2.5 Hz, 1 H), 5.50 (broad s, 1 H), 5.70 (d, J = 10 Hz, 1 H), 6.50 (d, J = 10 Hz, 1 H).

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.30; H, 9.17.

Irradiation of the signal at δ 5.50 changed the absorption at δ 3.18 into a doublet, each member of which was split into a doublet (J = 17 and 2.5 Hz). Irradiation at δ 2.25 produced the same effect on the signal at δ 3.18 as did irradiation at 5.50.

When a solution of ca. 100 mg of **6** in 0.5 mL of acetone-d_6 containing 0.01 equiv of NaOD and 0.10 mL of D_2O was allowed to stand for ca. 15 min, the following changes in the NMR spectrum were observed: the signal at δ 3.18 disappeared, whereas the signal at δ 2.82 changed from a doublet to a broad singlet; the signal at δ 5.50 became much sharper and appeared as a doublet ($J \sim 2$ Hz). When ca. 100 mg of **6** was treated with excess NaOH in methanol, a mixture of compounds (77 mg) could be isolated. Chromatography on Florisil (75% ether in hexane) yielded 40 mg of a pale yellow oil, tentatively identified as **8**: IR (CCl_4) 3420, 2960, 2860, 1662, 1622, 1607 cm^{-1}; NMR δ (CCl_4) 1.20 (s, 6 H), 1.27 (s, 3 H), 3.03 (s, 1 H), 6.00 (s, 1 H), 6.08 (d, J = 10 Hz, 1 H), 6.73 (d, J = 10 Hz, 1 H).

Irradiation of 1b in Glacial Acetic Acid. A solution of 1.00 g (0.00495 mol) of **1b** in 250 mL of freshly distilled glacial acetic acid was irradiated for 0.75 h. The excess solvent was removed at reduced pressure and the resulting yellow oil taken up in ether/water. Extraction of the ether with saturated aqueous sodium bicarbonate followed by drying and removal of solvent yielded 1.31 g (101%) of a yellow oil. This material was carefully chromatographed on Florisil, with each fraction being monitored by TLC. The only identifiable material that was isolated was eluted with 25% ether in hexane. This fraction yielded 0.920 g (71%) of **5b**: mp 64–66 °C (from hexane); IR (CCl_4) 2990, 2920, 2870, 1737, 1718, 1610 cm^{-1}; NMR δ (CCl_4) 1.05 (s, 3 H), 1.12 (s, 3 H), 1.17 (s, 3H), 1.93 (s, 3 H), 3.73 (t, J = 3 Hz, 1 H), 5.97 (t, J = 1.6 Hz, 1 H); UV λ_{max} (95% EtOH) 241 nm (ϵ 11 800).

Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.39; H, 8.43.

Registry No.—1a, 55659-72-8; **1b**, 64057-42-7; **3**, 64090-80-8; **4a**, 64057-43-8; **4b**, 64057-44-9; **5b**, 64057-45-0; **6**, 64070-26-4; **8**, 64057-46-1; (−)-2-carone, 5561-14-8; methyl vinyl ketone, 78-94-4; (−)-3-(2-oxobutan-4-yl)-2-carone, 64057-41-6; *cis*-6-(2-chloropropan-2-yl)-3-oxo-9-methyl-Δ^4-octahydronaphthalene, 64057-47-2.

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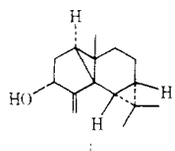

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(16) Examination of models of **14** indicates that it is more sterically crowded than **13** because of the β-methyl group on the dimethylcyclopropane ring. Steric crowding is particularly severe in **14a** where a methyl substituent is present at C-4.
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A Convenient Preparation of Methyl 2,5-Dihydro-2-oxo-3-furancarboxylate

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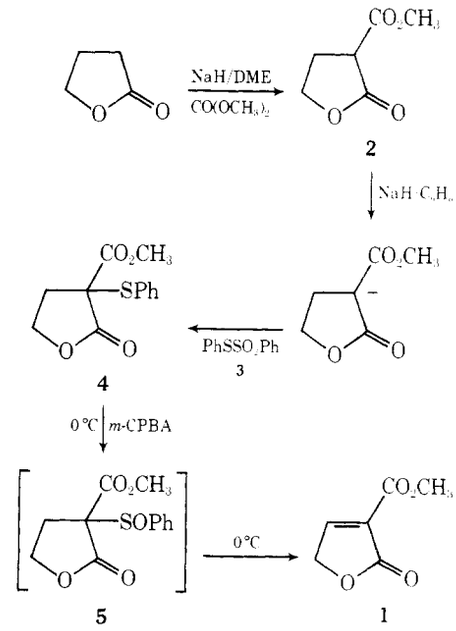
Received June 10, 1977

We have recently had need for the C-5 synthon methyl 2,5-dihydro-2-oxo-3-furancarboxylate (**1**) within the context of several total synthetic efforts. Compound **1** can serve as an electron-deficient olefin both in the Michael addition reaction and the Diels–Alder reaction, thus providing a convenient entry into a variety of complex molecular systems. Careful search of the literature revealed that, while several closely related systems were known,[1] compound **1** itself was unknown. The previously described syntheses of compounds related to **1** proved not to be synthetically applicable to the preparation of **1** itself.[1] As a result, we have developed a new approach to the synthesis of **1** (Scheme I) which, in principle, should be general for the synthesis of a variety of systems related to **1**.

Butyrolactone, on treatment with diethyl carbonate and sodium hydride in dimethoxyethane (DME), affords the corresponding carbomethoxy lactone **2** in 72% yield. Treatment of **2** with sodium hydride gives rise to the corresponding β-dicarbonyl anion which, on reaction with the sulfide sulfone **3**, undergoes thiophenylation to compound **4** in 55% yield. Reaction of the β-dicarbonyl anion derived from **2** with diphenyl disulfide does not yield compound **4** as the starting materials are recovered unreacted, even after prolonged reaction times. Thus, for unreactive anions such as those derived from β-dicarbonyl systems the sulfide sulfone **3** is a clearly superior thiophenylating agent.[2]

Scheme I



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Conversion of compound **4** into compound **1** was accomplished by oxidation with *m*-chloroperbenzoic acid in methylene chloride and *tert*-butyl alcohol at 0 °C. This oxidation reaction, even at 0 °C, leads directly to the unsaturated lactone **1**. Presumably the transformation of **4** into **1** involves the intermediacy of the sulfoxide **5**, which undergoes elimination of the elements of PhSOH at unusually low temperatures.[3] The low temperature for this elimination-type reaction is clearly reminiscent of the behavior exhibited by organoselenium compounds[4] and the thermal lability of **5** is most probably due to the β-dicarbonyl residue present in the molecule.

Experimental Section

Infrared spectra were taken on a 467 Perkin-Elmer spectrophotometer. ^{1}H NMR spectra were obtained on a Joel MH-100 spectrometer in the solvent indicated with tetramethylsilane as the internal reference and are expressed as δ values, with the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra were taken on a Dupont 21-490B instrument.

Preparation of 2. To a 2-L Morton flask equipped with mechanical stirrer, addition funnel, and condenser was added sodium hydride (28 g, 50% dispersion in mineral oil). The sodium hydride was washed five times with hexane, dried under a stream of nitrogen, and then covered with DME (300 mL). Dimethyl carbonate (73.5 mL) was added followed by butyrolactone (25 g, 0.29 mol, 21 mL) and the resulting mixture was then stirred and warmed to 45 °C. After 15 min, a vigorous evolution of gas occurred and the reaction solidified. Heating was discontinued and the reaction was allowed to stand for 2 h at room temperature. Sufficient ice water was added to permit stirring, whereupon 6 N HCl (150 mL) was added. The resulting mixture was extracted with $CHCl_3$ (3 × 75 mL), dried by vacuum filtration through $MgSO_4$, and then evaporated to give an orange oil. Distillation of this oil gave 29 g of **2** (72% yield): bp 110 °C (0.5 mm); IR ($CHCl_3$) 1778 and 1740 cm^{-1}; NMR ($CDCl_3$) δ 2.55 (m, 2 H), 3.5 (m, 1 H), 3.7 (s, 3 H), 4.28 (m, 2 H); MS parent *m/e* 144.

Preparation of 3. To a solution of diphenyl disulfide (50 g, 0.229 mol, 1 M in ether) contained in a 1-L three-necked flask equipped with magnetic stirrer, addition funnel, and condenser was added 40% peracetic acid (100 mL) dropwise (1 drop/s) at 0–5 °C. The reaction mixture was allowed to slowly warm to room temperature, stirred for 12 h, treated with more 40% peracetic acid (10 mL), and stirred an additional 4 h at room temperature. The reaction was poured into a 2-L Erlenmeyer flask and celite then added followed by the slow addition of K_2CO_3 (120 g). The resulting mixture was stirred for 20 min at room temperature and filtered under vacuum, and the filtrate was evaporated to dryness to yield 45 g of **3** as a white crystalline solid, mp 35–37 °C (lit.[5] mp 37.5–38.5 °C).

Preparation of 4. Sodium hydride (2.06 g, 50% dispersion in mineral oil) was placed in a three-neck flask equipped with reflux condenser. After washing five times with hexane and drying over nitrogen, the sodium hydride was covered with 70 mL of benzene, whereupon the lactone ester **2** (5 g, 35.7 mm) was added. Compound **3** (10.7 g) was then added (as a solid) and the resulting mixture was heated at 100 °C for 2.5 h. After cooling to room temperature, ice followed by water was added to the reaction mixture and the resulting two-phase system was then extracted with $CHCl_3$ (3 × 50 mL) and dried by filtration through $MgSO_4$, and the filtrate was evaporated to dryness to yield 8.8 g of crude material which, by NMR analysis, contained 74% of the desired product **4**. Of this crude mixture 5.1 g was filtered (under vacuum) through 30 g of silica gel G (10–40 μm), eluted first with 520 mL of hexane:ether (4:1), followed by 350 mL of hexane:ether (1:1). Evaporation of the latter eluent gave 2.8 g (55% yield) of compound **4** suitable for conversion into the lactone **1**. Spectral properties of compound **4** obtained in this manner are as follows: IR ($CHCl_3$) 1775 and 1735 cm^{-1}; NMR ($CDCl_3$) δ 2.85 (m, 2 H), 3.8 (s, 3 H), 4.22 (m, 2 H), 7.5 (m, 5 H); MS parent *m/e* 252.

Preparation of 1. Compound **4** (2 g, 8.06 mm), 1 M in CH_2Cl_2, was treated dropwise at 0 °C with *m*-chloroperbenzoic acid (1.8 g) dissolved in a mixture of CH_2Cl_2 (6 mL) and *t*-BuOH (2 mL). After addition of the peracid was complete, the reaction was stirred for 2 h at 0 °C. Saturated sodium bicarbonate was added and the mixture was extracted with $CHCl_3$ (3 × 20 mL), dried over anhydrous sodium sulfate for 2 h, filtered under vacuum, and evaporated to dryness to yield a white solid which on crystallization from Et_2O:$CHCl_3$ gave 0.87 g (79% yield) of white crystals: mp 103–105 °C; IR ($CHCl_3$) 1820 (shoulder), 1785, and 1733 cm^{-1}; NMR ($CDCl_3$) δ 3.8 (s, 3 H), 5.05 (d, 2 H), 6.42 (m, 1 H); MS parent *m/e* 142. Anal. Calcd for $C_6H_6O_4$: C, 50.70; H, 4.23; O, 45.07. Found: C, 50.61; H, 4.32.

Acknowledgments. We thank the National Institutes of Health (Grant No. CA-21469) and the Hoffmann–LaRoche Corp. for support of this work.

Registry No.—**1**, 63731-11-3; **2**, 19406-00-9; **3**, 1212-08-4; **4**, 63731-12-4; dimethyl carbonate, 616-38-6; butyrolactone, 96-48-0; diphenyl disulfide, 882-33-7.

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Chiroptical Properties of Pelletierine and Anaferine

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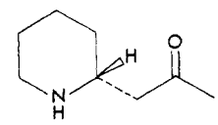
Received March 29, 1976

The alkaloid (−)-pelletierine **1** [1-(2-piperidyl)propan-2-one] has been shown to have the D configuration (= *R*) by the isolation of L-(−)-pipecolic acid on chromic acid oxidation of (+)-pelletierine,[1] while the closely related natural anaferine[2] [1,3-bis(2-piperidyl)propan-2-one] appears to be the meso isomer.[3] However, since it has been reported[4] that the resolved enantiomers of anaferine racemize readily, and that under the same conditions the racemate is converted into the meso form[5] in aqueous solution, it remains possible that natural anaferine



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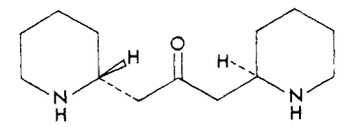

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is one of the optically active forms and undergoes isomerization during the isolation procedure. Since resolved (−)-1,3-bis(2-piperidyl)propan-2-one yielded D-(+)-pipecolic acid on chromic acid oxidation,[6] resolved (−)-anaferine possesses the D,D configuration (= *R*,*R*) **2**.

From recent work on the ORD and CD spectra of 2-alkylpiperidines[7] it is clear that the negative plain curve below 225 nm found (in addition to a negative Cotton effect at 280 nm for the n → π* transition of the ketone) in an earlier ORD spectrum of (−)-pelletierine sulfate[8] is due to the π → π* absorption of the ketone and cannot be used for configurational assignments by comparison with 2-alkylpiperidines. However, such a comparison can be made if the rotational contribution of the ketone chromophore is removed by chemical means which do not interfere with the asymmetric center.

The keto group in (−)-pelletierine sulfate was converted to the dimethyl ketal by reaction with methanolic hydrogen chloride[9] at room temperature. The resulting solution then

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