Phase Transfer-Catalyzed Reactions between Polysulfide Anions and α,β-Unsaturated Carbonyl Compounds

Eitan B. Krein and Zeev Aizenshtat*

Department of Organic Chemistry and Casali Institute, Energy Research Center, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Received December 29, 1992®

Ammonium polysulfide reacts with α,β-unsaturated ketones and aldehydes under PTC (phase transfer catalysis) conditions in a rather different manner than it does in homogeneous systems. 1,3-Diphenyl-2-propen-1-one (chalcone, 1) and 4-phenyl-3-buten-2-one (benzylideneacetone, 3) give sulfur-linked dimers (mainly disulfides). 3-Phenyl-2-propen-1-al (cinnamaldehyde) polymerizes. 1,5-Diphenyl-1,4-pentadien-3-one (dibenzylideneacetone, 7) gives the known six-membered ring thianones and new seven-membered ring 1,2-dithiepanones 9 along with a polymer. Carvone gives a disulfide dimer that converts to a mixture of bicyclic sulfur-containing compounds. Sodium polysulfide is much less effective because of the base-induced decomposition of either the products or the intermediates. Sodium sulfide reacts in the same manner as it does in homogenous systems.

Introduction

The addition of sulfur nucleophiles to activated C═C double bonds is well known. Many such reactions are phase transfer catalyzed.[1-3] Polysulfide anions are strong nucleophiles. It has been shown theoretically,[4] as well as experimentally,[5] that polysulfides are better nucleophiles than sulfides. The enhanced reactivity of polysulfides can play an important role in the formation of natural sulfur compounds.[4,5]

The reactions between sodium polysulfide and various α,β-unsaturated carbonyl compounds have been studied.[4,6-9] The most investigated reactions are those of chalcone (1) and some of its derivatives, which give thiolanes (tetrahydrothiophenes) as the major products in saturated ethanolic solutions of sodium polysulfide. Under similar conditions, other α,β-unsaturated compounds give complex mixtures, which in some cases contain organic polysulfides, five-membered heterocycles, and polymers.

Reports of heterogeneous phase transfer-catalyzed reactions of polysulfides are scarce. The only reaction described previously is the reaction between alkyl halides and sodium disulfide or sodium trisulfide. The products of this reaction were organic di- and trisulfides.[10]

The objectives of our research were (1) to study whether polysulfide anions react with α,β-unsaturated carbonyl compounds in heterogeneous systems with quaternary ammonium salts as phase transfer agents, (2) to study the product distributions in such systems, and (3) to try to explain the differences observed between homogeneous and heterogeneous systems.

This report presents the results of the phase transfer-catalyzed reactions of some α,β-unsaturated carbonyl compounds (ketones and an aldehyde) with ammonium or sodium polysulfide ($(NH_4)_2S_x$, Na_2S_x) and compares these reactions to the phase transfer-catalyzed reactions of the same compounds with sodium monosulfide (Na_2S).

Results and Discussion

The solvents used were toluene and THF. Halogenated solvents (such as CH_2Cl_2 and chloroform), which are very common in PTC (phase transfer catalysis) experiments, were avoided in order to prevent the reaction of the solvents with the polysulfide nucleophiles.

The transfer of polysulfide ions into the organic phase can be confirmed by the appearance of an orange-red coloration of the organic layer immediately after the addition of the quaternary ammonium salt (didecyldimethylammonium bromide, DDAB). The visible spectrum of the organic solution is dominated by the absorbance at 451 nm of the hexasulfide ion (S_6^{2-}),[11,12] which does not exist in the spectrum of the aqueous solution. The identification of S_6^{2-} is supported by the results of the analogues reaction of polysulfides with tetrabutylammonium bromide, which gives the orange-red solid salt $(Bu_4N)_2S_6$.[13] The shorter wavelength absorbances in the spectrum of the organic solution correspond to shorter polysulfide chains.[14]

1,3-Diphenyl-2-propen-1-one (Chalcone, 1). The reactions of chalcone with various sulfur nucleophiles had

---

® Abstract published in *Advance ACS Abstracts*, October 1, 1993.

[1] (a) Weber, W. P.; Gokel, G. W. *Reactivity and Structure Concepts in Organic Chemistry. Vol. 4: Phase Transfer Catalysis in Organic Synthesis*; Springer-Verlag: New York, 1977; pp 221–233. (b) Starks, C. M.; Liotta, C. L. *Phase Transfer Catalysis—Principles and Techniques*; Academic Press: New York, 1978. (c) Dehmlow, E. V.; Dehmlow, C. L. *Phase Transfer Catalysis, Monographs in modern Chemistry 011*; VCH: Weinheim, 1980.

[2] Landini, D.; Rolla, F. *Synthesis* **1974**, 565–566.

[3] Kuwajima, I.; Murofushi, T.; Nakamura, E. *Synthesis* **1976**, 602–604.

[4] LaLonde, R. T.; Ferrara, L. M.; Hayes, M. P. *Org. Geochem.* **1987**, *11*, 563–571.

[5] Vairavamurthy, A.; Mopper, K. Mechanistic Studies of Organosulfur (Thiol) Formation in Coastal Marine Sediments. In *Biogenic Sulfur in the Environment*; Saltzman, E. S., Cooper, W. J., Eds.; ACS Symposium Series 393; American Chemical Society: Washington, DC, 1989; pp 232–242.

[6] Reinecke, M. G.; Morton, D. W.; Del Mazza, D. *Synthesis* **1983**, 160–161.

[7] LaLonde, R. T.; Horenstein, B. A.; Schwendler, K.; Fritz, R. C.; Florence, R. A.; Ekiel, I.; Smith, I. C. P. *J. Org. Chem.* **1983**, *48*, 4049–4052.

[8] LaLonde, R. T.; Florence, R. A.; Horenstein, B. A.; Fritz, R. C.; Silveira, L.; Clardy, J.; Krishman, B. S. *J. Org. Chem.* **1985**, *50*, 85–91.

[9] LaLonde, R. T.; Codacovi, L. M.; Cun-heng, H.; Cang-fu, X.; Clardy, J.; Krishman, B. S. *J. Org. Chem.* **1986**, *51*, 4899–4905.

[10] Hase, T. A.; Perakyla, H. *Synth. Commun.* **1982**, *12*, 947–950.

[11] Pinon, V.; Lelieur, J. P. *Inorg. Chem.* **1991**, *30*, 2260–2264.

[12] Benaichouche, M.; Bosser, G.; Paris, J.; Plichon, V. *J. Chem. Soc., Perkin Trans. 2* **1991**, 817–823.

[13] Teller, R. G.; Krause, L. J.; Houshalter, R. C. *Inorg. Chem.* **1983**, *22*, 1809–1812.

[14] Giggenbach, W. *Inorg. Chem.* **1972**, *11*, 1201–1207.

[15] Licht, S.; Hodes, G.; Manassen, J. *Inorg. Chem.* **1986**, *25*, 2486–2489.

0022-3263/93/1958-6103$04.00/0

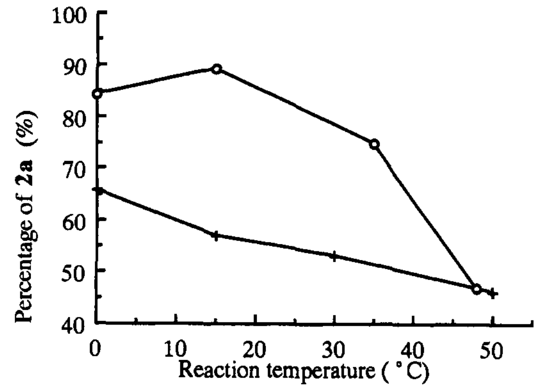


Figure 1. Effect of temperature on the percentage of **2a** (in the mixture of **2a** and **2b**) in toluene (O) and in THF (+).

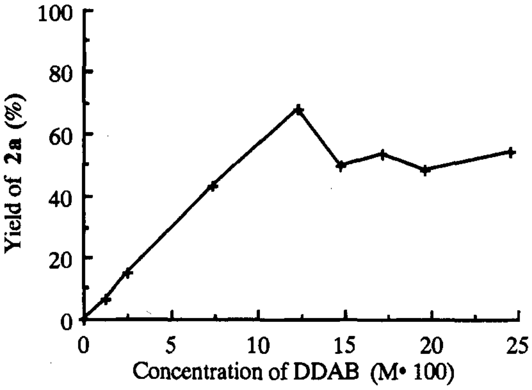
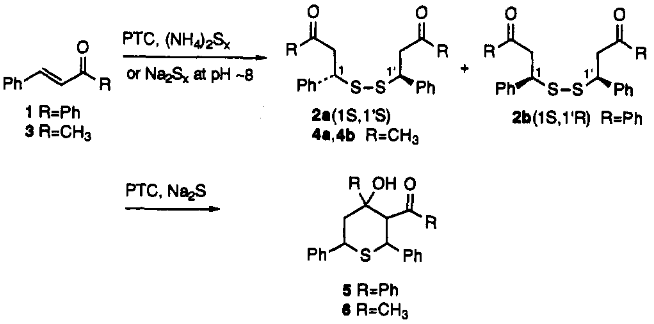


Figure 2. Effect of DDAB concentration on the yield of **2a** in toluene after 2 h.

Scheme I. PTC Reactions of 1 or 3 and Ammonium or Sodium Polysulfide and Sodium Sulfide



previously been studied under different conditions.[4-9,16,17] The major products with sodium polysulfides were five-membered heterocycles (thiophenes and thiolanes).

Under the PTC conditions applied here, chalcone (1) reacted with ammonium polysulfide (at ambient temperature or lower) to give the two diastereomers of disulfide 2 (Scheme I). The identity of known diastereomer **2a** was confirmed by the agreement of its physical and spectroscopic data with those in the literature.[17,18] Diastereomer **2a** was determined by X-ray difraction to be the racemic isomer (mixture of 1*S*,1′*S* and 1*R*,1′*R*). (See the ORTEP representation in the supplementary material.) The elemental analysis and the ^{13}C-NMR spectrum of **2b** were almost identical to those of **2a**. The ^{1}H-NMR chemical shifts of the protons at the two chiral centers of **2b** differed from those of **2a** by 0.1 ppm. There were also smaller differences in the chemical shifts of the other nonaromatic protons of the two compounds. On the basis of these data, **2b** was identified as the new meso (1*R*,1′*S*) diastereomer of disulfide 2. Racemic diastereomer **2a** was obtained almost exclusively when the reaction was carried out in toluene at rt or lower, since it precipitated during the reaction. When the reaction was carried out at temperatures higher than rt or in THF, the concentration of **2b** increased until a 1:1 ratio was reached in both solvents at 50 °C (see Figure 1). This behavior indicates that the two diastereomers equilibrate in solution. Equilibration fits the fact that the ratio of the two isomers changed from 9:1 (racemic/meso) to approximately 1:1 when the solvent was changed from toluene to THF and the mixture was left to equilibrate.

At higher temperatures (70 °C), small amounts of bis(1,3-diphenyl-3-oxo-1-propyl) sulfide, identified by the agreement of its ^{1}H-NMR spectrum and its mp with those in the literature,[17] were formed.

The cation of the polysulfide was found to have a striking influence on the product distribution. Under conditions similar to those described above, 1 did not react with sodium polysulfide, either in toluene or in THF. However, when the pH of the solution was reduced with H_2SO_4 to a value of about 8, 1 reacted to give **2a**. Furthermore, disulfide **2a** decomposed to 1 under PTC conditions with sodium sulfide. When sodium monosulfide was used, known thianol 5 (R = Ph, Scheme I), which had been previously prepared in ethanol,[17] was obtained.

The catalytic effect of the quaternary ammonium salt was checked by increasing the concentration of DDAB. Figure 2 shows the increasing yield of **2a** after 2 h at 0 °C at low DDAB concentrations. When the reaction was carried out without the ammonium salt, no **2a** was observed by ^{1}H-NMR after 2 h; if the reaction mixture was stirred for another 72 h at rt, **2a** was formed in 30% yield, probably as a result of interface reaction.

***trans*-4-Phenyl-3-buten-2-one (Benzylideneacetone, 3).** The reactions between ketone 3 and sulfur nucleophiles had previously been found[17,19] to be very similar to those of chalcone, and this similarity was also valid under PTC conditions. Ketone 3 gave two diastereomers of disulfide 4 (Scheme I). The selective formation of one of the two diastereomers (**4a**) in toluene and at low temperatures further supports the reversibility of the addition of polysulfides. The identity of disulfide **4a** was confirmed by the agreement of its physical and spectroscopic data with those in the literature and by the resemblance of its ^{1}H-NMR spectrum to that of disulfide **2a**. Like 1, compound 3 did not react with sodium polysulfide at high pH values and gave disulfide **4a** in the presence of H_2SO_4 (at pH of ~8). With sodium monosulfide, known thianol 6 (R = CH_3) was formed.

1,5-Diphenyl-1,4-pentadien-3-one (Dibenzylideneacetone, 7). 1,4-Dien-3-one 7 is known to react with H_2S under basic catalysis to give the two diastereomers of thianone 10.[20] Under PTC conditions, polymerization and cyclization compete (Scheme II). The main product with ammonium polysulfide (>70%) was a polymer (8) containing 24–28% of sulfur, indicating the presence of di- or trisulfide linkages. Desulfurization of this polymer with

---

(16) Fromm, E.; Hubert, E. *Ann.* **1912**, *394*, 301–309.

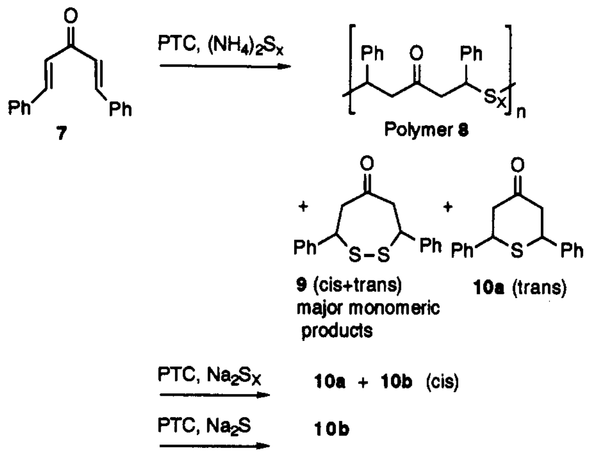
(17) Del Mazza, D.; Reinecke, M. G. *J. Org. Chem.* **1981**, *46*, 128–134.

(18) Tanaka, H.; Yokoyama, A. *Chem. Pharm. Bull.* **1960**, *8*, 275–279.

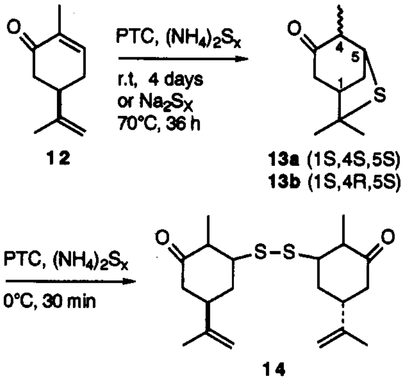
(19) Forward, G. C.; Whiting, D. A. *J. Chem. Soc. C* **1969**, 1647–1652.

(20) Baxter, C. A. R.; Whiting, D. A. *J. Chem. Soc. C* **1968**, 1174–1178.

Scheme II. PTC Reactions of 7 and Ammonium or Sodium Polysulfide and Sodium Sulfide



Scheme III. PTC Reactions of 12 with Ammonium Polysulfide

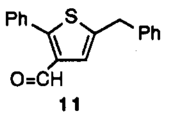


Raney nickel gave 1,5-diphenyl-3-pentanone (and in some cases also 1,5-diphenyl-3-pentanol which was probably formed as a result of Raney nickel reduction of the ketone). The formation of these products indicates that polymerization is caused by polysulfidic linking of the unsaturated ketone, in a way similar to that of the above dimerizations of 1 and 3, without the formation of carbon–carbon bonds.

Under high dilution, monomeric cyclic products were formed. The main products were the two stereoisomers of new 3,7-diphenyl-1,2-dithiepan-5-one (9), along with smaller amounts of *trans*-2,6-diphenylthian-4-one (10a). Compound 10 was identified by the agreement of its physical and spectroscopic data with those of an authentic sample and those in the literature.[20] New dithiepanone 9 was identified by X-ray diffraction analysis of the *cis* isomer (9a) and by ^{1}H-NMR, MS, and elemental analysis. The ORTEP representation for *cis*-3,7-diphenyl-1,2-dithiepan-5-one (9a) is presented in the supplementary material.

Compounds 9a and 9b were not obtained with sodium polysulfide under similar conditions. The *trans* (10a) and *cis* (10b) diastereomers of 2,6-diphenyl-4-thianone were the only monomeric products under these conditions. Sodium monosulfide gave only the kinetic *cis* isomer.[20] The formation of organic monosulfides from the reaction with sodium polysulfide may indicate a higher concentration of monosulfide ions in the sodium polysulfide solution in comparison with the ammonium polysulfide solution, which is indeed expected at high pH values.[14,15]

3-Phenyl-2-propenal (Cinnamaldehyde). Cinnamaldehyde had been shown to react with sodium polysulfide to give thiophene 11 (and the ethyl ester of the corresponding acid) in very low yields.[8] In our research, thiophene 11 was formed also in very low yields under PTC conditions with sodium polysulfide at 85 °C, but no reactions were observed at rt.



11

Cinnamaldehyde polymerized with ammonium polysulfide at rt. Elemental analysis showed that the polymer contains 30% S, 3.7% N, 60% C, 5.2% H and practically *no* oxygen. The IR spectrum showed the disappearance of the absorbances of both the C=O and C=C double bonds. No absorbance of any oxygen-containing functional group could be detected. ^{1}H-NMR spectrum showed only a wide aromatic peak around 7.2 ppm, which is typical of aromatic polymers. Raney Nickel desulfurization gave propylbenzene.

(5*R*)-2-Methyl-5-(1-methylethenyl)-3-cyclohexen-1-one (Carvone) (12). Carvone (12) had been shown to react with hydrogen sulfide under basic catalysis to give a β-substituted monosulfide dimer, 3-mercaptohydrocavone, and bicyclic thiane 13a.[21]

Under PTC conditions with polysulfides, 12 reacted differently under thermodynamic control than under kinetic control (Scheme III). The two diastereomers of thiane 13 were formed at rt or higher (70 °C) after several hours (thermodynamic control). Known (1*S*,4*S*,5*S*)-4,7,7-trimethyl-6-thia-1,5-bicyclo[3.2.1]octan-3-one (13a) was identified in the mixture by ^{1}H-NMR (methyl doublet at δ 1.18 ppm). The second, new isomer (13b) (methyl doublet at δ 1.07 ppm) was chromatographically separated, and its structure was established by X-ray diffraction analysis. The stereochemical configuration was found to be 1*S*,4***R***,5*S*, which explains the difference between the ^{1}H-NMR spectra of 13a and 13b. Compounds 13a and 13b were also formed in lower yields with sodium polysulfide.

At 0 °C without a solvent and after short reaction times (kinetic control), 12 reacted with ammonium polysulfide in the presence of DDAB to give new dicarvone disulfide 14 [bis(2-methyl-5-(1-methylethenyl)-3-oxocyclohexyl) disulfide] (Scheme III). This compound was identified by its mass spectrum and elemental analysis and by comparison of its ^{1}H-NMR spectrum with that of the monosulfide [bis(2-methyl-5-(1-methylethenyl)-3-oxocyclohexyl) sulfide] and of the thiophenol adduct [2-methyl-5-(1-methylethenyl)-3-(phenylthio)cyclohexan-1-one].[22] When a sample of 14 was left to equilibrate for 24 h under PTC conditions with ammonium polysulfide, it was converted quantitatively to a mixture of thermodynamically stable compounds 13a (~75%) and 13b (~25%). This shows that the formation of disulfide 14 is reversible, as was shown also for 1 and 2.

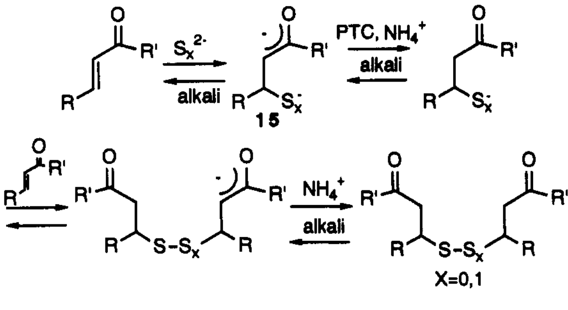
The results presented here show the ability of quaternary ammonium salts to serve as phase transfer catalysts for polysulfide ions and the catalytic effect of this transfer on nucleophilic Michael additions of such ions. The results clearly demonstrate the striking influence of the reaction

---

(21) Hargeaves, M.; McDougall, R.; Rabari, L. *Z. Naturforsch, B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1535–1539.

(22) Solladie, G.; Hutt, J. *Bull. Soc. Chim. Fr.* **1986**, *21*, 643–644.

Scheme IV. Proposed Mechanism for the Formation or Decomposition of (Di)sulfidic Linkages between α,β-Unsaturated Carbonyl Compounds under PTC Conditions



conditions on the type of product obtained. Solvent and pH (determined by the cation) are shown to be the major influencing parameters. Three different experimental conditions can be compared: alkali polysulfide in ethanol, ammonium polysulfide under PTC conditions, and alkali polysulfide under PTC conditions.

LaLonde[4,7-9] showed that with concentrated ethanolic alkali solutions the first nucleophilic attack, in which enolate ion 15 ($x > 1$, Scheme IV) is formed, is followed by two consecutive nucleophilic attacks that form first a C–C bond by a Michael or an aldol reaction and then a C–S bond. This sequence leads to the formation of a thiolane ring.

In contrast, our research shows that, under PTC conditions, ammonium polysulfide reacts directly to form disulfide dimers, disulfide heterocycles, or polysulfide polymers. Such conditions are therefore preferable for "simple" Michael addition of polysulfides because they prevent the "interfering" enolate activity. The most reasonable mechanism for this reaction is suggested in Scheme IV, and its principal steps are the Michael addition of the polysulfide anion to two, α,β-unsaturated carbonyl groups and the quenching of the two enolate ions, probably with several equilibrating intermediates. The isomerizations of **2a** to **2b** and of **14** to **13** (and probably of **4a** to **4b**) indicate the reversibility of the reaction. Functional groups other than enones, such as the non-activated double bond of carvone, may interact with the polysulfide function to give more complex structures such as **13**.

Under PTC conditions, sodium polysulfide, quite surprisingly, failed to give either thiolane and thiophenes or disulfide products. This outcome can be explained by the observed decomposition of the β-disulfide ketones under highly basic conditions. This decomposition indicates the easy elimination of polysulfides from β-polysulfide enolates. Quenching the enolate ions by lowering the pH value to about 8 prevents this elimination and indeed produces the expected disulfides. It is noteworthy that sodium monosulfide produces organic sulfides under high pH PTC conditions. The stability of the six-membered rings in **5**, **6**, and **10** and the precipitation of aldols **5** and **6** may explain this behavior.

An unsaturated aldehyde such as cinnamaldehyde may react in a similar way to **1** and **3**, but the aldehyde group reacts further. The details of the mechanism of formation and the structure of the polymer are not clear. The absence of oxygen and the disappearance of both the C=C double bond and the carbonyl group, along with the fact that no carbon–carbon bonds are formed (as evident from Raney nickel depolymerization to propylbenzene), suggest that sulfur is replacing the oxygen. The known transformation of carbonyls to thioacetal bridges,[23-25] possibly via the formation of imines,[26,27] along with Michael addition, may explain these observations.

Conclusions

The reactions of polysulfide anions under PTC conditions have been scarcely studied. The research presented here gives the first results of such reactions with α,β-unsaturated carbonyl compounds. The products obtained under such conditions are completely different from those obtained under homogeneous (usually ethanolic) conditions, and this difference gives additional evidence for the mechanism of the addition of polysulfides to activated C=C double bonds. The reaction of polysulfide anions in a two-phase system, with catalysis by quaternary ammonium salts, proved to be an efficient method to synthesize organic carbonyl sulfides, especially disulfides. When conjugated dienones are used, some new 1,2-disulfidic cyclic systems can be prepared. This work shows that ammonium polysulfide is more active in this reaction than sodium polysulfide. Unsaturated aldehydes are too active and polymerize under the reaction conditions.

Experimental Section

General. Melting points are uncorrected. Unless otherwise noted, all starting materials were purchased from Aldrich Chemical Co., Inc. Ammonium polysulfide was purchased from BDH. ^{1}H- and ^{13}C-NMR spectra were obtained in $CDCl_3$ solutions in 5-mm NMR tubes at 200 or 400 MHz. GC and GC/MS were carried out as previously described.[28]

General Procedures. Ammonium polysulfide was prepared by adding 0.25 g (1 mmol) of elemental sulfur (S_8) to 10 mL of an aqueous solution of commercial ammonium polysulfide (approximately 10% (w/v) H_2S) and stirring until all the solid sulfur disappeared. Sodium polysulfide was prepared by dissolving 10 g (41.7 mmol) of $Na_2S{\cdot}9H_2O$ in 10 mL of distilled water, adding 2 g (7.8 mmol) of elemental sulfur, and stirring until all of the solid sulfur dissolved. Solutions of sodium sulfide were similarly prepared without elemental sulfur. In a typical reaction, 1 g of a ketone or an aldehyde was dissolved in 10 mL of toluene or THF and added to the polysulfide solution. The two-phase medium was magnetically stirred, and 50 mg of didecyldimethylammonium bromide (DDAB) was added (as a 75% weight gel in water). A deep brown-red color immediately developed in the organic phase, as a result of the transfer of polysulfide ions into it. The reaction solutions were stirred under N_2 until no starting material was detected on a TLC plate and/or in the H^1-NMR spectrum. When THF was used, 200 mL of water was added to remove the polysulfide and the THF, and the residual oily matter was dissolved in 50 mL of CH_2Cl_2. The organic solution was washed repeatedly with small portions of water until the washings were colorless. The solution was dried over $MgSO_4$, and the solvent was evaporated. Mixtures were chromatographically separated on a silica gel column with a mixture of ether and hexane as an eluent. If a solid product precipitated during the reaction, it was filtered, washed with cold ethanol, dried, and recrystallized from a suitable solvent.

(1*S*,1′*S*)-Bis(1,3-diphenyl-3-oxo-1-propyl) Disulfide (2a). The usual procedure with ammonium polysulfide and toluene was performed with 1.30 g (6.25 mmol) of chalcone. The solutions were stirred overnight at rt, and filtration afforded **2a** (0.71 g, 47% yield) as a solid. Recrystallization from ethyl acetate gave 0.66 g (44%) of colorless prisms: mp 156 °C (lit.[18] mp 156.5 °C);

---

[23] Thiel, M.; Asinger, F. *Angew. Chem.* **1957**, *610*, 17–24.
[24] Asinger, F.; Thiel, M.; Lipfert, G. *Angew. Chem.* **1959**, *627*, 195–212.
[25] Magnusson, B. *Acta Chem. Scand.* **1959**, *13*, 1031–1032.
[26] Magnusson, B. *Acta Chem. Scand.* **1962**, *16*, 1536–1538.
[27] Magnusson, B. *Acta Chem. Scand.* **1963**, *17*, 273–275.
[28] Cohen, Y.; Aizenshtat, Z. *J. Anal. Appl. Pyrol.* **1992**, *22*, 153–178.

IR (Nujol) 1678 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 7.89 (d, *J* = 4.5 Hz, 4H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 4H), 7.28 (m, 10H) 4.36 (dd, *J* = 5.5, 8.6 Hz, 2H), 3.78 (dd, *J* = 5.5, 17.2 Hz, 2H), 3.56 (dd, *J* = 8.7, 17.1 Hz, 2H) ppm; ^{13}C-NMR δ 196.8, 139.8, 136.6, 133.2, 128.6, 128.6, 128.2, 128.1, 127.9, 49.4, 43.3 ppm. For X-ray diffraction data, see the supplementary material. Anal. Calcd for $C_{30}H_{26}O_2S_2$: C, 74.63; H, 5.43; S, 13.3. Found: C, 74.89; H, 5.64; S, 13.0.

Preparation of 2a with Sodium Polysulfide. When the usual procedure was preformed with sodium polysulfide and 1, no products were formed either in toluene or in THF. Therefore, a solution of 10% H_2SO_4 in water was added to a solution of sodium polysulfide until the appearance of elemental sulfur suspension (about pH 7). Then, a solution of 2 g of 1 in 10 mL of toluene and 50 mg of DDAB were added. The suspended elemental sulfur dissolved, and the organic layer became orange. A few drops of H_2SO_4 were added until the color disappeared, and $Na_2S{\cdot}9H_2O$ was added until pH 8 was obtained. The medium was stirred overnight. The solids, which contained disulfide **2a** and elemental sulfur, were filtered and washed thoroughly with ammonium polysulfide to remove the elemental sulfur. The residual white solid (1.84 g, 79% yield) was identified by ^{1}H-NMR as disulfide **2a**.

(1*S*,1′*R*)-Bis(1,3-diphenyl-3-oxo-1-propyl) Disulfide (2b). The usual procedure with ammonium polysulfide and THF was performed at rt for 2 h to afford 1 g of a viscous, yellowish oil, which solidified on standing (85% yield of crude **2a** and **2b**). A sample of this mixture was analyzed by ^{1}H-NMR and was found to contain only **2a** and **2b**. The ratio of the two isomers (1:1) was determined from the integration ratio between the two sets of double doublets for the protons at the α-position to the disulfide groups (4.36 ppm for **2a** and 4.26 ppm for **2b**).

A sample of 2.5 g of a reaction mixture prepared in THF at 70 °C from 3 g of 1 was found by ^{1}H-NMR to contain 90% of a 1:1 mixture of diastereomers **2a** + **2b** (33% overall yield of each) and 10% of the monosulfide (14% yield). The mixture was crystallized from ethyl acetate, and the crystals of the racemic isomer (**2a**) were filtered. The residual oil contained 17% of the monosulfide and 83% of a mixture of 17% **2a** and 66% **2b**. This mixture was chromatographed twice on a silica column with a 1:1 mixture of ether and hexane as eluent to yield a colorless oil, which slowly solidified. A sample was recrystallized from cold ethyl acetate to give 30 mg (1%) of pure **2b** as a white powder: mp 79 °C; IR (Nujol) 1680 cm^{-1} (C=O); ^{1}H-NMR δ 7.89 (d, *J* = 4.5 Hz, 4H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 4H), 7.28 (m, 10H) 4.26 (dd, *J* = 6.0, 8.2 Hz, 2H), 3.75 (dd, *J* = 6.0, 17.3 Hz, 2H), 3.53 ppm (dd, *J* = 8.4, 17.2 Hz, 2H); ^{13}C-NMR δ 196.9, 139.8, 136.7, 133.2, 128.6, 128.6, 128.2, 128.1, 127.9, 49.2, 43.3 ppm. Anal. Calcd for $C_{30}H_{26}O_2S_2$: C, 74.63; H, 5.43. Found: C, 74.34; H, 5.23.

White needles of the monosulfide (10 mg, 0.5%) crystallized after 5 days from the same fraction: mp 92–4 °C (lit.[17] mp 102–104 °C); ^{1}H-NMR δ 7.83 (d, 4H), 7.53 (t, 2H), 7.40 (t, 4H), 7.20 (m, 10H) 4.47 (t, 2H), 3.55 (d, 2H), 3.52 (d, 2H).

Reaction of Chalcone (1) and Sodium Sulfide. Chalcone (1) was treated as usual with sodium sulfide at rt for 16 h. The white precipitate was filtered and dissolved in CH_2Cl_2, the solution was dried over $MgSO_4$, and the solvent was evaporated. The 0.77 g of crude product was crystallized from ethyl acetate to afford 0.41 g (38%) of pure thiane **5**, which was identified by comparison of its physical and spectroscopic data with those in the literature[17] (see the supplementary material for detailed information).

Bis(1-phenyl-3-oxo-1-butyl) Disulfide (4a and 4b). In toluene: *trans*-4-phenyl-3-buten-2-one (**3**) (1.5 g) was treated as usual with ammonium polysulfide in an ice bath for 3 h to afford 0.75 g (41%) of **4a**; recrystallization of a sample from ethyl acetate gave colorless needles: mp 118 °C (lit.[19] mp 125 °C); IR (Nujol) 1707 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 7.40 (m, 10H), 4.09 (dd, *J* = 6.0, 8.5 Hz, 2H), 3.16 (dd, *J* = 6.0, 17.0 Hz, 2H), 2.97 (q, *J* = 8.5 Hz, 2H), 2.04 (s, 6H) ppm; ^{13}C-NMR δ 205.2, 139.6, 128.7, 128.1, 128.0, 128.0, 49.0, 48.4 ppm. Anal. Calcd for $C_{20}H_{22}O_2S_2$: C, 67.00; H, 6.19. Found: C, 66.82; H, 6.20.

In THF: a mixture of diastereomers **4a** and **4b** (75% yield of both) was obtained as usual from 1 g of **3** with ammonium polysulfide. The ratio of **4a** to **4b** was 55:45 (41% yield of **4a** and 34% of **4b**): ^{1}H-NMR of **4b** 7.30 (m, 10H), 4.00 (dd, *J* = 6.3, 8.4 Hz, 2H), 3.14 (dd, *J* = 6.0, 16.7 Hz, 2H), 2.94 (q, *J* = 8.4 Hz, 2H), 2.03 (s, 6H) ppm.

Reaction of 3 and Sodium Polysulfide. When 2.3 g of **3** was treated exactly as described for **1**, 0.41 g (15%) of **4a** was obtained after crystallization from ethyl acetate. No disulfides or other products were formed when the pH of the solution was not lowered.

Reaction of 3 and Sodium Sulfide. The usual procedure using 1.5 g of **3** in 5 mL in toluene yielded after 2.5 h at rt 0.44 g (26%) of crude thiane **6**. A sample of the filtered solid was crystallized from ethyl acetate to give white, square crystals, which were identified as thianol **6** by comparison of its physical and spectroscopic data with those in the literature[19] (see the supplementary material for detailed information).

Reaction of 1,5-Diphenyl-1,4-dien-3-one (Dibenzylideneacetone) (7) and Ammonium Polysulfide. A very viscous, brown-red oil (**8**) was obtained when **7** was treated as usual either in toluene or in THF. ^{1}H-NMR of this product showed the broad absorbances typical of polymers: δ 7.0–7.5 and around 4.5, 3.9, and 3.0 ppm; IR (neat) 1711 cm^{-1} (C=O). Anal. Found: C, 67.55; H, 5.25; S, 24.0. When this reaction was conducted at 85 °C, the sulfur percentage rose to 28% (C, 61.95; H, 4.88).

Desulfurization of Polymer 8. A solution of 100 mg of **8** in 5 mL of toluene was stirred under N_2 with approximately 3 g of prewashed Raney Nickel in 10 mL of ethanol for 1 h. The liquid was decanted and washed with water. The dried toluene solution was analyzed on a GC equipped with a sulfur-specific FPD detector and was found to contain two compounds that did not contain sulfur. The mixture was chromatographed on silica gel with a 1:1 mixture of ether/hexane as eluent. A sample of each fraction was purified on a silica TLC plate. The first fraction contained 1,5-diphenyl-3-pentanone, and the second contained 1,5-diphenyl-3-pentanol. The two compounds were also synthesized by alternative procedures, which gave identical products. Synthetic procedures and spectroscopic data can be found in the supplementary material.

Reaction of 7 with Ammonium Polysulfide at High Dilution. A solution of 2 g (8.5 mmol) of **7** in 60 mL of THF was added dropwise over a period of 40 min to a PTC system containing 10 mL of ammonium polysulfide, 0.26 g (1 mmol) of elemental sulfur, and 300 mL of THF. The mixture was then stirred for another 90 min. The reaction mixture was treated as described above to afford 2.85 g of a very viscous, yellow liquid. This mixture was found by ^{1}H-NMR to contain 66% of polymer **8**, 15% of **9a**, 15% of **9b** (about 17% overall yield of each), and 5% of **10a** (about 6% overall yield). A 2-g portion of this mixture was chromatographed on silica gel with a mixture of ether and hexane as eluent. The fraction eluted with 25% ether was further separated by careful fractional crystallization from hexane to afford 120 mg (5%) of **9a** and 10 mg (0.5%) of **10a**. The next fraction, eluted with 30% ether, yielded 80 mg (3%) of **9b**. A sample of **9a** was slowly crystallized from hexane to afford crystals suitable for X-ray diffraction analysis, which confirmed it to be the *cis* isomer of 3,7-diphenyl-1,2-dithiepan-5-one (see the supplementary material).

9a (*cis*): white needles; mp 115 °C; IR 1715 cm^{-1} (C=O); ^{1}H-NMR (at 328 K) δ 7.30–7.42 (m, 10H), 4.12 (dd, *J* = 12.2, 4.4 Hz, 2H), 3.80 (t (wide at room temperature), *J* = 10.9 Hz, 2H), 3.00 ppm (dd, *J* = 4.1, 11.1 Hz, 2H); ^{13}C-NMR (at 324 K) δ 206.5, 140.6, 129.0, 128.1, 126.9, 51.5 (wide), 50.9 (wide) ppm; mass spectrum *m/z* 300 (11) $M^{\cdot+}$, 236 (19) $[M - S_2]^+$, 196 (50) $[M - PhCHCH_2]^+$, 132 (25) $[PhCHCH_2CO]^+$, 131 (100) $[PhCHCHCO]^+$. Anal. Calcd for $C_{17}H_{16}OS_2$: C, 67.96; H, 5.37; S, 21.34. Found: C, 68.21; H, 5.24; S, 21.18.

9b (*trans*): white powder; mp 133 °C; IR 1710 cm^{-1} (C=O); ^{1}H-NMR (at 328 K) δ 7.30 (m, 10H), 4.54 (dd, *J* = 4.5, 10.5 Hz, 2H), 3.55 (dd, *J* = 10.5, 13.0 Hz, 2H), 3.27 (dd, *J* = 4.5, 13.0 Hz, 2H) ppm, at room temperature all peaks appear as wide absorbances; ^{13}C-NMR (at 324 K) δ 206.6, 139.8, 128.9, 128.2, 127.3, 53.4 (wide), 52.5 (wide) ppm; mass spectrum *m/z* 300 (21) $M^{\cdot+}$, 268 (12) $[M - S]^+$, 236 (31) $[M - S_2]^+$, 196 (54) $[M - PhCHCH_2]^+$, 132 (22) $[PhCHCH_2CO]^+$, 131 (100) $[PhCHCHCO]^+$. Anal. Calcd for $C_{17}H_{16}OS_2$: C, 67.96; H, 5.37. Found: C, 67.87; H, 5.34.

Reaction between 3-Phenyl-2-propenal (Cinnamaldehyde) and Ammonium Polysulfide. A solution of 2 g of cinnamaldehyde was treated as usual at rt for 12 h to afford 1.51 g of a yellow polymer. Thermal decomposition of this polymer began at 100 °C: IR (neat) 3026, 2917, 1945, 1874, 1804, 1602, 1493, 1452, 1378, 1248, 1178, 1158, 1080, 1030, 967, 852, 762, 728, 699 cm^{-1}; ^{1}H-NMR 7.2 ppm (wide peak). Anal. Found: C, 59.61; H, 5.23; N, 3.66; S, 29.68. GCMS analysis of the Raney nickel desulfurization products of this polymer (as described above for 8) showed propylbenzene: m/z 120 (25, M$^+$), 91 (10, PhCH$_2^+$).

Reaction between Cinnamaldehyde and Sodium Polysulfide. A solution of 2 g of cinnamaldehyde was treated as usual for 17 h at 85 °C to afford a viscous, red oil. The ^{1}H-NMR spectrum showed high amounts of polymers. This crude mixture was chromatographed on silica gel with a 1:9 mixture of ether/hexane as eluent. The first fraction contained 60 mg (1.5%) of thiophene 11 as a yellow liquid: ^{1}H-NMR (CDCl$_3$) δ 9.79 (s, 1H), 7.56 (s, 1H), 7.35 (m, 10H), 4.13 (s, 2H); (C$_6$D$_6$) δ 9.82 (s, 1H), 7.37 (s, 1H), 7.10 (m, 10H), 3.65 (s, 2H) (in agreement with the literature[8]); mass spectrum m/z 279 ([M + 1]$^{\bullet+}$, 27), 278 (M$^{\bullet+}$, 100), 277 ([M − 1]$^+$, 45).

Reaction of (*R*)-(−)-Carvone (12) with Ammonium Polysulfide. A mixture of 5 mL (32 mmol) of 12, 10 mL of ammonium polysulfide, 2 g (7.8 mmol) of elemental sulfur, and 50 mg DDAB (without a solvent) was stirred at rt for 4 days, at which time no 12 was observed by ^{1}H-NMR. The brown liquid was washed with ammonium polysulfide to remove elemental sulfur and then treated as described above. GC analysis showed **13a** and **13b** (in a 1:1 ratio) as the only constituents. The mixture was chromatographed on silica with a hexane/ether mixture as the eluent. A 1:1 hexane/ether mixture eluted a fraction enriched with **13b**, which was purified by several crystallizations from hexane to afford 250 mg (1.4 mmol, 4%) of white crystals of **13b**: mp 67–8 °C; IR (Nujol) 1710 cm^{-1} (C═O); ^{1}H-NMR δ 3.46 (wide s, 1H), 2.70 (m, 3H), 2.40 (m, 3H), 1.43 and 1.37 (s, each 3H), 1.07 (d, J = 6.5 Hz, 3H) ppm; ^{13}C-NMR δ 209.2, 54.8, 52.5, 52.2, 49.6, 44.9, 41.1, 34.0, 27.1, 13.7 ppm; MS m/z 184 (36) [M]$^{\bullet+}$, 169 (6) [M − CH$_3$]$^+$, 115 (16) [C$_6$H$_{11}$S]$^+$, 113 (100) [C$_6$H$_9$S]$^+$. Anal. Calcd for C$_{10}$H$_{16}$OS: C, 65.17; H, 8.75; S, 17.40. Found: C, 65.10; H, 9.05; S, 17.10. A sample was analyzed by X-ray diffraction, and the structure is given in the supplementary material. The second, known isomer, **13a**, was identified by ^{1}H-NMR and GCMS: ^{1}H-NMR δ 3.46 (wide s, 1H), 2.70 (m, 3H), 2.40 (m, 3H), 1.43 (s, 6H), 1.18 (d, J = 7.4 Hz, 3H) ppm; MS identical to **13b**.

When the reaction was carried out at 0 °C with 3 mL (19 mmol) of 12, a red mass was formed after 30 min. This mass was washed twice with water and then mixed with hexane, and the white crystals which separated were filtered and dissolved in CH$_2$Cl$_2$. The solution was dried over MgSO$_4$, and evaporation gave 0.64 g (1.7 mmol 19%) of a white solid. Recrystallization from ethanol yielded 0.25 g of 14 as white needles: mp 153 °C; IR 1715 (C═O), 1650 (C═C) cm^{-1}; ^{1}H-NMR δ 4.82 (s, 2H), 4.76 (s, 2H), 3.46 (dd, J = 3.8, 8.5 Hz, 2H), 2.86 (m, 4H), 2.50 (m, 4H), 2.28 (ddd, J = 13.5, 12.5, 1.0 Hz, 2H), 1.97 (m, 2H) 1.77 (s, 6H), 1.17 (d, J = 7.0 Hz, 6H); ^{13}C-NMR δ 209.2, 146.6, 110.4, 55.7, 48.0, 45.8, 40.2, 34.5, 20.9, 12.6 ppm; mass spectrum m/z 366 (7) [M]$^{\bullet+}$, 216 (9) ["carvone + H$_2$S$_2$"]$^+$, 150 (14) [carvone]$^+$, 116 (100). Anal. Calcd for C$_{20}$H$_{30}$O$_2$S$_2$: C, 65.53; H, 8.25; S, 17.50. Found: C, 65.65; H, 8.21; S, 17.40.

Reaction of (*R*)-(−)-Carvone (12) with Sodium Polysulfide. The usual procedure at 70 °C for 36 h converted 42% of 12 to a 1:1 mixture of **13a** and **13b** (determined by GC). No products were obtained at rt.

Conversion of 14 to 13. A sample of 20 mg (0.05 mmol) of 14 was stirred in a PTC system containing 3 mL of toluene, 3 mL of ammonium polysulfide, 0.11 g (0.4 mmol) of elemental sulfur, and 10 mg of DDAB at rt for 24 h. The resulting brown mixture contained approximately 75% of **13a** and 25% of **13b** (determined by H-NMR). Neither 14 nor 12 was observed.

Acknowledgment. We wish to thank Prof. Johanan Blum, Prof. Yoel Sasson, and Prof. Saul Patai for their helpful comments and Dr. Shmuel Cohen for X-ray analysis.

Supplementary Material Available: ORTEP representations of **2a**, **9a**, and **13b** and additional experimental details (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.