J. Org. Chem. **1983**, *48*, 4049–4052 **4049**

Formation of 2,4-Diaroyl-3,5-diarylthiolanes from Chalcones and Polysulfide. Scope, Conditions, and the Thiolane NMR

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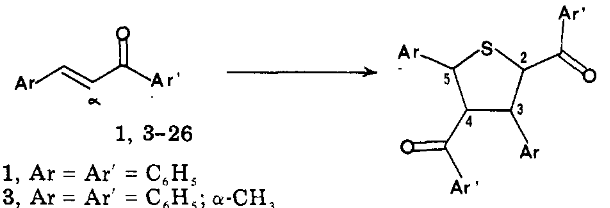
Received February 8, 1983

Conditions favorable for converting (*E*)-chalcone to 2,4-dibenzoyl-3,5-diphenylthiolane by polysulfide were determined. High-resolution ^{1}H NMR analysis of the resulting thiolane, and similar thiolanes, indicated that the four protons attached to the saturated ring were either all trans or that two contiguous pairs were trans and the third cis. Several chalcones possessing bromo, carbethoxy, chloro, cyano, methoxy, methyl, methylenedioxy, and nitro groups were treated with sodium polysulfide in ethanol to ascertain the effect of these substituents on the conversion of chalcones to 2,4-diaroyl-3,5-diarylthiolanes. α- and β-methylchalcones were also investigated. Electron-donating and bulky groups substituted on the aryl rings inhibited the formation of thiolanes, as did methyl substitution at the α- and β-olefinic positions.

A preliminary account[1] demonstrated sodium polysulfide's varied courses of action in converting (*E*)-chalcone (1) to 2,4-dibenzoyl-3,5-diphenylthiolane (2) or 1,3-diphenyl-3-thioxopropan-1-one. This paper concerns the conditions that favor the diastereoselective formation of thiolane 2 from (*E*)-chalcone (1), the effect of substitution at aryl and olefinic carbon, compatible functional groups, the assignments of the five-membered ring ^{1}H and ^{13}C NMR signals, and the relative configurations of the four contiguous chiral centers. This work also complements and confirms recently obtained findings from another laboratory which is concerned with the reaction of polysulfides with various α,β-unsaturated compounds.[2]



1, 3–26

2, Ar = Ar = C_6H_5

1, Ar = Ar' = C_6H_5
3, Ar = Ar' = C_6H_5; α-CH_3
4, Ar = Ar' = C_6H_5; β-CH_3
5, Ar = 2-$CH_3C_6H_4$; Ar' = C_6H_5
6, Ar = C_6H_5; Ar' = 2'-$CH_3C_6H_4$
7, Ar = 4-$CH_3C_6H_4$; Ar' = C_6H_5
8, Ar = C_6H_5; Ar' = 4' = $CH_3C_6H_4$
9, Ar = 2,4,6-$(CH_3)_3C_6H_2$; Ar' = C_6H_5
10, Ar = C_6H_5; Ar' = 2',4',6'-$(CH_3)_3C_6H_2$
11, Ar = C_6H_5; Ar' = 4'-BrC_6H_4
12, Ar = 3-ClC_6H_4; Ar' = C_6H_5
13, Ar = 4-ClC_6H_4; Ar' = C_6H_5
14, Ar = C_6H_5; Ar' = 4'-ClC_6H_4
15, Ar = 3-$CH_3OC_6H_4$; Ar' = C_6H_5
16, Ar = C_6H_5; Ar' = 3'-$CH_3OC_6H_4$
17, Ar = 4-$CH_3OC_6H_4$; Ar' = C_6H_5
18, Ar = C_6H_5; Ar' = 4'-$CH_3OC_6H_4$
19, Ar = 3,4-$(CH_3O)_2C_6H_3$; Ar' = C_6H_5
20, Ar = 3,4-$OCH_2OC_6H_3$; Ar' = C_6H_5
21, Ar = 4-$CH_3OC_6H_4$; Ar' = 4'-$CH_3OC_6H_4$
22, Ar = 3-$CH_3OC_6H_4$; Ar' = 3'-$CH_3OC_6H_4$
23, Ar = 4-$O_2NC_6H_4$; Ar' = C_6H_5
24, Ar = 4-$(CH_3)_2NC_6H_4$; Ar' = C_6H_5
25, Ar = 4-NCC_6H_4; Ar' = C_6H_5
26, Ar = 4-$C_2H_5OOCC_6H_4$; Ar' = C_6H_5

Reaction Conditions. Originally[3] the formation of 2 was carried out by treating chalcone (1) with an anhydrous ethanolic solution saturated with sodium polysulfide. The efficacy of these conditions, including the necessity of using a saturated polysulfide solution, was confirmed in a study that demonstrated the thiolane structure of the single solid product.[4] The dehydrogenation of the thiolane to 2,4-dibenzoyl-3,5-diphenylthiophene demonstrated that the two chalcone units had been incorporated in the thiolane in a head to tail fashion.[1]

Our recent study shows that saturated polysulfide solutions in 95% or 70% aqueous ethanol or in methanol or 2-propanol may replace solution in anhydrous ethanol with no apparent loss in conversion or diastereoselectivity.

The use of various alkali polysulfide thiating agents has been studied. Treatment of (*E*)-chalcone in anhydrous ethanol with sodium polysulfide prepared from anhydrous Na_2S and sulfur offered no advantage over the less costly $Na_2S\cdot 9H_2O$ in 95% ethanol. Likewise no advantage was evident when Li_2S or K_2S replaced $Na_2S\cdot 9H_2O$.

Studies have been carried out to ascertain the effect of changing the sulfur content of a saturated sodium polysulfide solution. A constant mole ratio (1:0.64) of $Na_2S\cdot 9H_2O$ to chalcone was employed in conversions carried out in a constant volume of 95% ethanol. The sulfur to $Na_2S\cdot 9H_2O$ ratio (mol/mol) was reduced in two unit increments from 12:1 to 2:1. When this ratio fell below 8:1 the yield remained the same but the TLC of the solid product showed several spots, a result contrasting with the single spot observed when the ratio was 8:1 or greater. At a ratio of 4:1 at least seven isomers were detected by TLC. The mass spectrum, showed a fragmentation pattern virtually identical with that of the single diastereomer, obtained when the $S/Na_2S\cdot 9H_2O$ ratio was eight or more,

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[1] LaLonde, R. T. *J. Chem. Soc., Chem. Commun.* **1982**, 401.

[2] We wish to thank Professor Manfred Reinecke for sending us the proofs of his paper prior to its publication. See: Reinecke, M. G.; Morton, D. W.; Del Mazza, D. *Synthesis* **1983**, 160.

[3] Fromm, E.; Hubert, E. *Justus Liebigs Ann. Chem.* **1912**, *394*, 301.

[4] Del Mazza, D.; Reinecke, M. G. *J. Org. Chem* **1981**, *46*, 128.

0022-3263/83/1948-4049$01.50/0

while the ^{13}C NMR revealed extra resonances in the 45–65 ppm saturated carbon region where the spectrum of **2** revealed only four. The same result was obtained when commercial Na_2S_4 was used in excess of chalcone.

The previously proposed mechanism[4] for the formation of thiolane indicates the displacement of an equilibrium through product insolubility and/or product stability as a necessary element for thiolane formation. Our results show that the sulfur content of the polysulfide is another essential factor in controlling the selectivity of the thiolane-forming process.

Effect of Substitution. Chalcones **3**–**26** were treated at room temperature with a 95% ethanolic solution saturated with sodium polysulfide, which was prepared from sulfur and $Na_2S \cdot 9H_2O$ in a mole-to-mole ratio of (10–12):1. Crude product mixtures were examined routinely by TLC for the presence of unconverted chalcone and by ^1H NMR (60 MHz) and mass spectrometry for the presence of a thiolane product. The appearance of the molecular ion peak and ^1H resonance in the region 4.5–5.5 ppm were taken as indicators of the presence of a thiolane. The thiolane was then purified by recrystallization; yields are reported in Table II in the Experimental Section. The thiolane was then examined by ^1H (100 MHz) and ^{13}C NMR and mass spectrometry in order to secure the structure in each case. The NMR of all, except one, showed the same general pattern. The signals in the general region 4.5–5.5 ppm of the ^1H NMR (100 MHz) consisted of two resonances, each approximating a doublet, located at 5.1–5.4 ppm and a multiplet at 4.7–4.8 ppm. The totally decoupled ^{13}C NMR showed a signal near 65 ppm and three signals at higher field in the range 57–53 ppm. The mass spectra of all thiolanes were consistent with that reported[4] for the parent thiolane, **2**. The parent thiolane and the thiolanes resulting from chalcones **5** and **18** were examined at still higher resolution in order to determine the $^3J_{H-H}$ values of the thiolane ring-carbon protons. The thiolane resulting from chalcone **18** represented one of the several substituted arylthiolanes whose 100-MHz NMR exhibited the same general resonance pattern as the parent thiolane while the thiolane resulting from chalcone **5** was examined at 360 MHz because its 4.5–5.5 ppm resonance pattern determined at 100 MHz appeared different from those of the other thiolanes. This result suggested initially a different stereochemistry for the thiolane from **5**. Particulars are given and discussed below in the section entitled "NMR".

Table II shows that the yields of thiolanes range from 10% to 96% but not all chalcones give thiolanes. Those chalcones from which no thiolanes could be obtained were 4,4′-dimethoxy **21** and 4-dimethylamino **24**, whose highly electron-donating substituents would tend to destabilize the formation of the enolates[4] required for the different bond-forming steps; α- and β-methyl **3** and **4** 2,4,6-trimethyl- **9**, and 2′,4′,6′-tetramethyl **10**, whose failure to form thiolanes can be attributed partly to a steric factor and partly to the electron-donating capacity of the methyl groups; and 4-nitro **23**, whose unsurprising reduction by polysulfide completely dominated. The failure of 4,4′-dimethoxy **21** and 4-nitrochalcones (**23**) to yield thiolanes confirms the recently published observations of Reinecke et al.[2] Table II also shows that another potentially incompatible group, the cyano group, survives when the chalcone **25** is treated with polysulfide at room temperature, even though nitriles are reported to react with sulfides under similar conditions.[5] The standard conditions employing hydrated sodium sulfide and 95% ethanol at room temperature are sufficiently moderate to allow the transformation of the carbethoxy-substituted chalcone **26** to its thiolane in fair yield. The relatively lower yield of thiolane produced from the 2-methyl-substituted chalcone **5** is consistent with the influence of the steric factor. A steric influence of another sort is indicated by the greater reactivity of (*E*)-chalcone (**1**) than its *Z* isomer. Under the standard procedure whereby **1** was converted to **2**, mixtures of the *E* and *Z* isomers gave crude product mixtures in which the unconsumed chalcone always was enriched in the *Z* isomer. However the only thiolane product was the single diastereomer **2**.

Table I. ^1H and ^{13}C NMR Values for the Saturated Ring of 2,4-Dibenzoyl-3,5-diphenylthiolane (2)

position	^1H, ppm	^{13}C, ppm	$^3J_{H-H}$, Hz	$^1J_{C-H}$, Hz
2	5.28	55.3	(2-3) 8.7	144
3	4.78	54.6	(3-4) 11.9	138
4	4.73	65.5	(4-5) 10.3	134
5	5.12	57.1		150

In the crossed reaction, equimolar quantities of chalcones **1** and 3-methoxy **15** were treated with sodium polysulfide according to the standard procedure. This yielded a product mixture containing at least one crossed thiolane, and likely two, as indicated by TLC, HPLC, and the appearance of the molecular ion at *m*/*z* 478 in the mass spectrum. That the crossed thiolanes are formed directly from the chalcones and not indirectly by equilibrium of two initially formed thiolanes was determined in an auxiliary experiment wherein a mixture of the thiolanes from chalcones **1** and **15** was treated under thiolane-forming conditions. No crossed thiolane was observed.

NMR Studies. The 300-MHz ^1H NMR chemical shifts and coupling constants are given in Table I for the saturated ring protons of the parent thiolane **2**. A simulated spectrum was superimposable in intensities and positions for 18 peaks and shoulders. The two lowest field signals are essentially doublets when observed at 300 MHz and therefore were assigned to the protons at C-2 and C-5. Complete identification of proton resonances was achieved by examining the spectrum of 2,4-dibenzoyl-3,5-diphenylthiolane-*3,5*-d_2, which was prepared by condensing benzaldehyde-α-d_1 with acetophenone in the presence of alcoholic sodium hydroxide and subsequently treating 1,3-diphenyl-2-propen-1-one-*3*-d_1 with a 95% ethanol solution saturated with sodium polysulfide. The spectrum showed two singlets corresponding in chemical shift to the lowest and highest field signals in the ^1H NMR of the unlabeled sample. The assignments indicated in Table I were made accordingly.

Similarly the chemical shift values for the thiolane resulting from 4-methoxychalcone (**18**) were found at 5.24 (d), 5.11 (d), 4.77 (m), and 4.55 (m) ppm. The coupling constants were determined to have values of 8.9, 11.7, and 10.3 Hz. Nearly the same set of $^3J_{H-H}$ values (8.9, 11.1, and 11.1 Hz) were observed for the thiolane resulting from the 2-methylchalcone (**5**). However the chemical shift values (5.48 (d), 5.31 (d), 5.10 (dd), and 4.81 (t) ppm) were more equally separated within a slightly wider chemical shift range, a finding which explained why the 100-MHz ^1H NMR appeared different from those of all the other thiolanes.

The ^{13}C chemical shifts for the four saturated ring carbons and the $^1J_{C-H}$ values of parent thiolane **2** are also given in Table I. The spectrum of the doubly deuterated thiolane showed two lines at 55.3 and 65.5 ppm, thus distinguishing C-2 and C-4. The further distinction of C-2 from C-4 was achieved by correlating the assigned ^1H

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(5) Mc Gregor, J. H. *J. Chem. Soc.* **1950**, 736.

resonances with ^{13}C resonances in a "crossover experiment"[6] for which the same doubly labeled sample was employed in order to simplify the partially decoupled ^{13}C spectra. The results demonstrated that the lower field, 65.5 ppm, ^{13}C resonance was coupled to the C-4 proton (4.73 ppm) and the higher field, 55.3 ppm, resonance was coupled to the C-2 proton (5.28 ppm). The lower chemical shift of C-2 relative to C-4 could be attributed in part to the smaller number of β-substituents[7] for the former carbon. The higher (57.1 ppm) and lower chemical shifts (54.5 ppm) for the two remaining pair of lines in the spectrum of the unlabeled sample were assigned to C-5 and C-3, respectively, in a similar experiment employing an unlabeled sample.

^1H NMR studies restrict the number of possible configurations once common well-defined assumptions are made regarding the thiolane conformation. The experimental values of $J_{3,4}$ and $J_{4,5}$ for **2** are very high (11.9 and 10.3 Hz, respectively). From the dependence of vicinal coupling constants on torsional angles,[8] it can be shown that for cisoidal hydrogen atoms such high values of coupling constants are expected only for a nearly planar ring (with endocyclic torsional angles <15°). Such a conformation is very improbable for a ring with large substituents, and therefore the high experimental values of $J_{3,4}$ and $J_{4,5}$ suggest a trans arrangement of substituents on C-3, C-4, and C-5 and a conformation in which all these substituents are quasi-equatorial. However, for this conformation, ^1H NMR cannot determine the configuration at C-2: the experimental value of $J_{2,3} = 8.7$ Hz can be explained by both cis and trans configurations. However, a cis arrangement of C-2 benzoyl and C-5 hydrogen has been proposed[4] to rationalize the appearance of ions m/z 209 and 239 in the mass spectrum of **2**. Thus on the basis of the latter rationale and the results of our NMR analysis, the relative configuration of **2** is trans-anti-trans.[9] It appears from the general similarity of the saturated carbon ^1H resonance pattern and the $^3J_{H-H}$ values determined from thiolane **2** and the thiolanes resulting from chalcones **5** and **18** that the configuration of the single crystalline diastereomer isolated in each transformation is the same.

Attempts were made to predict the ^{13}C chemical shifts based on literature values for thiolane[10] and the substituent effects in acyclic compounds of the phenyl and benzoyl moieties.[11] The predicted values differed from their experimental counterparts by 4 to 10 ppm. Clearly more relevant data from cyclic sulfur compounds are required. The ^{13}C chemical shifts are of little value in assigning the configuration at C-2.

Experimental Section

NMR Measurements. ^1H NMR spectra were determined in $CDCl_3$ solution in 5-mm tubes at 300 MHz on a Bruker CXP-300 spectrometer, at 360 MHz on a Bruker WM 360 spectrometer,[12] and at 100 MHz on a Varian XL-100 spectrometer. Spectra were simulated by using a LAOCOON III program. Fully noise decoupled, partially decoupled, and fully coupled ^{13}C NMR spectra were determined in 5- and 12-mm tubes at 25.2 MHz on a Varian XL-100 spectrometer. The "crossover experiment" carried out on 2,4-dibenzoyl-3,5-diphenylthiolane-*3,5*-d_2 used proton-decoupling frequencies of 500 and 1000 Hz upfield and 1500 and 2000 Hz downfield from Me_4Si to obtain four residual couplings for each of the two saturated unlabeled carbons. Each of the two sets of four residual coupling constants were analyzed mathematically by a computer program to obtain the least-squares straight lines and their intercepts.

Materials. Benzaldehyde-α-d_1 was obtained from Merck and the alkali sulfides from Alfa Products. All chalcones except two were prepared from the aldehyde and the acetophenone by alkali-catalyzed condensations and purified by recrystallization according to the literature. The exceptions were α- and β-methylchalcones **3** and **4**, which were condensed according to the literature from the appropriate aldehyde and ketones by an acid-catalyzed process.

Thiolane Formation. A 22.5-mmol quantity of the powdered alkali sulfide was weighed out in the hood in a round-bottom flask containing a magnetic stirrer bar. Thereafter 20–40 mL of an alcohol solvent was added and the mixture was stirred vigorously. A 250-mmol quantity of sulfur was added slowly and the resulting mixture was stirred about 30 min. In the series of experiments carried out to determine the effect of changing the S/S^{-2} ratio, 270-, 225-, 180-, 135-, 90-, and 45-mmol quantities of sulfur were added to the stirred suspension of $Na_2S{\cdot}9H_2O$ in 30 mL of 95% ethanol. Thereafter a 14.4-mmol quantity of chalcone was added, and the resulting mixture was stirred at ambient temperature for 24 h or until the solution became so viscous that it could no longer be stirred. After a total of 48–72 h at room temperature, the bulk of the solvent was removed at the rotary evaporator.

The residue was dissolved in 100–125 mL of CH_2Cl_2, and 40 mL of H_2O was added. The resulting mixture was filtered. The CH_2Cl_2 solution was separated from the filtrate and then washed repeatedly (3–5 times) with 25-mL quantities of 20% aqueous $(NH_4)_2S$ solution until a TLC of the CH_2Cl_2 solution showed no sulfur remaining. Thereafter the CH_2Cl_2 solution was washed (2–3 times) with 25–30-mL quantities of water and once with brine. The CH_2Cl_2 solution was then concentrated at the rotary evaporator and the concentrate was then analyzed: by TLC (7.5 × 2.5 cm Baker-flex Silica gel 1B2-F and/or E. Merck 20 × 5 cm Silica gel GF254 using hexane–ethyl acetate mixtures) for the presence of sulfur, unconverted chalcone, and products; by electron impact mass spectrometry (Finnigan 4021) for the determination of molecular weight and trace amounts of sulfur; and by ^1H NMR (60 MHz) for the appearance of resonance in the 4.5–5.5 ppm region which indicated thiolane formation. Recrystallization of the thiolane was from the solvent indicated in Table II.

The standard procedure described above was employed also to convert 3.43 mmol of 1,3-diphenyl-2-propen-1-one-*3*-d_1 to the doubly labeled thiolane with 5.42 mmol of $Na_2S{\cdot}9H_2O$ and 59.4 mol of sulfur in 5 mL of 95% ethanol. The crude dry product was dissolved in 25 mL of boiling glacial acetic acid and filtered while hot, and the filtrate was allowed to cool to room temperature. This yielded 1.26 mmol (73%) of a first crop: mp 213.5–214.5 °C; TLC (7.5 × 2.5 Baker-flex Silica gel 1B2-F using hexane–ethyl acetate, 4:1) R_f 0.35 but no sulfur at R_f 0.66.

Treatment of (*Z*)- and (*E*)-Chalcone with Sodium Polysulfide. According to the procedure of Lutz and Weiss,[13] a solution of (*E*)-chalcone (**1**) in isooctane solution was irradiated by sunlight and then placed in the freezer. The oil which settled to the bottom in time was separated by decantation and centrifugation, analyzed by GLC and HPLC to establish the starting ratio of *Z* to *E* isomers, and then treated with sodium polysulfide according to the standard procedure above. The crude product mixture was analyzed by HPLC (Partisil 10/25, M9 eluted with petroleum ether–EtOAc, 6:1). As an example of one such experiment, a 14.4 mmol, 2:3 mixture of (*Z*)- and (*E*)-chalcone gave

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[6] Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds"; Wiley: New York, 1981; p 275.

[7] Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; p 57.

[8] Haosnoot, C. A. G.; de Leeuw, F. A. A. M.; Altona, C. *Tetrahedron* **1980**, *36*, 2783.

[9] One should consider the stereochemical assignment based on mass spectral fragmentation with some reservation. The rationale[4] for the appearance of m/z 209 and 239 requires migration of hydrogen from C-5 to the C-2 carbonyl. Only if this migration occurs suprafacially in a concerted process and without prior bond breaking elsewhere in the molecule does the mass spectral results constitute evidence for making configurational assignments.

[10] Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds"; Wiley: New York, 1981; p 261.

[11] Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden: London, 1976; p 37.

[12] We wish to thank Dr. M. Balakrishnan of Bristol Laboratories for determining these spectra.

[13] Lutz, R. E.; Weiss, J. O. *J. Am. Chem. Soc.* **1955**, *77*, 1814.

Table II. Percentage Yields and Physical Properties of Thiolanes Produced from Chalcones

	thiolane[a]			TLC	
chalcone[b]	% yield[c]	mp, °C	recryst. from	PE[d]:EtOAc	R_f
1	72–96	211–212	AcOH	4:1	0.35
3	0				
4	0				
5	17	201–203	EtOAc–EtOH	2:1	0.56
6	38	141–146.5	EtOH	3:1	0.66
7	51	227–228	AcOH	2:1	0.54
8	52	212–213	AcOH	2:1	0.57
9	0				
10	0				
11	60	206–207	AcOH	4:1	0.47
12	73	193–194	AcOH	4:1	0.35
13	72	190.5–191.5	AcOH	2:1	0.56
14	51	197–199	EtOAc–EtOH	2:1	0.60
15	73	126–127.5	EtOH	2:1	0.42
16	67	155–158	AcOH	2:1	0.45
17	75	165–166	AcOH	2:1	0.38
18	78	180–184	AcOH	2:1	0.32
19	61	134–139	EtOH	1:1	0.31
20	58	201–201.5	EtOAc	2:1	0.52[e]
21	0				
22	41	105.5–106.5	Et_2O–CH_2Cl_2	2:1	0.29
23	0				
24	10[f]				
25	47[g]	124–130	CCl_4	1:1	0.64
26	52[h]	171–173	EtOAc	2:1	0.44

[a] Satisfactory elemental analyses (±0.4 for C, H, S) (performed by Bristol Laboratories) were reported for all the newly prepared thiolanes (**5–8**, **11–20**, **22**, **25**, **26**). [b] All the chalcones were employed in 14.4-mmol amounts except **3** and **5**, which were employed in 5.7- and 13.7-mmol quantities, respectively. [c] Percentage yield after one recrystallization of the crude product from the solvent indicated. [d] The mobile phase for TLC consisted of mixtures of low-boiling petroleum ether (PE) and ethyl acetate in the relative amounts indicated by the ratio. [e] The TLC plate was developed two times. [f] The percentage yield represents the crude product mixture consisting of unconverted chalcone and thiolane. The presence of the latter was indicated by the ^{1}H NMR resonance at 4.5–5.5 ppm and the molecular ion at *m/z* 534. [g] The percentage yield represents the amount of pure glasslike material obtained after flash chromatography of the crude product mixture on silica gel 60 employing PE–EtOAc (1:1). Mass, ^{1}H and ^{13}C NMR, and infrared spectra were consistent with the expected thiolane product. Successive triturations of the glasslike product with CH_2Cl_2–CCl_4 and finally pure CCl_4, rotary evaporation of the solvent after each trituration, and drying of the final faintly yellow powder at 0.03 torr at 50 °C for several hours gave the product whose properties are indicated and whose elemental analysis revealed the association of 1 mol of CCl_4. [h] Flash chromatography employing PE–EtOAc (2:1) replaced washing with 20% aqueous $(NH_4)_2S$ solution to remove sulfur.

2.99 g of sulfur-free crude product whose HPLC indicated a *Z* to *E* ratio of chalcones in excess of 10:1 in addition to thiolane **2**.

Crossed Thiolane Formation. A mixture consisting of 0.48 mmol each of chalcones **1** and **15** was added in one portion to a previously prepared mixture of 1.50 mmol of $Na_2S{\cdot}9H_2O$ and 17 mmol of sulfur in 1.5 mL of 95% ethanol, and the resulting mixture was stirred at 25 °C for 24 h and then treated according to the standard workup procedure indicated above. Thereby was obtained 193 mg of solid whose TLC (2.5 × 7.5 cm Silica gel 1B2-F plates developed with petroleum ether–EtOAc, 2:1) showed three spots, R_f 0.52, 0.48, and 0.42, of which the first and third corresponded to the thiolanes previously prepared from the pure chalcones **1** and **15** alone. The size and intensity of the second spot were about twice that of the first or third alone. Mass spectra of the product mixture gave peaks *m/z* 448, 478, and 508 in the ratio 1.00:1.52:0.43 which corresponded to the molecular ions of the thiolane from **1**, crossed thiolanes, and the thiolane from **15**, respectively. Also observed were fragmentation ions *m/z* 209, 239, and 269 which were observed in a ratio of 1.0:1.9:0.8. HPLC (Partisil 10/25, M9 eluted with petroleum ether–EtOAc, 2:1, at 3.1 mL/min) V_e 1.57, 1.88, and 2.30 (in a ratio of 25:43:23), the first of which corresponded to the thiolane **2** and the third to the thiolane from **15**.

In a related experiment, 0.23-mmol quantities each of the thiolanes from chalcones **1** and **15** were dissolved in 0.2–0.3 mL of THF and added in one portion to a stirred mixture of 0.72 mmol of $Na_2S{\cdot}9H_2O$ and 7.64 mmol of sulfur in 0.7 mL of 95% EtOH and 0.2 mL of THF, the latter solvent being used to assist the solubilization of the starting thiolanes. The resulting mixture was stirred for 3 days at 25 °C. Solvents were removed at the rotary evaporator and the residue was mixed with methylene chloride. Workup of the resulting mixture was carried out according to the standard workup procedure and thereby was obtained 190 mg of solid whose TLC (2.5 × 7.5 cm Silica gel) 1B2-F plates developed with petroleum ether–EtOAc, 2:1) showed two spots: R_f 0.52 and 0.42 corresponding to the starting thiolanes. The mass spectrum revealed molecular ions at 448 and 508 in an intensity ratio of 1.00:0.27 and fragment ions at *m/z* 209, 239, and 269 in a ratio 1.00:1.26:0.28.

Acknowledgment. The support of this work by Bristol Laboratories (Syracuse) is gratefully acknowledged.

Registry No. (*E*)-**1**, 614-47-1; **2**, 87172-17-6; (*E*)-**3**, 14182-01-5; (*E*)-**4**, 22573-24-6; (*E*)-**5**, 22966-01-4; **5** (thiolane), 87116-42-5; (*E*)-**6**, 13565-43-0; **6** (thiolane), 87116-43-6; (*E*)-**7**, 22252-14-8; **7** (thiolane), 87173-08-8; (*E*)-**8**, 14802-30-3; **8** (thiolane), 87136-14-9; (*E*)-**9**, 87172-18-7; (*E*)-**10**, 55800-30-1; (*E*)-**11**, 22966-23-0; **11** (thiolane), 87116-44-7; (*E*)-**12**, 22966-13-8; **12** (thiolane), 87116-45-8; (*E*)-**13**, 22252-16-0; **13** (thiolane), 87172-19-8; (*E*)-**14**, 22966-22-9; **14** (thiolane), 87172-20-1; (*E*)-**15**, 22966-05-8; **15** (thiolane), 87116-46-9; (*E*)-**16**, 22966-24-1; **16** (thiolane), 87116-47-0; (*E*)-**17**, 22252-15-9; **17** (thiolane), 87172-21-2; (*E*)-**18**, 22966-19-4; **18** (thiolane), 87172-22-3; (*E*)-**19**, 53744-27-7; **19** (thiolane), 87136-15-0; (*E*)-**20**, 54619-91-9; **20** (thiolane), 87116-48-1; (*E*)-**21**, 41564-67-4; (*E*)-**22**, 87116-40-3; **22** (thiolane), 87116-49-2; (*E*)-**23**, 2960-55-6; (*E*)-**24**, 22965-98-6; **24** (thiolane), 87116-50-5; (*E*)-**25**, 22966-17-2; **25** (thiolane), 87116-51-6; (*E*)-**26**, 87116-41-4; **26** (thiolane), 87116-52-7; Na_2S, 1313-82-2; Li_2S, 12136-58-2; K_2S, 1312-73-8.