Tetrahedron Vol. 42, No. 11, pp 2803 to 2808, 1986
Printed in Great Britain.

0040-4020/86 $3.00 + .00
Pergamon Journals Ltd.

REDUCTIVE METALLATION

A GENERAL PREPARATIVE METHOD FOR HYDROCARBON ALLYLMETALLIC COMPOUNDS

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(*Received in U.S.A.* 13 *May* 1985)

Abstract—Because of the great ease of preparation of allyl phenyl sulfides and their smooth reductive lithiation using lithium naphthalenide or 1-(dimethylamino)naphthalenide, these are ideal substrates for a particularly versatile preparative method for allylic anions. The lithio compounds react with aldehydes and ketones readily and with moderate regioselectivity. The allyltitanium compounds formed by addition of titanium tetraisopropoxide react with enals with very high regioselectivity and stereoselectivity. The allyltitanium compound derived from 2-phenylthio-1-methylenecyclohexane adds in a 1,2-fashion to crotonaldehyde at the secondary terminus of the allylic system. The potassium salt of this adduct undergoes the anion-accelerated oxy Cope rearrangement to the product of formal 1,4-addition of the crotonaldehyde to the primary terminus. The rearrangement product is an aldehyde which is also synthetically useful, undergoing the Lewis acid catalyzed ene reaction to produce a ring-closed product.

Although allyl anions bearing heteroatoms at one or both termini have been widely used in organic synthesis,[1] only the simplest members of the class of allyl anions lacking such substituents are ordinarily used, probably because general methods for their syntheses have not been available. Until recently, the preparation of allyl Grignard reagents was often plagued by coupling reactions; although that problem has apparently now been solved,[2] complex allyl halides are usually difficult to prepare in a regiospecific manner.† Allyllithium itself, prepared by the lithiation of allyl phenyl ether,[4] and crotyllithium,[5] prepared by tin–lithium exchange, are both employed extensively; however, the methods used for the preparation of these two species have not been generally applicable since more complex allylic phenyl ethers are not generally available and until very recently the same could be said for allyl stannanes although Trost and Herndon's recent preparative method[6] for the latter may allow tin–lithium exchange to become a major pathway to allyllithiums, one which is complementary to the method described herein. Finally, deprotonation of alkenes with organopotassium reagents is sometimes of use in preparing certain allylpotassium species[7] but if there is more than one type of proton that can be removed, the desired isomer may not necessarily be the one that is produced.

In this paper, we demonstrate that treatment of allyl phenyl sulfides with radical anions is a general and practical method for the generation of allyllithiums and that the 1,2-adducts with enals at the most-hindered terminus and the 1,4-adducts at the least-hindered terminus can be obtained by proper manipulations. However, it is appropriate first to outline the general utility of this powerful method for the production of anions and to highlight its complementary character to the most common methods in current use for preparing organolithium compounds. Early work in our laboratory[8] and that of Screttas[9] established that the phenylthio group could be readily replaced by a lithium atom in several types of organic compounds by treating the latter with lithium naphthalenide (LN), which is easily prepared by dissolving lithium metal in a solution of naphthalene in tetrahydrofuran (THF). The classes of organolithium species which were originally produced in this way included simple alkyllithiums as well as sulfur stabilized alkyl- and vinyllithiums.[8,9] More recently, reports from other laboratories have confirmed the utility of the method for producing unstabilized alkyllithiums[10a] and sulfur stabilized alkyllithiums.[10b]

Because of difficulties encountered in separating products derived by silylation of the anion from the naphthalene byproduct, the lithium 1-(dimethylamino)-naphthalenide (LDMAN) reagent was developed.[11] The great ease of removal of the basic byproduct, DMAN, by washing the reaction mixture with dilute acid solved the problem completely and this reagent proved so generally useful that we now use it routinely for reductive lithiations. The reductive lithiation behavior of the two reagents appears to be identical but it should be pointed out that unlike LN, which can be prepared and stored for several days at ambient temperature and can be titrated,[12] LDMAN must be prepared and stored below −45° and a method of titrating it has not been devised.

It has been shown that reductive lithiation with LDMAN or LN of alpha-(phenylthio)ethers is a general method of generation of alpha-lithioethers and the technology has been utilized in a two-flask synthesis of the brevicomins.[13] Among the alpha-lithioethers that can be formed in this way are 1-lithio-1-methoxycyclopropanes, which react with conjugated aldehydes and ketones to provide allylic alcohols capable of rearranging under mildly acidic conditions to 2-vinylcyclobutanones;[14] the latter undergo interesting acid-induced ring expansions to five- or six-

† Certain allylmagnesium compounds have been prepared by heating allyl naphthyl ethers or allyl phenyl sulfides with magnesium metal in refluxing THF. The process in the case of the latter substrates is presumably related to the reductive lithiations of such materials that we present below but the yields of the organomagnesium compounds vary widely.[3]

membered rings,[15] reactions with vinylmetallics to yield eight-membered rings,[16] and reductions to alcohols which undergo base-induced ring expansions to cyclohexenols.[17] The alpha-lithio derivatives of five- and six-membered cyclic ethers are also readily available by reductive lithiation of the phenylthio precursors, which are prepared from lactones in a one-flask transformation.[18] Reductive lithiation has been shown to be an excellent method, the only general one, for preparing alpha-lithiosilanes which are useful in the Peterson olefination.[10b,19] The substrates can be prepared by reductive lithiation of a thioacetal followed by silylation[10b,11,19] or, in the case of 1-lithio-1-silylcyclopropanes,[20] by several different one-flask connective methods.[21] In the cyclopropane series, this has provided a facile method for preparing allylidenecyclopropanes,[19,22] which undergo thermal ring expansions to produce ring systems such as hydrazulenes.[22]

LN and LDMAN have also been used to prepare certain vinyllithiums without sulfur substituents[19,23] and an enolate anion[24] from a phenylthioether precursor. Finally, LDMAN has been used for production of a 2-(trialkylsilyloxy)vinyllithium from the corresponding vinyl phenylselenyl ether.[25]

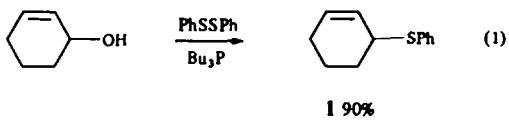
The great versatility and power of this method of anion generation derive from: (1) the great ease of production of the phenylthio precursors; (2) the considerable stability of the latter towards nucleophilic displacement and elimination (compare with halides, for example); (3) the smooth reductive metallations which usually occur at temperatures at which the anions being generated are stable; and (4) the complementary nature of this method to the electrophile exchange[26] that is nearly always used by synthetic chemists to produce organolithium species. In electrophile exchange, it appears likely that the rate-determining step is formation of the anion itself and there is thus a direct relationship between its stability and its ease of production. On the other hand, we believe that in reductive metallation with radical anions the rate-determining step is production of a carbon radical, a step which is preceded by a reversible electron transfer from the reducing agent to the phenylthio substrate;† since the stability order of radicals is frequently opposite that of anions, the rate-determining radical formation has profound consequences with regard to ease of anion production and interesting stereochemical consequences as well.

There are two types of evidence for our mechanistic hypothesis. The first is the excellent correlation between the ease of anion production and the stability of the putative radical precursor; for example, tertiary anions are produced with greater ease than are secondary[19] and cyclopropyl[19] anions while those at sp^2 carbon atoms‡ are produced more sluggishly. The second is that reductive lithiation of 2-(phenylthio)-tetrahydropyrans yields the axial lithioether as the proximate product; this is readily rationalized by a radical intermediate.[18]

Two heteroatom-substituted allylmetallics have already been prepared by reductive metallation. In our laboratory, a sulfur stabilized allyllithium, which could not be prepared by deprotonation, was generated easily by reductive lithiation[11,27] and Hoffmann[28] has produced methoxyallyl anions by reductive metallation.

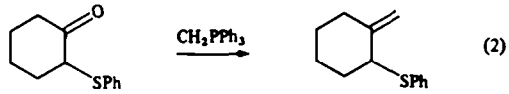
RESULTS AND DISCUSSION

The great ease of preparation of allylic phenylthio ethers is illustrated by three of many conceivable facile methods shown in Eqs (1)–(3).§‖ The symmetrical anion from the reduction of **1** with lithium naphthalenide formed an adduct with benzophenone in satisfactory yield (Eq. 4). The unsymmetrical allyllithium prepared from **2** by the use of LDMAN, as expected, gave mixtures of regioisomers with acrolein and crotonaldehyde; the results with the latter are shown in Eq. (5) in which **4** is a mixture of two diastereomers in the ratio 3:2.



(1)

1 90%



(2)

2 93%

Regioselectivity of the anion derived from **2** was easily achieved by using allyltitanium(IV) complexes as had been demonstrated in the pioneering work of Sato *et al.*,[31] Reetz,[32] Seebach and Weidmann,[33] Yamamoto and co-workers,[34] and Hoppe.[35-37] We chose to use the inexpensive titanium tetraisopropoxide. Treatment of the anion from **2** with this reagent followed by crotonaldehyde resulted in a high yield of two diastereomers (9:1) of a single regioisomeric 1,2-addition product (**4**, Eq. 6). A similar sequence starting from **3** provided complete stereoselectivity as well as regioselectivity (Eq. 7). The gratifying regio- and stereoselectivity, which was expected on the basis of the previous work,[31-36] is presumably due to a chair 6-member ring transition state in which the carbonyl O atom is complexed to the metal which, in turn, is bonded to the least-hindered terminus of the allylic system.[41]

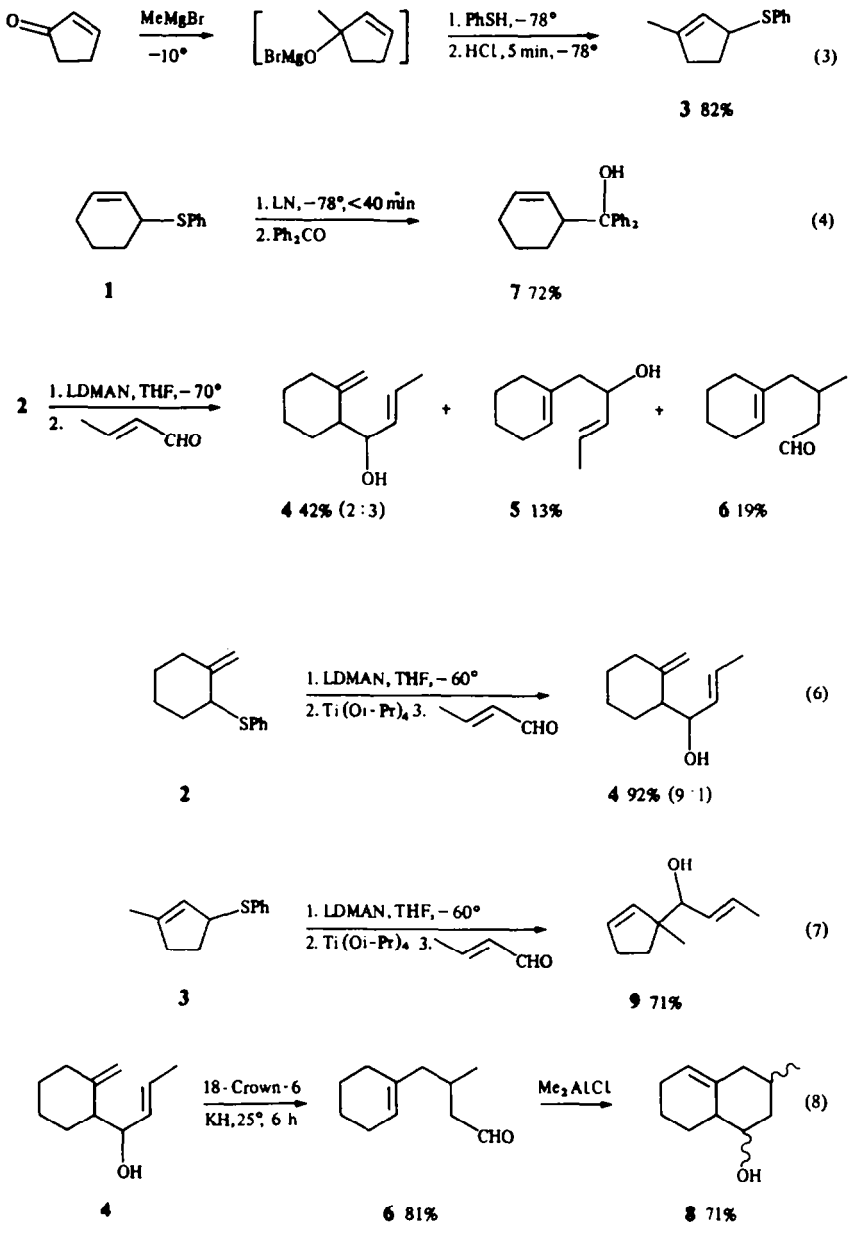
The 1,2-addition product **4** of the allyl anion derived from **2** can be converted to the 1,4-addition product **6** at the opposite terminus by means of the anion-accelerated oxy Cope rearrangement.[43] Thus, treatment of **4** with potassium hydride and a catalytic quantity of 18-crown-6 at room temperature in THF provided **6** in 65% yield (81% based on consumed reactant). The utility of such a product is shown by its ring closure in the presence of dimethylaluminum

† This interpretation differs from the assertion by Screttas that the electron-stransfer step is usually rate determining.[9]

‡ We have found that 2-(phenylthio)furan and 1-cyclohexenyl phenyl sulfide, unlike nearly all others that we have studied, are inert to reductive lithiation below 0° (unpublished observations of S. Nolan and D. Rattigan).

§ The reaction shown in Eq. (1) is an adaptation of the method used by Nakagawa and Hata in the nucleoside series which was based on a reaction originated by Mukaiyama.[29]

‖ The last step of Eq. (3) is analogous to the production of allylic phenylthio ethers by the reaction of the corresponding alcohols with benzenethiol and zinc iodide.[30]



chloride[44] to **8**, which appeared to be a single compound of unknown stereochemistry (Eq. 8); the structure of **8** was confirmed by Swern oxidation[45] to a known conjugated enone.

Reductive lithiation of allylic phenylthio ethers with radical anions thus shows promise of being a general and versatile method of generating allylic anions which can be made to attack enals regioselectively both with regard to the anion and the electrophile. We shall later communicate the results of our attempts, only partially successful at present, to reverse the regioselectivity of these reactions. The proximate adducts of the allylic anions with conjugated enals and the oxy Cope rearrangement products of these adducts are of considerable potential synthetic use.

EXPERIMENTAL

M.ps were determined on a Thomas–Hoover Unimelt Capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin–Elmer 247 grating infrared spectrophotometer, calibrated with a polystyrene film. ^{1}H-NMR spectra were recorded on a Bruker WH-300 spectrometer with TMS as an internal standard. Data are reported as follows: chemical shift, multiplicity (s: singlet, d: double, t: triplet, q: quartet, m: multiplet, br: broad), coupling constant, integration and assignment. Low-resolution mass spectra were recorded on an LKB-9000 combined gas chromatograph–mass spectrometer. Exact mass spectra were obtained on a CH-5 double focusing Varian Mat mass spectrometer.

1. *3-(Phenylthio)cyclohexene* (**1**).[46] A mixture of diphenyl disulfide (13.1 g, 60.0 mmol), tri-n-butylphosphine (17.5 ml, 80.0 mmol) and C_6H_6 (100 ml) was stirred for 2 h at 25°. To this mixture a soln of 2-cyclohexen-1-ol (1.96 g, 20.0 mmol) in 5 ml of THF was added. After 16 h at 25°, the soln was treated with 10% NaOH aq and the solvent was evaporated. The residue was taken up in ether, washed with 10% NaOH aq (2 × 100 ml), dried ($MgSO_4$) and concentrated to give a yellow oily residue which when purified by column chromatography (hexanes) gave 3.24 g (90%) of **1**. IR (neat) 1580, 1470, 1430, 1200, 1080, 1060 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.5–7.1 (m, 5H, aromatic),

5.9–5.7 (m, 2H, vinyl), 3.85 (m, 1H, CH—Sph), 2.1–1.5 (m, 6H); MS (15 eV) *m/z* 190 (M^+, 40%), 81 ($M^+ - SPh$, 85%), 80 ($M^+ - HSPh$, 100%).

2. 2 - *Methylene* - 1 - (*phenylthio*)*cyclohexane* (**2**).[4,7] To a mixture of methyltriphenylphosphonium bromide (18.75 g, 52.5 mmol) and t-BuOK (6.1 g, 55 mmol) under argon, just enough THF was added to dissolve the solids. After the mixture had been stirred at 25° for 1 h, a soln of 2-(phenylthio)cyclohexanone[4,8] (10.3 g, 50.0 mmol) in 20 ml of THF was added dropwise and the mixture was heated at reflux for 2 h. The solvent was evaporated and replaced with hexane (100 ml) and the mixture was filtered and concentrated. The residue was purified by chromatography on a short column to give 9.5 g (93%) of **2**. IR (neat) 1580, 1470, 1420, 1080, 1060 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.4–7.2 (m, 5H, aromatic), 4.7 (br s, 2H, vinyl), 3.9 (t, J = 4.5 Hz, 1H, CH—SPh), 2.55 (m, 1H), 2.1 (m, 1H), 2.0–1.4 (m, 6H). MS *m/z* 204 (M^+); exact mass: calc for $C_{13}H_{16}S$: 204.0971; found: 204.0973.

3. 1 - *Methyl* - 3 - (*phenylthio*)*cyclopentene* (**3**). A soln of 16 ml of MeMgBr (3.0 M, 48 mmol) and 20 ml of THF was cooled to −10° with stirring under an atmosphere of argon. To this soln was added dropwise 2-cyclopenten-1-one (1.0 ml, 12 mmol) in 10 ml of THF. After 30 min, the resulting soln was cooled to −78°, thiophenol (1.37 ml, 13.2 mmol) in 10 ml of THF was added, and HCl gas was passed through for 5 min. The mixture was stirred for another 10 min before 10% NaOH aq was added and the solvent was evaporated. The residue was taken up in ether and the soln was washed successively with 10% NaOH and H_2O, dried ($MgSO_4$), filtered and concentrated. The residue was purified by flash chromatography (5% EtOAc in hexanes) to yield 2.03 g (85%) of **3** as an oil. IR (neat) 1640, 1580, 1470, 1430, 1090 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.40–7.15 (m, 5H, aromatic), 5.40 (br s, 1H, vinyl), 4.28 (m, 1H, CH—SPh), 2.45–2.27 (m, 2H, =CMe—CH_2—), 2.25–2.10 (m, 1H), 2.10–1.95 (m, 1H), 1.75 (s, 3H, CH_3). MS *m/z* 190 (M^+); exact mass: calc for $C_{12}H_{14}S$: 190.0815; found: 190.0816.

4. 1-(1 - *Methylene* - 2 - *cyclohexyl*)trans - 2 - *buten* - 1 - *ol* (**4**). To a soln of LDMAN[19] (34.6 mmol) in THF was added dropwise the sulfide **2** (3.20 g, 15.7 mmol) in 20 ml of THF at −60°; the color of the soln changed from dark green to brown when the LDMAN was consumed. To this mixture at −78° titanium tetraisopropoxide (10.3 ml, 35 mmol) was added dropwise. After 30 min at −78°, the soln was treated with crotonaldehyde (4.0 ml, 48 mmol) in 10 ml of THF, and it was stirred for another 10 min. The mixture was quenched with sat NH_4Cl aq at the same temp, diluted with ether, filtered through Celite, and concentrated. The residue was dissolved in ether, washed successively with 10% NaOH aq and 10% HCl, dried ($MgSO_4$), and concentrated. The dried product was purified by flash chromatography (4% EtOAc in hexanes) to provide 2.4 g (90%) of **4** as a mixture of diastereomers. A small quantity of the pure major isomer could be obtained by flash chromatography using the same eluant. The diastereomer ratio (a : b = 9 : 1) of **4** was determined by integration of the methylene protons (=CH_2). For **4**: IR (neat) 3350, 1670, 1430, 960, 890 cm^{-1}; **4a** (major): ^{1}H-NMR ($CDCl_3$) δ 5.75 (dq, J = 15.1, 6.5 Hz, 1H, =CH—Me), 5.40 (ddq, J = 15.1, 8.2, 1.6 Hz, 1H, —CH=CH—Me), 4.90 (t, J = 1.1 Hz, 1H, =CH_2), 4.80 (d, J = 1.8 Hz, 1H, =CH_2), 4.15 (dd, J = 8.2, 9.3 Hz, 1H, —CHOH—), 2.30–1.45 (m, 10H), 1.75 (dd, J = 6.5, 1.6 Hz, =CH—CH_3). **4b**:† ^{1}H-NMR ($CDCl_3$) δ 5.65 (dq, J = 15.3, 6.3 Hz, 1H, =CH—Me), 5.55 (ddq, J = 15.3, 6.7, 1.4 Hz, 1H, —CH=CH—Me), 4.73 (s, 1H, =CH_2), 4.68 (s, 1H, =CH_2), 4.34 (dd, J = 6.7, 6.9 Hz, 1H, CHOH), 2.25–1.40 (m, 10H), 1.69 (dd, J = 6.3, 1.4 Hz, 3H, =CH—CH_3). MS (mixture) *m/z* 148 ($M^+ - H_2O$); exact mass: calc for $C_{11}H_{16}$ ($M^+ - H_2O$): 148.1252; found: 148.1252.

5. (1 - *Cyclohexen* - 3 - *yl*)*diphenylmethanol* (**7**). To a soln of LN (1.0 mmol)[9,12] in THF at −78° was added dropwise the sulfide **1** (91 mg, 0.50 mmol) in 5 ml of THF. After 20 min at −78°, the soln was treated with benzophenone (90 mg, 0.55 mmol) in 5 ml of THF. The mixture was quenched with 5% NaOH aq and concentrated. The residue was dissolved in ether and the organic layer was washed successively with 10% NaOH aq and water, dried ($MgSO_4$) and concentrated. The crude product was purified by flash chromatography (5% EtOAc in hexanes) to obtain 96 mg (72% yield) of the alcohol **7**. M.p. 61–62°; IR (neat) 3600, 1650, 1610, 1490, 1440, 1340, 1160, 1060 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.65–7.10 (m, 10H, aromatic), 5.95 (m, 1H, vinyl), 5.49 (m, 1H, vinyl), 3.45 (br s, 1H, CH—COH), 2.20 (s, 1H, OH), 2.0 (m, 2H), 1.78 (m, 1H), 1.64–1.40 (m, 3H). MS (15 eV) *m/z* 247 ($M^+ - OH$, 11%), 183 ($Ph_2C{=}OH^+$, 100%), 105 (Ph—C≡O^+, 62%).

6. 1 - (1 - *Methylene* - 2 - *cyclohexyl*) - 2 - *propen* - 1 - *ol*. The title compound was prepared in 72% (174 mg) yield from **2** (326 mg, 1.60 mmol) as a 4 : 1 mixture of stereoisomers, following the procedure described for **4**. For the mixture: IR (neat) 3420, 1670, 1630 1440, 980 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 6.0–5.7 (m, 1H, CH=CH_2, isomeric), 5.35–5.10 (m, 2H, CH=CH_2, isomeric), 4.90 (d, J = 1.6 Hz, 1H, =CH_2, major isomer), 4.83 (d, J = 1.8 Hz, 1H, =CH_2, major isomer), 4.75 (s, 1H, =CH_2, minor isomer), 4.70 (s, 1H, =CH_2, minor isomer), 4.42 (m, 1H, CHOH, minor isomer), 4.19 (dd, J = 8.3, 8.9 Hz, 1H, CHOH, major isomer), 2.25–2.10 (m, 3H, isomeric), 1.90–1.40 (m, 7H, isomeric); MS *m/z* 134 ($M^+ - H_2O$); exact mass: calc for $C_{10}H_{14}$ ($M^+ - H_2O$): 134.1096; found: 134.1096. For the major isomer: ^{1}H-NMR ($CDCl_3$) δ 5.80 (ddd, J = 1.6, 10.1, 17.1 Hz, 1H, CH=CH_2), 5.32 (dd, J = 1.6, 17.1 Hz, 1H, CH=CH_2, *trans*), 5.23 (dd, J = 1.6, 10.1 Hz, 1H, CH=CH_2, *cis*), 4.90 (d, J = 1.6 Hz, 1H, C=CH_2), 4.83 (d, J = 1.8 Hz, 1H, C=CH_2), 4.19 (dd, J = 8.3, 8.9 Hz, 1H, CHOH), 2.25–2.10 (m, 3H), 1.90–1.40 (m, 7H).

7. 1 - (3 - *Methylcyclopenten* - 3 - *yl*) - 2 - *buten* - 1 - *ol* (**9**). The alcohol **9** was prepared in 71% (174 mg) yield from the sulfide **3** (240 mg, 1.70 mmol) following the procedure described for **4**. IR (neat) 3400, 1430, 1370, 1010, 960 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 5.85–5.40 (m, 4H, vinyl), 3.87 (d, J = 8 Hz, 1H, CHOH), 2.45–2.30 (m, 2H), 2.0 (m, 1H), 1.73 (dd, J = 0.6, 6.4 Hz, 3H, =CH—CH_3), 1.65–1.40 (m, 2H), 1.01 (s, 3H, CH_3); MS *m/z* 137 ($M^+ - Me$); exact mass: calc for $C_9H_{13}O$ ($M^+ - Me$): 137.0968; found: 137.0966.

8. *Reaction of the sulfide* **2** *with LDMAN and crotonaldehyde*. To a soln of LDMAN (3.77 mmol) in THF at −78° was added dropwise the sulfide **2** (0.340 g, 1.66 mmol) in 10 ml of THF. After 15 min, the soln was treated with crotonaldehyde (152 ml, 1.82 mmol) in 5 ml of THF and it was stirred for another 10 min. The mixture was quenched with saturated NH_4Cl aq and concentrated. The residue was dissolved in ether, the organic layer was washed successively with 10% NaOH aq and 10% HCl, dried ($MgSO_4$), and concentrated. The crude product was purified by flash chromatography (5% EtOAc in hexanes) to provide 50 mg (19%) of the aldehyde **6** and a mixture of 150 mg (55%) of the alcohols **4** and **5** in the ratio of 3 : 1. See exp. 4 for the spectrum of **4** and exp. 9 for that of **6**. For 1-(1-cyclohexenyl)-3-penten-2-ol (**5**): IR (neat) 3400, 2900, 2850, 1440, 1010, 960 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 5.68 (ddq, J = 15.3, 6.4, 0.6 Hz, 1H, CH=CH—CH_3), 5.54 (br s, 1H, CH=C), 5.47 (ddq, J = 15.3, 6.7, 1.5 Hz, 1H, CH=CH—CH_3), 4.13 (m, 1H, CHOH), 2.20–1.80 (m, 5H), 1.80–1.40 (m, 6H), 1.70 (dd, J = 0.6, 6.4 Hz, 3H, CH_3). MS *m/z* 166 (M^+); exact mass: calc for $C_{11}H_{18}O$: 166.1358; found: 166.1359.

9. 4 - (1 - *Cyclohexenyl*) - 3 - *methylbutanal* (**6**). To a suspension of KH (150 mg, 3.8 mmol) in 80 ml of THF at 25° was added a soln of the alcohol **4** (288 mg, 1.74 mmol) in 10 ml of THF, and a soln of 18-crown-6 (0.5 g, 2.0 mmol) in 5 ml of THF. The mixture was stirred for 6 h at 25°, quenched with sat NH_4Cl aq and concentrated. The crude product was purified by flash chromatography (5% EtOAc in hexanes) to yield 188 mg (65%) of the aldehyde **6** and 55 mg (19%) of the starting material. For **6**: IR (neat) 2820, 2740, 1720, 1400, 890 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 9.75 (t, J = 2.3 Hz, 1H, CHO), 5.40 (m, 1H,

† The ^{1}H-NMR spectrum of the minor isomer **4b** was obtained by subtraction of the spectrum of **4a** from that of the mixture.

vinyl), 2.45–2.35 (m, 1H), 2.35–2.10 (m, 2H), 2.10–1.80 (m, 6H), 1.80–1.40 (m, 3H), 0.93 (d, J = 6.4 Hz, 3H, CH—C<u>H</u>$_3$), 0.94 (m, 1H); MS *m/z* 166 (M^+); exact mass: calc for $C_{11}H_{18}O$: 166.1361; found: 166.1358.

10. 1,2,3,4,6,7,8,8a - *Octahydro* - 1 - *hydroxy* - 3 - *methylnaphthalene* (**8**). To a soln of **6** (188 mg, 1.13 mmol) in 20 ml of dry CH_2Cl_2 at −78° was added dropwise 3.4 ml of Me_2AlCl (1.4 M in hexanes, 4.7 mmol). The reaction was followed by TLC. After 2 h, the mixture was treated with sat NaH_2PO_4 aq and extracted twice with ether. The combined ether extracts were washed with 10% HCl and water, dried ($MgSO_4$) and concentrated. The crude product was purified by flash chromatography (10% EtOAc in hexanes) to obtain 145 mg (71%) of the alcohol **8** as a white solid. M.p. 58.5°; IR (neat) 3550, 1400, 1175, 1025 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 5.65 (s, 1H, vinyl), 3.87 (m, 1H, C<u>H</u>OH), 2.28–2.10 (m, 2H), 2.1–1.6 (m, 8H), 1.47 (m, 1H), 1.35 (d, J = 7.5 Hz, 1H, O<u>H</u>), 1.23 (ddd, J = 2.0, 11.2, 12.1 Hz, 1H), 0.91 (d, J = 6.3 Hz, 3H, CH_3). (Based upon irradiation experiments, the methyl and the hydroxyl groups are presumably *trans*.) MS *m/z* 148 ($M^+ - H_2O$); exact mass: calc for $C_{11}H_{16}$ ($M^+ - H_2O$): 148.1252; found: 148.1252.

11. 1,2,3,4,5,6,7,8 - *Octahydro* - 3 - *methyl* - 1 - *oxo* - *naphthalene*.[15] To a soln of DMSO (71 μl, 1.0 mmol) in 1 ml of CH_2Cl_2 under argon at −78° was added a soln of oxalyl chloride (47 μl, 0.5 mmol) in 5 ml of CH_2Cl_2. To this mixture was added dropwise a soln of **8** (50 mg, 0.3 mmol) in 3 ml of CH_2Cl_2. After 15 min, the mixture was treated with Et_3N (0.2 ml, 1.5 mmol) and the cold bath was removed. After 1 h, the mixture was treated with sat NH_4Cl aq and concentrated. As before, the residue was dissolved in ether, washed with 10% HCl and H_2O, dried ($MgSO_4$) and concentrated. The crude product on flash chromatographic separation gave 36.8 mg (73.6%) of the conjugated enone and 13.0 mg (26%) of the starting material. IR (neat) 1650, 1630 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.46 (dd, J = 2.4, 14.4 Hz, 1H), 2.30–1.90 (m, 8H), 1.75–1.60 (m, 2H), 1.60–1.45 (m, 2H), 1.03 (d, J = 6.4 Hz, 3H, CH—C<u>H</u>$_3$). MS *m/z* 164 (M^+); exact mass: calc for $C_{11}H_{16}O$: 164.1200; found: 164.1201.

Acknowledgements—We thank the National Institutes of Health for financial support (GM 22760), the National Science Foundation for funds used to purchase the 300 MHz Bruker NMR instrument used in this study (CHE 7905185), Dr Alvin Marcus for recording the mass spectra, and Professor Manfred Reetz for providing several references.

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