Experimental Section

General.—Spectra were recorded on Beckman IR-8, Varian HA-100, Atlas CH7, and CEC 110B instruments.[6] Varian-Aerograph 1200 and A90P instruments were used for glc with columns (A) 0.01 in. × 25 ft UCONLB550X capillary, (B) 0.125 in. × 7 ft 2.5% KOH–2.5% Carbowax 4000 on 80/100 Chromosorb W, and (C) 0.25 in. × 4 ft 20% SF96 on Chromosorb. Analyses were performed at Galbraith Laboratories.

2-Phenyl-1-trimethylsiloxy-1-vinylcyclononane (1).—A solution of 1 g (4.7 mmol) of 2-phenyl-1-cyclononanone[8] in 5 ml of dry THF was added under nitrogen at room temperature to 15 ml of 1 *M* vinyllithium in THF (diluted Ventron solution). The reaction was stirred for 15 min and was then quenched with 5 ml of saturated ammonium chloride and extracted with pentane. The pentane solution was washed with water and dried over magnesium sulfate. Analysis by gc (column A at 135°) showed a 60% conversion (other runs with longer reaction times did not give significantly greater conversion). The alcohol was purified by chromatography on SilicAR, eluting with pentane to remove a substantial amount of nonpolar material and then with 3% ether–pentane, which gave unreacted ketone (36%) and the desired alcohol[7] (45% yield) as a low-melting solid: ir (CS_2) 2.8, 3.42, 14.4 μ; nmr (CCl_4) δ 7.12 (s, 5), 5.82, 4.74, 4.68 (ABC pattern, J = 12, 17 Hz, 3), 2.8 (m, 1), 1.0–1.8 (m, 15).

The alcohol was converted to the trimethylsilyl derivative by stirring with Tri-Sil Concentrate (Pierce Chemical Co.) and dimethyl sulfoxide as described previously.[1b] The product was purified by preparative gas chromatography on column C at 160°, which gave 1 as a semisolid: ir (neat) 3.42, 6.75, 6.90, 8.04, 9.42, 11.15, 12.0, 13.3, 14.35 μ; nmr (CCl_4) δ 7.2 (m, 5), 5.52, 4.92, 4.84 (ABC pattern, J = 17, 10, 2 Hz, 3), 2.8 (m, 1), 1.2–2.2 (m, 14), 0.12 (s, 9); mass spectrum m/e 316.221 (calcd for $C_{20}H_{32}OSi$, m/e 316.222).

4-Phenylcycloundecanone (2).—Ampoules were prepared and sealed as described previously.[1b] The ampoules were heated in an aluminum block oven which was regulated with a Cole Palmer Model 1300 temperature controller. Most runs utilized 10 mg of gc-purified sample in a 10-ml ampoule. A run using a 0.8-ml ampoule and 0.2 g of sample that had only been purified by vacuum transfer gave similar results when heated for 16 hr at 280° except that the amount of ketone formed during pyrolysis was much higher (64% *vs.* 13%) and the yield was only 60%. Analysis of the product mixture before hydrolysis using a glc–mass spectrometer combination (column B) showed two rearranged trimethylsilyl compounds and a third component which was identified as 2.

Hydrolysis of the mixture as described earlier[1b] gave only one product, 2: ir (neat) 3.42, 5.88, 6.70, 6.90, 13.25, 14.35 μ; nmr (CCl_4) δ 7.5 (m, 5), 2.4–2.9 (m, 5), 1.3–2.1 (m, 14).

Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.89. Found: C, 83.23; H, 9.67.

Acknowledgment.—We thank the Research Corporation for Cottrell Research Grant support.

Registry No.—1, 42031-17-4; 2, 42031-18-5; 2-phenyl-1-cyclononanone, 14996-80-6.

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(6) We thank the University of Oregon for the use of their CEC mass spectrometer.

(7) Two diastereomers are possible. The alcohol used showed only one peak on gc (columns A and B). The later chromatography fractions (not used) showed minor amounts of another alcohol with a slightly longer retention time.

Di- and Trimethyl-2-cyclohexenones

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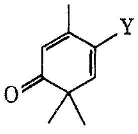
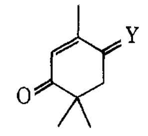
In connection with a problem of terpene synthesis 4-methoxy-3,6,6-trimethyl-2,4-cyclohexadienone (**1a**) was needed as starting material as a consequence of which the following reactions were investigated.

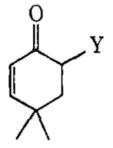


1a, Y = OMe
b, Y = H

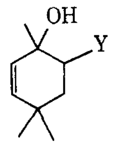


2a, Y = H_2
b, Y = H, Br
c, Y = H, OAc
d, Y = O
e, Y = H, OMe

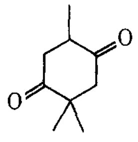
Treatment of 3,6,6-trimethyl-2-cyclohexenone (**2a**),[1] prepared by the interaction of methylmagnesium iodide with 4,4-dimethyl-2-cyclohexenone (**3a**)[2] followed by chromic acid oxidation of the resultant carbinol (**4a**), with *N*-bromosuccinimide yielded bromo ketone **2b**, which suffered facile dehydrobromination producing dienone **1b** but could be converted into the keto ester **2c** on exposure to silver acetate. Lithium aluminum hydride reduction of **2c**, followed by manganese dioxide oxidation of the intermediate diol, gave the diketone **2d**. Unfortunately, neither ketalation of the latter or its dihydro derivative **5** under a variety of conditions[3] nor enol ether formation of **2d** succeeded.



3a, Y = H
b, Y = Br
c, Y = OMe
d, Y = OAc
e, Y = OH



4a, Y = H
b, Y = OMe



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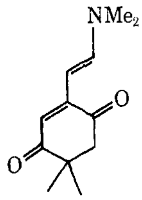

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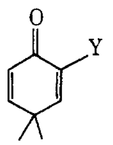
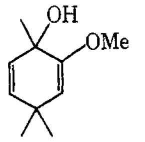
An alternative route toward the desired product was based on an attempt to introduce the methoxyalkene function into the framework of cyclohexenone **3a**. While selenium dioxide oxidation of the latter yielded dienone **7a**,[4] treatment of **3a** with cupric bromide afforded **3b**,[4] whose exposure to methanolic silver nitrate led to the keto ether **3c**. Interaction of the latter with methylmagnesium iodide and the resultant carbinol **4b** with chromic acid produced the ether **2e**. Unfortunately, various attempts to dehydrogenate **2e** failed.



7a, Y = H
b, Y = OH
c, Y = OMe



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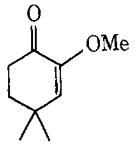

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(1) J. M. Conia and F. Rouessac, *Bull. Soc. Chim. Fr.*, 1925 (1963).

(2) (a) E. L. Eliel and C. A. Lukach, *J. Amer. Chem. Soc.*, **79**, 5986 (1957); (b) E. D. Bergmann and R. Corett, *J. Org. Chem.*, **23**, 1507 (1958); (c) J. M. Conia and A. Le Craz, *Bull. Soc. Chim. Fr.*, 1937 (1960); (d) F. G. Bordwell and K. M. Wellman, *J. Org. Chem.*, **28**, 1347 (1963); (e) J. W. Lewis and R. L. Meyers, *J. Chem. Soc. C*, 753 (1971).

(3) Treatment of **2d** with bis(dimethylamino)methoxymethane afforded the condensation product **6** [*cf.* R. F. Borch, C. V. Grudzinskas, D. A. Peterson, and L. D. Weber, *J. Org. Chem.*, **37**, 1141 (1972)].

(4) F. G. Bordwell and K. M. Wellman, *J. Org. Chem.*, **28**, 2544 (1963).

Finally, alkaline hydrolysis of keto ester **3d**, previously prepared by the lead tetraacetate oxidation of 4,4-dimethyl-2-cyclohexenone (**3a**),[2d] yielded ketol **3e**. Oxidation of the latter with bismuth oxide, followed by base-induced O-methylation, led to cyclohexadienones **7b** and **7c**, consecutively. Interaction of the methoxy ketone **7c** with methyllithium afforded carbinol **8**, whose Collins oxidation[5] gave the desired methoxy ketone **1a**. Since selenium dioxide oxidation of keto ether **9**, a recently reported product of the ready condensation of isobutyraldehyde and methoxymethyl vinyl ketone,[6] leads to dienone **7c**, its aforementioned transformation into **1a** makes available a facile, four-step synthesis of the dienone **1a**.

Experimental Section

Melting points, determined on a Reichert micro hot stage, are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer. Unless otherwise noted, proton magnetic resonance spectra of deuteriochloroform solutions containing tetramethylsilane (δ 0 ppm) as internal standard were taken on a Varian Associates Model A-60 spectrometer.

3,3,6-Trimethyl-2-cyclohexenone (2a).—A solution of methylmagnesium iodide, from 2.9 g of magnesium, 8.1 ml of methyl iodide, and 100 ml of ether, was added dropwise over a 1-hr period to an ice-cold solution of 10.0 g of 4,4-dimethyl-2-cyclohexenone (**3a**) in 50 ml of ether. The mixture was refluxed for 1 hr and stirred at room temperature for 14 hr. Saturated ammonium chloride solution (200 ml) was added, the mixture was shaken, and the organic layer was separated and evaporated. A suspension of 10.0 g of chromium trioxide in 200 ml of acetic acid was added dropwise to a solution of the residual carbinol **4a** (12 g) in 50 ml of acetic acid and the mixture was kept at room temperature for 16 hr. It then was diluted with water and extracted with ether. The extract was washed with sodium bicarbonate solution and water and evaporated. Chromatography of the residue (7.0 g) on neutral alumina (activity I) and elution with 1:1 pentane–ether yielded 4.7 g of liquid **2a**: bp 87–89° (16 Torr) [lit.[1] bp 86–88° (15 Torr)]; ir (neat) 5.98 (s, C=O), 6.09 μ (m, C=C); pmr (CCl_4) δ 1.03 (s, 6, Me_2), 1.6–2.5 [m, 4, $(CH_2)_2$], 1.92 (broad s, 3, olefinic Me), 5.63 (q, 1, J = 2 Hz, olefinic H); literature[1] spectra identical.

3,6,6-Trimethyl-2,4-cyclohexadienone (1b).—A solution of 10.0 g of **2a** and 13.0 g of N-bromosuccinimide in 250 ml of carbon tetrachloride was refluxed under nitrogen for 20 min. The mixture then was cooled and filtered. Evaporation of the filtrate yielded 17.0 g of unstable, oily bromo ketone **2b**: ir (neat) 5.96 (s, C=O), 6.12 μ (m, C=C); pmr δ 1.11 (s, 3, Me), 1.22 (s, 3, Me), 1.2–1.5 (m, 2, CH_2), 2.13 (t, 3, J = 2 Hz, olefinic Me), 4.88 (m, 1, BrCH), 5.87 (p, 1, J = 2 Hz, olefinic H). A mixture of 5.0 g of the latter and 10 g of calcium carbonate in 70 ml of N,N-dimethylacetamide was refluxed under nitrogen for 30 min. It was cooled and filtered and the filtrate was diluted with water and extracted with ether. The extract was evaporated and the residual oil (2.5 g) was chromatographed on silica gel. Elution with 5:1 hexane–ether gave 2.0 g of oil whose distillation afforded colorless liquid **1b**: bp 66–67° (4.7 Torr); ir (neat) 6.00 (s, C=O), 6.33 μ (m, C=C); pmr δ 1.19 (s, 6, Me_2), 2.07 (d, 3, J = 2 Hz, olefinic Me), 5.88 (m, 1, H-2), 6.04 (dd, 1, J = 10, 2 Hz, H-4), 6.30 (d, 1, J = 10 Hz, H-5).

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.17; H, 8.83.

4-Acetoxy-3,6,6-trimethyl-2-cyclohexenone (2c).—A solution of 12.0 g of bromo ketone **2b** and 15.0 g of silver acetate in 50 ml of acetic acid was stirred at room temperature for 24 hr. The mixture was filtered and the filtrate was diluted with water and extracted with ether. The extract was washed with sodium bicarbonate solution and with water, dried over sodium sulfate, and evaporated. Distillation of the residue (8.9 g) gave 3.9 g of oil whose chromatography on alumina (activity IV) and elution with 10:1 hexane–ether gave liquid keto ester **2c**: uv (EtOH) λ_{max} 229 nm (ε 13,900); ir (neat) 5.75 (s, C=O), 5.97 μ (s); pmr δ 1.17 (s, 6, Me_2), 1.95 (t, 3, J = 1 Hz, olefinic Me), 1.9–2.2 (m, 2, CH_2), 2.13 (s, 3, acetyl Me), 5.75 (m, 1, oxymethine), 5.84 (m, 1, olefinic H).

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.61; H, 8.27.

2,5,5-Trimethyl-2-cyclohexene-1,4-dione (2d).—A solution of 17.9 g of keto ester **2c** in 250 ml of dry ether was added to a suspension of 16.4 g of lithium aluminum hydride in 750 ml of ether and the mixture was kept at room temperature for 3 hr. A sodium sulfate slurry saturated with water was added and the mixture was shaken and filtered. Evaporation of the filtrate gave 13.1 g of oily enediol: ir (neat) 2.97 (s, OH), 6.02 μ (w, C=C). A mixture of 12.9 g of the latter and 150 g of activated manganese dioxide in 350 ml of ether was stirred at room temperature under nitrogen for 20 hr. It was filtered and the filtrate was evaporated. Crystallization of the residual solid (6.7 g) from hexane and sublimation yielded yellow, crystalline **2d**: mp 85°; uv (EtOH) λ_{max} 242 nm (ε 15,200); ir (Nujol) 5.94 (s, C=O), 6.13 μ (m); pmr δ 1.24 (s, 6, Me_2), 2.01 (d, 3, J = 2 Hz, olefinic Me), 2.77 (s, 2, CH_2), 6.52 (m, 1, olefinic H).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 71.23; H, 8.17.

2,2,5-Trimethyl-1,4-cyclohexanedione (5).—A mixture of 0.70 g of diketone **2d** and 10 g of zinc dust in 40 ml of acetic acid was stirred at room temperature for 10 min. It was filtered and the filtrate was diluted with water and extracted with ether. Evaporation of the extract yielded 0.51 g of a solid whose crystallization from hexane and sublimation gave colorless, crystalline diketone **5**: mp 52–54°; ir (Nujol) 5.85 μ (s, C=O); pmr δ 1.17 (s, 6, Me_2), 1.19 (d, 3, J = 6 Hz, Me), 2.61 (s, 2, H_2-3), 2.6–2.8(m, 3, H-5 and H_2-6).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.26; H, 8.97.

2-(*trans*-β-Dimethylaminovinyl)-5,5-dimethyl-2-cyclohexene-1,4-dione (6).—A solution of 200 mg of diketone **2d** and 4.0 ml of bis(dimethylamino)methoxymethane in 10 ml of benzene was refluxed under nitrogen for 18 hr. It was poured into water and extracted with ether. The exatract was evaporated and the residue (210 mg) was chromatographed on alumina (activity III). Elution with hexane led to recovery of 160 mg of starting ketone, while elution with 20:1 hexane–ether gave 30 mg of solid whose sublimation yielded orange, crystalline **6**: mp 96–98°; uv (EtOH) absorption at 448 nm; ir (Nujol) 5.88 (s, C=O), 6.06 (s, C=O and C=C), 6.18 (s), 6.44 μ (s); pmr δ 1.21 (s, 6, Me_2), 2.73 (s, 2, CH_2), 2.98 (s, 6, NMe_2), 4.93 7.40 (d each, 1 each, J = 14 Hz, vinyl methines), 6.14 (s, 1, H-3).

Anal. Calcd for $C_{12}H_{17}O_2N$: mol wt, 207.1259. Found: mol wt, 207.1261 (mass spectrum).

4,4-Dimethyl-6-methoxy-2-cyclohexenone (3c).—A suspension of 29.4 g of cupric bromide in 150 ml of methanol was added dropwise during a 1-hr period to a refluxing solution of 8.0 g of ketone **3a** in 100 ml of methanol and the refluxing was then continued for 4 hr The cooled solution was filtered, the precipitate was washed with ether, and the combined organic solutions were reduced to a volume of 100 ml under vacuum at room temperature. Water was added and the mixture was extracted with ether. Evaporation of the extract and distillation of the residue yielded 11.1 g of oil whose redistillation gave a colorless liquid which crystallized on standing. Crystallization from hexane gave bromo ketone **3b**: bp 77–79° (0.2 Torr); mp 44–45° (lit.[4] mp 47.5°); ir (film) 5.91 (s, C=O), 12.25 μ (m, CBr) (lit.[4] 5.92 and 12.20 μ, respectively); pmr δ 1.23 (s, 3, Me), 1.26 (s, 3, Me), 2.40 (d, 1, J = 11 Hz, H-5), 2.42 (dd, 1, J = 8, 2 Hz, H-5), 4.87 (dd, 1 J = 11, 8 Hz, BrCH), 5.92 (d, 1, J = 11 Hz, H-2), 6.72 (dd, 1, J = 11, 2 Hz, H-3). A mixture of 8.0 g of **3b**, 7.7 g of silver nitrate, and 0.1 ml of 70% perchloric acid in 75 ml of methanol was stirred at room temperature for 2 hr. It was filtered and the filtrate was concentrated to 30 ml under vacuum at room temperature. Water was added and the mixture was extracted with ether. The extract was evaporated and the residue (6.5 g) was chromatographed on alumina (activity II) and eluted with 5:1 hexane–ether. Distillation of the eluate (1.3 g) afforded liquid keto ether **3c**: bp 55° (0.25 Torr); ir (neat) 5.95 (s, C=O), 6.21 μ (w, C=C); pmr δ 1.20 (s, 3, Me), 1.27 (s, 3, Me), 1.90 (d, 1, J = 12 Hz, H-5), 2.02 (d d, 1, J = 7, 2 Hz, H-5), 3.52 (s, 3, OMe), 3.89 (dd, 1, J = 12, 7 Hz, H-6), 5.75 (d, 1, J = 10 Hz, H-2), 6.61 (dd, 1, J = 10, 2 Hz, H-3).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.31; H, 9.21.

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(5) R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, **35**, 4000 (1970).

(6) E. Wenkert, N. F. Golob, S. S. Sathe, and R. A. J. Smith, *Syn. Commun.*, **3**, 205 (1973).

4-Methoxy-3,6,6-trimethyl-2-cyclohexenone (2e).—A solution of methylmagnesium iodide, from 360 mg of magnesium and 1 ml of methyl iodide in 50 ml of ether, was added dropwise over a 0.5-hr period to an ice-cold solution of 1.55 g of keto ether **3c** in 25 ml of dry ether and the mixture was stirred at room temperature for 14 hr. Saturated ammonium chloride solution (100 ml) was added and the ether solution was separated and evaporated. A suspension of 1.27 g of chromium trioxide in 20 ml of acetic acid was added to a solution of the residual carbinol stereoisomer mixture **4b** (1.62 g) in 10 ml of acetic acid and the mixture was kept at room temperature for 4 hr. It then was poured into water and extracted with ether. Evaporation of the extract, chromatography of the residue (0.97 g) on alumina (activity IV), and elution with hexane yielded an oil whose distillation gave 780 mg of ketone **2e**: bp 75° (0.5 Torr); uv (EtOH) λ_{max} 232 nm (ϵ 9900); ir (neat) 5.98 (s, C=O), 6.12 μ (m, C=C); pmr δ 1.12 (s, 3, Me), 1.16 (s, 3, Me), 1.0–2.3 (m, 2, CH_2), 1.99 (t, 3, J = 2 Hz, olefinic Me), 3.43 (s, 3, OMe), 3.98 (m, 1, OCH), 5.74 (m, 1, olefinic H).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.51; H, 9.69.

Dienones 7.—A mixture of 500 mg of ketone **3a** and 1.3 g of selenium dioxide in 4 ml of water and 20 ml of dioxane was refluxed for 30 hr. It was filtered and the filtrate was diluted with water and extracted with ether. The extract was evaporated and the residue (390 mg) was chromatographed on alumina (activity IV). Elution with 20:1 pentane–ether gave 70 mg of liquid 4,4-dimethyl-2,5-cyclohexadienone (**7a**), ir and pmr identical with those cited in the literature.[4,7]

A solution of 9.6 g of keto ester **3d**[2d] in 125 ml of 0.5 *N* aqueous potassium hydroxide and 125 ml of methanol was kept at room temperature under nitrogen for 10 min. It was brought to pH 6 with acetic acid and evaporated under vacuum at room temperature. Extraction of the residue with ether, evaporation of the extract, and distillation of the residue gave 5.0 g of liquid 4,4-dimethyl-6-hydroxy-2-cyclohexenone (**3e**): bp 50° (0.2 Torr); ir (neat) 2.86 (m, OH), 5.92 (s, C=O), 6.15 μ (m, C=C); pmr δ 1.19 (s, 3, Me), 1.27 (s, 3, Me), 1.89 (d, 1, J = 13 Hz, H-5), 2.12 (dd, 1, J = 7, 2 Hz, H-5), 4.38 (dd, 1, J = 13, 7 Hz, H-6), 5.92 (d, 1, J = 10 Hz, H-2), 6.68 (dd, 1, J = 10, 2 Hz, H-3). A mixture of 2.8 g of the latter and 9.3 g of bismuth trioxide in 40 ml of acetic acid was kept at 100° for 10 min. It then was cooled, diluted with ether, and filtered. The precipitate was washed thoroughly with ether and the combined washings and filtrate were washed with saturated sodium bicarbonate solution and with water and evaporated. Distillation of the residue yielded 1.5 g of liquid 4,4-dimethyl-2-hydroxy-2,5-cyclohexadienone (**7b**): bp 53–54° (0.3 Torr); uv (EtOH) λ_{max} 238 nm (ϵ 6300), 283 (2440); ir (neat) 2.92 (m, OH), 6.06 (br s, C=O), 6.23 μ (w, C=C); pmr δ 1.31 (s, 6, Me_2), 5.98 (d, 1, J = 2 Hz, H-3), 6.18 (d, 1, J = 10 Hz, H-6), 6.82 (dd, 1, J = 10, 2 Hz, H-5).

Anal. Calcd for $C_8H_{10}O_2$: C, 69.55; H, 7.30. Found: C, 69.31; H, 7.50.

A mixture of 1.4 g of **7b**, 2.2 g of anhydrous potassium carbonate, and 5 ml of methyl iodide in 70 ml of dry acetone was stirred at room temperature for 18 hr. It was filtered and the filtrate was evaporated. Chromatography of the residue (1.6 g) on alumina (activity II) and elution with 10:1 hexane–ether yielded 720 mg of oil whose distillation produced liquid 4,4-dimethyl-2-methoxy-2,5-cyclohexadienone (**7c**): bp 81° (0.3 Torr); uv (EtOH) λ_{max} 238 nm (ϵ 9200), 283 (3100); ir (neat) 6.05 (s, C=O), 6.15 (s, C=C), 6.26 μ (s); pmr δ 1.31 (s, 6, Me_2), 3.62 (s, 3, OMe), 5.71 (d, 1, J = 2 Hz, H-3), 6.18 (d, 1, J = 10 Hz, H-6), 6.79 (dd, 1, J = 10, 2 Hz, H-5).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found C: 70.75; H, 7.96.

A mixture of 26.8 g of keto ether **9**[6] and 23.2 g of selenium dioxide in 192 ml of glacial acetic acid and 1.5 l. of dry *tert*-amyl alcohol was refluxed under nitrogen for 24 hr. It was filtered and the filtrate was concentrated at atmospheric pressure and finally evaporated fully under vacuum. A methylene chloride solution of the residual oil was washed with 5% sodium hydroxide solution and saturated brine solution, dried over potassium carbonate, and evaporated. Distillation of the residue gave 20.4 g of dienone **7c**, physical properties identical with those of the above sample.

4-Methoxy-3,6,6-trimethyl-2,4-cyclohexadienone (1a).—A solution of 180 ml of ethereal 1.5 *M* methyllithium was added to a stirring solution of 20.4 g of **7c** in 300 ml of ether under nitrogen at such rate as to assure gentle refluxing. After 14 hr water was added and the organic solution was separated, dried over potassium carbonate, and evaporated. The residual ketol **8** (22.3 g) [ir (neat) 2.90 (m, OH), 5.95 (m, C=C), 6.11 μ (m); pmr δ 1.05 (s, 3, Me), 1.11 (s, 3, Me), 1.37 (s, 3, carbinol Me), 3.57 (s, 3, OMe), 4.54 (s, 1, β-methoxy olefinic H), 5.53 (broad s, 2, olefinic Hs)] was used in the next reaction without further purification. Dry chromium oxide (13.5 g) was added to a stirring solution of 21.3 g of pyridine, distilled from barium oxide, in 350 ml of methylene chloride. After 15 min 2.78 g of **8** in 5 ml of methylene chloride was added to the mixture and stirring was continued for 15 min. The mixture was poured into ether and washed with 5% sodium hydroxide solution and 10% cupric sulfate solution. The organic solution was dried over magnesium sulfate and evaporated. Distillation of the residue gave 1.77 g of liquid ketone **1a**: bp 55° (0.2 Torr); ir (neat) 6.01 (s, C=O), 6.10 (s, C=C), 6.32 μ (s); pmr δ 1.19 (s, 6, Me_2), 2.03 (s, 3, olefinic Me), 3.57 (s, 3, OMe), 5.04 (s, 1, H-5), 5.85 (s, 1, H-2).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.45; H, 8.42.

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Registry No.—**1a**, 42116-94-9; **1b**, 23438-76-8; **2a**, 23438-77-9; **2b**, 42116-96-1; **2c**, 42116-97-2; **2d**, 38770-37-5; **2e**, 42116-99-4; **3a**, 1073-13-8; **3b**, 40441-34-7; **3c**, 42117-25-9; **3d**, 42117-26-0; **3e**, 42117-27-1; **5**, 42117-27-2; **6**, 42087-03-6; **7b**, 42117-29-3; **7c**, 42117-30-6; **8**, 42117-31-7; **9**, 42117-32-8; methyl iodide, 74-88-4; bis(dimethylamino)methoxymethane, 1186-70-5.

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(7) E. W. Garbisch, *J. Org. Chem.*, **30**, 2109 (1965); G. Legler and B. Quiring, *Tetrahedron*, **23**, 2683 (1967); H. E. Zimmerman, E. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *J. Amer. Chem. Soc.*, **89**, 6589 (1967).

An Improved Method for the Synthesis of Aliphatic Sulfinic Acids

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Despite their importance as polymerization activators[1] and as proposed intermediates in photochemical smog systems,[2] no simple one-step method appears to be available for the synthesis of aliphatic sulfinic acids in high yields and purity. For example, in the most important preparation,[3] the reduction of sulfonyl chlorides with zinc, iron, aluminium, or magnesium, the yields are reduced and the work-up is complicated by further reduction to disulfides and mercaptans.

Another favored method,[3] the treatment of organometallic compounds (RMgX and RLi) with sulfur dioxide, though preferable in cases where the sulfonyl chloride is unstable, suffers similarly from complications arising from competing side reactions. During the course of a study of the photochemical reactions of excited sulfur dioxide with hydrocarbons[4] we found it necessary to devise a synthesis capable of yielding

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(1) C. S. Marvel and R. S. Johnson, *J. Org. Chem.*, **13**, 822 (1948).

(2) P. A. Leighton, "Photochemistry of Air Pollution," Academic Press, New York, N. Y., 1961, p 298.

(3) For reviews see W. E. Truce and A. M. Murphy, *Chem. Rev.*, **48**, 69 (1951); M. Quaedvlieg in "Enzyklopädie der organischen Chemie," E. Müller, Ed., Fourth ed, Band 9, Georg Thieme Verlag, Stuttgart, 1955, p 343.

(4) R. D. Penzhorn, L. Stieglitz, W. G. Filby, and K. Günther, *Chemosphere*, **3**, 111 (1973).