carbonate, evaporated, and extracted with ether. The ether solution was washed with sodium bicarbonate solution and brine, dried, and evaporated. Purification by HPLC (elution with petroleum ether/ethyl acetate, 30:1) gave **2** (6.33 g, 60%); IR (neat, cm^{-1}) 2940, 1678, 1618; ^1H NMR (90 MHz, $CDCl_3$) δ 2.8 (m, 1 H), 2.5–2.2 (m, 4 H), 2.1 (m, 3 H), 2.0–1.3 (m, 4 H), 0.97 (s, 3 H), 0.82 (s, 3 H); MS, m/z calcd (M^+) 178.1358, obsd 178.1362.

(3*R,3a*R**,7a*S**)-Tetrahydro-3,7,7-trimethyl-4(3a*H*)-indanone (3).** Ketone **2** (2.69 g, 15.1 mmol) and 10% palladium on carbon (300 mg) in acetic acid (50 mL) was shaken under an atmosphere of hydrogen (50 psi) for 12 h. The solution was filtered and added to a mixture of ether and water. The biphasic mixture was neutralized with solid potassium carbonate. The aqueous layer was extracted with ether and the combined ether phases were washed sodium bicarbonate solution and brine prior to drying and solvent evaporation. There was obtained 2.61 g (96%) of **3**: IR (neat, cm^{-1}) 2940, 2865, 1710, 1460, 1365, 900, 710; ^1H NMR (90 MHz, $CDCl_3$) δ 2.68 (t, J = 7.5 Hz, 1 H), 2.5–1.4 (series of m, 10 H), 1.25 (d, J = 6 Hz, 3 H), 1.24 (s, 3 H), 0.93 (s, 3 H); ^{13}C NMR ($CDCl_3$) ppm 215.13, 54.50, 53.83, 38.72, 37.93, 34.78, 31.13, 29.74, 28.64, 27.79, 25.85, 16.32; MS, m/z calcd (M^+) 180.1514, obsd 180.1519.

Trimethylsilyl Enol Ether 4. A tetrahydrofuran solution (10 mL) of **3** (100 mg, 0.56 mmol) was added during 1 h to lithium diisopropylamide (0.73 mmol) in the same solvent (10 mL) at −78 °C. An 0.6-mL aliquot of a centrifuged solution containing no precipitate (triethylamine hydrochloride) was drawn off by syringe from a mixture of chlorotrimethylsilane (1.68 mL), triethylamine (2 mL), and tetrahydrofuran (4 mL) and added to the cold (−78 °C) enolate anion solution. The reaction mixture was allowed to warm to room temperature and poured into a mixture of petroleum ether (60 mL) and ice-cold saturated sodium bicarbonate solution (60 mL). The organic phase obtained after thorough shaking was dried and evaporated to give 130 mg (93%) of **4** as a colorless oil: IR (neat, cm^{-1}) 2960, 2280, 1650, 1460, 1250, 1180; ^1H NMR (90 MHz, $CDCl_3$) δ 4.60 (d, J = 5 Hz, 1 H), 3.4 (m, 1 H), 2.4–1.0 (series of m, 8 H), 0.99 (d, J = 6.5 Hz, 3 H), 0.88 (s, 3 H), 0.80 (s, 3 H), 0.11 (s, 9 H); MS, m/z calcd (M^+) 252.1909, obsd 252.1915.

(3*R,3a*S**,7a*S*)-Tetrahydro-3,7,7-trimethyl-4(3a*H*)-indanone (6).** Ketone **3** (4.83 g, 27 mmol) was stirred with sodium methoxide in methanol (from 1.0 g of sodium metal in 100 mL of methanol) for 8 h. The mixture was evaporated to one-half its volume, poured into ammonium chloride solution, and extracted with ether. The combined ether layers were washed with sodium bicarbonate solution and brine, dried, and evaporated to give 4.19 g (85%) of **6**: IR (neat, cm^{-1}) 2940, 2060, 1710; ^1H NMR (90 MHz, $CDCl_3$) δ 2.5–1.4 (series of m, 11 H), 1.02 (s, 3 H), 0.92 (d, J = 4 Hz, 3 H), 0.90 (s, 3 H); MS, m/z calcd (M^+) 180.1514, obsd 180.1519.

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.98; H, 11.24.

Trimethylsilyl Enol Ether 7. Ketone **6** (1.0 g, 5.56 mmol) in tetrahydrofuran (10 mL) was added to a cold (−78 °C) solution of lithium diisopropylamide (7.23 mmol) in tetrahydrofuran (30 mL) over 1 h. This solution was treated with a portion (5.6 mL) of a mixture of trimethylsilyl chloride (3.4 mL), triethylamine (4 mL), and tetrahydrofuran (8 mL). This mixture was spun in a centrifuge tube to settle the white precipitate formed and the supernatant that was added to the enolate solution was free of any precipitate. The reaction mixture was stirred at ambient temperature for 1 h and poured into petroleum ether. The petroleum ether solution was washed with sodium bicarbonate solution and brine, dried, and evaporated to give **7** (1.43 g, 100%): IR (neat, cm^{-1}) 2940, 2860, 1640, 1245, 1195, 895, 830; ^1H NMR (90 MHz, CCl_4/CH_2Cl_2) δ 4.3 (m, 1 H), 3.4 (m, 1 H), 2.1–1.1 (series of m, 8 H), 1.0 (d, J = 2 Hz, 3 H), 0.85 (s, 3 H), 0.75 (s, 3 H), 0.10 (s, 9 H); MS, m/z calcd (M^+) 252.1909, obsd 252.1915.

(3*R,3a*S**,7a*S**)-Tetrahydro-5-isopropylidene-3,7,7-trimethyl-4(3a*H*)-indanone (8).** A solution of **7** (1.43 g, 5.56 mmol) in dichloromethane (10 mL) was added to a cold (−78 °C) solution of 2,2-dimethoxypropane (0.75 mL, 6.5 mmol) and titanium(IV) chloride (2.75 mL, 5.56 mmol) in dichloromethane (50 mL). The reaction mixture was allowed to warm to room temperature during 5 h and then treated carefully with water at −78 °C. The mixture was poured into water and extracted with ether. The combined ether phases were washed with water and brine, dried, and evaporated. The residue was admixed with diazabicycloundecene (1.52 g, 10 mmol) and molecular sieves (3-Å, 1.25 g) in dichloromethane (25 mL) and was heated at the reflux temperature for 8 h. This mixture was filtered, poured into 10% hydrochloric acid, and extracted with ether. The combined ether solutions were washed with sodium bicarbonate solution and brine, dried, and evaporated. Purification by HPLC (elution with petroleum ether/ethyl acetate, 40:1) gave **8** (700 mg, 58%); IR (CCl_4, cm^{-1}) 2940, 2860, 1685, 1625, 1450, 1360; ^1H NMR (90 MHz, $CDCl_3$) δ 2.6–2.0 (m, 4 H), 1.9 (s, 3 H), 1.75 (s, 3 H), 1.6–1.2 (m, 5 H), 1.10 (d, J = 6 Hz, 3 H), 1.00 (s, 3 H), 0.95 (s, 3 H); MS, m/z calcd (M^+) 220.1827, obsd 220.1833.

Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.46, H, 10.98.

(3*R,3a*S**,7a*S**)-Tetrahydro-3,3′,3′,7,7-pentamethylspiro[indan-5(4*H*),2′-oxiran]-4-one (9).** Ketone **8** (260 mg, 1.18 mmol) in acetic acid (5 mL) previously saturated with potassium acetate was cooled to 15 °C. To this solution was added 38% peracetic acid (222 mg, 1.18 mmol). The reaction mixture was warmed to room temperature, stirred for 24 h, poured into ether and water, neutralized with solid potassium carbonate, and extracted with ether. The ether layer was washed with sodium bicarbonate solution and brine, dried, and evaporated to give **9** as colorless crystals (210 mg, 75%): mp 91.0–91.5 °C (from petroleum ether); IR (CCl_4, cm^{-1}) 2940, 2860, 1725, 1455, 1380, 1370, 1235; ^1H NMR (90 MHz, $CDCl_3$) δ 2.5–1.5 (series of m, 9 H), 1.45 (s, 3 H), 1.25 (s, 3 H), 1.15 (s, 3 H), 1.10 (d, J = 6 Hz, 3 H), 1.10 (s, 3 H); ^{13}C NMR ($CDCl_3$) ppm 206.52, 70.15, 63.48, 60.20, 57.35, 46.36, 33.56, 31.80, 31.37, 29.25, 24.64, 20.39, 19.66; MS, m/z calcd (M^+) 236.1776, obsd 236.1784.

Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: C, 76.07; H, 10.21.

Acknowledgment. This research was supported by the National Institutes of Health (Grant GM-28468).

Registry No. **1**, 1073-13-8; **2**, 91763-57-4; **3**, 96041-18-8; **4**, 96041-19-9; **6**, 96041-20-2; **7**, 96041-21-3; **8**, 96041-22-4; **9**, 96041-23-5; 2-(2-bromoethyl)-2-methyl-1,3-dioxolane, 37865-96-6.

Structural Effects on Intramolecular Furan Cycloadditions

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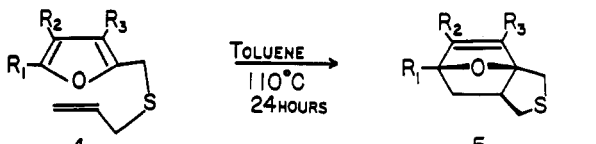
Received November 26, 1984

The intramolecular Diels–Alder reaction has been a valuable tool for the construction of polycyclic ring systems.[1] The versatility of furan as the diene in this process has been demonstrated by elaboration of its cycloadducts into aromatic systems,[2] oxabicyclo[2.2.1.]heptane systems,[3] and cis-2,5-disubstituted tetrahydrofuran products.[4] We are interested in utilizing these cycloadducts for the preparation of highly substituted tetrahydrofuran natural product systems such as **1**.[5] In this work we demonstrate

(1) (a) Fallis, A. G. *Can. J. Chem.* **1984**, *62*, 183. (b) Ciganek, E. *Org. React. (N.Y.)*, in press.
(2) (a) Bilovic, D. *Croat. Chem. Acta* **1968**, *40*, 15. (b) Best, W. M.; Wege, D. *Tetrahedron Lett.* **1981**, *22*, 4877. (c) Van Royen, L. A.; Mijngheer, R.; D. clercq, P. J. *Tetrahedron Lett.* **1983**, *24*, 3145. (b) Pelter, A.; Singaram, B. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1383.
(3) Mukaiyama, T.; Iwasawa, N. *Chem. Lett.* **1981**, 29.
(4) Iten, P. K.; Hofmann, A. A.; Eugster, C. H. *Helv Chem. Acta* **1979**, *62*, 2202.
(5) Kirfel, A.; Will, G.; Wiedenfeld, H.; Roeder, E. *Cryst. Struct. Commun.* **1980**, *9*, 363.

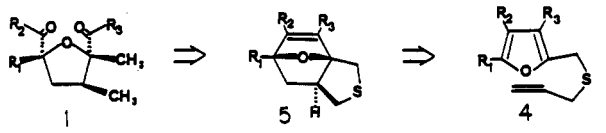
0022-3263/85/1950-1770$01.50/0

Table I[11]



	4 R1	R2	R3	YIELD 5 (%)
a. (2a)	H	H	H	23
b.	CH_3	H	H	18
c.	$PhCH_2OCH_2$	H	H	30
d.	H	CH_3	H	40
e.	H	H	CH_3	77
f.	CH_3	CH_3	H	60
g.	CH_3	$PhCH_2OCH_2$	H	48
h.	CH_3	H	CH_3	60
i.	H	$PhCH_2OCH_2$	$PhCH_2OCH_2$	84
j.	CH_3	CH_3	CH_3	92

that one can use furfuryl allyl sulfides as precursors for tetrahydrofuryl rings, and we report the preparation and cycloaddition results of a series of these furan derivatives.



The ease with which these furan cycloadduts undergo a retro-cycloaddition has thus far limited their use in synthesis. This problem has been countered in several cases by placement of bulky substituents[6] or metal coordinating groups[7] in the side chain, using cyclodextrin as a complexing agent[8] and constructing this side chain within a ring.[9] These efforts have aimed toward increasing the occurrence of those conformations which allow for proper approach of diene and dienophile. Recently, we have found that nuclear substitution of the furan also has a great influence on this reaction, leading to as high as 92% yield of product.

Initially, we tested the reactivity of simple furfuryl sulfides **2**, having modified dienophiles. These compounds were prepared via the alkylation of furfuryl mercaptan with the appropriate alkenyl halide. These furans were then refluxed in toluene for 24 h at which time all systems had reached their equilibrium mixtures.[10] In general, the reactions were devoid of any side products, allowing for approximately 90% recovery of materials after purification.

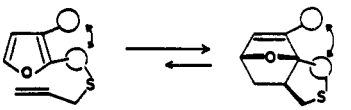
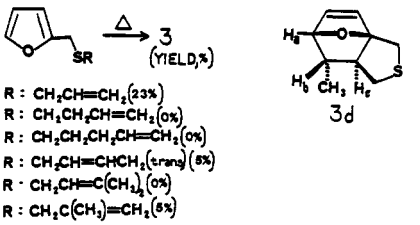
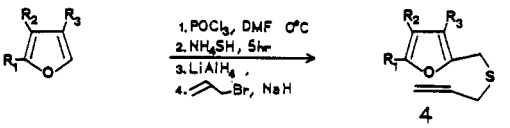


Figure 1.

Whereas the unsubstituted compound **2a** yielded 23% of its cycloadduct after 24 h, those furans having extended or substituted olefins, **2b–f**, afforded little or no product under these conditions.



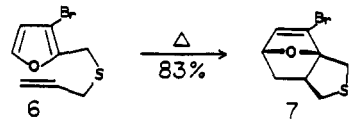
When derivatives having substitution of the furan nucleus were cyclized, more useful results were obtained. At least one example of each substitution pattern was synthesized using either methyl or (benzyloxy)methyl substituents. As before, the furan derivatives were heated at 110 °C to give equilibrium mixtures, and the results are shown in Table I. In many cases these reactions produced synthetically useful quantities of products. Although the anomalous differences between the two substituents (compare entries 2 and 3; 6 and 7) are difficult to explain, two general conclusions can be drawn from this data: (1) the greater the substitution on the furan ring, the higher the yield of product and (2) substituents at C-3 have the greatest influence on the reaction. The sulfides **4a–i**, which were not available from known thiols were prepared via a four-step process involving (1) Vilsmeier formylation of the furan ring, (2) reductive thiolation to form the furfuryl disulfide,[11] (3) reduction to the corresponding thiol, and (4) alkylation with allyl bromide. The total yield of this sequence ranged from 50% to 60% following purification of the final sulfide.



The relative stereochemistry of the cycloadducts is expected to be that of the previous examples, i.e., arising from "exo" of the dienophile side chain.[12] This is further substantiated by analysis of the ^1H NMR spectrum of cycloadduct **3d** obtained from (*E*)-2-butenyl furfuryl sulfide (**2d**). The coupling constant between protons Ha_a and H_b of 4.53 Hz indicates the stereochemistry as shown for **3d** with H_b and H_c in the exo and endo positions, respectively.

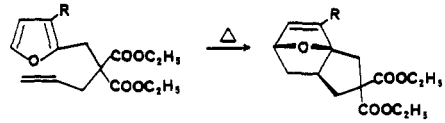
Since the electronic effect cannot wholly explain these results (compare entries 4 vs. 5), we suspect that a steric effect is also occuring. Substituents at C-3 experience an eclipsing ortho interaction with the side-chain methylene (Figure 1) which is partially relieved upon formation of the cycloadduct due to a skewing of these two groups. This interaction also occurs with a C-4, C-5 substitution pattern for the same reason and is greatest with the tetrasubstituted furan (entry 10). The relative unimportance of electronic effects is further established by reaction of the bromo derivative **6**, prepared from the known 3-bromo-

(6) (a) Gschwend, H. W.; Hillman, M. J.; Visis, B.; Rodenbaugh, R. K. *J. Org. Chem.* **1976**, *41*, 104. (b) Sternbach, D.; Rossana, D. *Tetrahedron Lett.* **1982**, *23*, 303.
(7) Mukaiyama, T.; Tsuji, T.; Iwasawa, N. *Chem. Lett.* **1979**, *697*.
(8) Sternbach, D.; Rossana, D. *J. Am. Chem. Soc.* **1982**, *104*, 5853.
(9) Van Royen, L. A.; Mijngheer, R.; De Clerg, R. J. *Tetrahedron Lett.* **1982**, *23*, 3283.
(10) The reactions were monitored by TLC and halted when no further change was noted. The ratio of furan starting material and cycloadduct was obtained by integration of the ^1H NMR spectra, and these materials were than isolated and weighted. Each compound was resubmitted to the reaction conditions until ^1H NMR spectra of both mixtures were identical.
(11) Kipnis, F.; Levy, I.; Ornfelt, J. *J. Am. Chem. Soc.* **1949**, *71*, 2270.
(12) Parker, K. A.; Adamchuk, M. R. *Tetrahedron Lett.* **1978**, 1689.



6 7

furfuraldehyde.[13] If the substituent electronic effects were significant, one might expect the furan diene to be less reactive, but, in fact, an 83% yield of cycloadduct is produced. To test the generality of this steric effect, we studied the diesters **8a,b** which were obtained from the condensation of furfuraldehyde and 3-methylfurfuraldehyde with diethyl malonate, hydrogenation to the furfuryl malonate, and allylation. Whereas furan **8a** is



8a. R:H
b. R:CH₃

9a. 40%
b. 82%

known to undergo cycloaddition in refluxing benzene over 6 days to produce a 40% yield of cycloadduct,[12] we found that **8b** afforded an 82% yield of product after only 6 h in refluxing toluene. Application of this structural effect in the stereoselective synthesis of highly substituted tetrahydrofuran ring systems is ongoing.

Experimental Section

NMR spectra were recorded with Varian EM-390 and XL-200 spectrometers as solutions in $CDCl_3$. Chemical shifts are reported in parts per million relative to Me_4Si as internal standard. High resolution mass spectra were obtained on a Kratos MS-50TA spectrometer. Chromatography was performed with an MPLC system or by circular chromatography (Chromatotron Model 7924, Harrison Research, Palo Alto, CA). Thin layer chromatographic (TLC) analysis was performed on EM Reagents silica gel 60 F-254 plates, 0.25 mm. Reactions were run in oven-dried glassware under a static N_2 atmosphere. Tetrahydrofuran and ether were distilled prior to use from Na metal. All alkenyl halides were used as purchased.[14]

A. Synthesis of Furans 2a–f. To a suspension of 0.19 g (4.8 mmol) of NaH (60% in mineral oil) in 50 mL of THF at 0 °C is added 0.5 g (4.4 mmol) of furfuryl mercaptan[14] in 5 mL of THF dropwise, causing evolution of H_2 gas. After this mixture was stirred for 30 min at room temperature, the alkenyl halide (6.6 mmol) was added. When TLC analysis showed the reaction to be complete, the mixture was recooled to 0 °C and quenched with saturated NH_4Cl solution. This solution was partitioned between ether and H_2O, and the aqueous layer was separated and extracted twice more with ether. The combined ether extracts were washed with brine, dried over Na_2SO_4, and concentrated to give the crude product as an oil. Chromatographic purification in each case was performed with CH_2Cl_2–hexane mixtures.

2-[(Allylthio)methyl]furan (2a): oil; ^1H NMR (90 MHz, $CDCl_3$) δ 7.25 (1 H, br s), 6.2 (1 H, dd), 6.07 (1 H, d), 5.68 (1 H, m), 5.25 (1 H, s), 4.98 (1 H, d), 3.62 (2 H, s), 3.1 (2 H, d); HRMS, $C_8H_{10}OS$ calcd 154.045 182, obsd 154.044 533.

2-[(3-Butenylthio)methyl]furan (2b): oil; ^1H NMR (90 MHz, $CDCl_3$) δ 7.2 (1 H, br s), 6.5 (1 H, dd), 6.03 (1 H, d), 5.65 (1 H, m), 4.95 (1 H, d), 4.84 (1 H, s), 3.6 (2 H, s), 2.0–2.6 (4 H, m); HRMS, $C_9H_{12}OS$ calcd 168.060 82, obsd 168.060 206.

2-[(4-Pentenylthio)methyl]furan (2c): oil; ^1H NMR (90 MHz, $CDCl_3$) δ 7.3 (1 H, br s), 6.25 (1 H, dd), 6.12 (1 H, d), 5.71 (1 H, m), 5.05 (1 H, d), 4.86 (1 H, s), 3.7 (2 H, s), 2.52 (2 H, t), 2.15 (2 H, q), 1.7 (2 H, q); HRMS, $C_{10}H_{14}OS$ calcd 182,076 45, obsd 182.076 158.

2-[(*trans*-2-Butenylthio)methyl]furan (2d): oil; ^1H NMR (90 MHz, $CDCl_3$) δ 7.34 (1 H, br s), 6.27 (1 H, t), 6.14 (1 H, d), 5.5 (2 H, m), 3.66 (2 H, s), 3.1 (2 H, d), 1.75 (3 H, d); HRMS, $C_9H_{12}OS$ calcd 168.060 82, obsd 168.061 220.

2-[(3-Methyl-2-butenylthio)methyl]furan (2e): oil; ^1H NMR (90 MHz, $CDCl_3$) δ 7.23 (1 H, br s), 6.21 (1 H, dd), 6.1 (1 H, d), 5.15 (1 H, t), 3.65 (2 H, s), 3.2 (2 H, d), 1.72 (3 H, s), 1.6 (3 H, s); HRMS, $C_{10}H_{14}OS$ calcd 182.076 46, obsd 182.075 975.

2-[(2-Methyl-2-propenylthio)methyl]furan (2f): oil; ^1H NMR (90 MHz, $CDCl_3$) δ 7.3 (1 H, br s), 6.24 (1 H, dd), 6.1 (1 H, d), 4.84 (2 H, m), 3.6 (2 H, s), 3.08 (2 H, s), 1.8 (3 H, s); HRMS, $C_9H_{12}OS$ calcd 168.060 82, obsd 168.060 206.

B. Cycloaddition Reactions of 2a–f. The sulfide (5 mmol) was refluxed in 10 mL of toluene for 24 h at which time the reaction mixture was cooled and concentrated. ^1H NMR analysis of the crude oil was followed by chromatographic repurification or separation of the constituents via chromatotron. In all cases, the polarity of the cycloadduct was greater than its precursor.

3a: oil; ^1H NMR (90 MHz, $CDCl_3$) δ 6.33 (2 H, AB q), 4.98 (1 H, d), 3.27 (2 H, AB q), 3.02 (1 H, dd), 2.7 (1 H, t), 2.2 (1 H, ddd), 1.8 (1 H, ddd), 1.45 (1 H, dd).

3d: oil; ^1H NMR (200 MHz, $CDCl_3$) δ 6.43 (1 H, d), 6.36 (1 H, dd), 4.83 (1 H, dd, J = 4.53, 2.9), 3.23 (2 H, AB q), 3.09 (1 H, dd), 2.73 (1 H, t), 2.17 (1 H, m), 1.5–1.8 (1 H, m), 0.83 (3 H, d).

3f: oil; ^1H NMR (90 MHz, $CDCl_3$) δ 6.45 (1 H, dd), 6.3 (1 H, d), 4.95 (1 H, br d), 3.28 (2 H, s), 2.9 (2 H, AB q), 2.12 (1 H, dd), 1.15 (1 H, d), 1.02 (3 H, s).

C. Synthesis of Substituted Furans 4b–j. The preparation of sulfide **4c** will be used as an example of the general procedure.

i. Vilsmeier Formylation. To a stirred mixture of 1 g of $POCl_3$ (7 mmol) and 0.5 g of dimethylformamide (7 mmol) at 0 °C was added 1.4 g (5 mmol) of 2-[(benzyloxy)methyl]furan[15] over 30 min. After being stirred at 0 °C for 30 min, the mixture was heated to 40 °C for 10 min and poured slowly into 10 g of ice. Cautiously, this was neutralized with Na_2CO_3 and workup procedures for **2a–f** were followed. This aldehyde can be used directly without further purification.

ii. Disulfide Formation. The NH_4SH reagent was prepared as from Kipnis et al.[11] This solution was added to an ice-cold ethanol solution of the crude aldehyde from part i. The ice bath was removed and the amber solution was stirred at room temperature for 2 h. In some cases, mild heating was required to complete the reaction. The volatile components were removed via aspirator, and the dark crude oil was azeotroped several times with toluene before the next step.

iii. Mercaptan Formation. The crude disulfide from part ii was dissolved in 10 mL of THF and added dropwise to a stirred suspension of $LiAlH_4$ (3.75 mmol) in 50 mL ether at 0 °C. After the mixture was stirred at room temperature for 1 h, the ice bath was replaced and 0.15 mL of H_2O was added cautiously, followed by 0.15 mL of 15% NaOH and 0.45 mL of H_2O. The suspension was stirred vigorously for 30 min and the solids were filtered and rinsed with ether. The ether solution was washed with brine, dried over Na_2SO_4, and concentrated.

iv. Allylation. The same alkylation procedure for formation of **2a–f** above was followed using the crude mercaptan produced in part iii to give **4c**.

5-[(Benzyloxy)methyl]-2-[(allylthio)methyl]furan (4c): oil; ^1H NMR (90 MHz, $CDCl_3$) δ 7.35 (5 H, s), 6.2 (1 H, d), 6.1 (1 H, d), 4.7 (1 H, m), 5.17 (1 H, s), 5.02 (1 H, d), 4.65 (2 H, s), 4.55 (2 H, s), 4.44 (2 H, s), 3.15 (2 H, d).

5-Methyl-2-[(allylthio)methyl]furan (4b). 5-Methyl-2-furfuraldehyde[14] was treated as in parts ii–iv to give **4b**: oil; ^1H NMR (90 MHz, $CDCl_3$) δ 5.98 (1 H, d), 5.83 (1 H, d), 5.7 (1 H, m), 5.17 (1 H, s), 5.00 (1 H, m), 3.58 (2 H, s), 3.1 (2 H, d), 2.27 (3 H, s); HRMS, $C_9H_{12}OS$ calcd 168.061 220, obsd 168.061 051.

4-Methyl-2-[(allylthio)methyl]furan (4d). 4-Methyl-2-furfuraldehyde was prepared from the reaction of 4-methyl-2-lithiofuran[16] and dimethylformamide. Parts ii–iv were followed to produce **4d**: oil; ^1H NMR (90 MHz, $CDCl_3$) δ 7.04 (1 H, s), 5.97 (1 H, s), 5.68 (1 H, m), 5.15 (1 H, s), 5.00 (1 H, d), 3.56 (2 H, s), 3.1 (2 H, d), 2.00 (3 H, s).

3-Methyl-2-[(allylthio)methyl]furan (4e). 3-Methyl-2-furfuraldehyde was prepared from 3-methyl-2-(hydroxy-

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methyl)-furan.[17] To a suspension of 6.2 g (0.07 mol) of MnO_2 in 100 mL of CH_2Cl_2 was added 2 g (0.018 mol) of the alcohol with vigorous stirring. After 6 h the reaction mixture was filtered through a small pad of Celite, rinsed with CH_2Cl_2, and concentrated to yield the crude aldehyde. Parts ii–iv were followed to produce **4e**: oil; ^1H NMR (90 MHz, $CDCl_3$) δ 7.25 (1 H, d), 6.18 (1 H, d), 5.8 (1 H, m), 5.2 (1 H, d), 5.1 (1 H, s), 3.65 (2 H, s), 3.17 (2 H, d), 2.00 (3 H, s); MS, *m/e* 168 (M^+), 167, 123, 95.

4,5-Dimethyl-2-[(allylthio)methyl]furan (4f). 2,3-Dimethylfuran[18] was treated as in parts i–iv to produce **4f**: oil; ^1H NMR (90 MHz, $CDCl_3$) δ 5.85 (1 H, s), 5.68 (1 H, m), 5.15 (1 H, d), 5.00 (1 H, m), 3.52 (2 H, s), 3.1 (2 H, d), 2.17 (3 H, s), 1.8 (3 H, s).

4-[(Benzyloxy)methyl]-5-methyl-2-[(allylthio)methyl]-furan (4g). Addition of 3 g (0.027 mol) of 3-(hydroxymethyl)-2-methylfuran[19] to a suspension at 0 °C of 1.6 g (0.04 mol) of NaH (60% in mineral oil) in 100 mL of THF was performed over 15 min. The ice bath was removed and the mixture was stirred at room temperature for 30 min. To this suspension was added 9.2 g (0.054 mol) of benzyl bromide, and the mixture was stirred overnight. Upon completion of the reaction by TLC analysis, the mixture was cooled to 0 °C and quenched via dropwise addition of saturated NH_4Cl solution. The usual workup provided the crude benzyl ether which was distilled prior to use at 82.5–94 °C (0.1–0.08 mm). Parts i–iv were followed to produce **4g**: oil; ^1H NMR (90 MHz, $CDCl_3$) δ 7.3 (5 H, s), 6.04 (1 H, s), 5.68 (1 H, m), 5.17 (1 H, s), 5.00 (1 H, d), 4.46 (2 H, s), 4.25 (2 H, s), 3.55 (2 H, s), 3.1 (2 H, d), 2.23 (3 H, s); HRMS, $C_{17}H_{20}O_2S$ calcd 288.118 29, obsd 288.117 134.

3,5-Dimethyl-2-[(allylthio)methyl]furan (4h). 3,5-Dimethyl-2-(hydroxymethyl)furan[20] was oxidized as in the preparation of **4d**, and the resulting aldehyde was treated as in parts ii–iv to produce **4h**: oil; ^1H NMR (90 MHz, $CDCl_3$) δ 5.65–6.0 (1 H, m), 5.7 (1 H, s), 5.19 (1 H, d), 3.6 (3 H, s), 3.13 (2 H, d), 2.24 (3 H, s), 1.93 (3 H, s); HRMS, $C_{10}H_{14}OS$ calcd 182.076 46, obsd 182.076 158.

3,4-Bis(hydroxymethyl)-2-[(allylthio)methyl]furan (4i). 3,4-Bis(hydroxymethyl)furan[21] was benzylated as above for **4g** using 2 molar equiv of benzyl bromide. The resulting furan was used directly in crude form for parts i–iv to produce **4i**: oil; ^1H NMR (90 MHz, $CDCl_3$) δ 7.33 (11 H, s), 5.68 (1 H, m), 5.15 (1 H, d), 5.00 (1 H, s), 4.64 (2 H, s), 4.48 (4 H, s), 4.4 (4 H, s), 3.1 (2 H, d); HRMS, $C_{24}H_{26}O_3S$ calcd 394.160 12, obsd 394.161 242.

3,4,5-Trimethyl-2-[(allylthio)methyl]furan (4j). 3,4,5-Trimethylfuran[22] was treated as in parts i–iv to produce **4j**: oil; ^1H NMR (90 MHz, $CDCl_3$) δ 5.68 (1 H, m), 5.17 (1 H, d), 5.00 (1 H, s), 3.56 (2 H, s), 3.1 (2 H, d), 2.17 (3 H, s), 1.87 (3 H, s), 1.84 (3 H, s); HRMS, $C_{11}H_{16}OS$, calcd (fragment) $C_8H_{11}O$ 123.080 93, obsd 123.080 869; calcd (fragment) C_4H_7S, calc. 87.02681; exp. 87.026582.

3-Bromo-2-[(allylthio)methyl]furan (6). 3-Bromo-2-furfuraldehyde[13] was treated as in parts ii–iv to produce **6**: oil; ^1H NMR (90 MHz, $CDCl_3$) δ 7.3 (1 H, d), 6.35 (1 H, d), 5.77 (1 H, m), 5.27 (1 H, s), 5.15 (1 H, d), 3.65 (2 H, s), 3.15 (2 H, d).

Diethyl (3-Methylfurfuryl)allylmalonate (8b). Diethyl (3-methylfurfuryl)malonate was produced in an analogous manner to diethyl furfurylmalonate[23] from 3-methyl-2-furfuraldehyde (see **4e** above) and allylated as in part iv to produce **8b**: oil; ^1H NMR (90 MHz, $CDCl_3$) δ 7.2 (1 H, d), 6.13 (1 H, d), 5.7 (1 H, m), 5.17 (1 H, br s), 5.04 (1 H, br s), 4.2 (4 H, q), 3.25 (2 H, s), 2.64 (2 H, d), 1.98 (3 H, s), 1.3 (6 H, t); HRMS, $C_{16}H_{22}O_5$ calcd 294.146 59, obsd 294.145 746.

D. Cycloaddition of 4b–j, 6, and 8b. These reactions were performed as for **2a–f**. See Table I and text for yields and ref 10 for methods of analysis.

5b: oil; ^1H NMR (90 MHz, $CDCl_3$) δ 6.25 (2 H, AB q), 3.2 (2 H, AB q), 2.98 (1 H, dd), 2.7 (1 H, t), 2.27 (1 H, ddd), 1.55 (2 H, m), 1.6 (3 H, s).

5c: oil; ^1H NMR (90 MHz, $CDCl_3$) δ 7.35 (5 H, s), 6.4 (2 H, s), 4.63 (2 H, s), 3.87 (2 H, s), 3.35 (2 H, s), 3.05 (1 H, dd), 2.75 (1 H, t), 2.32 (1 H, m), 1.4–1.7 (2 H, m).

5d: oil; ^1H NMR (90 MHz, $CDCl_3$) δ 4.82 (1 H, s), 4.7 (1 H, d), 3.25 (2 H, AB q), 3.04 (1 H, dd), 2.7 (1 H, t), 2.27 (1 H, m), 1.86 (3 H, d), 1.6–1.8 (1 H, m), 1.45 (1 H, dd).

5e: oil; ^1H NMR (90 MHz, $CDCl_3$) δ 5.94 (1 H, d), 4.85 (1 H, d), 3.15 (2 H, AB q), 2.98 (1 H, dd), 2.67 (1 H, t), 2.14 (1 H, ddd), 1.81 (3 H, d), 1.75 (1 H, m), 1.48 (1 H, dd).

5f: oil; ^1H NMR (90 MHz, $CDCl_3$) δ 5.84 (1 H, br s), 3.2 (2 H, AB q), 3.06 (1 H, dd), 2.74 (1 H, t), 2.32 (1 H, m), 1.75 (3 H, d), 1.54 (3 H, s), 1.2–1.7 (2 H, m).

5g: oil; ^1H NMR (90 MHz, $CDCl_3$) δ 7.35 (5 H, s), 6.2 (1 H, s), 4.5 (2 H, s), 4.1 (2 H, d), 3.23 (2 H, d), 3.04 (1 H, dd), 2.75 (1 H, t), 2.35 (1 H, m), 1.61 (3 H, s), 1.3–1.7 (2 H, m).

5h: oil; ^1H NMR (90 MHz, $CDCl_3$) δ 5.8 (1 H, d), 3.18 (2 H, AB q), 3.00 (1 H, dd), 2.75 (1 H, t), 2.27 (1 H, m), 1.84 (3 H, d), 1.6 (3 H, s), 1.5–1.7 (2 H, m).

5i: oil; ^1H NMR (90 MHz, $CDCl_3$) δ 7.33 (10 H, s), 5.00 (1 H, d), 4.47 (4 H, d), 4.15 (4 H, d), 3.34 (2 H, AB q), 3.09 (1 H, dd), 2.72 (1 H, t).

5j: oil; ^1H NMR (90 MHz, $CDCl_3$) δ 3.15 (2 H, AB q), 2.97 (1 H, dd), 2.7 (1 H, t), 2.17 (1 H, m), 1.67 (3 H, s), 1.65 (3 H, s), 1.5 (3 H, s), 1.2–1.7 (2 H, m).

7: oil; ^1H NMR (90 MHz, $CDCl_3$) δ 7.23 (1 H, s), 4.98 (1 H, dd), 3.3 (2 H, AB q), 3.05 (1 H, dd), 2.72 (1 H, t), 2.32 (1 H, m), 1.84 (1 H, dt), 1.6 (1 H, dd).

9b: oil; ^1H NMR (90 MHz, $CDCl_3$) δ 5.73 (1 H, d), 4.76 (1 H, d), 4.14 (4 H, dq), 2.6 (2 H, AB q), 2.45 (1 H, dd), 2.07 (1 H, dd), 1.79 (3 H, d), 1.3–1.8 (3 H, m).

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Chlorination of 1-Hexyne and 3-Hexyne in Acetic Acid and Methanol

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Received October 3, 1984

The literature contains conflicting reports concerning the chlorination of aliphatic alkynes in nucleophilic solvents. Hennion et al. found that the chlorination of 1-hexyne (1) occurred in methanol[1] and acetic acid[2] with predominate solvent incorporation; however, a recent study[3] in acetic acid reported only the *Z* dichloride. It is reported that anti addition of chlorine to 1 occurs in methanol[2] and syn addition in acetic acid,[2,3] whereas anti addition of chlorine along with predominate solvent incorporation was found for 3-hexyne (2) in acetic acid.[3,4] Because of our interest in the stability of bridged halonium

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0022-3263/85/1950-1773$01.50/0