favorably with an authentic sample prepared from the reaction of 1 with heptanal.

(*SS*)-4-Methyl-1-(*N*-methylphenylsulfonimidoyl)-2-pentanol (3d) was obtained (ca. 83 ± 5%) as a mixture of diastereomers from the reduction of (*SS*)-4-methyl-1-(*N*-methylphenylsulfonimidoyl)-2-pentanone **(2d)** with diborane at −78 °C. TLC (2:1 hexane/ethyl acetate) indicated the presence of a small amount of starting material in the mixture, but ^{1}H NMR indicated it to be less than 5%. In order not to alter the diastereomeric ratio produced, we did not remove the contaminant but allowed it to be carried along with the hydroxy sulfoximine to the next step. TLC and spectral data compared favorably with an authentic sample prepared by the reaction of (+)-1 with 3-methylbutanal.

(*SS*)-3,3-Dimethyl-1-(*N*-methylphenylsulfonimidoyl)-2-butanol (3b) was obtained (92%) as a mixture of diastereomers (ca. 8:1) from the reduction of (*SS*)-3,3-dimethyl-1-(*N*-methylphenylsulfonimidoyl)-2-butanone **(2b)** by diborane at −78 °C. TLC (2:1 hexane/ethyl acetate) and spectral data compared favorably with an authentic sample prepared by the reaction of (+)-1 with 2,2-dimethylpropanal.

Acknowledgment. We thank the National Science Foundation for support of this work.

Registry No. (+)-(*S*)-1, 33993-53-2; (*S*)-2a, 78742-26-4; (±)-2a, 80446-95-3; (*S*)-2b, 78742-25-3; (*S*)-2c, 80422-46-4; (*S*)-2d, 80422-47-5; 3a (isomer 1), 33903-51-4; 3a (isomer 2), 72174-41-5; (±)-3a (*R**,*R**), 80446-96-4; (±)-3a (*R**,*S**), 80446-97-5; 3b (isomer 1), 78742-30-0; 3b (isomer 2), 78742-34-4; 3c (isomer 1), 80422-48-6; 3c (isomer 2), 80422-49-7; 3d (isomer 1), 80422-50-0; 3d (isomer 2), 80422-51-1; (*S*)-4a, 1445-91-6; (*S*)-4b, 1517-67-5; (*S*)-4c, 6169-06-8; (*S*)-4d, 14898-80-7; benzonitrile, 100-47-0; 2,2-dimethylpropanonitrile, 630-18-2; heptanonitrile, 629-08-3; 3-methylbutyronitrile, 625-28-5; 2-phenylethanol, 60-12-8.

Reactions of 3-(Phenylthio)-3-buten-2-one with Cycloalkanones. A New Approach to Fused Phenols

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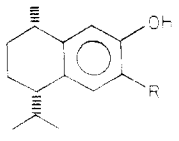
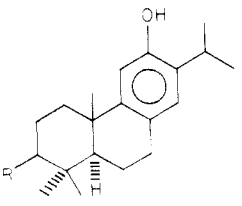
Received August 10, 1981

Synthesis and properties of 3-(phenylthio)-3-buten-2-one (**7**) have been described. The butenone **7** reacted with lithium cycloalkanone enolates to give ketols **14** or diketones **15** in good yields, which were easily transformed into fused phenols **17** by the treatment with *p*-toluenesulfonic acid or sodium ethoxide, respectively. Oxidative elimination of the sulfenyl group of **14a** afforded also 2-naphthol **17a**. Tetrahydronaphthalene **23**, a key intermediate of calamenene **1a** and calamenenal **1b**, was successfully synthesized by this approach by starting from *l*-carvone (**19**). Bicyclo[2.2.2]octanone **25** was obtained in the reaction of **7** with kinetic enolate of 2-cyclohexen-1-one in 84% yield.

Fused β-phenols are important structural units in natural products, for example, 7-hydroxycalamenene (**1a**), 7-hydroxycalamenenal (**1b**),[1] ferruginol (**2a**),[2] and hinokiol (**2b**).[3] Synthesis of these units has been based on the

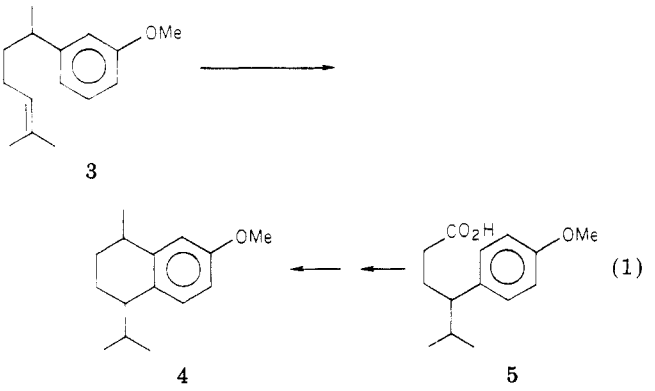


1a, R = Me
b, R = CHO



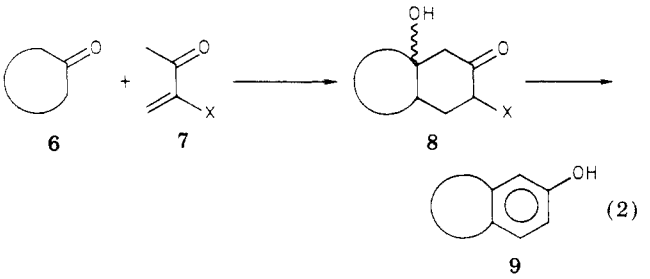
2a, R = H
b, R = OH

electrophilic substitution starting from phenol derivatives (eq 1).[4] However, this process has many limitations: (i) generation of the precursors **3** and **5** involved several nonconvergent steps; (ii) undesired products were accompanied by cationic species, and therefore yields were often low; (iii) the stereochemistry of substituents on the alicyclic



(1)

rings was not controlled. To overcome these limitations, we can envision a new strategy based on annelative method where readily available cycloalkanones **6** will react with 3-buten-2-one derivatives **7** to give ketols **8**, followed by aromatization (eq 2). This approach is closely related to

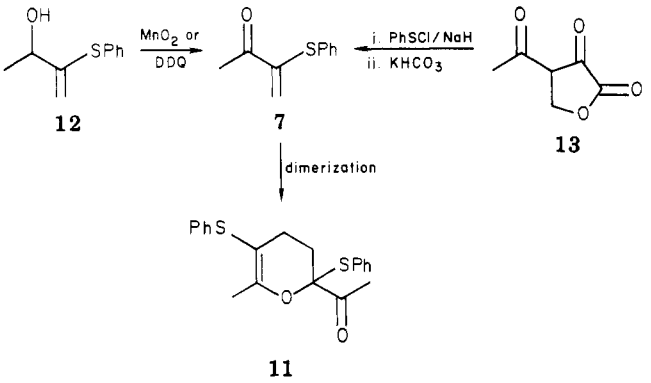


(2)

(1) (a) Rowe, J. W.; Toda, J. K. *Chem. Ind. (London)* **1969**, 922. (b) Lindgren, O. B.; Svahn, C. M. *Phytochemistry* **1968**, *7*, 1407; *Chem. Abstr.* **1968**, *69*, 65131.
(2) (a) Brandt, C. W.; Neubauer, L. G. *J. Chem. Soc.* **1939**, 1031. (b) King, F. E.; King, T. J.; Topliss, J. G.; *Ibid.* **1957**, 573. (c) Ohashi, M., Maruishi, T.; Kakisawa, H. *Tetrahedron Lett.* **1968**, 719.
(3) (a) Chow, Y.; Erdtman, H. *Acta Chem. Scand.* **1962**, *16*, 1296. (b) Matsumoto, T.; Usui, S.; Kawashima, H.; Mitsuki, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 581.
(4) (a) Bohlmann, F.; Mailahn, W. *Chem. Ber.* **1981**, *114*, 1091. (b) Alexander, J.; Rao, G. S. K. *Tetrahedron* **1971**, *27*, 645.

0022-3263/82/1947-1200$01.25/0

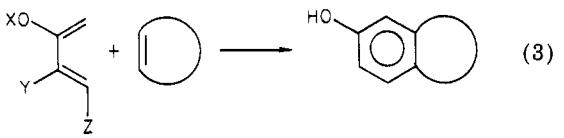
Scheme I



Boger's "phenol annelation" method,[5] which appeared at the same time as our preliminary communication,[6] wherein the eliminating group was attached to α-position of cyclohexanone instead of the butenones.

The choice of substituents X is significant for successful transformation because they are required to stabilize carbanions and be eliminated oxidatively, and therefore we considered sulfenyl group to be suitable.[7] Although many modified 3-buten-2-one reagents have been reported for total synthesis of natural products,[8] the corresponding sulfur analogues have been little known unfortunately. Synthesis of 3-(phenylthio)-3-buten-2-one (7) by Tishchenko's method[9] was doubtful, and McMurry described that its annelation was absolutely unsuccessful owing to polymerization.[10]

Other approaches to the phenol rings via Diels–Alder reactions of suitably functionalized dienes **10** with dienophiles have been recently suggested by Danishefsky[11] and Trost[12] (eq 3). Thus, the reagent **7** is of interest also as a synthon of **10**.



(3)

10, X = Ac(SiMe$_3$); Y = SAr(H); Z = H(OMe)

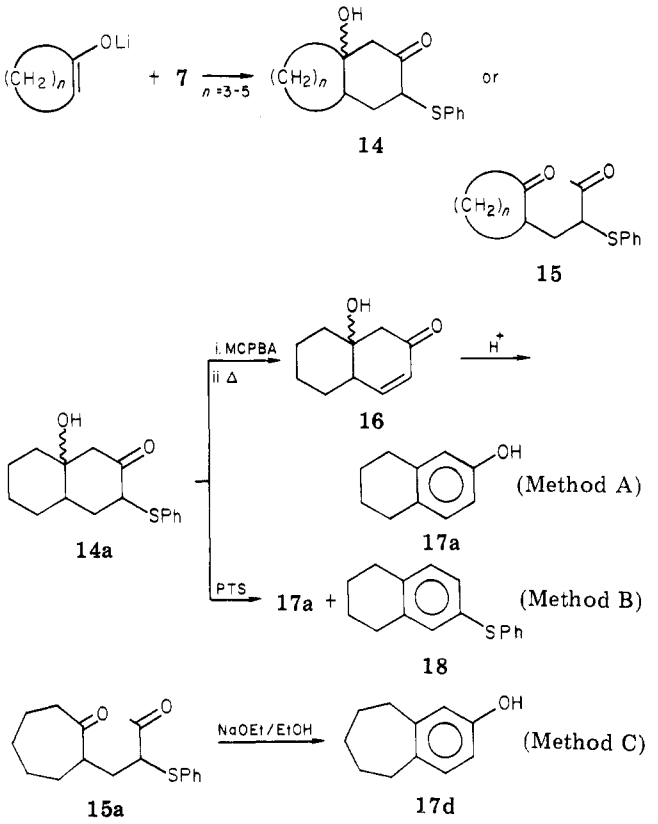
From such a point of view, we report herein the synthesis and properties of **7** and the reactions with cycloalkanones to yield fused phenols, especially calamenene derivatives.

Results and Discussion

Synthesis and Properties of 3-(Phenylthio)-3-buten-2-one (7).[13] It has been reported that treatment of 4-hydroxy-3-(phenylthio)-2-butanone with zinc chloride gave the butenone **7**,[9] but the conditions were too severe to isolate **7**, and the product was truly the dimer of **7**, 2-acetyl-2,5-bis(phenylthio)-6-methyl-3,4-dihydropyran (**11**), in our investigation. We examined oxidation of 3-(phenylthio)-3-buten-2-ol (**12**) with various reagents (Scheme I). Oxidation with MnO_2[14] and Jones reagent yielded diphenyl disulfide instead of **7**. Treatment with less reactive MnO_2[15] and DDQ gave **7** in 32% and 52% yields, respectively. Reaction of 3-acetyl-2-oxo-γ-butyrolactone (**13**) with phenylsulfenyl chloride and subsequent degradation afforded the butenone **7** in 90% yield, alternatively.

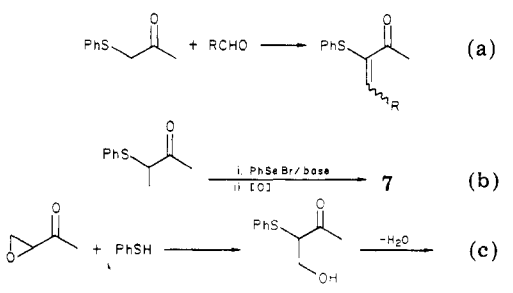
While the butenone **7** was relatively stable in acidic solution, exposure of **7** to alkaline solution resulted in the formation of the dimer **11** and diphenyl disulfide (see Experimental Section). NMR analyses showed that half of the butenone **7** had been changed to the dimer **11** after 30 h in chloroform at room temperature. Accordingly, the

Scheme II



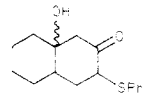
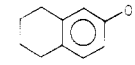
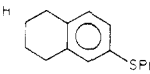
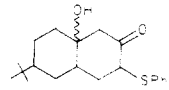
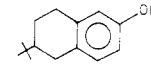
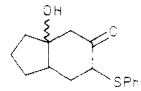
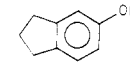
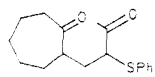
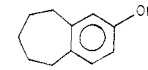
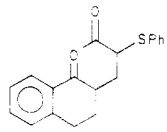
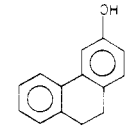
(5) Boger, D. L.; Mullican, M. D. *J. Org. Chem.* **1980**, *45*, 5002.
(6) Takaki, K.; Okada, M.; Yamada, M.; Negoro, K. *J. Chem. Soc., Chem. Commun.* **1980**, 1183.
(7) Davidson, A. H., Hodgson, P. K. G.; Howells, D.; Warren, S. *Chem. Ind. (London)* **1975**, 455.
(8) For a review, see: Jung, M. E. *Tetrahedron* **1976**, *32*, 3.
(9) Tishchenko, I. G.; Malashko, P. M. *Khim. Gerotsikl. Soedin.* **1966**, 483; *Chem. Abstr.* **1967**, *66*, 28407.
(10) Ksander, G. M.; McMurry, J. E.; Johnson, M. *J. Org. Chem.* **1977**, *42*, 1180.
(11) (a) Danishefsky, S.; Kitahara, T. *J. Am. Chem. Soc.* **1974**, *96*, 7807. (b) Danishefsky, S.; Hirama, M.; Gombatz, K.; Hirayama, T.; Berman, E.; Schuda, P. *Ibid.* **1978**, *100*, 6536.
(12) (a) Trost, B. M.; Ippen, J.; Vladuchick, W. C. *J. Am. Chem. Soc.* **1977**, *99*, 8116. (b) Trost, B. M. Vladuchick, W. C.; Bridge, A. J. *Ibid.* **1980**, *102*, 3554.

(13) We examined other methods as follows:



Although 4-alkyl-3-(phenylthio)-3-buten-2-ones were prepared by these methods, they were not practical for a large-scale synthesis of **7** because of low yields, polymerization, and impurity.
(14) Goldman, I. M.; *J. Org. Chem.* **1969**, *34*, 1979.
(15) Attenburrow, J.; Cameron, A. F. B.; Chapman, J. H.; Evans, R. M.; Hems, B. A.; Jansen, A. B. A.; Walker, T. *J. Chem. Soc.* **1952**, 1094.

Table I. Synthesis of Fused Phenols 17 from Butenone 7 and Cycloalkanones via Ketols 14 or Diketones 15

ketone	ketol or diketone[a]	yield,[b] % (ratio of diastereomers)[c]	method	phenol	yield,[b,d] %
	 14a	80 (1:3)	A B	 17a  18	70 + 0 74 + 21
	 14b	95 (1:1.5)	B	 17b	94
	 14c	68 (1:1.5)	B	 17c	98
	 15a	85[e]	C	 17d	86
	 15b	67 (1:2)	C	 17e	42

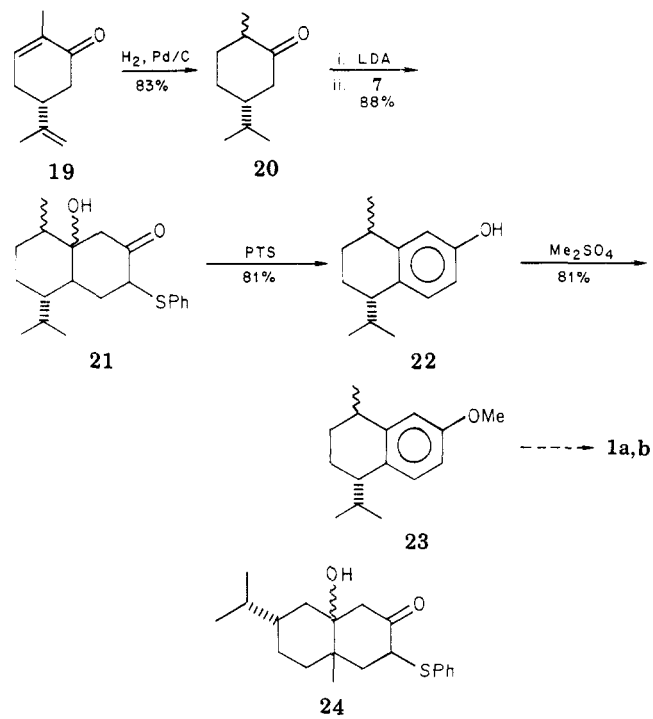
[a] Reaction conditions: −70 °C (1 h) to room temperature (4.5 h). [b] Yields of isolated products. [c] Determined by NMR and GC. [d] Based on ketols or diketones. [e] Ratio was not determined clearly.

butenone **7** should be treated at low temperature to avoid dimerization in the synthesis and reactions.

Synthesis of Fused Phenols. The butenone **7** was reacted with lithium cyclohexanone enolate at −70 °C for 1 h then at room temperature for 4.5 h to give 8a-hydroxy-3-(phenylthio)-2-decalone (**14a**) in 80% yield as a mixture of two diastereomers in a ratio of 1:3 (Scheme II). GC analyses of the mixture showed two close peaks, and that of the main product was the peak with the longer retention time. In the NMR spectrum, the two signals of the hydroxy group appeared at 3.33 and 4.40 ppm, the former being assignable to the *trans*-hydroxy group and the latter to the cis on the basis of the literature.[16] In addition, 8a-hydroxy-2-decalone (**26**) derived from **14a** as mentioned below was also a mixture in the same ratio as for **14a**. Accordingly, the mixture was stereoisomeric with respect to the ring junctions. On the other hand, reaction of **7** with cycloheptanone enolate under similar conditions afforded 2-[(3-oxo-2-(phenylthio)butyl]cycloheptanone (**15a**) in 85% yield instead of ketol.[17]

Aromatization of the ketol **14a** has been achieved by the following two methods. Oxidation of **14a** with *m*-chloroperbenzoic acid and subsequent elimination of the sulfoxide group[18] gave a mixture of 9-hydroxy-$\Delta^{3(4)}$-2-octalone (**16**) and 5,6,7,8-tetrahydro-2-naphthol (**17a**) in a ratio of 2:1, followed by acid treatment to afford **17a** in a total yield of 70% (method A). More conveniently, treatment of **14a** with *p*-toluenesulfonic acid gave readily the phenol **17a** and 6-(phenylthio)-1,2,3,4-tetrahydronaphthalene (**18**) in 74% and 21% yields, respectively (method B). In the cases of other ketols **14**, the (phenylthio)naphthalenes corresponding to **18** were not detected under similar conditions. On the contrary, when the diketone **15a** was exposed to sodium ethoxide in order to get ketol **14**, 2-hydroxy-6,7,8,9-tetrahydro-5*H*-benzocycloheptene (**17d**) was obtained directly in 86% yield and was produced presumably

Scheme III



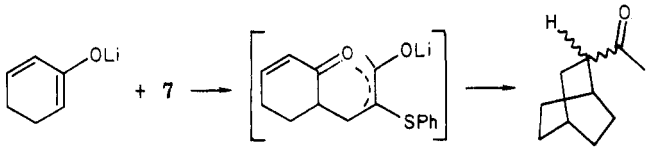
(16) Marshall, J. A.; Fanta, W. I. *J. Org. Chem.* **1964**, *29*, 2501.
(17) Whether the ketones would cyclize or not depends on the reaction conditions and the substrates. Cyclization of conjugated ketones and seven-membered ketones needs a generally prolonged reaction time and heating: Takaki, K.; Nakagawa, K.; Negoro, K. *J. Org. Chem.* **1980**, *45*, 4789. In the case of cyclohexanone, a long reaction time and heating (40 °C) caused the formation of the dehydrated product, 3-(phenylthio)-$\Delta^{1(9)}$-2-octalone (<9%), together with **14a**.
(18) Trost, B. M.; Salzmann, T. N.; Hiroi, K. *J. Am. Chem. Soc.* **1976**, *98*, 4887.

via the ketol and enone under alkaline conditions[19] (method C). These results are summarized in Table I.

The results described above showed the general utility of this method for the synthesis of fused phenols, and we applied it to the synthesis of 1-isopropyl-4-methyl-6-methoxy-1,2,3,4-tetrahydronaphthalene (**23**) which was a key compound of calamenene **1a** and calamenenal **1b**[20] (Scheme III).

l-Carvone (**19**) was hydrogenated to give carvomenthone (**20**) wherein the C-2 methyl was epimeric but was used in the next step without separation, because the two diastereomers were chromatographically homogeneous in this state and could be separable in the final products.[1] Reaction of the ketone **20** with the butenone **7** gave ketol **21** after gentle heating, and fortunately ketol **24**, an undesired product derived from thermodynamic enolate of **20**, was not present. The ketol **21** was readily aromatized to phenol **22**, followed by methylation to afford methoxynaphthalene **23** in good yield.

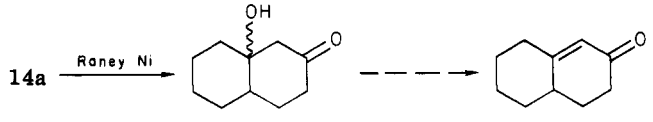
Other Reactions of Butenone 7. In order to get further information about the reactivities of **7**, we studied the reaction with the kinetic enolate of 2-cyclohexen-1-one which would yield the $\Delta^{7(8)}$-2-octalone derivative by simple cyclization or bicyclo[2.2.2]octanone by double Michael additions.[21] 5-Acetylbicyclo[2.2.2]octan-2-one (**25**) was



25

indeed obtained in 84% yield as a mixture of exo and endo products in a ratio of 1:1, where the phenylsulfenyl group was eliminated under reaction conditions.[22]

The butenone **7** was also applicable to the usual annelation reaction since the ketol **14a** was desulfurized before aromatization with Raney Ni to give 8a-hydroxy-2-decalone (**26**) in 91% yield which was readily converted to $\Delta^{1(9)}$-2-octalone (**27**).[16]



26 27

Conclusion

Although treatment of the butenone **7** demands some care so that it does not dimerize, synthesis of fused phenols is accomplished in high yields by simple operations, formation of undesired byproducts is suppressed, and each intermediate can be isolated if desired. Since β-phenol units are attached regioselectively to readily available cycloalkanones, this method provides a wide utility for a variety of ring sizes where stereochemistry of substituents on the alicyclic rings is generally unchanged. Furthermore, introduction of functionalities at the γ-position of the phenol rings is expected on utilization of the ketols and diketones before aromatization, and this is now under investigation.

Experimental Section

Melting points were measured with a Yanagimoto micro melting point apparatus and uncorrected. IR spectra were recorded with a Hitachi 215 spectrophotometer. ^{1}H NMR spectra were obtained from a JEOL PMX-60, and chemical shifts are reported in parts per million on the δ scale from intenal tetramethylsilane. Mass spectra were taken with a Hitachi RMU-6D mass spectrometer. Microanalyses were determined on a Yanagimoto CHN-Corder, Type II. GLC analyses were performed on a KOR-70 equipped with an FID and on a G-80 with a TCD and a 2 m × 3 mm i.d. column of 10% OV-17 and 10% SE-30 on Chromosorb W. Column chromatography was carried out on Wakogel C-300 (silica gel).

Synthesis of 3-(Phenylthio)-3-buten-2-one (7). Procedure A. Bromine (111.9 g, 0.70 mol) was added to a stirred solution of phenyl vinyl sulfide (95.2 g, 0.70 mol) in ether (500 mL) with cooling in an ice bath. After the mixture was stirred for 1 h, DBU (106.6 g, 0.70 mol) in ether (100 mL) was added to the mixture, and stirring was continued for 1 h at 0 °C. Then the mixture was poured into water (200 mL), extracted with ether, dried over sodium sulfate, concentrated, followed by distillation in vacuo to give 136.0 g (90%) of phenyl α-bromovinyl sulfide: bp 70–73 °C (2 mm); IR (neat) 1580 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.82 (d, J = 2.0 Hz, 1 H), 5.92 (d, J = 2.0 Hz, 1 H), 7.17–7.60 (m, 5 H). A solution of the bromovinyl sulfide (6.45 g, 30 mmol) in dry THF (100 mL) was treated with 1.56 M *n*-butyllithium (21.2 mL, 33 mmol) under N_2 at −70 °C, and the mixture was stirred for 1 h at this temperature. Then, acetaldehyde (1.59 g, 36 mmol) in THF (60 mL) was added dropwise to the mixture, and stirring was continued at −70 °C for 1 h and at room temperature for 1 h. Aqueous ammonium chloride solution (5%, 50 mL) was added to the mixture, and the organic layer was extracted with ether, dried over sodium sulfate, and concentrated. Distillation of the residue in vacuo gave pure 3.73 g (69%) of 3-(phenylthio)-3-buten-2-ol (**12**): bp 88–92 °C (2 mm); IR (neat) 3350, 1600 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.14 (d, J = 6.0 Hz, 3 H), 2.13 (s, 1 H, OH), 4.33 (q, J = 6.0 Hz, 1 H), 4.93 (s, 1 H), 5.45 (s, 1 H), 7.07–7.60 (m, 5 H).

A suspension of MnO_2 (30 g, 345 mmol), prepared by Attenburrow's method,[15] and the alcohol **12** (3.51 g, 20 mmol) in chloroform (150 mL) was stirred for 20 h at room temperature. The reaction mixture was filtered, and the filtrate was concentrated in vacuo. The residue contained the butenone **7** in 32% yield by GC and NMR analyses.

The alcohol **12** (1.0 g, 5.6 mmol) was added to a stirred solution of DDQ (1.25 g, 5.5 mmol) in dry benzene (100 mL) with cooling in an ice bath. After the mixture was stirred for 24 h at 0 °C, the solvent was removed in vacuo, and the residue was diluted with ether, washed with 20% aqueous sodium hydroxide solution, and dried over sodium sulfate. Concentration of the solvent gave **7** (52%) and diphenyl disulfide (10%).

Similar oxidation of **12** with MnO_2 prepared by Goldman's method[14] (10 equiv, hexane, 14 h, 0 °C) and with Jones reagent[23] (2 equiv, acetone, 30 min, 0 °C) gave diphenyl disulfide in 83% and 73% yields, respectively, and the butenone **7** was not isolated.

Procedure B (Modified McMurry Method[10]). Anhydrous 3-acetyl-2-oxo-γ-butyrolactone (**13**; 4.26 g, 30 mmol) prepared according to the established method[24] was treated with a suspension of sodium hydride (0.79 g, 33 mmol) in dry THF (30 mL) with cooling under N_2. The mixture was stirred until evolution of H_2 had ceased, and then phenylsulfenyl chloride (3.61 g, 25 mmol) in dry THF (30 mL) was added to the mixture. After being stirred for 3 h at room temperature, the mixture was cooled to 0 °C, 20% aqueous $KHCO_3$ solution (80 mL) was added to the mixture cautiously to avoid vigorous heat generation, and additional stirring was continued for 30 min. The organic layer was

(19) Treatment of the ketols **14** with sodium ethoxide gave polymeric tar.
(20) The compound **23** was also converted to cadalenal and cadalene.[1]
(21) White, K. B.; Reusch, W. *Tetrahedron* **1978**, *34*, 2439.
(22) The phenylsulfenyl group was recovered as diphenyl disulfide. The stereochemistry of **25** suggested that the substituent was eliminated after formation of the bicyclo[2.2.2]octanone ring, since endo selectivity and slight epimerization at C-5 were observed in the reaction of methyl vinyl ketone with cyclohexenone derivatives.[21]
(23) (a) Vanstone, A. E.; Whitehurst, J. S. *J. Chem. Soc. C* **1966**, 1972. (b) Glotter, E.; Greenfield, S.; Lavie, D. *Ibid.* **1968**, 1646. (c) Burstein, S. H.; Ringold, H. J.; *J. Am. Chem. Soc.* **1967**, *89*, 4722.
(24) Nield, C. H.; *J. Am. Chem. Soc.* **1945**, *67*, 1145.

quickly extracted with ether and dried over sodium sulfate in a refrigerator. Evaporation of the solvent below 0 °C in vacuo gave 4.02 g (90%) of the butenone **7** as yellow crystals which melted at room temperature. GC and NMR analyses showed that the purity of the crystals was 98%, and therefore they were used in the next reactions without further purification.[25] 3-(Phenylthio)-3-buten-2-one (**7**): IR (Nujol) 1670, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.37 (s, 3 H), 5.27 (d, J = 1.0 Hz, 1 H), 6.07 (d, J = 1.0 Hz, 1 H), 7.00–7.50 (m, 5 H); mass spectrum (70 eV), m/e 178 (M^+).

Properties of Butenone 7. The butenone **7** (0.30 g, 1.7 mmol) in MeOH (25 mL) was treated with 5% aqueous HCl (1 mL) at 0 °C for 3 h, and the mixture was extracted with ether, dried over $MgSO_4$, and concentrated in vacuo below 0 °C. The residue contained **7**, the dimer **11**, and diphenyl disulfide in 59%, 35%, and 6% yields, respectively. Similar treatment of **7** with 5% aqueous NaOH solution gave the dimer **11**, diphenyl disulfide, and unknown product in 30%, 40%, and 30% yields, respectively, and **7** was not recovered. The butenone **7** was converted quantitatively to the dimer **11** by gentle heating. Then, the stability of **7** was measured at room temperature (25 °C) by NMR ($CDCl_3$, 9.4 wt %), and the ratio of **7** to **11** was as follows: 98:2 (0 h), 73:27 (6.5 h), 48:52 (30 h), 35:65 (52 h), 27:73 (80 h). 2-Acetyl-2,5-bis(phenylthio)-6-methyl-3,4-dihydropyran (**11**): mp 77–77.5 °C (EtOH); IR (neat) 1710, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.98 (s, 3 H), 2.07–2.43 (m, 7 H), 6.95–7.58 (m, 10 H); mass spectrum (70 eV), m/e 356 (M^+).

Anal. Calcd for $C_{20}H_{20}O_2S_2$: C, 67.40; H, 5.66. Found: C, 67.45; H, 5.73.

The dimer was changed to 2-acetyl-6-methyl-3,4-dihydro-2*H*-pyran (Raney Ni, EtOH, reflux, 8 h) in 65% yield and identified with an authentic sample.[26]

The reagent **7** can be prepared on a large scale and stocked in a refrigerator for about 3 months as crystals or a THF solution.

Reactions of Butenone 7 with Lithium Cycloalkanone Enolates. General Procedure. Cycloalkanone (30 mmol) was added to a solution of LDA (33 mmol) in dry THF (30 mL) at −70 °C under N_2, and stirring was continued for 3 h. The butenone **7** (5.27 g, 30 mmol) in dry THF (40 mL) was added to the mixture, and the resulting solution was stirred for 1 h at −70 °C and then allowed to warm to room temperature for 4.5 h. After addition of saturated aqueous ammonium chloride solution (40 mL) to the mixture, the water layer was separated and extracted with ether. The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated in vacuo to give yellow oil, which was chromatographed on silica gel with hexane, benzene, and benzene–ether.

8a-Hydroxy-3-(phenylthio)-2-decalone (14a): mp 167–168 °C (acetone–hexane); IR (Nujol) 3450, 1700 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 1.00–2.00 (m, 11 H), 2.15–2.85 (m, 2 H), 3.33 (s, 0.75 H, OH), 4.40 (s, 0.25 H, OH), 4.15–4.60 (m, 1 H), 7.00–7.60 (m, 5 H); mass spectrum (70 eV), m/e 276 (M^+).

Anal. Calcd for $C_{16}H_{20}O_2S$: C, 69.54; H, 7.30. Found: C, 69.47; H, 7.35.

In this reaction, 3-(phenylthio)-$\Delta^{1(9)}$-2-octalone was sometimes obtained as a byproduct: <9% yield; colorless oil; IR (neat) 1660, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10–2.90 (m, 11 H), 3.60–4.13 (m, 1 H), 5.75–6.00 (m, 1 H), 7.03–7.73 (m, 5 H).

6-*tert*-Butyl-8a-hydroxy-3-(phenylthio)-2-decalone (14b): mp 196–198 °C (acetone–hexane); IR (Nujol) 3450, 1700 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 0.82 (s, 9 H), 0.98–3.20 (m, 12 H), 3.33 (s, 0.6 H, OH), 3.55–3.92 (m, 1 H), 4.40 (s, 0.4 H, OH), 7.00–7.50 (m, 5 H).

Anal. Calcd for $C_{20}H_{28}O_2S$: C, 72.26; H, 8.49. Found: C, 72.60; H, 8.74.

3a-Hydroxy-6-(phenylthio)hexahydro-5-indanone (14c): IR (neat) 3450, 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05–2.53 (m, 10 H), 2.95–3.40 (m, 2 H), 3.63–4.10 (m, 1 H), 7.00–7.66 (m, 5 H).

2-[3-Oxo-2-(phenylthio)butyl]cycloheptanone (15a): IR (neat) 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12–2.15 (m, 10 H), 2.25 (s, 3 H), 2.32–3.08 (m, 3 H), 3.55–3.88 (m, 1 H), 7.11–7.48 (m, 5 H).

2-[3-Oxo-2-(phenylthio)butyl]-α-tetralone (15b): IR (neat) 1710, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60–2.23 (m, 4 H), 2.30 (s, 3 H), 2.77–3.17 (m, 3 H), 3.90–4.30 (m, 1 H), 7.03–7.60 (m, 8 H), 7.83–8.10 (m, 1 H).

Aromatization of the Ketols 14 and Diketones 15. Method A. MCPBA (80%, 431 mg, 2.0 mmol) in dichloromethane (20 mL) was added to a solution of the diketone **14a** (0.50 g, 1.81 mmol) in dichloromethane (40 mL) with cooling at −10 °C and then stirring was continued for 1 h at room temperature. The mixture was treated with 10% aqueous sodium sulfite solution (3 × 30 mL), and the water layer was extracted with dichloromethane. The combined organic layers were washed with 10% aqueous sodium bicarbonate solution (2 × 30 mL) dried over sodium sulfate, and concetrated to give yellow residue. The byproduct 8a-hydroxy-3-(phenylsulfonyl)-2-decalone crystallized from the residue on standing and was filtered: 56 mg (10%); mp 185–186 °C (EtOH); IR (Nujol) 3500, 1715, 1305, 1145 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90–1.97 (m, 10 H), 2.02–2.48 (m, 4 H), 3.85–4.23 (m, 1 H), 7.18–7.72 (m, 3 H), 7.92–8.23 (m, 2 H).

Anal. Calcd for $C_{16}H_{20}O_4S$: C, 62.32; H, 6.54. Found: C, 62.17; H, 6.52.

The filtrate (445 mg) was dissolved in benzene (20 mL) and treated with sodium carbonate (168 mg) under reflux for 4 h. After filtration, the mixture was concentrated to give 0.27 g of residue which contained the phenol **17a** and 9-hydroxy-$\Delta^{3(4)}$-2-octalone (**16**: IR (neat) 3400, 1680, 1580 cm^{-1}) in a ratio of 1:2 as determined by GC. A solution of this mixture and *p*-toluenesulfonic acid monohydrate (130 mg, 0.68 mmol) in benzene (15 mL) was refluxed for 3.5 h. After cooling, the mixture was washed with 10% aqueous sodium bicarbonate solution and brine, dried over sodium sulfate, and concentrated to give 188 mg (70%) of 5,6,7,8-tetrahydro-2-naphthol (**17a**): mp 56–57 °C (hexane–benzene); IR (neat) 3300, 1600, 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40–2.10 (m, 4 H), 2.33–3.00 (m, 4 H), 5.10 (br, 1 H, OH), 6.37–7.17 (m, 3 H); mass spectrum (70 eV), m/e 148 (M^+). The product **17a** was identified with a commercially available authentic sample.

Method B. A solution of the ketol **14a** (1.0 g, 3.6 mmol) and *p*-toluenesulfonic acid monohydrate (171 mg, 0.9 mmol) in benzene (60 mL) was refluxed for 6.5 h. After cooling, the mixture was poured into 10% aqueous sodium carbonate solution (60 mL) and extracted with benzene, and the extract was dried over sodium sulfate and concentrated in vacuo. The residue was chromatographed on silica gel. The phenol **17a** was obtained in 74% yield (0.39 g). 6-(Phenylthio)-1,2,3,4-tetrahydronaphthalene (**18**) was also isolated [0.18 g (21%); mass spectrum (70 eV), m/e 240 (M^+)], was changed to 1,2,3,4-tetrahydronaphthalene by the treatment with Raney Ni (EtOH, reflux, 8.5 h, 24% yield), and was identified with an authentic sample.

Method C. A solution of the diketone **15a** (4.78 g, 16.5 mmol) and sodium ethoxide (16.5 mmol) in absolute ethanol (40 mL) was stirred at room temperature for 4 h and then heated to 50 °C for 1.5 h. After cooling, the mixture was poured into chilled water, neutralized with hydrochloric acid, extracted with ether, dried over sodium sulfate, and concentrated. Distillation of the residue gave 2.30 g (86%) of 2-hydroxy-6,7,8,9-tetrahydro-5*H*-benzocycloheptene (**17d**); bp 150 °C (4 mm, Kugelrohr); IR (neat) 3350, 1600, 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26–1.97 (m, 6 H), 2.42–2.86 (m, 4 H), 5.38 (br, 1 H, OH), 6.38–7.10 (m, 3 H); mass spectrum (70 eV), m/e 162 (M^+).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.70; H, 9.10.

6-*tert*-Butyl-5,6,7,8-tetrahydro-2-naphthol (17b): mp 99–100 °C (hexane–benzene); IR (neat) 3300, 1610, 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (s, 9 H), 1.07–2.29 (m, 3 H), 2.30–3.10 (m, 4 H), 4.80 (br, 1 H, OH), 6.27–7.10 (m, 3 H); mass spectrum (70 eV), m/e 204 (M^+).

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.54; H, 9.80.

5-Indanol (17c): bp 80 °C (2 mm; bath temperature); IR (neat) 3350, 1600, 1570 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.82–2.38 (m, 2 H), 2.80 (t, J = 6.5 Hz, 4 H), 4.67 (br, 1 H, OH), 6.43–7.56 (m, 3 H); mass spectrum (70 eV), m/e 134 (M^+). This product was identified with a commercially available authentic sample.

3-Hydroxy-9,10-dihydrophenanthrene (17e): bp 180 °C (3 mm, Kugelrohr); IR (neat) 3300, 1605, 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.77 (s, 4 H), 3.90 (br, 1 H, OH), 6.50–7.83 (m, 7 H);

(25) A small amount of the dimer **11** was contained (<2%), but short-path distillation was unsuccessful.

(26) Alder, K.; Offermanns, H.; Rüden, E. *Chem. Ber.* **1941**, *74*, 905.

mass spectrum (70 eV), m/e 196 (M^+).

Anal. Calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.40; H, 6.21.

Carvomenthone (20). A solution of *l*-carvone (**19**; 23.0 g, 153 mmol) in ethanol (230 mL) containing 1.75 g of palladium on carbon (5%) was hydrogenated (1 kg/cm^2) until the calculated amount of hydrogen (2 equiv) was absorbed. The mixture was filtered, and the solvent was evaporated in vacuo. Distillation of the residue gave 19.5 g (83%) of the product **20**: bp 101-103 °C (21 mm); IR (neat) 1715 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.70-1.23 (m, 9 H), 1.23-2.00 (m, 6 H), 2.00-2.67 (m, 3 H).

8a-Hydroxy-5-isopropyl-8-methyl-3-(phenylthio)-2-decalone (21). Carvomenthone (**20**; 12.0 g, 78 mmol) was added to a stirred solution of LDA (86 mmol) in dry THF (140 mL) at -78 °C under N_2, and stirring was continued for 2 h. The butenone **7** (13.9 g, 78 mmol) in dry THF (80 mL) was added dropwise to the mixture, and the resulting solution was stirred for 2 h at -78 °C, allowed to warm to room temperature for 6 h, and then stirred at 40 °C for 2 h. After addition of 10% hydrochloric acid (20 mL), the mixture was extracted with ether, washed with brine, dried over sodium sulfate, and concentrated to give 26.9 g of yellow oil. The oily residue (10 g) was chromatographed on silica gel (benzene-ether, 1:1) to give 8.48 g (88%) of the ketol **21**: mp 157-159 °C (hexane-benzene); IR (Nujol) 3450, 1710 cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 0.90-1.07 (m, 9 H), 1.07-3.10 (m, 12 H), 3.33 (s, 0.7 H, OH), 3.83 (br, 1 H), 4.20 (s, 0.3 H, OH), 7.13-7.87 (m, 5 H).

Anal. Calcd for $C_{20}H_{28}O_2S$: C, 72.26; H, 8.49. Found: C, 72.54; H, 8.40.

5-Isopropyl-8-methyl-5,6,7,8-tetrahydro-2-naphthol (22). A solution of the ketol **21** (1.20 g, 3.6 mmol) and *p*-toluenesulfonic acid monohydrate (171 mg, 0.9 mmol) in benzene (150 mL) was refluxed for 6 h. After cooling, the mixture was poured into 10% aqueous sodium bicarbonate solution, extracted with benzene, dried over sodium sulfate, and concentrated in vacuo. Kugelrohr distillation afforded 0.60 g (81%) of the naphthol **22**: bp 130 °C (3 mm); IR (neat) 3350, 1610, 1580 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.71, 0.75, 0.91, 1.00 (4 d, J = 6.5, 6.5, 7.0, 7.0 Hz, respectively, total 6 H), 1.23 (d, J = 7.0 Hz, 3 H), 1.40-3.03 (m, 7 H), 4.47 (br, 1 H, OH), 6.47-7.67 (m, 3 H).

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.61; H, 9.87.

1-Isopropyl-4-methyl-6-methoxy-1,2,3,4-tetrahydronaphthalene (23). A solution of the naphthol **22** (200 mg, 0.98 mmol), dimethyl sulfate (189 mg, 1.5 mmol), and powdered potassium carbonate (621 mg, 4.5 mmol) in dry acetone (40 mL) was refluxed for 3 h. The mixture was filtered and concentrated. Kugelrohr distillation gave 173 mg (81%) of the naphthalene **23**: bp 130 °C (3 mm); IR (neat) 1605, 1570, 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.71, 0.75, 0.97, 1.00 (4d, J = 6.5, 6.5, 7.0, 7.0 Hz, respectively, total 6 H), 1.26 (d, J = 7.0 Hz, 3 H), 1.40-3.07 (m, 7 H), 3.77 (s, 3 H), 6.53-7.37 (m, 3 H); mass spectrum (70 eV), m/e 218 (M^+).

Anal. Calcd for $C_{15}H_{22}O$: C, 82.51; H, 10.16. Found: C, 82.89; H, 9.89.

5-Acetylbicyclo[2.2.2]octan-2-one (25). 2-Cyclohexen-1-one (0.96 g, 10 mmol) in dry THF (10 mL) was added to a stirred solution of LDA (11 mmol) and HMPA (11 mmol) in dry THF (10 mL) at -50 °C under N_2, and stirring was continued for 1 h. The butenone **7** (1.78 g, 10 mmol) in dry THF (10 mL) was added dropwise to the mixture, and the resulting solution was allowed to stir for 1 h at -50 °C and then for 12 h at room temperature. The mixture was quenched by addition of saturated aqueous ammonium chloride solution (20 mL), and the organic layer was separated. The water layer was extracted with ether, and the combined extracts were washed with brine, dried over sodium sulfate, and concentrated. The residue was chromatographed on silica gel to give 1.40 g (84%) of the octanone **25**: IR (neat) 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.08-2.13 (m, 7 H), 2.22 (s, 3 H), 2.27-3.17 (m, 4 H); mass spectrum (70 eV), m/e 166 (M^+).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.91; H, 8.30.

8a-Hydroxy-2-decalone (26). The ketol **14a** (0.90 g, 3.3 mmol) was treated with excess Raney Ni in ethanol (60 mL) under reflux for 26 h. After filtration, the mixture was concentrated to give 0.50 g (91%) of crystals: mp 151-152 °C (hexane-acetone); IR (Nujol) 3300, 1700 cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 0.95-1.83 (m, 11 H), 1.93-2.63 (m, 4 H), 3.33 (s, 0.75 H, OH), 4.20 (s, 0.25 H, OH); mass spectrum (70 eV), m/e 168 (M^+).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.72; H, 9.50.

Registry No. **7**, 13522-48-0; **11**, 19718-58-2; **12**, 77202-27-8; **13**, 61203-07-4; **14a** (isomer 1), 80485-41-2; **14a** (isomer 2), 80485-42-3; **14b** (isomer 1), 80485-43-4; **14b** (isomer 2), 80485-44-5; **14c** (isomer 1), 80485-45-6; **14c** (isomer 2), 80485-46-7; **15a**, 77202-26-7; **15b** (isomer 1), 80485-47-8; **15b** (isomer 2), 80485-48-9; **16**, 77202-25-6; **17a**, 1125-78-6; **17b**, 80485-49-0; **17c**, 1470-94-6; **17d**, 1659-93-4; **17e**, 79144-22-2; **18**, 77202-24-5; **19**, 6485-40-1; **20** (isomer 1), 5206-83-7; **20** (isomer 2), 7065-48-7; **21**, 80485-50-3; **22**, 80485-51-4; **23**, 32178-69-1; **25** (isomer 1), 80485-52-5; **25** (isomer 2), 80513-96-8; **26** (isomer 1), 20591-71-3; **26** (isomer 2), 20721-86-2; phenyl vinyl sulfide, 1822-73-7; phenyl α-bromovinyl sulfide, 80485-53-6; acetaldehyde, 75-07-0; diphenyl disulfide, 882-33-7; phenylsulfenyl chloride, 931-59-9; 2-acetyl-6-methyl-3,4-dihydro-2*H*-pyran, 28450-02-4; 3-(phenylthio)-$\Delta^{1(9)}$-2-octalone, 80485-54-7; 8a-hydroxy-3-(phenylsulfonyl)-2-decalone, 80485-55-8; 2-cyclohexen-1-one, 930-68-7; cyclohexanone, 108-94-1; 4-*tert*-butylcyclohexanone, 98-53-3; cyclopentanone, 120-92-3; cycloheptanone, 502-42-1; α-tetralone, 529-34-0.

Dianions Derived from α-Halo Acids. The Darzens Condensation Revisited

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The dianions of α-halo carboxylic acids are readily generated by the addition of the acids to 2 equiv of lithium diisopropylamide at low temperatures. When the mixture warms to room temperature dimeric products are formed. When aldehydes and ketones were added to the cooled solutions of the dianions and the reaction mixtures were allowed to warm to room temperature, followed by acid quench, glycidic acids were formed. The glycidic acids, per se, were often too unstable to be isolated and purified but could be analyzed by conversion to their methyl esters with diazomethane. When the reactions were quenched prematurely, α-chloro-β-hydroxy carboxylic acids were isolated. Homologated aldehydes and ketones were obtained from the glycidic acids by catalytic and thermal decarboxylation methods.

Extensions of the carbon backbone of aldehydes and ketones are important transformations in synthetic chemistry. The Darzens glycidic ester condensation[1] (eq 1) provided one of the early methods for carbonyl homolo-

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