the failure to isolate a ring cleavage product from norbornanone under similar conditions.[11]

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References and Notes

(1) (a) M. Braun, R. Dammann, and D. Seebach, *Chem. Ber.*, **108,** 2368 (1975); (b) A. Sidani, J. Marchand-Brynaert, and L. Ghosez, *Angew. Chem., Int. Ed. Engl.*, **13,** 267 (1974); (c) W. T. Brady and G. A. Scherubel, *J. Am. Chem. Soc.*, **95,** 7447 (1973); (d) L. Ghosez, R. Montaigne, A. Roussel, H. Vanlierde, and P. Mollet, *Tetrahedron,* **27,** 615 (1971); (e) M. Rey, S. Roberts, A. Dieffenbacher, and A. S. Dreiding, *Helv. Chim. Acta,* **53,** 417 (1970).

(2) (a) B. M. Trost, D. E. Keeley, and M. J. Bogdanowicz, *J. Am. Chem. Soc.*, **95,** 3068 (1973); (b) B. M. Trost and D. E. Keeley, *ibid.*, **96,** 1252 (1974); (c) B. M. Trost and M. J. Bogdanowicz, *ibid.*, **95,** 5321 (1973).

(3) (a) J. E. Baldwin, G. A. Höfle, and D. W. Lever, Jr., *J. Am. Chem. Soc.*, **96,** 7125 (1974); (b) J. R. Wiseman and H. F. Chan, *ibid.*, **92,** 4749 (1970); (c) J. K. Crandall and D. R. Paulson, *J. Org. Chem.*, **33,** 991, 3291 (1968).

(4) For reviews see B. M. Trost, *Acc. Chem. Res.*, **7,** 85 (1974); B. M. Trost, *Fortschr. Chem. Forsch.*, **41,** 1 (1973); D. Seebach in "Methodender Organischen Chemie (Houben-Weyl-Müller)", Band 1v/4, Georg Thieme, Stuttgart, 1971.

(5) (a) B. M. Trost, M. J. Bogdanowicz and J. Kern, *J. Am. Chem. Soc.*, **97,** 2218 (1975); (b) B. M. Trost, M. Preckel, and L. M. Leichter, *ibid.*, **97,** 2224 (1975).

(6) B. M. Trost and T. N. Salzmann, *J. Am. Chem. Soc.*, **95,** 6840 (1973); B. M. Trost, T. N. Salzmann, and K. Hiroi, *ibid.*, in press.

(7) Also see E. Cossement, R. Biname, and L. Ghosez, *Tetrahedron Lett.*, 997 (1974).

(8) To a solution of 10.0 g (66.7 mmol) of 7-methylspiro[3.5]non-5-en-1-one in 500 ml of methanol was added 40 g (183 mmol) of diphenyl disulfide and 10 g (183 mmol) of sodium methoxide. Reflux continued until TLC analysis utilizing benzene as eluting solvent indicated the absence of starting material (R_f ~0.6) and the presence of product (R_f ~0.7). The time was normally about 5 days. The reaction was cooled and washed with three portions of aqueous sodium chloride solution. The ether layer was dried and evaporated in vacuo to give the crude product. Chromatography on silica gel eluting with benzene purified the ring cleaved product. In one run, beginning with 150 mg (1.0 mmol) of this cyclobutanone, 870 mg (4.0 mmol) of diphenyl disulfide, and 160 mg (3.0 mmol) of sodium methoxide in 10 ml of methanol gave 320 mg (80%) of pure 3-carbomethoxy-3-[2′,2′-bis(phenylthioethyl)]-6-methylcyclohex-1-ene. In the large-scale reaction, the crude thioacetal was dissolved in 400 ml of methanol containing 20 g of iodine and refluxed for 1.5 h. The solution was diluted with ether and washed with two portions of saturated aqueous sodium thiosulfate solution, two portions of saturated aqueous sodium bicarbonate solution, and one portion of saturated aqueous sodium chloride solution. After drying and evaporation in vacuo, the oil was distilled at 110–112 °C (0.3 mm) to give 10 g (62%) of pure 3-carbomethoxy-3-[2′,2′-bis(methoxyethyl)]-6-methylcyclohex-1-ene.

(9) T. Cohen, D. Kuhn, and J. R. Falck, *J. Am. Chem. Soc.*, **97,** 4749 (1975); S. Yamamoto, M. Shiono, and T. Mukaiyama, *Chem. Lett.*, 961 (1973); T. Mukaiyama, K. Narasaka, and M. Furusato, *J. Am. Chem. Soc.*, **94,** 8641 (1972); E. J. Corey and D. Seebach, *J. Org. Chem.*, **31,** 4097 (1966).

(10) T. Cohen, G. Herman, J. R. Falck, and A. J. Mura, Jr., *J. Org. Chem.*, **40,** 812 (1975).

(11) For cleavage of α-bissulfenylated cycloalkanones of ring sizes larger than four, see J. A. Marshall and D. E. Seitz, *J. Org. Chem.*, **40,** 534 (1975).

Barry M. Trost,* James H. Rigby
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

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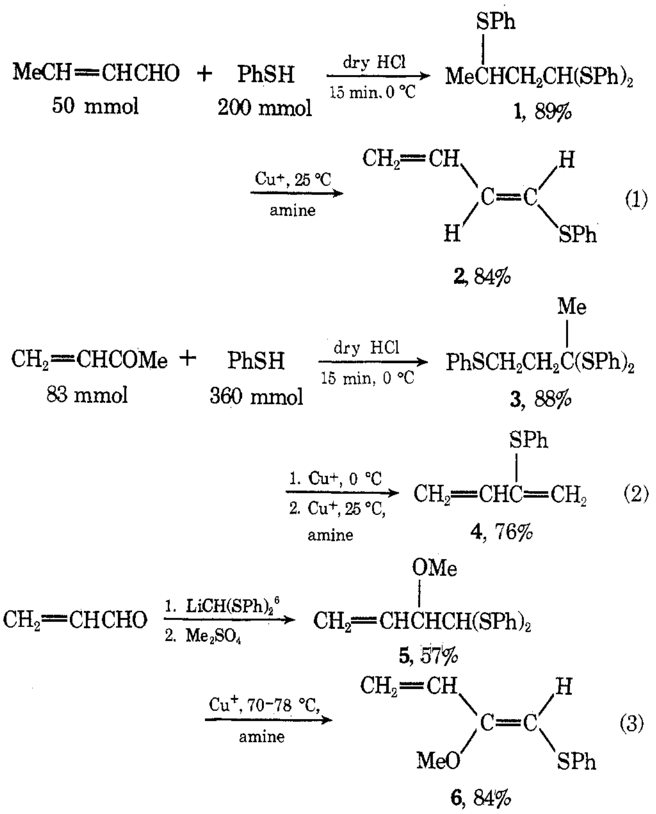
Removal of Sulfur Groups from Molecules by Copper(I). Preparation of Sulfur-Substituted 1,3-Dienes for the Diels–Alder Reaction[1]

Summary: The elimination of thiophenol by copper(I) from readily prepared precursors leads in good yield to several useful phenylthio-subtituted Diels–Alder dienes including (*Z*)-1-phenylthio-2-methoxy-1,3-butadiene which yields a *m*-methoxy adduct with methyl vinyl ketone.

Sir: We wish to report a simple procedure for the preparation of 1,3-dienes which are substituted by phenylthio groups. Because of the great versatility of sulfur in organic compounds, the Diels–Alder adducts of these dienes should be of considerable value in synthesis.

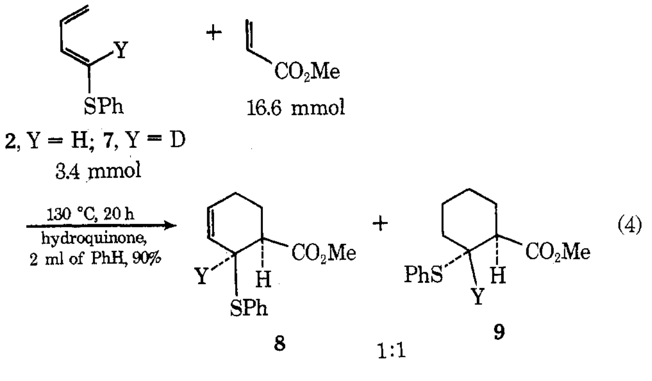
Our procedure consists of the copper(I)-induced removal[2] of one or two thiophenol molecules from readily available diene precursors; eq 1–3 are given as examples.[3,4]

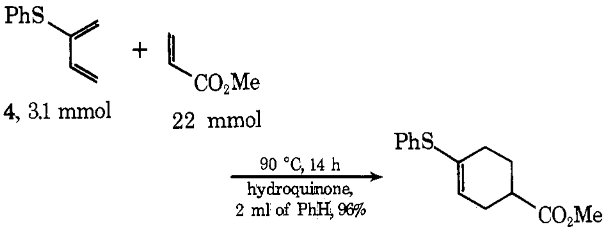


A typical procedure for performing the elimination step follows. A solution of 2.87 mmol of 1,1,3-tris(phenylthio)butane (**1**) in 2 ml of tetrahydrofuran was added at 0 °C to a solution of 15.5 mmol of the benzene complex of cuprous trifluoromethanesulfonate [Cu_2-$C_6H_6(CF_3SO_3)_2$][7] and 17.6 mmol of diisopropylethylamine dissolved in 120 ml of benzene and the solution was allowed to stir at 25 °C for 14 h. The mixture was passed rapidly through a short silica column, and the light yellow oil which was eluted with ether was submitted to molecular distillation (45–50 °C/0.02 mmHg) in the presence of a small quantity of hydroquinone to give 84% diene as a colorless oil. More concentrated solutions resulted in some polymerization and reduced yields.

As indicated previously,[2] the temperature required for the elimination depends upon the stability of the carbonium ion left after the removal of a thiophenoxide ion. In the case of **1**, the reaction cannot be stopped after the loss of one thiophenol molecule. In the case of **3**, however, the product of loss of one thiophenol molecule, 1,3-bis(phenylthio)-2-butene,[5,8] must be warmed to 25 °C in the presence of cuprous ion in order to convert it to the diene **4.**

The dienes **2** and **6** are stereochemically homogeneous[9] and are assumed to be *E* and *Z*, respectively, on the basis of their ready reactions with dienophiles. Dienes **2, 4,** and **6** gave well-characterized Diels–Alder adducts (eq 4–6)[12] in the





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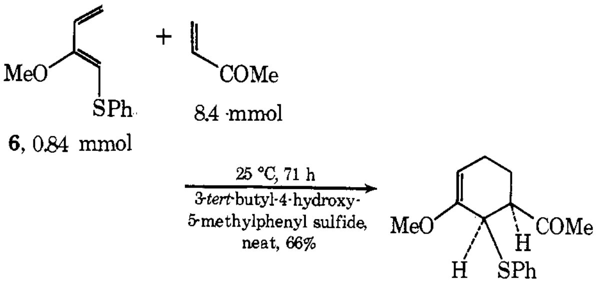

(6)

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presence of a trace of radical polymerization inhibitor. The yields in the equations are not optimized and are for purified adducts.

Evans[14] has shown that **2** is capable of condensing with methyl vinyl ketone and maleic anhydride and that its sulfoxide forms useful Diels–Alder adducts with electron-rich dienophiles. In order to demonstrate that the adducts in reaction 4 do not include an allylic rearrangement product[15] of **8** and/or **9**, the C_1 proton of **1** was readily removed (CH_3Li–HMPA) and replaced by deuterium (D_2O); the resulting diene (**7**) gave an adduct lacking NMR peaks for the protons labeled Y in **8** and **9**. The structures of **8** and **9** (Y = H) were confirmed by 250-MHz ^{1}H NMR decoupling experiments on the mixture.

The structure of **11** was unequivocally established by the same technique. The absorption at 3.83 ppm for the CHS proton appeared as a broad doublet (J = 4.0 Hz) which collapsed to a broad singlet upon irradiation at the frequency of the methine hydrogen adjacent to the carbonyl. The signal for the latter, an eight-line multiplet centered at 2.71 ppm, collapsed to a clean doublet of doublets ($J_{\text{ax-ax}}$ = 13 Hz; $J_{\text{ax-eq}}$ = 2.5 Hz) upon irradiation at 3.83 ppm. Thus, the acetyl group is equatorial and adjacent to a quasiaxial phenylthio group.

The syntheses herein described of dienes substituted by phenylthio groups are far superior in yield, simplicity, and stereospecificity to any thus far reported.[11,13,14,16] The importance of these dienes lies in their Diels–Alder adducts which bear synthetically manipulatable functionality in fixed regiospecific relationships. Adduct **11** is a striking example in that the potential ketone function is meta to the acetyl group in contrast to the para orientation of the alkoxy groups in adducts of other 2-alkoxybutadienes.[17,18] The exploitation of these now accessible dienes and their adducts is receiving considerable attention in our laboratory and will be described in due course.

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References and Notes

(1) Taken in part from the Ph.D. Thesis of Albert J. Mura, Jr., University of Pittsburgh, 1976.
(2) (a) T. Cohen, G. Herman, J. R. Falck, and A. J. Mura, Jr., *J. Org. Chem.*, **40**, 812 (1975); (b) T. Cohen, D. Kuhn, and J. R. Falck, *J. Am. Chem. Soc.*, **97**, 4749 (1975).
(3) New compounds gave satisfactory spectral and elemental composition data.
(4) In addition to these examples, we have prepared 1,3-bis(phenylthio)-1,3-butadiene by the procedures of eq 1 and 2 starting with commercial $MeCOCH_2CH(OMe)_2$ as well as 1-phenylthio-2-methyl-1,3-butadiene by elimination of thiophenol from 1,3-bis(phenylthio)-2-methyl-1-butene;[5] both undergo Diels–Alder reactions and are thus, presumably, of *E* configuration.
(5) T. Cohen, D. A. Bennett, and A. J. Mura, Jr., *J. Org. Chem.*, **41**, 2506 (1976).
(6) Preparation of bis(phenylthio)methane: K. Uneyama, H. Namba, and S. Oae, *Bull. Chem. Soc. Jpn.*, **41**, 1928 (1968). Preparation of lithio derivative: E. J. Corey and D. Seebach, *J. Org. Chem.*, **31**, 4097 (1966).
(7) R. G. Salomon and J. K. Kochi, *J. Am. Chem. Soc.*, **95**, 3300 (1973).
(8) If the amine is present during the first stage of the reaction at 0 °C, 2,4-bis(phenylthio)-1-butene, the undesirable product of Hofmann elimination, is also formed.
(9) Diene **2** gave a single peak on a support coated (OV-17) open tubular (SCOT) GC column[10] which is capable of almost complete separation of the *E* and *Z*[11] isomers. Diene **6** gave one TLC spot and its ^{1}H NMR spectrum exhibited a very sharp methyl peak at 3.70 and other absorptions at 4.98–5.60 (8-line multiplet, 2 H, CH_2), 5.78 (s, 1 H, SCH), 5.93–6.43 (quart., 1 H, vinyl), and 7.06–7.50 ppm (m, 5 H, aromatic).
(10) Perkin-Elmer Corp.
(11) E. N. Prilezhaeva, V. N. Petrov, and A. N. Khudyakova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **5**, 1097 (1968); *Engl. Trans.*, **5**, 1042 (1968).
(12) The Diels–Alder adduct of **4** with maleic anhydride was also prepared and was found to have the reported melting point.[13]
(13) K. D. Gundermann and P. Holtmann, *Angew. Chem., Int. Ed. Engl.*, **5**, 668 (1966).
(14) D. A. Evans, C. A. Bryan, and C. L. Sims, *J. Am. Chem. Soc.*, **94**, 2891 (1972).
(15) H. Kwart and N. Johnson, *J. Am. Chem. Soc.*, **92**, 6064 (1970).
(16) Samples of diene **2** prepared as in ref 2 and 14 (the latter kindly supplied by Dr. Sarah Danishefsky) were contaminated by *Z* isomer. A newly reported preparation of **2** proceeds in poor yield and in unspecified stereochemistry: I. Kuwajima, K. Sugimoto, and T. Murofushi, *Chem. Lett.*, 625 (1974).
(17) Reviews of Diels–Alder reactions: Y. A. Titov, *Russian Chem. Rev.*, **31**, 267 (1962); J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **5**, 211 (1966); **6**, 16 (1967).
(18) For a particularly elegant solution to the problem raised by the failure of 2-alkyl-1,3-butadienes to give meta Diels–Alder adducts as major products, see G. Büchi and J. E. Powell, Jr., *J. Am. Chem. Soc.*, **92**, 3126 (1970).
(19) (a) Andrew Mellon Predoctoral Fellow. (b) Undergraduate Research Participant.

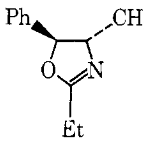
Theodore Cohen,* Albert J. Mura, Jr.[19a]
David W. Shull, Elaine R. Fogel[19b]
Robert J. Ruffner,[19b] **J. R. Falck**
Chemistry Department, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Received July 27, 1976

Preparation and Alkylation of a New Chiral Oxazoline from L-Serine

Summary: A new chiral oxazoline was prepared from L-serine, and its alkylation leads to asymmetric induction which is the reverse of that observed for other oxazolines.

Sir: The use of chiral oxazolines in the preparation of optically active α-substituted carboxylic acids has been demonstrated by Meyers. For example, lithiation of **1** followed by treatment



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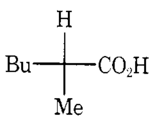

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with 1-iodobutane gives an alkylated oxazoline which may be converted by acidic hydrolysis into (*S*)-(+)-2-methylhexanoic acid, **2**, with 78% optical purity.[1] We wish to report the preparation of a new chiral oxazoline related to **1**, along with some unexpected results from preliminary studies of its alkylation and hydrolysis.

The new chiral oxazoline was prepared from the methyl ester hydrochloride, **3**, of L-serine which was converted by sequence 1 through 4 and **5a** to **5b**.[2] Reaction of **3** with ethyl propionimidate[3] in dichloromethane at room temperature for