5,5′-dithiobis(2-nitrobenzoic acid), Whitesides et al. (ref 24) found a single line with slope $\beta_{nuc} = 0.36$, whereas Wilson et al. (ref 35) found two parallel lines of slope $\beta_{nuc} = 0.48$ with the rates for aromatic thiols being about fivefold higher than those for aliphatic thiols of the same pK_a.
(42) For purposes of reference, some values of β_{nuc} for reactions of thiol anions follow: with acetaldehyde (ref 43), 0.1; with benzene oxide (ref 44) or ethylene oxide (ref 38), 0.2 and 0.3; with *p*-nitrothiophenyl acetate (ref 45), 0.27; with *p*-nitrophenyl acetate (ref 39), 0.38; with 5,5′-dithiobis(2-nitrobenzoic acid) (note 41), 0.36 or 0.48; with *N*-*p*-2-benzimidazolylphenylmaleimide (ref 46), 0.42; with acrylonitrile (ref 47), 0.45; with chloroacetamide (ref 37), ~1; with 1,2-dithiolane (ref 34), ~1.
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(51) I.e., $R^1SH + R^2SSCONHR \rightarrow R^1SSR^2 + COS + H_2NR$, with no $R^1SSCONHR$ formed. Note the close analogy of this result to the reported thiol-induced fragmentation of sulfenylthiocarbonates to give unsymmetrical disulfides: $R^1SH + R^2SSCOOCH_3 \rightarrow R^1SSR^2 + COS + CH_3OH$. See S. J. Brois, J. F. Pilot, and H. W. Barnum, *J. Am. Chem. Soc.*, **92**, 7629–7631 (1970).
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α-Ketoketene Dithioacetal Chemistry. 1. Alternate Modes of Lithium Aluminum Hydride Reduction. Regio- and Stereospecific vs. Reduction–Alkylation–Fragmentation

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Abstract: Two modes of lithium aluminum hydride reduction for α-ketoketene dithioacetals have been established. One pathway proceeds in a regio- and stereospecific manner illustrating for the first time that such reductions on acyclic α,β-unsaturated ketones can in fact be stereospecific. A second pathway arises when a steric interaction in an early intermediate forces the reaction to proceed through a reduction–alkylation–fragmentation mechanism. Lithium aluminum hydride reduction of 3,3-bis(methylthio)-1-phenylpropen-1-one (**5**) gave α-[2,2-bis(methylthio)ethyl]benzenemethanol (**8**) in 93% yield. The regio- and stereospecificity of the reduction of **5** was established by reduction with lithium aluminum deuteride which gave [α*S*(*S*)]-α-[2,2-bis(methylthio)ethyl-1-*d*]-benzenemethanol-α-*d* (**9**) in 92% yield. Analysis by ^1H NMR established the formation of a single diastereomer. Reduction of **5** with lithium aluminum hydride followed by quenching with DCl–D_2O gave α-[2,2-bis(methylthio)ethyl-2-*d*]benzenemethanol (**10**) in 90% yield thus establishing the presence of an organoaluminum intermediate in the reduction. Reduction of 3,3-bis(methylthio)-1-phenylpropen-1-one-2-*d* (**11**) with lithium aluminum hydride gave [α*S*(*R*)]-α-[2,2-bis(methylthio)ethyl-1-*d*]benzenemethanol (**12**) which had the opposite configuration at carbon-2 to that of **9**. In contrast to the above reductions, lithium aluminum hydride reduction of 1-phenyl-2-(1,3-thiolan-2-yl)ethanone (**13**) gave 2,2′-(2-phenyl-1,3-propanediylidene)bis(1,3-dithiolane) (**14**) and benzaldehyde (**15**). Reduction of **13** with lithium aluminum deuteride gave 2,2′-(2-phenyl-1,3-porpanediylidene-2-*d*)bis(1,3-dithiolane) (**21**) and deuteriobenzaldehyde (**22**). Lithium aluminum hydride reduction of 2-(1,3-dithan-2-ylidene)-1-phenylethanone (**23**) gave α-phenyl-1,3-dithane-2-ethanol (**24**) in 95% yield and reduction of **23** with lithium aluminum deuteride gave the corresponding α-phenyl-1,3-dithane-2-ethanol-2-*d* (**25**). The organoaluminum intermediate V, resulting from the reduction of **23**, was characterized by ^{13}C NMR and shown to be symmetrical.

Some 30 years ago, Nystrom and Brown[1] reported that lithium aluminum hydride (LAH) reduction of cinnamic acid (**1**) unexpectedly gave dihydrocinnamyl alcohol (**4**) (eq 1) rather than cinnamyl alcohol. This was to be the first of several reports[2] in which LAH reduction of acyclic α,β-unsaturated carbonyl compounds resulted in carbon–carbon double-bond

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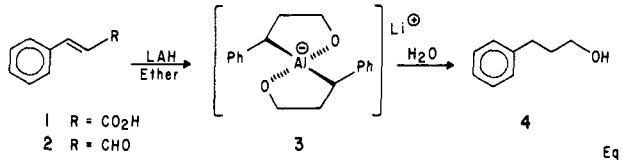


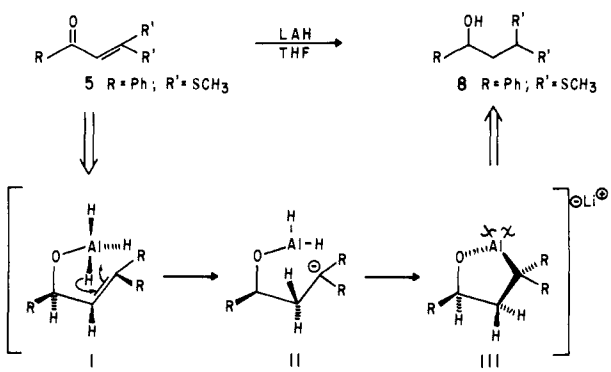
Eq I

reduction in addition to the expected carbonyl reduction. Hochstein and Brown[3] extended this reduction to cinnamaldehyde (**2**) and, through LAH reduction/deuterolysis and chemical transformation of the reduction product (**4**), were able to determine the sites of hydride addition. To explain their results, the novel cyclic organoaluminum compound **3** was suggested as an intermediate in the reaction.

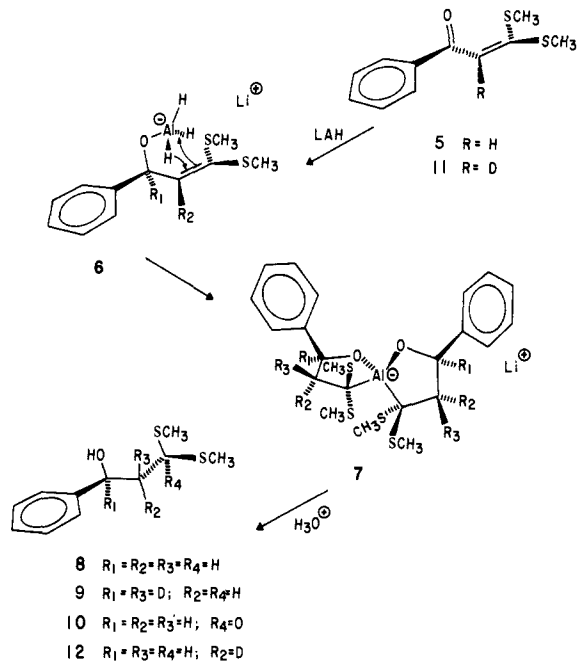
Since these initial reports, a number of studies have been conducted on both α,β-unsaturated carbonyl compounds as well as allylic alcohols to probe the stereochemistry and thus the mechanism of this type of hydride reduction. Results to date, although ambiguous, suggest that the LAH reduction of acyclic α,β-unsaturated carbonyl compounds is in fact a nonstereospecific process.[4] The ambiguities surrounding reductions of α,β-unsaturated ketones stems from the lack of a suitable system that will first undergo the required regiospecific carbonyl reduction and then proceed in a favorable manner to provide a product with unequivocal answers concerning stereochemistry. Reduction of allylic alcohols on the other hand has provided explicit details concerning the stereospecificity of double-bond reductions in such systems. Specifically, Bordon,[5a] and more recently Wong and Gray,[5b] has obtained results which clearly indicate that reduction of an allylic alcohol, in at least two cases, is a stereospecific process and likely proceeds via the as yet uncharacterized cyclic organoaluminum intermediate postulated by Hochstein and Brown.[3]

During the course of an investigation to explore the chemistry of α-ketoketene dithioacetals, it occurred to us that LAH reduction of **5** could conceivably result in the formation of a β-hydroxy dithioacetal **8** in which double-bond reduction as well as carbonyl reduction had taken place. The success of this investigation in fact rested on the likelyhood of **5** first undergoing a regiospecific carbonyl reduction and secondly giving a product suitable for stereochemical evaluation. While the steric and electronic factors that influence the course of the above reduction are not well defined.[1,2a,3,4a,b,6] there does appear to be a need for a substituent on the terminus (i.e., C-3) of the double bond that can stabilize the incipient negative charge that arises in going from I to III during the course of the reduction[7] (see Scheme I). α-Ketoketene dithioacetal **5** seemed to meet these requirements and in fact a sulfur stabilized intermediate such as III was reported during the course of this study by Wong and Gray.[5b] Should this reduction be successful, we would expect to generate the novel organometallic intermediate III which is similar to that postulated by Hochstein and Brown.[3] Protonolysis of intermediate III would give the β-hydroxy dithioacetal **8.** By conducting the reduction with LAD the stereospecificity of the reaction could easily be

Scheme I



Scheme II



analyzed by ^1H NMR since the methine proton at C-3 in **8** forms an ABX pattern where $J_{AX} \neq J_{BX}$. If the LAD reduction resulted in the collapse of only one of the couplings to the methine proton at C-3, we should see a single AX pattern reflecting the presence of a single diastereomer and thus a stereospecific process. If on the other hand, the LAD reduction results in the methine proton at C-3 remaining as an ABX pattern, we can conclude that we have a mixture of diastereomers, and thus a nonstereospecific process.

Data and Results

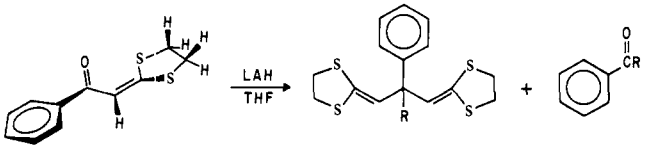
Reduction of α-ketoketene dithioacetal **5**[8] with LAH in tetrahydrofuran, followed by acid quench, gave a 93% yield of the β-hydroxy dithioacetal **8** as a clear oil (see Scheme II). The ^1H NMR of **8** contained doublet of doublets at δ 4.95 (J = 4.5, J = 8.5 Hz) corresponding to the C-1 proton and δ 3.80 (J = 6.5, J = 8.5 Hz) corresponding to the C-3 proton thereby confirming that reduction of this unsaturated system proceeded with carbonyl reduction along with carbon-carbon double-bond reduction. To determine the regio- and stereospecificity of this reduction, **5** was reduced with LAD under the same conditions as above. The LAD reduction gave the dideuterio-β-hydroxy dithioacetal **9** (92%) in which deuterium was incorporated at C-1 and C-2. This experiment indicated that the LAH reduction of α-ketoketene dithioacetal **5** proceeded by the same mechanism as the LAH reduction of cinnamic acid and cinnamaldehyde. The ^1H NMR of **9** contained a doublet at δ 3.80 (J = 8.5 Hz) corresponding to the C-3 proton and thus revealed that the reduction had indeed produced a single diastereomer since the 6.5-Hz coupling to the proton at C-3 was absent. Quenching the LAH reaction with 20% DCl/D_2O afforded the 3-deuterio-β-hydroxy dithioacetal **10** which contained the doublet of doublets at δ 4.95 (J = 4.5, J = 8.5 Hz) but lacked a signal for the C-3 proton. This latter reaction supports the presence of an organometallic species such as **7** and firmly establishes the reaction pathway (see Scheme II).

To complete the detailed stereochemical analysis of this mechanism and to further illustrate the potential use of this reduction for stereospecific isotope labeling, 3,3-bis(methylthio)-phenyl-2-propen-1-one-*2-d* (**11**) was reduced with LAH. This reduction produced the 2-deuterio-β-hydroxy dithioacetal **12** (92%) which contains the opposite configuration at C-2 to

that found in reduction product **9.** This change in configuration at C-2 resulted in a 6.5-Hz coupling to H_4 from H_3 rather than the 8.5-Hz coupling to H_4 from H_2 observed in **9.** The ^1H NMR of **12** also revealed an 8.5-Hz coupling to H_1 which is in complete accordance with the configurational relationship expected between C-1 and C-2 based on the mechanism outlined in Scheme II (see Figure 1).

This reduction can be viewed as proceeding first with 1,2-hydride addition across the carbonyl carbon to give the alkoxyaluminum hydride salt **6.** Intramolecular hydride transfer to C-2 followed by C-Al bond formation then generates the cyclic organometallic species which upon protonation gives rise to **8.** This intramolecular process (i.e., **6** → **7**), as well as the formation of the cyclic organometallic intermediate, is consistent with the stereospecific process observed. One would not expect complete stereospecificity to arise from a polymeric equivalent of **7** since hydride attack would be just as likely from either side of the double bond.

In contrast to **5,** reduction of 1-phenyl-2-(1,3-thiolan-2-yl)ethanone[9] (**13**) with LAH followed by acidic workup gave an ivory white solid which by thin layer chromatography was a mixture of two compounds. When this solid was washed with ether and filtered, a pure compound was isolated. The ether filtrate was reduced in volume in vacuo to give a light yellow oil which after chromatography afforded a clear, sweet smelling oil that was readily identified as benzaldehyde (**15**) by IR, ^1H NMR, and GC-MS (eq 2). The crystalline product



Eq 2

was assigned structure **14** based on the following spectral and analytical data. Bisketene dithioacetal **14** exhibited a strong olefinic absorption in the IR spectrum at 1600 cm^{-1} and had a λ_{max} (EtOH) in the UV at 246 nm (ϵ 2250). Combustion analysis [Anal. ($C_{15}H_{16}S_4$) C, H, S.] and mass spectral data (parent ion at *m/e* 324) suggested $C_{15}H_{16}S_4$ as the molecular formula. The ^1H NMR of **14** indicated that there were two magnetically equivalent vinyl protons at δ 5.66 (d, J = 9 Hz) which were coupled to an adjacent methine proton at δ 4.30 (t, J = 9 Hz). The presence of two $-S-CH_2-CH_2-S-$ groups in **14** at δ 3.32, thus also magnetically equivalent, suggested the symmetrical structure assigned to **14.** Further support for this structure was acquired from the proton decoupled ^{13}C NMR (see Experimental Section), which exhibited nine lines rather than the fifteen which would have been expected for an unsymmetrical molecule based on the molecular formula.

The mechanism of this reaction appears to begin with 1,2-hydride reduction just as was observed with **5** (see Scheme III). However, the alkoxyaluminum hydride salt **16,** which in the case of **5** (see Scheme I) underwent intramolecular double-bond reduction at C-2, is unable to follow this pathway owing to a serious steric interaction between the hydrogens on the thiolane ring and the aluminum hydride moiety. Apparently this steric interaction prevents the alkoxyaluminum hydride component from achieving suitable positioning with respect to the double bond for hydride delivery. Alternatively, **16** undergoes subsequent 1,2-hydride reductions to give the tetraalkoxyaluminum intermediate **17.** Intermediate **17** is now capable of undergoing a sulfur-assisted intramolecular alkylation to give **18** which undergoes further reaction to give the tetraalkoxy intermediate **19.** Hydrolysis of **19** likely leads to the unstable diol **20** which would be expected to readily undergo acid-catalyzed fragmentation to give **14** and **15.**[10,11]

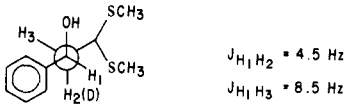
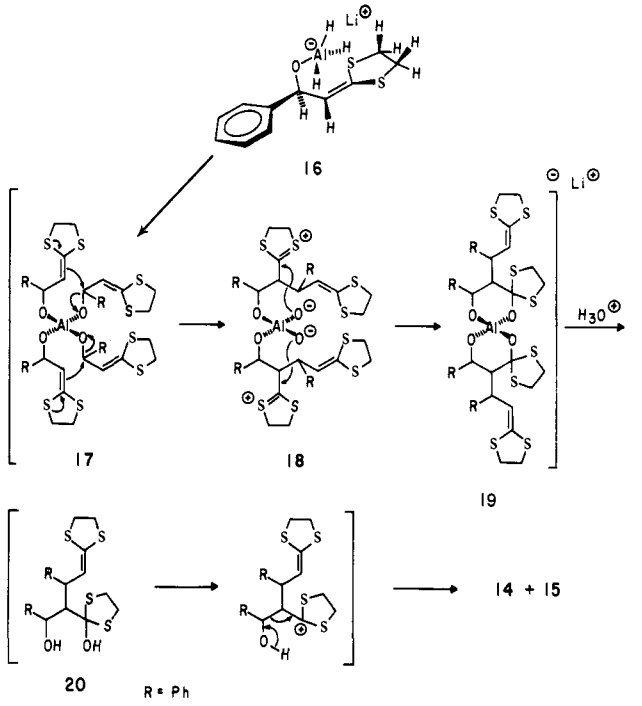


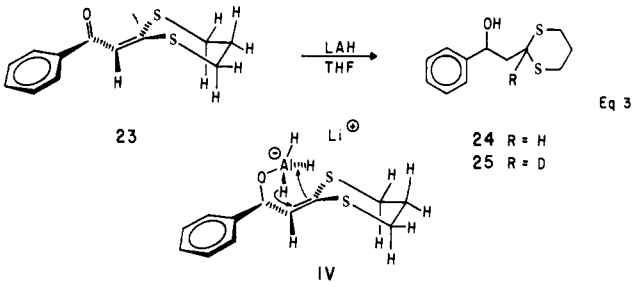
Figure 1.

Scheme III



Reduction of **13** with LAD gave the deuterated products **21** and **22.** The positioning of deuterium in these compounds is consistent with the mechanism outlined in Scheme III. Furthermore, reduction of **13** with 0.5 molar equiv of LAH or 1.0 molar equiv of sodium bis(2-methoxyethoxy)aluminum hydride gave complete conversion of **13** into **14** and **15** and thus supports the presence of the tetraalkoxyaluminum intermediate **17.**

To support our steric argument, we reduced α-ketoketene dithioacetal **23.**[12] Molecular models indicated that the steric interaction that had altered the reaction pathway in the case of **13** should not play a critical role (see IV) in reduction of **23.** Reduction of **23** with LAH gave **24**[13] (eq 3) in 95% yield and



Eq 3

therefore fully supported our argument. Quenching this reduction with 20% DCl/D_2O gave the C-3 deuterio product **25** which confirmed that the reduction of **5** and **23** proceeded by the same mechanism.

^{13}C NMR Observation of the Organoaluminum Intermediate. Direct observation and characterization of the cyclic organometallic intermediate (i.e., III) involved in this reduction has been attempted by ^1H NMR but was unsuccessful.[4a] We have successfully recorded the ^{13}C NMR of intermediate V (Figure 2) by conducting the reduction of **23** (LAH, 0.5 molar equiv, THF-d_8, 16 h) in a 10-mm NMR tube. As shown in Figure 2,

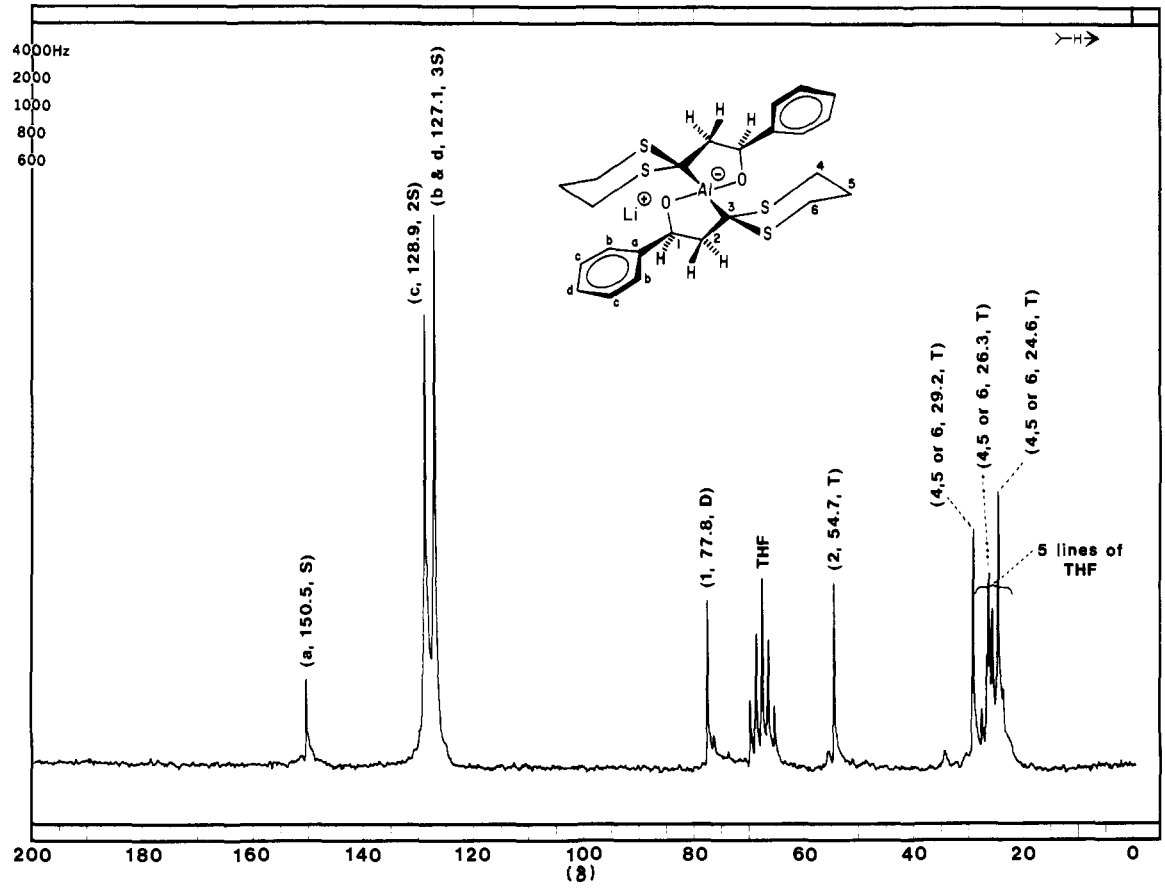


Figure 2. ^{13}C NMR spectrum of organoaluminum intermediate V. The center line of the quintet of the CD_2 in THF-d_8 was used as the internal reference and set to 67.9 ppm relative to Me_4Si. Multiplicities in the off-resonance decoupled spectra: s = singlet, d = doublet, t = triplet, q = quartet.

we observed nine of the expected ten lines in the proton decoupled spectrum of this symmetrical intermediate. The para carbon of the aromatic ring appeared as a shoulder on the ortho carbon line at 127.1 ppm. The absence of the carbon bonded directly to the aluminum atom (i.e., C-3) was not surprising and is likely a result of line broadening due to the nonpolar nature of THF.[14] In the coupled spectrum of V the C-H at C-1 appeared as a doublet (J_{C-H} = 143 Hz) with slight broadening due to the ortho protons of the aromatic ring while the CH_2 at C-2 appeared as a triplet (J_{C-H} = 128 Hz).

Conclusion

LAH reduction of α-ketoketene dithioacetals can proceed via a regio- and stereospecific mechanism to give β-hydroxy dithioacetals in high yield thus providing the first example of a stereospecific reduction of an α,β-unsaturated carbonyl compound. Utilizing LAD and/or deuterated starting materials provides quick access to a variety of stereospecifically labeled compounds. These reductions proceed through the symmetrical cyclic organoaluminum intermediate, characterized herein for the first time, which was postulated by Hochstein and Brown.

In certain other cases, because of unfavorable steric interactions a reduction-alkylation-fragmentation pathway results. Both mechanisms, the regio- and stereospecific and reduction-alkylation-fragmentation, begin via a regiospecific carbonyl reduction. The presence or absence of steric interactions in the resulting alkoxyaluminum hydride salt determines the course of the reaction.

Experimental Section

General. Mass spectra, infrared spectra, ultaviolet spectra, and combustion analysis were obtained by The Physical and Analytical Chemistry Department of The Upjohn Co. ^1H NMR spectra were obtained at 60 MHz in chloroform-*d* solutions containing tetramethylsilane as an internal standard. ^{13}C NMR spectra were obtained at 20 MHz on a Varian CFT-20 instrument in either chloroform-*d* or dimethyl sulfoxide-d_6 with tetramethylsilane as an internal standard. Infrared spectra were obtained on a Perkin-Elmer 197 spectrophotometer as mulls or neat liquids. Combustion analyses were also obtained from Micro-Analysis, Inc., Wilmington, Del. Thin-layer chromatography (TLC) was conducted by using Merck glass plates precoated with silica gel 60 F-254. The TLC plates were visualized by UV light or iodine. Column chromatography was conducted at medium pressure utilizing silica gel 60 (E. Merck, 230–400 mesh). All solvents for chromatography were reagent grade distilled in glass (Burdick and Jackson). All reductions described herein were conducted under an atmosphere of nitrogen with freshly distilled tetrahydrofuran (from LAH) in flamed glassware. The lithium aluminum hydride was purchased from Ventron (Alfa Division) and used as received. Lithium aluminum deuteride was purchased from Aldrich Chemical Co. All melting points are uncorrected. GC–MS was preformed on a Hewlett-Packard 5990A-5992A system. A 4-ft 3% Se-30 stainless steel column was used. All reductions were performed in the same manner and a representative experiment is given for the reduction of **5**.

3,3-Bis(methylthio)-1-phenylpropen-1-one (5). This compound was prepared by the method of Shahak and Sasson[8] in 55% yield and had the following spectral and analytical properties: mp 92.5–94 °C; IR (mull) 1625, 1610, 1595, 1570, 1495, 1475, 1235, 1060, 805, 760, 695 cm^{-1}; UV (EtOH) λ_{max} (ϵ) 220 (sh, 5350), 263 (7900), 279 (8250), 344 (19 050); ^1H NMR ($CDCl_3$, δ) 7.80–8.05 (m, 2 H, aromatic), 7.31–7.52 (m, 3 H, aromatic), 6.73 (s, 1 H, vinyl proton), 2.47 (s, 3 H, $-SCH_3$), 2.42 (s, 3 H, $-SCH_3$); mass spectrum, ions at *m/e* (rel intensity), 224 (24), 209 (56), 207 (24), 163 (15), 147 (10), 105 (100), 75 (12), 51 (29), 45 (9); ^{13}C NMR ($CDCl_3$, ppm) 185.10, 166.24, 139.21, 131.59, 128.37, 127.59, 109.31, 17.22, 14.88. Anal. ($C_{11}H_{12}OS_2$) C, H, S.

α-[2,2-Bis(methylthio)ethyl]benzenemethanol (8). A solution of 3,3-bis(methylthio)-1-phenylpropen-1-one (**5**, 2.24 g, 10 mmol) in THF (20 mL, freshly distilled from LAH) was added dropwise to a

suspension of LAH (380 mg, 10 mmol) in THF (50 mL) during the course of 5 min with stirring and under a blanket of nitrogen. The reaction was stirred at room temperature for 1.5 h and then carefully quenched by addition of ice. The reaction was further diluted with 2 N HCl (100 mL) and ethyl ether (100 mL). The ether layer was separated and the aqueous layer back-extracted with ether (2 × 75 mL). The combined organic extracts were dried ($MgSO_4$) and solvent was removed in vacuo to give 2.25 g of an almost colorless oil. This oil was chromatographed over 250 g of LC silica gel packed in 25% EtOAc–hexane. The column afforded 2.12 g (93%) of **8:** IR (neat) 3420, 1605, 1495, 1455, 1435, 1420, 1055, 760, 700 cm^{-1}; ^1H NMR ($CDCl_3$, δ) 7.33 (s, 5 H, aromatic), 4.95 (dd, 1 H, J = 4.5, J = 8.5 Hz, $ArCH(OH)CH_2$), 3.83 (dd, 1 H, J = 6.5, J = 8.5 Hz, $-CH_2CH(SCH_3)_2$), 3.60 (s, 1 H, exchanges with D_2O, -OH), 2.08 (m, 8 H, $-CH_2-$, $-SCH_3$); mass spectrum, ions at *m/e* (rel intensity) 228 (2), 180 (42), 133 (15), 107 (100), 105 (16), 79 (60), 77 (46), 75 (58), 74 (19), 51 (10), 45 (9); ^{13}C NMR ($CDCl_3$, ppm) 143.81, 128.33, 127.45, 125.69, 71.71, 50.98, 43.54, 12.47, 11.96. Calcd for $C_{11}H_{16}OS_2$: *m/e* (P) 228.0636. Found: *m/e* 228.0642. Anal. ($C_{11}H_{16}OS_2$) C, H, S.

[αS(S)]-α-[2,2-Bis(methylthio)ethyl-*1-d*]benzenemethanol-α-*d* (9). Compound **9** was reduced (LAD) and isolated in the same manner as described for **8** in 92% yield and had the following spectral and analytical properties: IR (neat) 3410, 1605, 1495, 1455, 1435, 760, 705 cm^{-1}; ^1H NMR ($CDCl_3$, δ) 7.33 (s, 5 H, aromatic), 3.83 (d, 1 H, J = 8.5 Hz $-CHDCH(SCH_3)_2$), 2.80 (s, 1 H, exchanges with D_2O, -OH), 2.10 (m, 7 H, -CHD-, $-SCH_3$); mass spectrum, ions at *m/e* (rel intensity) 230 (9), 181 (41), 134 (15), 108 (100), 80 (43), 78 (14), 77 (13), 76 (58), 75 (14), 43 (22). Calcd for $C_{11}H_{14}D_2OS_2$: *m/e* (P) 230.0772. Found: *m/e* 230.0768. Anal. ($C_{11}H_{14}D_2OS_2$) C, H, D, S.

α-[2,2-Bis(methylthio)ethyl-*2-d*]benzenemethanol (10). Compound **10** was obtained in 90% yield by LAH reduction of **5** followed by quenching with 20% DCl/D_2O. Workup and isolation follows that of compound **8.** Compound **10** had the following spectral and analytical properties: IR (neat) 3420, 1605, 1495, 1435, 1420, 760 cm^{-1}; ^1H NMR ($CDCl_3$, δ) 7.33 (s, 5 H, aromatic), 4.95 (dd, 1 H, J = 4.5, J = 8.5 Hz, $ArCH(OH)CH_2$), 2.55 (s, 1 H, exchanges with D_2O, OH), 2.10 (m, 8 H, $-CH_2-$, $-SCH_3$); mass spectrum, ions at *m/e* (rel intensity) 229 (8), 182 (12), 181 (74), 134 (26), 116 (15), 107 (100), 105 (17), 79 (48), 77 (24), 76 (81), 75 (22). Calcd for $C_{11}H_{15}DOS_2$: *m/e* (P) 229.0719. Found: *m/e* 229.0705. Anal. ($C_{11}H_{15}DOS_2$) C, H, D, S.

3,3-Bis(methylthio)-1-phenylpropen-1-one-*2-d* (11). Compound **11** was prepared from acetophenone-d_3 following the procedure of Shahak and Sasson[8] in 56% yield and had the following spectral and analytical properties: IR (mull) 1625, 1610, 1595, 1570, 1495, 1475, 1235, 1060, 805, 760, 695 cm^{-1}; ^1H NMR ($CDCl_3$, δ) 7.80–8.05 (m, 2 H, aromatic), 7.31–7.52 (m, 3 H, aromatic), 2.47 (s, 3 H, $-SCH_3$), 2.42 (s, 3 H, $-SCH_3$); mass spectrum, ions at *m/e* (rel intensity) 225 (26), 210 (75), 208 (37), 164 (16), 148 (11), 105 (100), 77 (53), 75 (10), 51 (16). Calcd for $C_{11}H_{11}DOS_2$: *m/e* (P) 225.0396. Found: *m/e* 225.0392. Anal. ($C_{11}H_{11}DOS_2$) C, H, D, S.

[αS(R)]-α-[2,2-Bis(methylthio)ethyl-*1-d*]benzenemethanol (12). Compound **12** was obtained in 92% yield by LAH reduction of **11** as described for reduction of **5.** Compound **12** had the following spectral and analytical properties: IR (neat) 3420, 1605, 1595, 1435, 1420, 760 cm^{-1}; ^1H NMR ($CDCl_3$, δ) 7.33 (s, 5 H, aromatic), 4.95 (d, 1 H, J = 8.5 Hz, $ArCH(OH)CHD-$), 3.83 (d, 1 H, J = 6.5 Hz, $-CHDCH(SCH_3)_2$), 2.68 (s, 1 H, exchanges with D_2O, -OH), 2.10 (m, 7 H, $-CHD-$, SCH_3); mass spectrum, ions at *m/e* (rel intensity) 229 (8), 182 (10), 181 (62), 134 (21), 107 (100), 105 (13), 79 (34), 77 (19), 76 (68), 75 (15). Calcd for $C_{11}H_{15}DOS_2$: *m/e* (P) 229.0719. Found: *m/e* 229.0705. Anal. ($C_{11}H_{15}DOS_2$), C, H, D, S.

2-(1,3-Dithiolan-2-ylidene)-1-phenylethanone (13). Compound **13** was prepared by the method of Shahak and Sasson[8] in 50% yield and had the following spectral and analytical properties: mp 80–81 °C (lit. mp 81 °C[9]); IR (mull) 1610, 1595, 1575, 1495, 1475, 1255, 1230, 1050, 765, 695 cm^{-1}; UV (EtOH) λ_{max} (ε) 214 (sh, 7000), 221 (sh, 5600), 259 (8100), 288 (5850), 345 (21 650); ^1H NMR ($CDCl_3$, δ) 7.28–8.08 (m, 2 H, aromatic), 7.34 (s, 1 H, vinyl proton), 7.35–7.60 (m, 3 H, aromatic), 3.40 (s, 4 H, $-SCH_2CH_2S-$); ^{13}C NMR ($CDCl_3$, ppm) 185.89, 168.08, 138.27, 131.96, 128.45, 127.78, 108.26, 38.89, 35.40; mass spectrum, ions at *m/e* (rel intensity) 222 (100), 194 (63), 145 (17), 110 (37), 105 (37), 89 (11), 85 (36), 77 (41). Anal. ($C_{11}H_{10}OS_2$) C, H, S.

2,2′-(2-Phenyl-1,3-propanediylidene)bis(1,3-dithiolane) (14). A solution of 2-(1,3-dithiolan-2-ylidene)-1-phenylethanone (**13,** 4.44 g, 20 mmol) in THF (30 mL) was added dropwise to a suspension of LAH (760 mg, 20 mmol) during the course of 15 min with stirring under a blanket of nitrogen. The reaction was stirred a total of 2 h at room temperature. The reaction was carefully quenched with ice and then further diluted with 2 N HCl (50 mL) and ethyl ether (50 mL). The organic layer was then separated and the aqueous layer back-extracted with ether (2 × 75 mL). The combined organic extracts were dried ($MgSO_4$) and solvent was removed in vacuo to give an almost white sweet smelling solid. This solid was thoroughly washed with ether (2 × 50 mL) and filtered to give 2.63 g (81%) of **14:** mp 185–186 °C; IR (mull) 1600, 1580, 1490, 1280, 830, 755, 695 cm^{-1}; UV (EtOH) λ_{max} (ε) 211 (2150), 246 (2250), 254 (2200, 257 (sh, 2150), 265 (sh, 1850), 269 (sh, 1450), 359 (314); ^1H NMR ($CDCl_3$, δ) 7.23 (s, 5 H, aromatic), 5.66 (d, 2 H, J = 9 Hz, vinyl protons), 4.30 (t, 1 H, J = 9 Hz, methine proton), 3.32 (s, 8 H, $-SCH_2CH_2S-$); ^{13}C NMR (Me_2SO-d_6, ppm) 142.89, 137.10, 128.50, 127.26, 126.40, 117.41, 53.23, 38.28, 37.08; mass spectrum, ions at *m/e* (rel intensity) 324 (100), 296 (9), 267 (2), 263 (17), 232 (41), 220 (50), 192 (80), 147 (66), 105 (59). Anal. ($C_{15}H_{16}S_4$) C, H, S. The ether filtrate was reduced in volume in vacuo to give a sweet smelling oil which after chromatography over 20 g of silica gel (25% EtOAc–hexane) gave 520 mg (98%) of benzaldehyde **15:** IR (neat) 3050, 2800, 2730, 1700, 1600, 1590, 1450, 1390, 1310, 1210, 1160, 740 cm^{-1}; ^1H NMR ($CDCl_3$, δ) 7.3–8.0 (m, 5 H, aromatic), 10.1 (s, 1 H, aldehyde proton); mass spectrum, ions at *m/e* (rel intensity) 107 (8), 106 (100), 105 (95), 78 (17), 77 (82), 74 (12), 51 (33).

2,2′-(2-Phenyl-1,3-propanediylidene-*2-d*)bis(1,3-dithiolane) (21). 2-(1,3-Dithiolan-2-ylidene)phenylethanone (**13,** 4.44 g, 20 mmol) was reduced with LAD (840 mg, 20 mmol) as described above. This reduction afforded 2.47 g (76%) of **21:** IR (mull) 3000, 2920, 1600, 1580, 1485, 1420, 1280, 920, 840 cm^{-1}; ^1H NMR ($CDCl_3$, δ) 7.23 (s, 5 H, aromatic), 5.66 (s, 2 H, vinyl protons), 3.32 (s, 8 H, $-SCH_2CH_2S-$); ^{13}C NMR (Me_2SO-d_6, ppm) same as that of **14** except the signal at 52.23 ppm was absent; mass spectrum, ions at *m/e* (rel intensity) 325 (57), 297 (6), 264 (10), 233 (43), 221 (53), 193 (100), 148 (98), 121 (23), 116 (61), 106 (32), 105 (61), 104 (28). Calcd for $C_{15}H_{15}DS_4$: *m/e* (P) 325.0197. Found: *m/e* 325.0204. Also isolated from this reaction was 500 mg (94%) of **22:** IR (neat) 3050, 2920, 2100, 2050, 1695, 1600, 1590, 1450, 1310, 1230, 1210, 790, 730 cm^{-1}; ^1H NMR ($CDCl_3$, δ) 7.20–8.00 (m, 5 H, aromatic); mass spectrum, ions at *m/e* (rel intensity) 108 (8), 107 (93), 106 (8), 105 (100), 79 (20), 78 (15), 77 (72), 51 (38).

2-(1,3-Dithian-2-ylidene)-1-phenylethanone (23). Compound **23** was prepared by the method of Shahak and Sasson[8] in 47% yield and had the following spectral and analytical properties: mp 52–54 °C (lit. 51–53 °C[12]); IR (mull) 1620, 1615, 1595, 1575, 1500, 1490, 1225, 780, 705, 695 cm^{-1}; UV (EtOH) λ_{max} (ε) 215 (sh, 7000), 260 (7400), 280 (sh, 5500), 353 (20 600); ^1H NMR ($CDCl_3$, δ) 7.9 (m, 2 H, aromatic), 7.42 (m, 3 H, aromatic), 7.29 (s, 1 H, vinyl proton), 2.95 (m, 4 H, $-CH_2S-$), 2.28 (m, 2 H, $-CH_2-$); mass spectrum, ions at *m/e* (rel intensity) 236 (78), 189 (15), 159 (71), 105 (100), 85 (20), 77 (62). Anal. ($C_{12}H_{12}OS_2$) C, H, S.

α-Phenyl-1,3-dithane-2-ethanol (24). Compound **24** was obtained in 95% yield by LAH reduction of 2-(1,3-dithan-2-ylidene)-1-phenylethanone (**23**) in the manner previously described. Compound **24** had the following spectral and analytical properties: mp 85–87 °C; IR (mull) 3400, 2930, 2900, 1600, 1495, 1450, 1420, 1280, 1050, 905, 910, 765, 710 cm^{-1}; UV (EtOH) λ_{max} (ε) 205 (11 800), 208 (sh, 11 350), 248 (922), 251 (924); ^1H NMR ($CDCl_3$, δ) 7.33 (s, 5 H, aromatic), 4.96 (dd, 1 H, J = 4.5, J = 8.5 Hz, $ArCH(OH)CH_2-$), 3.26 (dd, 1 H, J = 6.5, J = 8.5 Hz, $CH_2CH(SCH_2)_2CH_2$), 2.84 (m, 4 H, $-SCH_2CH_2CH_2S-$), 2.50 (s, 1 H, exchanges with D_2O, -OH), 2.10 (m, 4 H, alphatic); mass spectrum, ions at *m/e* (rel intensity) 240 (80), 222 (79), 134 (22), 133 (100), 119 (47), 107 (56), 106 (29), 105 (33), 79 (63), 77 (53). Calcd for $C_{12}H_{16}OS_2$: *m/e* (P) 240.0642. Found: *m/e* 240.0647. Anal. ($C_{12}H_{16}OS_2$) C, H, S.

α-Phenyl-1,3-dithane-2-ethanol-*2-d* (25). Compound **25** was prepared in the same manner as **24** except the reaction was quenched with 20% DCl/D_2O: IR (mull) 3400, 2170, 1600, 1495, 1055, 910, 760, 705 cm^{-1}; ^1H NMR ($CDCl_3$, δ) 7.33 (s, 5 H, aromatic), 4.96 (dd, 1 H, J = 4.5, J = 8.5 Hz, $ArCH(OH)CH_2$), 2.84 (m, 4 H, $(-SCH_2)_2CH_2$) 2.10 (m, 4 H, aliphatic); mass spectrum, ions at *m/e* (rel intensity) 241 (52), 222 (39), 147 (22), 135 (58), 134 (100), 120 (54), 108 (54), 106 (63), 105 (44), 77 (44). Calcd for $C_{12}H_{15}DOS_2$:

m/e (P) 241.0705. Found: *m/e* 241.0708. Anal. ($C_{12}H_{15}DOS_2$) C, H, D, S.

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Electron Transfer Induced Isomerization of *cis*-4,4′-Diphenylstilbene into Its Trans Form

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Abstract: The 4,4′-diphenylstilbenes, denoted by C and T for the cis and trans isomers, as well as $T^{-}\cdot$ and T^{2-}, were characterized spectroscopically and electrochemically. The disproportionation $2T^{-}\cdot,Na^{+} \rightleftarrows T + T^{2-},2Na^{+}$ has equilibrium constant in THF 0.04, $\Delta H = 18.2$ kcal/mol, and $\Delta S = 54$ cal/mol·deg, and its rate constant is 9.0×10^{8} M^{-1} s^{-1}. The cis–trans isomerization was studied in THF at ambient temperature in three systems: $T + T^{-}\cdot,Na^{+} + C$, $T^{2-},2Na^{+} + C$, and $B^{-}\cdot,Na^{+} + C$, B denoting biphenyl. In the first two systems the reaction is governed by the three interrelated equilibria, namely, $C + T^{-}\cdot,Na^{+} \rightleftarrows T + C^{-}\cdot,Na^{+}$ (K_1), $C + T^{2-},2Na^{+} \rightleftarrows C^{-}\cdot,Na^{+} + T^{-}\cdot,Na^{+}$, ($K_2 = K_1/K_{dispr}$), and $2T^{-}\cdot,Na^{+} \rightleftarrows T + T^{2-},2Na^{+}$ (K_{dispr}), the rate-determining step being $C^{-}\cdot,Na^{+} \rightarrow T^{-}\cdot,Na^{+}$ (k_i). The results give k_iK_1 or k_iK_2. In the last system the rapid electron transfer $B^{-}\cdot,Na^{+} + C \rightarrow B + C^{-}\cdot,Na^{+}$ produces momentarily high concentration of $C^{-}\cdot,Na^{+}$ and, since its disproportionation is favored, a relatively large amount of $C^{2-},2Na^{+}$. The latter rapidly isomerizes into $T^{2-},2Na^{+}$. Thus, in early stages of the reaction, the concentration of $T^{2-},2Na^{+}$ exceeds that expected for the disproportionation equilibrium had the reaction with $B^{-}\cdot,Na^{+}$ formed only $C^{-}\cdot,Na^{+}$ and then $T^{-}\cdot,Na^{+}$. This observation provides the evidence for the existence of $C^{2-},2Na^{+}$.

Several routes lead to conversion of *cis*-stilbene to its trans isomer. A direct thermal reaction is too slow to be observed at ambient temperature; it was studied[2a,b] at elevated temperatures exceeding 300 °C. Photoisomerization was extensively investigated;[2c,d] it leads to photostationary state. In a recent series of papers[3] we reported an isomerization process catalyzed by electron transfer. Reduction of *cis*-stilbene to its radical anion or dianion is followed by their spontaneous isomerization to the respective radical anion or dianion of *trans*-stilbene. Electron transfer from the latter to the unreduced *cis*-stilbene generates the original cis radical anions or dianions and continues the process.

Spontaneous isomerization of *cis*-stilbene radical anions, or their ion pairs, is slow, whereas the dianions, or their aggregates with cations, isomerize rapidly. Which of these two contributes more to the overall isomerization depends on the extent of disproportionation, 2 *cis*-stilbene$^{-}\cdot \rightleftarrows$ *cis*-stilbene + *cis*-stilbene^{2-}. For example, in hexamethylphosphoric triamide the radical anions are not associated with cations and the disproportionation constant is very low. Thus, virtually all the isomerization proceeds via radical anions. In contrast, in THF the radical anions are coupled with cations into ion pairs and the disproportionation constant is high. Under these conditions the dianions are the intermediates responsible for the isomerization.

We extended these studies to a derivative of stilbene, namely, the *p,p′*-diphenylstilbenes. Our results revealed again that isomerization of *cis*-*p,p′*-diphenylstilbene (C) may be induced by the radical anions or dianions of *trans*-*p,p′*-diphenylstilbene (T). Three equilibria are maintained in this system:

$$T^{-}\cdot,Na^{+} + C \rightleftarrows T + C^{-}\cdot,Na^{+}$$

$$T^{2-},2Na^{+} + C \rightleftarrows T^{-}\cdot,Na^{+} + C^{-}\cdot,Na^{+}$$

$$2T^{-}\cdot,Na^{+} \rightleftarrows T + T^{2-},2Na^{+}$$

A more powerful reducing agent, viz., sodium biphenylide, $B^{-}\cdot,Na^{+}$, converts some C into $C^{2-},2Na^{+}$, and then the spontaneous reaction

$$C^{2-},2Na^{+} \rightarrow T^{2-},2Na^{+}$$

produces $T^{2-},2Na^{+}$ in excess of what would be expected in disproportionation of equivalent amounts of $T^{-}\cdot,Na^{+}$.

The distinction between $C^{2-},2Na^{+}$ and $T^{2-},2Na^{+}$ is not required to account for that result. In fact, $C^{2-},2Na^{+}$ may be identical with $T^{2-},2Na^{+}$

Reagents and Their Characterization

trans-4,4′-Diphenylstilbene, subsequently referred to as T, was acquired commercially. The purchased material was

0002-7863/80/1502-3100$01.00/0