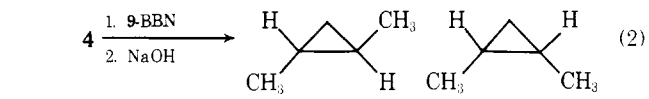
(*Z*)-1-Chloro-2-methyl-2-butene (**4**-*Z*) was obtained in a similar way from (*Z*)-2-methyl-2-butanoic (angelic) acid (**3**-*Z*).[10] In this case **3**-*Z* (99.5% *Z* isomer) gave **4**-*Z* consisting of 98.8 ± 0.4% *Z* isomer.[6,9] Configurations of angelic (**3**-*E*) and tiglic (**3**-*Z*) acids have been unequivocally established by x-ray analysis.[11] Thus the method of synthesis establishes configurations of the allylic chlorides. This assignment is confirmed by the NMR spectra. The vinyl proton shift is δ 5.43 for **4**-*Z* and δ 5.59 for **4**-*E* ($DCCl_3$). These values, and the shift differences, are in good agreement with values obtained by a model-compound method for calculating shifts of olefinic protons.[12]

The isomeric 1-chloro-2-methyl-2-butenes (**4**) were converted to dimethylcyclopropane by a method developed by Brown and Rhodes[3] which involves hydroboration with **9**-BBN. The pertinent data are summarized under eq 2.[9] Data for **4**-*E* and **4**-*Z* are averages for four and three independent experiments. The isomeric dimethylcyclopropanes were



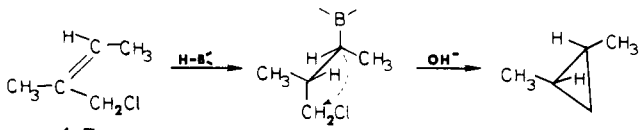
(2)

>99.9% **4**-**E** ⟶ 0.3 ± 0.1% 99.7 ± 0.1%

98.7 ± 0.1% **4**-**Z** ⟶ 96.3 ± 0.2% 3.7 ± 0.2%

identified by comparison of properties with authentic samples.[13]

Syn hydroboration[4] of **4**-*Z* leads to the erythro γ-chloroborane (**5**). Similarly **4**-*E* gives the threo diastereomer. Presumably cyclization involves coordination of the base with the boron atom to form an ate complex which undergoes 1,3-elimination.[3,4] The present results show that this proceeds with inversion of configuration of the carbon–boron center.



4-**Z** **5**

This stereochemical result is in contrast to that generally observed with organoboranes. Most nonradical reactions are stereospecific and proceed with retention of configuration of the carbon atom bonded to boron.[4] However, these cases differ mechanistically from the 1,3-elimination and involve migration of an alkyl group from boron to an adjacent electron deficient atom.[4] The base-promoted halogenation of organoboranes is presumably mechanistically related to the 1,3-elimination (electrophilic attack at a carbon atom bonded to boron in an ate complex)[4] and also proceeds with predominating inversion.[14]

The present data show that the cyclopropane synthesis (eq 1) is highly stereoselective. However, there is some loss of configuration in one of the steps. The greater loss with **4**-*Z* than with **4**-*E* suggests this occurs before the cyclization step because the conformation for concerted 1,3-elimination appears more favorable for the erythro chloroborane (**5**) than for the threo diastereomer. The slight loss could result from isomerization of the allylic chloride prior to reaction,[15] or a less than 100% syn addition.

The high stereoselectivity of this two-step transformation suggests that asymmetric hydroboration[16] followed by cyclization may be a useful method for preparing optically active disubstituted cyclopropanes.

Acknowledgment. This work was supported by the National Science Foundation (MPS76-15879) and the Air Force Office of Scientific Research (AFOSR-71-1974).

References and Notes

(1) (a) M. F. Hawthorne and J. A. Dupont, *J. Am. Chem. Soc.*, **80**, 5830 (1958); (b) M. F. Hawthorne, *ibid.*, **82**, 1886 (1960).
(2) P. Binder and R. Koster, *Tetrahedron Lett.*, 156 (1961).
(3) H. C. Brown and S. P. Rhodes, *J. Am. Chem. Soc.*, **91**, 2149 (1969).
(4) H. C. Brown, "Organic Synthesis via Boranes", Wiley-Interscience, New York, N.Y., 1975, and references therein.
(5) J. A. Marshall and J. H. Babler, *Chem. Commun.*, 993 (1968).
(6) All new compounds were identified by NMR, ir, and mass spectrometry.
(7) (a) E. I. Snyder, *J. Org. Chem.*, **37**, 1466 (1972); (b) E. W. Collington and A. I. Meyers, *ibid.*, **36**, 403 (1971).
(8) Isomeric composition determined by GC analysis of the methyl ester prepared with CH_2N_2.
(9) Isomeric compositions determined by GC as follows: methyl esters, 200 ft capillary 5% TCEP; allylic alcohols, 300 ft capillary 10% Carbowax 20 M; **4**, 100 ft capillary 5% SE30 or 10 ft × 1/8 in. column 3% SE30 on Varaport 30; 1,2-dimethylcyclopropanes, same as for **4**. Complete baseline resolution in all cases.
(10) H. House and G. Rasmusson, *J. Org. Chem.*, **26**, 4278 (1961).
(11) A. L. Porte and J. M. Robertson, *J. Chem. Soc.*, 817 and 825 (1959).
(12) S. W. Tobey, *J. Org. Chem.*, **34**, 1281 (1969); D. F. Ewing and K. A. W. Parry, *J. Chem. Soc. B*, 970 (1970). The model compounds used in the present work were *cis*- and *trans*-2-butene, allyl chloride, and *cis*- and *trans*-1-chloro-2-butene.
(13) W. E. Doering and P. La Flamme, *J. Am. Chem. Soc.*, **78**, 5447 (1956).
(14) H. C. Brown, N. R. De Lue, G. W. Kabalka, and H. C. Hedgecock, Jr., *J. Am. Chem. Soc.*, **98**, 1290 (1976).
(15) Equilibration of 2-methylbutenyl chloride gives 92.2% 3-chloro-2-methyl-1-butene, 7.6% **4**-*E*, and 0.2% **4**-*Z* (room temperature, ether with HCl and $SOCl_2$).
(16) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Am. Chem. Soc.*, **86**, 397 (1964).

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New Synthetic Reagents. 2-Methoxy-3-phenylthiobuta-1,3-diene. A Novel Annelating Agent

Sir:

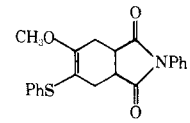
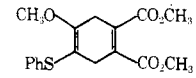
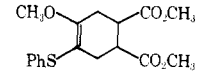
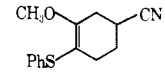
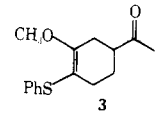
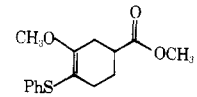
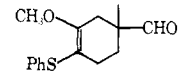
We wish to report the preparation of a versatile new diene, 2-methoxy-3-phenylthiobutadiene (**1**), which serves as an annelating agent to introduce a masked β-ketosulfide moiety as an integral part of the annelation. Such a structural feature has been shown to be versatile in elaborating organic structures.[1]

Moreover, the regiochemistry of the annelation indicates that the phenylthio, rather than the methoxy group, is controlling in the thermal process, whereas the methoxy group plays a greater controlling role in the catalyzed reaction—an unusual dichotomy.[2] *The ease of desulfurization of organic compounds suggests the application of this directive effect of sulfur as an approach for obtention of a regiochemistry that complements that obtained with the usual dienes* such as 2-methoxybutadiene.[2,3]

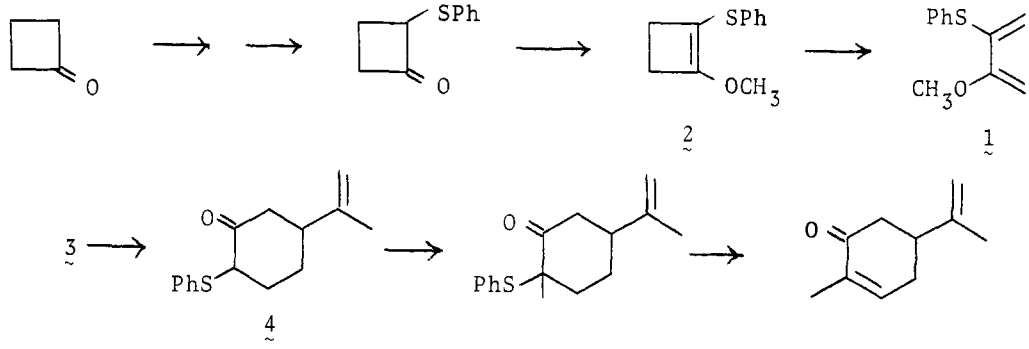
2-Phenylthiocyclobutanone,[4] prepared from 2-bromocyclobutanone[5] (PhSNa, DMF, 0°, 1 h), is O-methylated (KH, THF–DMF, $(CH_3O)_2SO_2$, −78° → 0°) to give 1-methoxy-2-phenylthiocyclobutene (**2**)[4] in 46% yield (from bromocyclobutanone). No purification of the intermediates starting from cyclobutanone is necessary. The cyclobutene **2** is purified on Baker alumina eluting first with hexane and then 1–2% ether in hexane. Pyrolysis, by dropping a hexane solution of **2** through a 40 cm hot tube packed with glass helices (150 ml free volume, flow rate ~500 ml/min, 340°) that has been pretreated with *O,N*-bistrimethylsilylacetamide, gives the desired diene **1**[4,6] in nearly quantitative yields. The sensitivity of the diene towards polymerization makes it desirable to place a trace amount of 2,6-di-*tert*-butyl-4-methylphenol as a stabilizer in the cold traps, and to store the diene over this stabilizer. We normally utilize the diene within a week of its preparation.

Reaction of diene **1** with dienophiles, either neat or in toluene solution at reflux, produces the desired adducts (see Table I).[7] The question of the regiospecificity was directly answered in the cases of entries 4, 5, and 7 and it is assumed that the same

Table I. Diels–Alder Reactions of 2-Methoxy-3-phenylthio-buta-1,3-diene

Entry	Dienophile	Conditions[a]	Adduct[b,e]	Yield (%)[f]
1	*N*-Phenylmaleimide	$PhCH_3$, 2 h	 **12**	71
2	Dimethyl acetylenedicarboxylate	$PhCH_3$, 2 h		61
3	Maleic anhydride	$PhCH_3$, 4 h		48[g]
4	Acrylonitrile	neat, 24 h	 **5**	63[c]
5	Methyl vinyl ketone	neat, 2 h	 **3**	75[c]
6	Methyl acrylate	neat, 24 h		65[d]
7	Methacrolein	neat, 24 h	 **6**	72[c]

[a] All reactions were performed at reflux in the presence of 2,6-di-*tert*-butyl-4-methylphenol as a stabilizer. [b] The major adduct is shown. [c] Major:minor >5:1. [d] Major:minor >3:1. [e] All compounds have been fully characterized by spectral means and elemental composition. See ref 4 for selected spectral data. [f] No attempt to optimize yields has been made. [g] The initial adduct was subjected to methanolysis and then diazomethane before isolation.

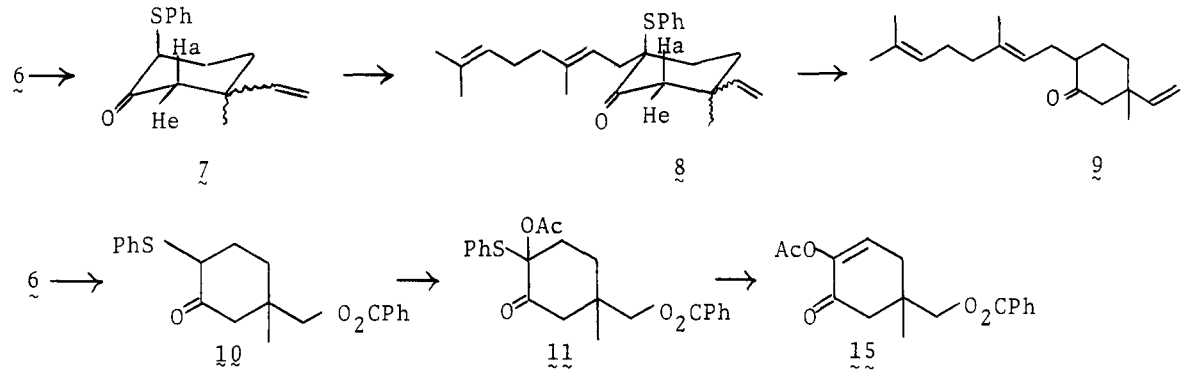


trend holds in the case of entry 6. Furthermore, the structural correlations provide illustrations of the utility of these intermediates in synthesis.

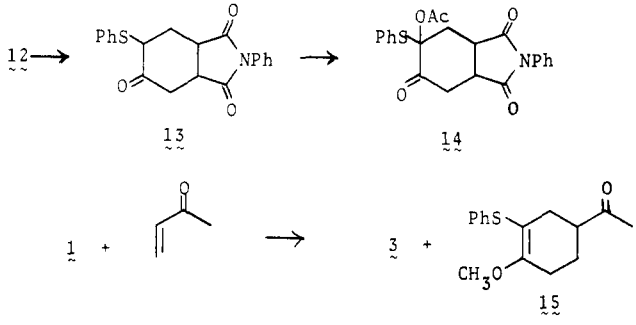
The β-ketosulfide moiety is present in a masked form and allows easy structural manipulation of the functional group of the dienophile. For example, the MVK adduct **3** undergoes a standard Wittig reaction ($Ph_3P^+CH_3Br^-$, *n*-C_4H_9Li, THF, 0° → 25°) and subsequent hydrolysis (4:1 THF:10% aqueous HCl, 20°)[8] to give the sulfenylated ketone **4**[5] in 52% yield. Regiospecific methylation[5] (NaH, THF, CH_3I, 4 h, 77% yield) and dehydrosulfenylation (MCPBA, CH_2Cl_2, −78°; add $(CH_3O)_3P$, reflux; 66% yield) produce carvone, identical in all respects with an authentic sample.[9] The acrylonitrile adduct **5** was correlated with **3** by reaction with methyllithium (ether, 20°) followed by selective hydrolysis of the resultant imine (oxalic acid, water, 25°).

The use of the ketosulfide unit for controlled alkylations of unsymmetrical ketones[1d] was illustrated with adduct **6**. Again, the aldehyde was subjected to standard Wittig conditions and subsequently hydrolyzed as above to give **7**[5] in 66% overall yield. Alkylation with geranyl bromide (NaH, THF, 20°, 63% yield) gives **8**.[5] It has been previously shown that the phenylthio group, in the absence of severe steric interactions, prefers the axial orientation and deshields the axial hydrogen on C-6 (Ha in **7** and **8**).[10] In each of these compounds, this proton appears as a pair of doublets (**7** δ 2.76 and 2.89, J = 14 Hz, **8** δ 3.28 and 3.40, J = 15 Hz) for the two isomers at C-5. In the product from the alternative Diels–Alder regioisomer, this proton would show further coupling to a methylene group. Reduction of the sulfide (6% Na–Hg, CH_3OH, Na_2HPO_4, 0°, 55% yield) gives the regiospecifically monoalkylated ketone **9**.[4]

A new application of the ketosulfide illustrates the utility of this annelation for the regiospecific formation of a diosphenol.[11] Reduction ($NaBH_4$, CH_3OH, 0°), benzoylation (PhCOCl, pyridine, 0°), and hydrolysis (50:1 CH_3CN:60% aqueous $HClO_4$, 0°) gives the benzoate **10**[4] in 60% overall yield. Lead tetraacetate (PhH, reflux, 10 min, 89% yield) smoothly acetoxylates the ketosulfide to give the α-diketone in a protected form, i.e., **11**.[4] Similarly, the ketosulfide **13**,[4] obtained by hydrolysis (50:1 CH_3CN:60% aq $HClO_4$) of the adduct **12**, undergoes smooth acetoxylation to **14**[4] under identical conditions. Conversion of **11** to the diosphenol, as its acetate **15**,[4] in a regiospecific fashion by the dehydrosulfenylation procedure (MCPBA, CH_2Cl_2, −78°, then reflux, 86%

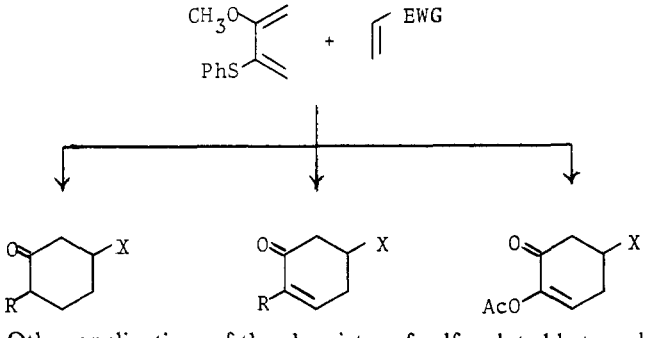


yield) completes the sequence. The presence of the vinyl proton as a triplet, δ 6.26, J = 4 Hz, confirms the regiochemistry of the initial adduct as assigned.



The reaction is subject to a marked acceleration by the addition of anhydrous magnesium bromide. Under these conditions the MVK adducts are formed in 91% isolated yield at room temperature; however, the ratio of **3**:**15** of >5:1 in the uncatalyzed reaction becomes approximately 1:1 in the catalyzed case in contrast to the normal trends for the Lewis acid catalyzed Diels–Alder reaction. Discussion of the controlling effect of the sulfur substituent over oxygen in the normal thermal mode and the tendency for reversal of this directive effect in the presence of a Lewis acid is postponed to the full paper.

The advantages of this novel annelating procedure are manifold. (1) The versatile β-ketosulfide moiety is introduced in a protected form—a fact that allows modification elsewhere. (2) We have demonstrated the transformations listed below.



Other applications of the chemistry of sulfenylated ketones[1] and diosphenols[13] further enhance the utility of this chemistry. (3) The regiochemistry observed here complements the normal regiochemistry obtained with 2-oxygenated dienes. The ease with which sulfur can be removed from organic molecules may make this a general approach to reversing the normal orientation of Diels–Alder reactions.

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References and Notes

(1) For some examples see (a) R. L. Autrey and P. W. Suillard, *J. Am. Chem. Soc.*, **90**, 4917, 4924 (1968); (b) B. M. Trost and T. Salzmann, *ibid.*, **95**, 6840 (1973); (c) P. A. Grieco, D. Boxler, and C. S. Pogonowski, *J. Chem. Soc., Chem. Commun.*, 497 (1974); (d) R. M. Coates, H. D. Pigott, and J. Ollinger, *Tetrahedron Lett.*, 3955 (1974); (e) P. G. Gassman, T. J. van Bergen, D. P. Gilbert, and B. W. Cue, Jr., *J. Am. Chem. Soc.*, **96**, 5495 (1974); (f) B. M. Trost, K. Hiroi, and S. Kurozumi, *ibid.*, **97**, 438 (1975); (g) P. A. Grieco and C. S. Pogonowski, *J. Chem. Soc., Chem. Commun.*, 72 (1975).

(2) For reviews see J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **5**, 211 (1966); **6**, 16 (1967); H. Wollweber in "Methoden der Organischen Chemie", E. Mueller, Ed., Band V/1c, Teil 3, Houben Weyl, 1970.

(3) For recent applications of novel dienes in synthesis see (a) S. Danishefsky and T. Kitahara, *J. Am. Chem. Soc.*, **96**, 7807 (1974); *J. Org. Chem.*, **40**, 538 (1975); (b) D. A. Evans, C. A. Bryan, and C. L. Sims, *J. Am. Chem. Soc.*, **94**, 2891 (1972); (c) H. Neunhoffer and G. Werner, *Justus Liebigs Ann. Chem.*, 437 (1973); (d) V. I. Zahorszky and H. Musso, *ibid.*, 1777 (1973); (e) Y. Gaoni, *Tetrahedron Lett.*, 2361 (1973); (f) E. Sonveaux and L. Ghosez, *J. Am. Chem. Soc.*, **95**, 5417 (1973); (g) E. J. Corey and A. P. Kozikowski, *Tetrahedron Lett.*, 2389 (1975); (h) S. D. Darling and N. Subramanian, *J. Org. Chem.*, **40**, 2851 (1975); (i) A. Demoulin, H. Goussin, A. M. Hesbain-Fisque, and L. Ghosez, *J. Am. Chem. Soc.*, **97**, 4409 (1975).

(4) All compounds have been fully characterized by spectral means and elemental composition. Selected spectral data are listed herein. 2-Phenylthiocyclobutanone: ir 1788, 1582, 1479 cm^{-1}; NMR δ 4.40 (t, J = 7, 1 H), 3.0 (m, 2 H), 2.44 (m, 1 H), 1.90 (m, 1 H). **1:** ir 1613, 1570, 1489 cm^{-1}; NMR δ 6.00 (1 H), 5.36 (1 H), 4.81 (1 H), 4.16 (1 H), 3.57 (3 H). **2:** 1622, 1578 cm^{-1}; NMR δ 3.95 (s, 3 H), 3.56 (t, J = 4, 2 H), 2.14 (t, J = 4, 2 H). **3:** ir 1715, 1639, 1582 cm^{-1}; NMR δ 7.2 (m, 5 H), 3.65 (s, 3 H), 1.18 (s, 3 H). **4:** ir 1709, 1645, 1584, 895 cm^{-1}; NMR 4.78 (m, 2 H), 3.74 (m, 1 H), 3.08 (m, 1 H), 1.78 (s, 3 H). **5:** ir 2250, 1640, 1582 cm^{-1}; NMR δ 7.26 (m, 5 H), 3.66 (s, 3 H), 2.92 (m, 1 H). **6:** ir 2710, 1728, 1639, 1579 cm^{-1}; NMR δ 9.45 (s, 1 H), 7.22 (m, 5 H), 3.69 (s, 3 H), 2.71 (d, J = 16 Hz, 1 H), 1.14 (s, 3 H). **10:** ir 1710, 1599, 1582 cm^{-1}; NMR δ 8.01 (m, 2 H), 4.12, 4.10 (s, 2 H), 3.79 (m, 1 H), 3.20 (d, J = 14 Hz, 0.6 H), 2.71 (d, J = 14 Hz, 0.6 H), 1.13, 1.10 (s, 3 H). **14:** ir 1715, 1595 cm^{-1}; NMR δ 7.38 (m, 10 H), 2.6–3.6 (m, 6 H), 2.06 (s, 3 H). **15:** ir 1765, 1723, 1710, 1695, 1655, 1600, 1584 cm^{-1}; NMR δ 7.77 (m, 2 H), 7.2 (m, 3 H), 6.26 (t, J = 4 Hz, 1 H), 4.10 (s, 2 H), 2.3–2.8 (m, 4 H), 2.24 (s, 3 H), 1.29 (s, 3 H).

(5) J. M. Conia and J. L. Ripoll, *Bull. Chim. Soc. Fr.*, 755 (1963).

(6) Hydrolysis of **1** to 2-phenylthiobut-1-en-3-one (phenylthio MVK equivalent) has been observed. NMR shows absorptions at δ 7.4 (m, 5 H), 6.12 (s, 1 H), 5.31 (s, 1 H), 2.32 (s, 3 H); ir 1695, 1647, 1579 cm^{-1}. For applications of the silyl derivative in synthesis see G. Stork and J. Singh, *J. Am. Chem. Soc.*, **96**, 6181 (1974).

(7) 2,3-Trimethylsiloxy-1,3-butadiene (J. J. Bloomfield, H. M. Frey, and J. Metcalfe, *Int. J. Chem. Kinet.*, **3**, 85 (1971)) does not serve as a diene in cycloadditions (unpublished results in these laboratories). Other 2,3-dialkoxy-1,3-butadienes do serve in Diels–Alder reactions. See J. R. Johnson, W. H. Jobling, and G. W. Bodamer, *J. Am. Chem. Soc.*, **63**, 131 (1941); R. K. Summerbell and G. J. Lestina, *ibid.*, **79**, 3878 (1957).

(8) Subsequent studies suggest that the use of 50:1 acetonitrile–60% aqueous perchloric acid at 0° is preferable for these hydrolyses.

(9) VPC analysis indicated >95% carvone compared to the presumed 2-methyl-4-isopropenylcyclohex-2-en-1-one, the latter deriving from the minor adduct.

(10) B. M. Trost, T. Salzmann, and K. Hiroi, *J. Am. Chem. Soc.*, in press.

(11) B. M. Trost, G. Massiot, and K. Hiroi, unpublished work. For the reactions of lead tetraacetate with sulfides see B. M. Trost and K. Hiroi, *J. Am. Chem. Soc.*, **97**, 6911 (1975), and references cited therein.

(12) (a) J. Sauer and J. Kredel, *Tetrahedron Lett.*, 731 (1966); (b) T. Inukai and T. Kojima, *J. Org. Chem.*, **36**, 924 (1971); (c) W. Kreiser, W. Haumesser, and A. F. Thomas, *Helv. Chim. Acta*, **57**, 164 (1974).

(13) H. R. Nace and D. H. Nelander, *J. Org. Chem.*, **29**, 1677 (1964); A. G. Schultz and D. S. Kashdan, *ibid.*, **38**, 3814 (1973); A. S. Kende and R. G. Eilerman, *Tetrahedron Lett.*, 697 (1973); K. M. Patel and W. Reusch, *Synth. Commun.*, **5**, 27 (1975); A. D. Schultz and R. D. Lucci, *J. Org. Chem.*, **40**, 1371 (1975).

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