Phenylcyclopropane-*trans*-2,2,3-d_3. 1,1-Dichloro-2-phenylcyclopropane-3-*d* (30 g, 0.16 mol) was placed with 300 ml of anhydrous ether in a 1-l., three-necked flask cooled in an ice bath. Metallic Na (40 g) was added in roughly 1-cm^3 pieces during the course of the reaction. At the same time, wet methanol (15 ml of D_2O and 90 ml of MeOD) was added dropwise with vigorous stirring. The addition of wet methanol required 2.5 h, but the addition of Na was finished in 2 h (the addition of Na should be faster than that of wet methanol). After completion of the reaction, any excess Na was removed by filtration with a Büchner funnel. The solution was washed with H_2O, and the ether layer was dried ($MgSO_4$). Distillation [60–62 °C (9 mm)] yielded 15 g (78%) of the product. The isomeric purity was over 87% by NMR analysis: NMR (CCl_4) δ 0.58 (d, J = 5 Hz, 1 H), 1.72 (d, J = 5 Hz, 1 H), 6.95 (m, 5 H).

Cyclopropane-*trans*-2,2,3-d_3-carboxylic Acid (4).[7] A solution of 15 g (0.124 mol) of phenylcyclopropane-*trans*-2,2,3-d_3 in 200 ml of HOAc and 20 ml of H_2O was placed in a 500-ml flask equipped with a sintered glass cylinder as an ozone inlet, as well as a gas outlet. Ozone was produced by electric discharge from a Welsbach T 23 ozonator and bubbled through the solution at 0 °C. Excess O_3 was decomposed by bubbling the exit gas through an aqueous solution of NaI. After a reaction period of 36 h, the starting material has almost gone, as indicated by the NMR spectrum of the total reaction mixture. Hydrogen peroxide (30%, 40 ml) was then added to the ozonolysis mixture, which was allowed to stand overnight at room temperature. Some palladium on charcoal was added to decompose any remaining peroxide. After the complete decomposition of the peroxide (overnight), the palladium/charcoal was filtered off with a Büchner funnel. The solvent was removed under reduced pressure at about 40 °C, and the residue was distilled to give 4.1 g of the cyclopropane-d_3-carboxylic acid: NMR (CCl_4) δ 1.2 (d, J = 4.5 Hz, 1 H), 1.5 (d, J = 4.5 Hz, 1 H).

Bromocyclopropane-2,2,3-d_3 (5). A mixture of 30 ml of 1,1,2,2-tetrachloroethane, 13.7 g (0.063 mol) of red mercuric oxide, and 10.8 g (0.125 mol) of cyclopropane-*trans*-2,2,3-d_3-carboxylic acid was placed in a 100-ml, three-necked flask equipped with a distilling receiver, a thermometer, and a stirrer. The mixture was heated to remove about 4 ml of H_2O and solvent. The solution was then cooled to about 70 °C, the distilling receiver was removed, and 20 g (0.125 mol) of Br_2 was added dropwise with stirring over a period of 15–20 min. Carbon dioxide evolved vigorously but ceased about115 min after the addition was completed. The condenser was replaced by a distillation column, and the mixture was distilled with stirring. The distillate below 75 °C was collected (4.5 g, 29%).

Acknowledgments. This work was supported by the National Science Foundation (Grant CHE75-05006), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Chevron Research Co.

Registry No.—**4**, 61377-11-5; **5a**, 61377-12-6; **5b**, 61377-13-7; *trans*-β-bromostyrene, 588-72-7; styrene-*trans*-β-*d*, 6911-81-5; 1,1-dichloro-2-phenylcyclopropane-*d*, 61377-09-1; phenylcyclopropane-*trans*-2,2,3-d_3, 61377-10-4.

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Favorskii-Type Rearrangement of Chlorinated Acetylacetone Monomethyl Enol Ethers. Presumptive Evidence for a Cyclopropane Dimethyl Acetal Intermediate

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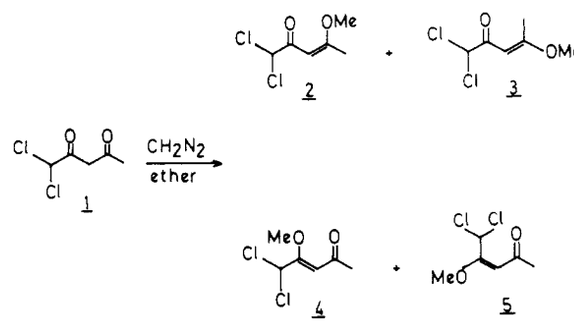
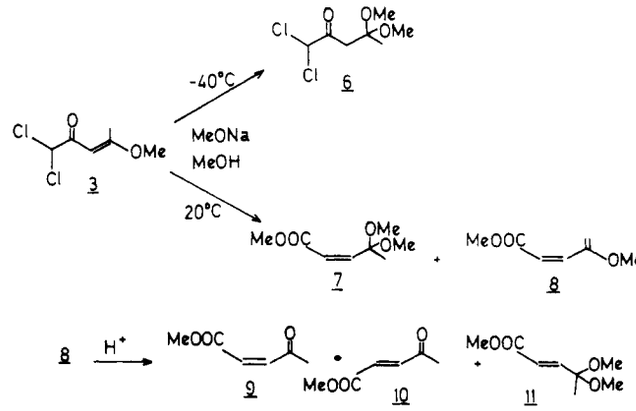
Our interest in the Favorskii rearrangement of dichlorinated methyl ketones[3,4] and the reactions of chlorinated 1,3-cyclohexanedione monomethyl enol ethers with sodium methoxide[5] prompted us to explore the reactivity of dichlorinated aliphatic β-diketone monomethyl enol ethers.

As model compounds the monomethyl enol ethers of 1,1-dichloro-2,4-pentanedione (**1**), prepared by condensation of methyl dichloroacetate and acetone in the presence of sodium using the method of Panizzi,[6] have been selected. Treatment of **1** with ethereal diazomethane initially gave four compounds: (*Z*)- and (*E*)-1,1-dichloro-4-methoxy-3-penten-2-one (**2, 3**); (*Z*)- and (*E*)-5,5-dichloro-4-methoxy-3-penten-2-one (**4, 5**)



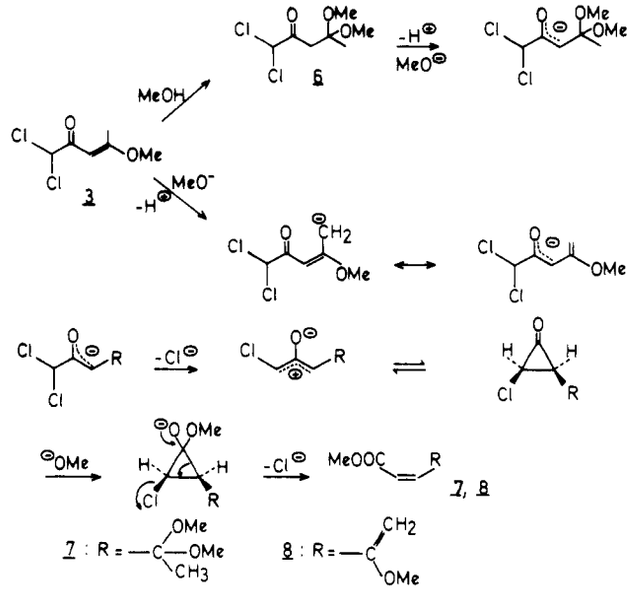
(14, 27, 6, and 24%, respectively). On distillation the *Z* compounds were completely isomerized into the more stable *E* compounds **3** and **5**, which, however, were thermally labile and decomposed on standing.

Treatment of (*E*)-1,1-dichloro-4-methoxy-3-penten-2-one (**3**) with 4 equiv of sodium methoxide in methanol (2.5 N) at −40 °C gave the methanol addition product 1,1-dichloro-4,4-dimethoxy-2-pentanone (**6**). At room temperature a mixture of *cis*-methyl 4,4-dimethoxy-2-pentenoate (**7**) and *cis*-methyl 4-methoxy-2,4-pentadienoate (**8**) was produced in a 1:4 ratio. Treatment of **8** with dilute acetic acid afforded a mixture of *cis*- and *trans*-methyl 4-oxo-2-pentenoate (**9** and **10**) and *trans*-methyl 4,4-dimethoxy-2-pentenoate (**11**).

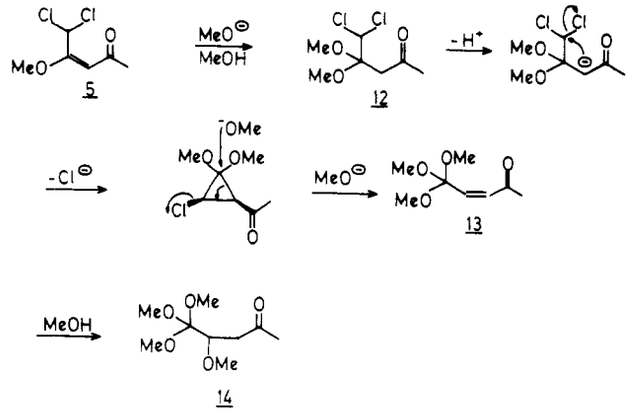


As found in the case of dichloromethyl ketones[3,4] the unsaturated esters **7** and **8** are in the cis configuration, which is in accordance with the mechanism proposed by Bordwell's

group.[7-9] A cyclopropanone intermediate was formed from the enolate by deprotonation and subsequent chloride expulsion, creating a zwitterion followed by a concerted disrotative ring closure. A stereospecific ring opening by a S_N2 attack gave the cis acrylic esters. The initial step in the formation of **7** consisted of methanol addition while in the case of compound **8** a deprotonation occurred yielding a terminal double bond.



The reaction of (*E*)-5,5-dichloro-4-methoxy-3-penten-2-one (**5**) with methanolic sodium methoxide at −40 °C afforded 5,5-dichloro-4,4-dimethoxy-2-pentanone (**12**) as the initial product. The Michael addition product **12** could be isolated at −40 °C and was fully characterized by spectroscopy. At room temperature compound **12** was further converted into a mixture of 5,5,5-trimethoxy-3-penten-2-one (**13**, 80%) and 4,5,5,5-tetramethoxy-2-pentanone (**14**, 20%). The assignment



of the stereochemistry of **13** could not be based on the NMR spectrum because the two olefinic protons exhibited the same chemical shift. However, we have reasons to believe that compound **13** has the cis configuration. Hydrolysis of **13** afforded a mixture of *cis*- and *trans*-methyl 4-oxo-2-pentenoate (**9, 10**). The presence of the cis isomer **9** indicated that in the reaction mixture **9** was predominantly formed as the cis compound rapidly isomerized to the trans form on standing or GLC analysis.

The formation of **13** could not be rationalized by ring opening of a cyclopropanone intermediate, but could proceed via deprotonation and ring closure producing a cyclopropanone dimethyl acetal. Nucleophilic attack of methoxide then causing ring cleavage provided the ortho ester **13**. Michael addition of methanol to **13** gave **14**. To our knowledge this type of reaction represents the first example of a Favorskii-type rearrangement of dichloromethyl ketone dimethyl acetals in which the intermediate is now a cyclopropanone dimethyl acetal instead of a cyclopropanone intermediate in the normal Favorskii rearrangement.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer as a thin film on sodium chloride plates. NMR spectra were taken on a Varian T-60 instrument in carbon tetrachloride with tetramethylsilane as internal reference.

Mass spectra were obtained from GC–MS couplings using a Pye Unicam 104 gas chromatograph (SE 30 5%, 1.5 m) connected with a AEI MS 20 mass spectrometer. The spectral data were obtained after preparative gas chromatography (Varian 1700, SE-30 12%, 3 m).

1,1-Dichloro-2,4-pentanedione (1). A mixture of 157 g (1 mol) of methyl dichloroacetate and 64 g (1.1 mol) of acetone was added to a suspension of 46 g (2 mol) of sodium powder in 500 ml of dry ether at 0 °C under stirring. After stirring overnight at room temperature the reaction mixture was carefully acidified with 350 ml of sulfuric acid (6 N) and the organic layer separated. The aqueous phase was extracted with ether (350 ml) and the combined ether extracts were dried ($MgSO_4$) and concentrated. Fractional distillation gave 74.5 g (45%) of **1**: bp 86–90 °C (14 mm) [lit.[6] bp 83 °C (7 mm)]; IR (NaCl) 3500–3100 (OH), 1750 ($CHCl_2CO$), 1630–1590 cm^{-1} (enolized β-diketone); NMR (CCl_4) δ 2.17 (s, 1, CH_3), 5.93 (s, 1, =CH), 5.97 (s, 1, $CHCl_2$), 12.76 (s broad, 1, OH); mass spectrum (70 eV) *m/e* (rel intensity) 157 (3), 155 (6), 153 (9), 86 (7), 85 (100), 84 (2), 83 (20), 43 (82), 41 (12).

Reaction of 1 with Diazomethane. A solution of 30 g of **1** in 100 ml of ether was treated with 500 ml of ethereal diazomethane solution, and the reaction mixture was kept overnight. Evaporation left an oil containing four isomeric enol ethers **2, 3, 4,** and **5** which were separated by GLC. Fractional distillation gave (*E*)-1,1-dichloro-4-methoxy-3-penten-2-one (**3**, 34%), bp 82–84 °C (14 mm), and (*E*)-5,5-dichloro-4-methoxy-3-penten-2-one (**5**, 13%), bp 114–116 °C (14 mm).

(*Z*)-1,1-Dichloro-4-methoxy-3-penten-2-one (2): NMR (CCl_4) δ 2.24 (s, 3, CH_3), 4.02 (s, 3, OCH_3), 5.76 (s, 1, $CHCl_2$), 6.06 (s, 1, =CH).

(*E*)-1,1-Dichloro-4-methoxy-3-penten-2-one (3): IR (NaCl) 3030 (=CH), 1690, 1610, 1595 cm^{-1} (COC=C); NMR (CCl_4) δ 2.30 (s, 3, CH_3), 3.79 (s, 3, OCH_3), 5.79 (s, 1, =CH), 5.83 (s, 1, $CHCl_2$); mass spectrum (70 eV) *m/e* (rel intensity) 182/84/86 (0.2), 100 (5), 99 (100), 59 (16), 43 (14).

(*Z*)-5,5-Dichloro-4-methoxy-3-penten-2-one (4): NMR (CCl_4) δ 2.13 (s, 1, CH_3), 3.91 (s, 1, OCH_3), 5.44 (s, 1, $CHCl_2$), 5.91 (s, 1, =CH).

(*E*)-5,5-Dichloro-4-methoxy-3-penten-2-one (5): IR (NaCl) 3040 (=CH), 1690, 1610 cm^{-1} (–COC=C); NMR (CCl_4) δ 2.20 (s, 3, CH_3), 3.80 (s, 3, OCH_3), 5.44 (s, 1, =CH), 7.72 (s, 1, $CHCl_2$); mass spectrum (70 eV) *m/e* (rel intensity) 182/84/86 (32), 171 (6), 169 (27), 167 (56), 149 (5), 147 (16), 89 (12), 43 (100).

Reaction of 3 with Sodium Methoxide. The solution of 5 g of enol ether **3** in 30 ml of methanol was added dropwise to 50 ml of methanolic sodium methoxide solution (2.5 N) at 20 °C under stirring and the reaction mixture was stirred for another hour followed by addition of 250 ml of water. Extraction with ether and concentration in vacuo afforded an oil which consisted of 25% **7** and 75% **8**. At low temperature the same reaction only provided **6**.

1,1-Dichloro-4,4-dimethoxy-2-pentanone (6): IR (NaCl) 1710 cm^{-1} (CO); NMR (CCl_4) δ 1.33 (s, 3, CH_3), 3.00 (s, 2, CH_2CO), 3.20 (s, 6, OCH_3), 6.03 (s, 1, $CHCl_2$).

***cis*-Methyl 4,4-Dimethoxy-2-pentenoate (7):** IR (NaCl) 1735 (COOMe), 1605 cm^{-1} (C=C); NMR (CCl_4) δ 1.41 (s, 3, CH_3), 3.10 (s, 6, OCH_3), 3.62 (s, 3, $COOCH_3$), 5.70 (d, 1, J = 12 Hz, HC=CH), 5.92 (d, 1, J = 12 Hz, HC=CH); mass spectrum (70 eV) *m/e* (rel intensity) 160 (3), 159 (47), 144 (10), 143 (100), 142 (12), 115 (43), 111 (30), 89 (17), 83 (60), 59 (13), 55 (14), 53 (15), 43 (43).

***cis*-Methyl 4-Methoxy-2,4-pentadienoate (8):** IR (NaCl) 1735 (COOMe), 1595 cm^{-1} (C=C); NMR (CCl_4) δ 3.56 (s, 3, OCH_3), 3.65 (s, 3, $COOCH_3$), 4.26 (d, 1, J = 2.5 Hz, $=CH_2$), 4.36 (d, 1, J = 2.5 Hz, $=CH_2$), 5.75 (d, 1, J = 12.3 Hz, HC=CH), 5.95 (d, 1, J = 12.3 Hz, HC=CH); mass spectrum (70 eV) *m/e* (rel intensity) 142 (69), 127 (31), 114 (6), 113 (68), 112 (12), 111 (56), 101 (12), 99 (50), 83 (75), 79 (18), 59 (97), 43 (100).

***cis*-Methyl 4-Oxo-2-pentenoate (9):** IR (NaCl) 1725 (COOMe), 1680, 1650 cm^{-1} (C=O, C=C); NMR (CCl_4) δ 2.27 (s, 3, CH_3CO), 3.74 (s, 3, $COOCH_3$), 6.06 (d, 1, J = 12.2 Hz, HC=CH), 6.30 (d, 1, J = 12.2 Hz, HC=CH); mass spectrum (70 eV) *m/e* (rel intensity) 128 (5), 114 (5), 113 (81), 97 (28), 85 (9), 69 (9), 59 (24), 55 (11), 54 (9), 53 (6), 43 (100).

***trans*-Methyl 4-Oxo-2-pentenoate (10):** IR (NaCl) 1730 (COOMe), 1675, 1650 cm^{-1} (CO, C=C); NMR (CCl_4) δ 2.38 (s, 3, CH_3CO), 3.86 (s, 3, $COOCH_3$), 6.63 (d, 1, J = 15.7 Hz, HC=CH), 7.00 (d, 1, J = 15.7 Hz, HC=CH); mass spectrum (70 eV) *m/e* (rel intensity) 128 (22), 114 (6), 113 (100), 98 (4), 97 (37), 85 (9), 69 (13), 59 (23), 55 (6), 54 (5), 53 (8), 43 (67).

***trans*-Methyl 4,4-Dimethoxy-2-pentenoate (11):** IR (NaCl) 1730 (COOMe), 1600 cm^{-1} (C=C); NMR (CCl_4) δ 1.33 (s, 3, CH_3), 3.13 (s, 6, OCH_3), 3.69 (s, 3, $COOCH_3$), 6.17 (d, 1, J = 16.0 Hz, HC=CH), 6.53 (d, 1, J = 16.0 Hz, HC=CH); mass spectrum (70 eV) *m/e* (rel intensity) 174 (23), 159 (36), 145 (30), 143 (100), 129 (60), 113 (23), 97 (37), 83 (24), 75 (11), 69 (14), 59 (10), 43 (33).

Reaction of (*E*)-5,5-Dichloro-4-methoxy-3-penten-2-one (5) with Sodium Methoxide. This reaction was carried out in the same way as in the case of **3**.

5,5-Dichloro-4,4-dimethoxypentan-2-one (12): NMR (CCl_4) δ 2.20 (s, 3, CH_3CO), 2.97 (s, 2, CH_2CO), 3.34 (s, 6, OCH_3), 5.87 (s, 1, $CHCl_2$).

***cis*-5,5,5-Trimethoxy-3-penten-2-one (13):** IR (NaCl) 1690, 1645 cm^{-1} (CO, C=C); NMR (CCl_4) δ 2.25 (s, 3, CH_3CO), 3.20 (s, 9, OCH_3), 6.33 (s, 2, HC=CH); mass spectrum (70 eV) *m/e* (rel intensity) 159 (3), 144 (8), 143 (100), 115 (12), 113 (6), 105 (37), 99 (14), 85 (8), 84 (45), 65 (46), 59 (18), 55 (8), 53 (6), 43 (33).

4,5,5,5-Tetramethoxy-2-pentanone (14): IR (NaCl) 1725 cm^{-1} (CO); NMR (CCl_4) δ 2.10 (s, 3, CH_3CO), 2.45–2.66 (m, 2, $CHCH_2CO$), 3.27 (s, 9, OCH_3), 3.37 (s, 3, OCH_3), 3.66–3.80 (m, 1, $-CHCH_2CO$); mass spectrum (70 eV) *m/e* (rel intensity) 175 (14), 106 (5), 105 (100), 99 (2), 75 (14), 59 (16), 43 (30).

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Registry No.—**1**, 53009-77-1; **2**, 61203-72-3; **3**, 61203-73-4; **4**, 61203-74-5; **5**, 61203-75-6; **6**, 61203-76-7; **7**, 61203-77-8; **8**, 61203-78-9; **9**, 19522-27-1; **10**, 2833-24-1; **11**, 42997-93-3; **12**, 61203-79-0; **13**, 61203-80-3; **14**, 61203-81-4; methyl dichloroacetate, 116-54-1; acetone, 67-64-1; diazomethane, 334-88-3; sodium methoxide, 124-41-4.

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(2) Postdoctoral Fellow, A.B.O.S.
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A Simple Synthesis of *trans*-8,10-Dimethyl-1(9)-octal-2-one via an Acid-Catalyzed Michael Reaction

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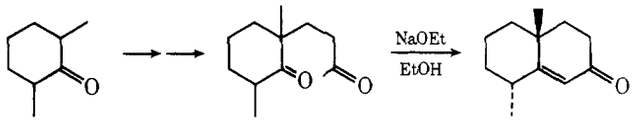
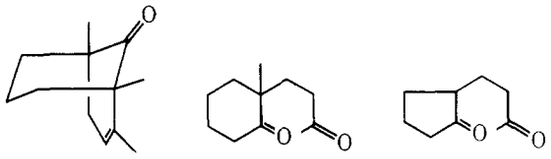
The structural similarity of *trans*-8,10-dimethyl-1(9)-octal-2-one (**1**) to the eudesmane sesquiterpenes makes it a valuable compound for natural product synthesis. Indeed, our concern with **1** stemmed from a project directed toward the synthesis of certain eudesmanolides. It is also of interest that octalone **1** has found commercial application as a flavorant and perfume constituent,[2] and was recently discovered to be a minor component of vetiver oil.[3] Use of **1**, however, has been limited by its unavailability. Failure of the Robinson annulation sequence to provide a viable route to this material has prompted other workers to develop new pathways to **1**.[4,5a] The alternate syntheses involve multistep conversion of 2,6-dimethylcyclohexanone to the 1,5 diketone **2** followed by a



2 **1**

high-yield base-catalyzed cyclization to **1**.[5] Although overall yields of **2** as high as 46% were realized, the reported pathways are four to five steps in length and would require considerable effort for the preparation of large quantities of material. We wish to report that a one-step synthesis of **2** may be effected via an acid-catalyzed Michael addition and that **2** so prepared undergoes the previously reported cyclization in high yield to the octalone **1**.

Our initial experiments were directed toward the preparation of **1** via the convenient acid-catalyzed Robinson annulation procedure developed by Heathcock, Ellis, McMurry, and Coppolino.[6] Earlier studies by Marshall and Schaeffer[5a] on the Wichterle reaction indicated, however, that acid-catalyzed aldol cyclization of the intermediate 1,5 diketone **2** might lead preferentially to the bridged enone **3**. This proved



3 **4** **5**

to be the case. When 2,6-dimethylcyclohexanone and methyl vinyl ketone were refluxed with sulfuric acid in benzene, the bicyclo[3.3.1]nonenone **3** was isolated as the major product. We found, however, that stopping the reaction after only a few minutes at reflux allowed chromatographic isolation of substantial quantities of the intermediate Michael adduct **2**.[7] Further experimentation showed that by conducting the reaction at 0 °C, **2** could be prepared in 50–58% yield (70–75% conversion) with concurrent formation of only a trace of the bridged enone **3**. The product was readily isolated by distillation.

Preliminary experiments suggest that this preparation of 1,5 diketones could have considerable generality. For example, sulfuric acid catalyzed addition at 0 °C of methyl vinyl ketone to 2-methylcyclohexanone and even cyclopentanone gave diones **4** and **5** in unoptimized yields of 55 and 31%, respectively.

Experimental Section

2,6-Dimethyl-2-(3-oxobutyl)cyclohexanone (2). A solution of 9.50 g (75 mmol, 10.3 ml) of 2,6-dimethylcyclohexanone, 5.25 g (75 mmol, 6.1 ml) of freshly distilled methyl vinyl ketone, and 50 ml of benzene was cooled to 0 °C under a drying tube. The mixture was stirred while 1.5 ml of concentrated sulfuric acid was added, and then allowed to stand at 0 °C for 2 h. The orange mixture was then stirred and second portions of methyl vinyl ketone (3.0 ml) and sulfuric acid (0.5 ml) were added. After an additional 2 h, final portions of methyl vinyl ketone (3.0 ml) and sulfuric acid (0.5 ml) were mixed with the dark reaction mixture. After standing for an additional 12 h at 0 °C, the orange reaction mixture was decanted from the dark polymer and poured into 100 ml of ether. The polymer was rinsed with a little fresh ether. The combined ethereal solutions were washed with 1 N sodium hydroxide and brine. The aqueous washings were back-extracted with ether, and the combined ether solutions were dried ($MgSO_4$) and the solvents removed at reduced pressure to give an orange oil (13.9 g).