Soc.* **1987**, *109*, 6396. (k) Posner, G. H.; Haces, A.; Harrison, W.; Kinter, C. M. *J. Org. Chem.* **1987**, *52*, 4836.

(2) (a) *Organic Chemistry of Sulfur*; Oae, S., Ed.; Plenum: New York, 1977. (b) Bernardi, F.; Mangini, E. *Organic Sulfur Chemistry: Theoretical & Experimental Advances*; Elsevier: Amsterdam, 1985.

(3) (a) Tao, Y. T.; Liu, C. L.; Lee, S. J.; Chou, S. S. P. *J. Org. Chem.* **1986**, *51*, 4718. (b) Chou, S. S. P.; Liou, S. Y.; Tsai, C. Y.; Wang, A. J. *J. Org. Chem.* **1987**, *52*, 4468.

(4) Chou, S. S. P.; Liou, S. Y.; Tsai, C. Y. *J. Chin. Chem. Soc.*, in press.

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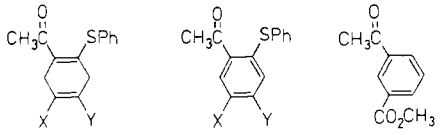
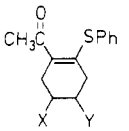
The major product **5** had ^{1}H NMR signals at δ 3.70 for the carbomethoxy group and δ 6.60 for the vinyl hydrogen. The corresponding signals for the minor product **6** appeared at δ 3.60 and 6.80. The Dreiding models of compound **5** and **6** indicated that the anisotropic deshielding effect of the acetyl group was significant for the carbomethoxy group of **5** and the vinyl hydrogen of **6**. To further substantiate this structural assignment, isomers **5** and **6** were separated by preparative HPLC and were then subjected to dehydrogenation conditions (refluxing in *p*-xylene over 5% Pd/C) to give the aromatized products **7** and **8**, respectively. As expected, compound **7** had a characteristic downfield hydrogen at δ 8.35 caused by the flanking acetyl and carbomethoxy groups. Furthermore, compound **5** was first oxidized to the sulfone by MCPBA (2.2 equiv) in dichloromethane at room temperature and then treated with potassium hydroxide in aqueous methanol to afford the desulfonylated product **9**, which clearly showed the meta substitution pattern in its ^{1}H NMR spectrum.



5, **6** **7**, **8** **9**

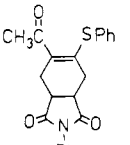
5, **7** : X = CO_2CH_3, Y = H
6, **8** : X = H, Y = CO_2CH_3

Similar reaction conditions converted methyl acrylate to the cycloadducts **10** and **11** in a ratio of 78:22 in excellent yield (entry 2). The reaction with methyl vinyl ketone required different conditions. The in situ generation of diene **3** from sulfolene **2** at high temperature caused methyl vinyl ketone to polymerize even in the presence of hydroquinone. Thus, diene **3** was first prepared, diluted in toluene, and was then refluxed with excess methyl vinyl ketone (entry 3, conditions D). Even under such conditions, only a 20% yield of a single regioisomeric cycloadduct **12** was obtained. Since methyl vinyl ketone is usually a more regioselective dienophile than methyl acrylate in the Diels–Alder reaction,[5] the single isomer obtained here was assigned to have the structure **12**. A more satisfactory yield of product **12** was obtained when anhydrous zinc chloride was added to the reaction mixture (entry 3, conditions F). Presumably, zinc chloride complexed with methyl vinyl ketone to lower its LUMO energy.[6] It is worth noting that zinc chloride did not have any beneficial effect in the case of methyl acrylate, but instead caused the polymerization of diene **2**, and no cycloaddition product was obtained.



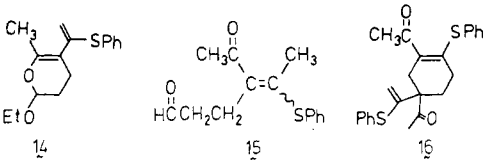
10 : X = CO_2CH_3, Y = H
11 : X = H, Y = CO_2CH_3
12 : X = $COCH_3$, Y = H

The reaction of sulfolene **2** with *N*-phenylmaleimide was carried out in benzene because both reactants were solids (entry 4). The highly reactive *N*-phenylmaleimide gave the cycloaddition product **13** in almost quantitative yield. The stereochemistry of the product was presumed to be cis.



13

When sulfolene **2** was heated with an electron-rich dienophile, ethyl vinyl ether, in a sealed tube at 200 °C, the dihydropyran derivative **14** was obtained (entry 5). Since ethyl vinyl ether is easily polymerized at high temperature in the presence of any acidic impurity, the addition of 1 equiv of triethylamine was necessary in order to get a good yield of product **14** (compare conditions A and C). Compound **14** has characteristic ^{1}H NMR absorptions at δ 4.85 (doublet of doublets) for the hemiacetal hydrogen and δ 5.20 and 5.08 for the two vinyl hydrogens. Thus, a completely chemo- and regiospecific hetero Diels–Alder reaction was observed. Ethyl vinyl ether reacted preferentially with the more electron deficient enone fragment of the diene **3**. Compound **14** was completely hydrolyzed after being left for 12 h in the $CDCl_3$ solution used for the proton NMR spectrum determination. The resulting solution indicated the formation of aldehyde **15** (*E*/*Z* mixtures)[7] and ethanol. The aldehyde **15** decomposed readily upon further storing in solution. In contrast to the high reactivity of ethyl vinyl ether, the reaction of sulfolene **2** with a less electron donating dienophile, isopropenyl acetate, gave only one regioisomeric dimerization product **16** from diene **3** (entry 6).



14 **15** **16**

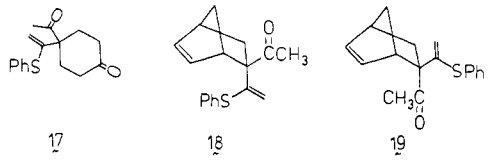
The diene **3** could also undergo cross Diels–Alder reactions with other dienes. However, to avoid self-dimerization of **3**, an electron-rich diene was required. It was found that 2-(trimethylsiloxy)-1,3-butadiene reacted with the sulfolene precursor **2** in a sealed tube at 200 °C to give the cyclohexanone derivative **17** (entry 7). In this reaction, 1 equiv of triethylamine was added to prevent the acid-catalyzed hydrolysis of 2-(trimethylsiloxy)-1,3-butadiene. The cross Diels–Alder reaction between these two dienes was completely chemo- and regiospecific, with the electron-deficient diene **3** reacting as the dienophile.

Reaction of cyclopentadiene with the sulfolene **2** at 200 °C led to dimerization of cyclopentadiene instead of the cross Diels–Alder reaction. However, if the diene **3** was first prepared and diluted with benzene and was then refluxed with cyclopentadiene, the cycloaddition products **18** and **19** could be obtained in a ratio of 89:11 (entry 8). The structural assignment was determined by an NOE study of the ^{1}H NMR spectra. Although isomers **18** and **19** could not be separated by HPLC, their 400-MHz ^{1}H NMR spectra were well resolved. The major isomer **18** had absorptions at δ 6.24 and 5.88 for the vinyl hydrogens on the ring whereas the corresponding hydrogens of the minor isomer appeared at δ 6.23 and 6.12, respectively. Irradi-

(5) See, for example, ref 1g,h.
(6) (a) Houk, K. N.; Strozier, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 4094. (b) Houk, K. N. *Acc. Chem. Res.* **1975**, *8*, 361. (c) Kahn, S. D.; Pau, C. F.; Overman, L. E.; Hehre, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 7381.

(7) Compound **15** had a characteristic ^{1}H NMR spectrum at δ 9.80 (1 H, t, J = 1.0 Hz) for the aldehyde proton. A mixture of *E* and *Z* isomers was obtained in a ratio of 1:1.2. The *E* isomer had absorptions for the acetyl methyl and the allyic methyl groups at δ 2.34 and 1.93, respectively. The corresponding peaks for the *Z* isomer appeared at δ 2.42 and 1.92.

ation at δ 6.24, which should simultaneously saturate the C3 hydrogen of both isomers, caused NOE enhancements for the ortho hydrogens of the phenyl group of the major isomer and the acetyl hydrogens of the minor isomer. Irradiation at δ 5.88 gave an NOE enhancement only for the ortho hydrogens of the phenyl group of the major isomer. Thus, the major isomer was assigned to have structure **18**, and the minor isomer, structure **19**. Since isomer **18** would be less stable than isomer **19** on the basis of steric considerations, the predominant formation of **18** indicated that the cross Diels–Alder reaction was under kinetic control.



17 18 19

In summary, the diene **3** or its sulfolene precursor **2** can react as both a diene and a dienophile with high chemo-, regio-, and stereoselectivity, giving cycloadducts with useful ring structures and functional groups. These results further extend the use of sulfur-substituted dienes in the Diels–Alder reaction. We are now studying the nucleophilic addition reactions of diene **3** and will report them in due course.

Experimental Section

Infrared spectra were recorded with a Beckman Acculab TM1 infrared spectrometer. ^{1}H NMR spectra were taken with a Varian-360L spectrometer, with tetramethylsilane as the internal standard. Mass spectra were recorded with a JEOL JMS-D-100 spectrometer. Elemental analyses were taken with a Perkin-Elmer 240C analyzer. High-performance liquid chromatography (HPLC) was carried out with a Shimadzu LC-6A chromatograph using LiChrosorb (Merck) as the column. Melting points were taken with a Mel-Temp apparatus and were uncorrected. The sealed tube used for thermolysis was made by Ace Glass (cat. no. 8648-23). The silica gel used for flash column chromatography was made by Merck (60 H). Dichloromethane and carbon disulfide were distilled from P_2O_5. Ether was distilled from lithium aluminum hydride, and ethyl vinyl ether was distilled frm sodium. Acetyl chloride was distilled with 10% quinoline. Triethylamine was distilled from calcium hydride. 3-(Phenylthio)-3-sulfolene (**1**)[8] and 2-(trimethylsiloxy)-1,3-butadiene[9] were prepared according to the literature.

3-Acetyl-4-(phenylthio)-3-sulfolene (2). To a suspension of aluminum chloride (1.17 g, 8.8 mmol) in carbon disulfide (20 mL) was added acetyl chloride (0.69 g, 8.8 mmol). This mixture was heated to gentle reflux, and solid 3-(phenylthio)-3-sulfolene (**1**) (1.00 g, 4.4 mmol) was added in one portion. The resulting mixture was heated at reflux overnight. After cooling to room temperature, the solvent was decanted. To the solid residue were added some crushed ice and concentrated HCl (10 mL). This was extracted with dichloromethane (20 mL × 3). The organic solution was then washed with water and saturated sodium bicarbonate solution and was dried ($MgSO_4$). After the removal of solvent by a rotary evaporator, the residue was passed through a flash column of silica gel, using hexane/ethyl acetate (3:1) as eluent, to give white crystalline solids (0.83 g, 70% yield): mp 149.5–150.5 °C; IR (KBr) 1650, 1520, 1310, 1235, 1200, 1130 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.30 (3 H, s), 3.60 (2 H, m), 4.15 (2 H, m), 7.40 (5 H, s); MS, *m/z* (relative intensity) 268 (M^+, 75), 204 (100), 171 (45). Anal. Calcd for $C_{12}H_{12}O_3S_2$: C, 53.71; H, 4.51. Found: C, 53.55; H, 4.54.

2-Acetyl-3-(phenylthio)-1,3-butadiene (3). Solid 3-acetyl-4-(phenylthio)-3-sulfolene (**2**) (0.11 g, 0.41 mmol) was mixed thoroughly with glass beads (5-mm diameter) in a round-bottomed flask. This was placed in a Kugelrohr apparatus (preheated at 170–180 °C) and was subjected to vacuum pyrolysis. The diene **3** was distilled at 3 mmHg in 2 h with ice cooling. The distillate was further purified by flash column chromatography, using hexane/ethyl acetate (3:1) as eluent, to give a colorless liquid (0.07 g, 80% yield): IR (neat) 3050, 1680, 1570, 1350, 1150 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.25 (3 H, s), 5.35 (1 H, s), 5.45 (1 H, s), 5.85 (2 H, s), 7.30 (5 H, m); MS, *m/z* (relative intensity) 204 (M^+, 100), 171 (40), 161 (60), 43 (100).

General Procedure for the Diels–Alder Reaction of Diene 3 or the Sulfolene Precursor 2. These reactions were carried out under six different sets of conditions (see Table I). General procedures together with typical reaction scales are shown as follows. A: A mixture of sulfolene **2** (0.09 g), hydroquinone (10 mg), and the unsaturated substrate (dienophile or diene, 10 equiv) was bubbled with nitrogen for 3 min and was then heated in a sealed tube at 200 °C for 4 h. After cooling to room temperature, the excess substrate was removed by rotary evaporation. The residue was passed through a flash column of silica gel, using hexane/ethyl acetate (4:1) as eluent, to give the purified products. B: The same as conditions A except that benzene (1 mL) was used as the solvent. C: The same as conditions A except that triethylamine (1 equiv) was also added, and during workup the dichloromethane extract was washed with 2% HCl. D: A mixture of diene **3** (0.21 g), hydroquinone (5 mg), and the unsaturated substrate (10–20 equiv) in toluene (1 mL) was heated at reflux under nitrogen for 24 h. E: The same as conditions D except that benzene (40 mL) was used as the solvent. F: A mixture of anhydrous zinc chloride (10 equiv), ether (2 mL), and methyl vinyl ketone (10 equiv) was stirred at room temperature for 15 min. To this was added a solution of diene **3** (0.07 g) in dichloromethane (6 mL). The resulting mixture was stirred at room temperature for 2 days and was poured into water. The solution was extracted with dichloromethane, and the organic solution was dried ($MgSO_4$) and evaporated to dryness.

Methyl 5-Acetyl-4-(phenylthio)-1,4-cyclohexadienecarboxylate (5) and Methyl 4-Acetyl-5-(phenylthio)-1,4-cyclohexadienecarboxylate (6). Conditions A. The two isomers were separated by HPLC. Compound **5**: mp 110–111 °C; IR (KBr) 1710, 1680, 1660, 1270, 1240 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.35 (3 H, s), 2.60–3.00 (2 H, m), 3.10–3.50 (2 H, m), 3.70 (3 H, s), 6.60 (1 H, m), 7.30 (5 H, m); HS, *m/z* (relative intensity) 288 (M^+, 92), 179 (100), 110 (58); exact mass calcd for $C_{16}H_{16}O_3S$ *m/z* 288.0820, found 288.0830. Compound **6**: mp 96–97 °C; IR (KBr) 1710, 1670, 1560, 1270, 1090 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.35 (3 H, s), 2.65–2.95 (2 H, m), 3.05–3.40 (2 H, m), 3.60 (3 H, s), 6.80 (1 H, m), 7.30 (5 H, m); MS, *m/z* (relative intensity) 288 (M^+, 94), 229 (59), 179 (100), 110 (76); exact mass calcd for $C_{16}H_{16}O_3S$ *m/z* 288.0820, found 288.0826. The structural assignments for compounds **5** and **6** were further confirmed by conversion to the aromatic derivatives, methyl 3-acetyl-4-(phenylthio)benzoate (**7**) and methyl 4-acetyl-3-(phenylthio)benzoate (**8**), respectively. A typical procedure is shown as follows. A mixture of **5** (50 mg) and 5% Pd/C (5 mg) in *p*-xylene was heated at reflux in the air for 3 h. After the removal of solvent, the residue was dissolved in ethyl acetate, filtered through Celite, and evaporated to give **7** (47 mg, 95% yield). Compound **7**: ^{1}H NMR ($CDCl_3$) δ 2.65 (3 H, s), 3.80 (3 H, s), 6.75 (1 H, d, *J* = 8.0 Hz), 7.35 (5 H, m), 7.70 (1 H, dd, *J* = 8.0, 1.5 Hz), 8.35 (1 H, d, *J* = 1.5 Hz). Compound **8**: ^{1}H NMR ($CDCl_3$) δ 2.60 (3 H, s), 3.75 (3 H, s), 7.35 (5 H, m), 7.50 (1 H, d, *J* = 1.0 Hz), 7.65 (1 H, d, *J* = 1.0 Hz), 7.65 (1 H, s). Compound **5** was further converted to methyl 3-acetylbenzoate (**9**) by the following procedures. To a mixture of **5** (30 mg, 0.1 mmol) in CH_2Cl_2 (5 mL) was added MCPBA (0.23 mmol) at room temperature. This was stirred for another 2 h at room temperature and was poured into saturated aqueous $Na_2S_2O_3$. The mixture was extracted with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$, and dried ($MgSO_4$). After the removal of solvent, the sulfone product obtained was dissolved in a mixture of methanol (2 mL) and water (0.5 mL), and KOH (1.0 mmol) was added. After being stirred at room temperature for 1 h, the reaction mixture was poured into water. Extraction with CH_2Cl_2, followed by drying and evaporation of the solvent, gave the pure **9** (15.7 mg, 85%):[10]

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(9) Jung, M. E.; McCombs, C. A. *Org. Synth.* **1980**, *58*, 163.

(10) Van Bekkum, H.; Kieboom, A. P. G.; Van de Putte, K. J. G. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 52.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.66 (3 H, s), 3.96 (3 H, s), 7.56 (1 H, t, J = 7.7 Hz), 8.17 (1 H, m), 8.23 (1 H, m), 8.60 (1 H, t, J = 1.5 Hz).

Methyl 3-Acetyl-4-(phenylthio)-3-cyclohexenecarboxylate (10) and Methyl 4-Acetyl-3-(phenylthio)-3-cyclohexenecarboxylate (11). Conditions A. These two isomers could not be separated by HPLC but the isomer ratio was determined by ^{1}H NMR spectra. Compound **10**: ^{1}H NMR ($CDCl_3$) δ 2.35 (3 H, s), 1.80–2.70 (7 H, m), 3.70 (3 H, s), 7.45 (5 H, m). Compound **11**: ^{1}H NMR ($CDCl_3$) δ 2.35 (3 H, s), 1.80–2.70 (7 H, m), 3.60 (3 H, s), 7.45 (5 H, m). The following spectral data were taken of the mixture: IR (neat) 1730 (br), 1685, 1605, 1540, 1440, 1250 cm^{-1}; MS, m/z (relative intensity) 290 (M^+, 89), 181 (100). Anal. Calcd for $C_{16}H_{18}O_3S$: C, 66.18; H, 6.25. Found: C, 65.96; H, 6.22.

2,4-Diacetyl-1-(phenylthio)cyclohexene (12). Conditions F. The product was purified by flash column chromatography using hexane/ethyl acetate (2:1) as eluent: IR (neat) 1701, 1654, 1535, 1353, 1250 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.65–2.20 (4 H, m), 2.20 (3 H, s), 2.37 (3 H, s), 2.55 (3 H, m), 7.25–7.45 (5 H, m); MS, m/z (relative intensity) 274 (M^+, 55), 165 (55), 123 (100). Anal. Calcd for $C_{16}H_{18}O_2S$: C, 70.04; H, 6.61. Found: C, 69.77; H, 6.69.

***N*-Phenyl-4-acetyl-5-(phenylthio)-1,2-*cis*-1,2,3,6-tetrahydrophthalimide (13). Conditions B**: mp 165–166 °C; IR (KBr) 1700, 1660, 1500, 1390, 1190 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.30 (3 H, s), 2.15–3.45 (6 H, m), 6.95–7.55 (10 H, m); MS, m/z (relative intensity) 377 (M^+, 100), 268 (21), 121 (32), 110 (21). Anal. Calcd for $C_{22}H_{19}NO_3S$: C, 70.01; H, 5.07; N, 3.71. Found: C, 69.97; H, 5.16; N, 3.81.

2-Ethoxy-6-methyl-5-[1-(phenylthio)ethenyl]-3,4-dihydro-2*H*-pyran (14). Conditions C: IR (neat) 1664, 1654, 1477, 1114, 1056, 1016 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.16 (3 H, t, J = 8.0 Hz), 1.60 (1 H, m), 1.68 (1 H, m), 1.87 (3 H, t, J = 1.5 Hz), 2.10 (1 H, m), 2.22 (1 H, m), 3.50 (1 H, m), 3.74 (1 H, m), 4.86 (1 H, dd, J = 2.3, 4.5 Hz), 5.08 (1 H, br s), 5.20 (1 H, br s), 7.26–7.40 (5 H, m); MS, m/z (relative intensity) 276 (M^+, 29), 167 (100), 95 (71).

2,4-Diacetyl-1-(phenylthio)-4-[1-(phenylthio)ethenyl]cyclohexene (16). Conditions A. The product was purified by flash chromatography using hexane/ethyl acetate (4:1) as eluent: ^{1}H NMR ($CDCl_3$) δ 1.90–2.30 (4 H, m), 2.15 (3 H, s), 2.35 (3 H, s), 2.70–2.85 (2 H, m), 4.70 (1 H, d, J = 1.5 Hz), 5.20 (1 H, d, J = 1.5 Hz), 7.30–7.45 (10 H, m); MS, m/z (relative intensity) 408 (M^+, 30), 299 (95), 152 (80), 110 (100).

4-Acetyl-4-[1-(phenylthio)ethenyl]cyclohexanone (17). Conditions C. The product was purifed by flash column chromatography using hexane/ethyl acetate (4:1) as eluent: mp 80–81 °C; IR (KBr) 1708, 1599, 1439, 1340, 1207, 879, 758 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.30 (3 H, s), 2.25–2.50 (8 H, m), 4.85 (1 H, d, J = 2.0 Hz), 5.40 (1 H, d, J = 2.0 Hz), 7.50 (5 H, m); MS, m/z (relative intensity) 274 (M^+, 64), 165 (100), 123 (31), 110 (26). Anal. Calcd for $C_{16}H_{18}O_2S$: C, 70.04; H, 6.61. Found: C, 69.80; H, 6.61.

5-*exo*-Acetyl-5-[1-(phenylthio)ethenyl]bicyclo[2.2.1]-hept-2-ene (18) and 5-*endo*-Acetyl-5-[1-(phenylthio)-ethenyl]bicyclo[2.2.1]hept-2-ene (19). Conditions E. The product was purified by flash column chromatography using hexane/ethyl acetate (10:1) as eluent. These two isomers could not be separated by HPLC, but the isomer ratio was determined by ^{1}H NMR. **18**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.52–1.55 (1 H, m), 1.72 (1 H, d, J = 8.2 Hz), 1.84 (1 H, dd, J = 11.9, 3.7 Hz), 2.17 (3 H, s), 2.29 (1 H, dd, J = 11.9, 2.6 Hz), 2.90 (1 H, m), 3.39 (1 H, m), 4.61 (1 H, d, J = 1.4 Hz), 5.35 (1 H, d, J = 1.4 Hz), 5.88 (1 H, dd, J = 5.6, 2.9 Hz), 6.24 (1 H, dd, J = 5.5, 2.9 Hz), 7.34–7.36 (3 H, m), 7.40–7.48 (2 H, m). **19**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.36 (1 H, m), 1.50 (1 H, m), 2.13 (1 H, dd, J = 10.0, 2.6 Hz), 2.28 (3 H, s), 2.30 (1 H, m), 2.82 (1 H, m), 3.47 (1 H, m), 4.54 (1 H, d, J = 1.5 Hz), 5.13 (1 H, d, J = 1.5 Hz), 6.12 (1 H, m), 6.23 (1 H, m), 7.30–7.45 (5 H, m). The following data were taken from the mixture: mp 62.5–64 °C; IR (KBr) 1712, 1596, 1359, 1218, 725 cm^{-1}; MS, m/z (relative intensity) 270 (M^+, 6), 161 (100), 95 (22). Anal. Calcd for $C_{17}H_{18}OS$: C, 75.51; H, 6.71. Found: C, 75.27; H, 6.68.

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Registry No. **1**, 64741-13-5; **2**, 116503-23-2; **3**, 116503-24-3; **5**, 116503-25-4; **6**, 116503-26-5; **7**, 116503-27-6; **8**, 116503-28-7; **9**, 21860-07-1; **10**, 116503-29-8; **11**, 116503-30-1; **12**, 116503-31-2; **13**, 116503-32-3; **14**, 116503-33-4; **16**, 116503-34-5; **17**, 116503-35-6; **18**, 116503-36-7; **19**, 116503-37-8; $HC{\equiv}CCO_2CH_3$, 922-67-8; $H_2C{=}CHCO_2CH_3$, 96-33-3; $H_2C{=}CHCOCH_3$, 78-94-4; $H_2C{=}CHOEt$, 109-92-2; $H_2C{=}C(CH_3)OAc$, 108-22-5; $H_2C{=}CHC(OSiMe_3){=}CH_2$, 38053-91-7; *n*-phenylmaleimide, 941-69-5; cyclopentadiene, 542-92-7.