Portions were removed at various times and subjected to spectrometric analysis at the UV maximum at 350 nm to measure the *p*-nitro(methylthio)benzene being formed. Although the portions were homogeneous solutions during the reactions, they were not during the UV spectral measurements at room temperature because the products were not sufficiently soluble in the buffer media at such a low temperature. Thus, acetonitrile was added to make the solutions homogeneous during measurement. The difference between absorption intensities at infinite time and a specified time indicated the amount of remaining **10**. Thus, the pseudo-first-order rate coefficients were calculated with a FACOM computer.

(13) Refer to: Perrin, D. D.; Dempsey, B. "Buffers for pH and Metal Ion Control"; Chapman and Hall: London, 1974.

Acknowledgment. We thank Professor R. L. Schowen, University of Kansas, for helpful discussions.

Registry No. 9, 70969-20-9; **10**, 73198-19-3; **11**, 73245-78-0; **12**, 68258-55-9; **13**, 68330-66-5; **14**, 29843-53-6; **15**, 73198-21-7.

Enones with Strained Double Bonds. 4. The Bicyclo[5.3.1]undecane System[1]

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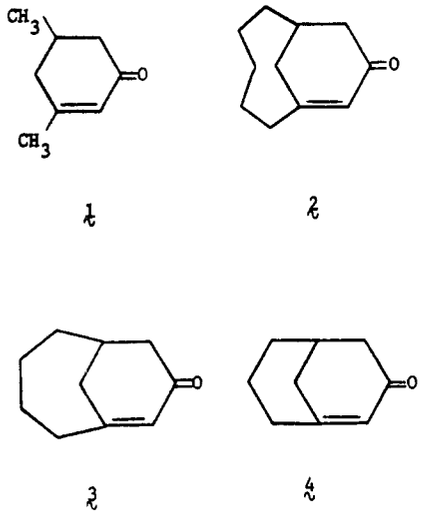
Bicyclo[5.3.1]undec-7-en-9-one (**2**) has been synthesized from cyclooctenone. This bicyclo[5.3.1] enone system **2** shows less tendency to add nucleophiles in a conjugate manner than is the case for the more strained bicyclo[4.3.1] enone **3** and bicyclo[3.3.1] enone **4**. Comparison of the ultraviolet spectra and the electrochemical reduction potentials of the monocyclic enone **1** and the bicyclic enones **2** and **3** indicates that these compounds absorb light at longer wavelengths and that they are more easily reduced to the corresponding anion radicals as distortion of the conjugated enone system increases. Force field calculations have been used to estimate the degree of distortion present in the enone systems of these bicyclic compounds.

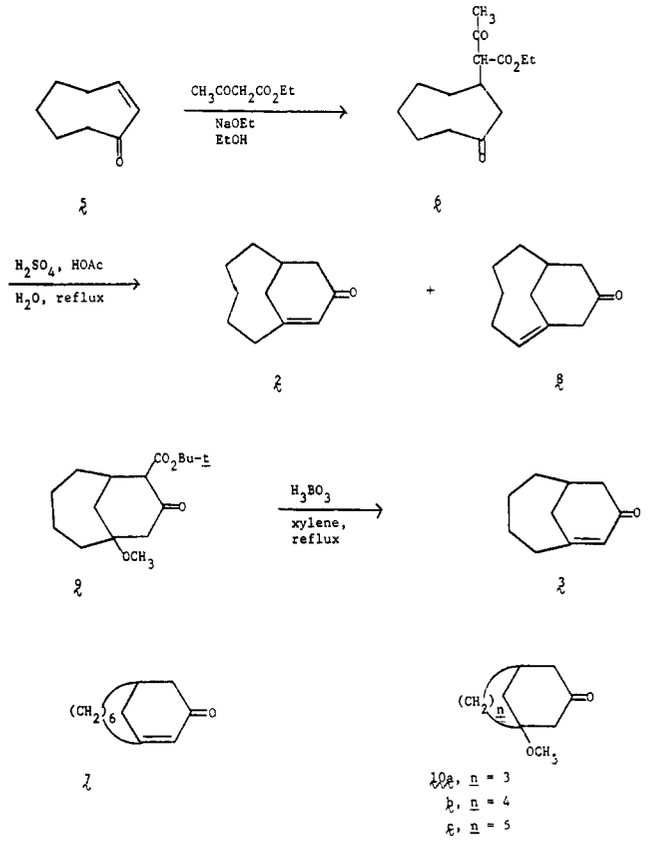
In continuing our study of enones with strained double bonds,[2] we wished to compare the properties of the series of enones **1**–**4**. In this series the distortion of the C=C



bond was expected to vary from essentially none (enone **1**) to substantial twisting in the enone **4**[2a,c] whose high reactivity has thus far prevented isolation. This paper reports the synthesis of the bicyclic enone **2** and compares certain of the chemical and physical properties of the series of enones **1**–**4**.

The synthesis of the enone **2** was accomplished by the Michael addition of ethyl acetoacetate to cyclooctenone (**5**, Scheme I) followed by treatment of the adduct **6** with

Scheme I



a refluxing mixture of H_2SO_4, HOAc, and H_2O. This synthesis, which is analogous to the method used earlier for the formation of the larger bicyclic enone **7**,[3] initially formed a mixture of the conjugated enone **2** and the un-

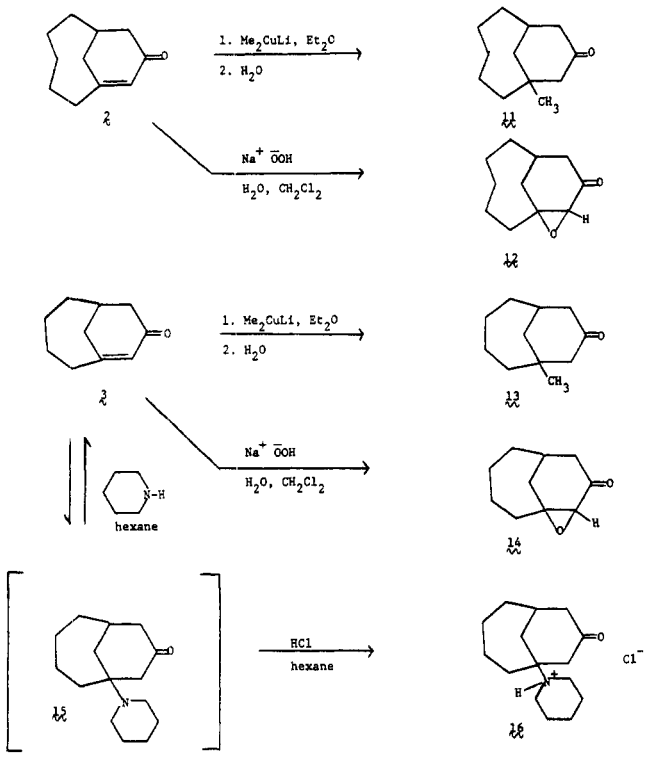
(1) This research has been supported by Public Health Service Grant R01-GM-20197 from the National Institute of General Medical Science. The exceution of this research was also assisted by Institutional Research grants from the National Science Foundation for the purchase of a mass spectrometer and a Fourier transform NMR spectrometer.

(2) (a) House, H. O.; Kleschick, W. A.; Zaiko, E. J. *J. Org. Chem.* **1978**, *43*, 3653. (b) House, H. O.; Lee, T. V. *Ibid.* **1979**, *44*, 2819. (c) House, H. O.; DeTar, M. B.; VanDerveer, D. *Ibid.* **1979**, *44*, 3793.

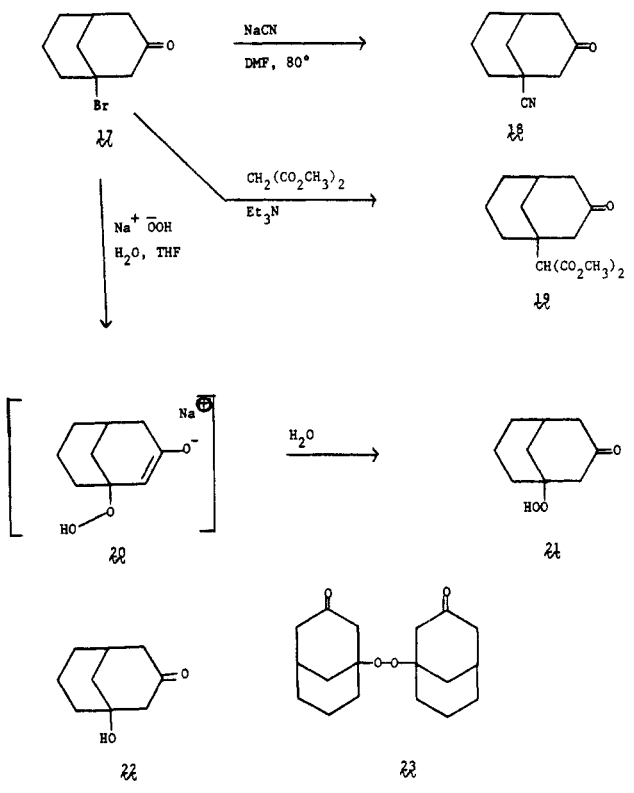
(3) Gioia, B.; Marchesini, A.; Andreeti, G. D.; Bocelli, G.; Sgarabotto, P. *J. Chem. Soc., Perkin Trans. 1* **1977**, 410.

0022-3263/80/1945-1800$01.00/0

Scheme II



Scheme III

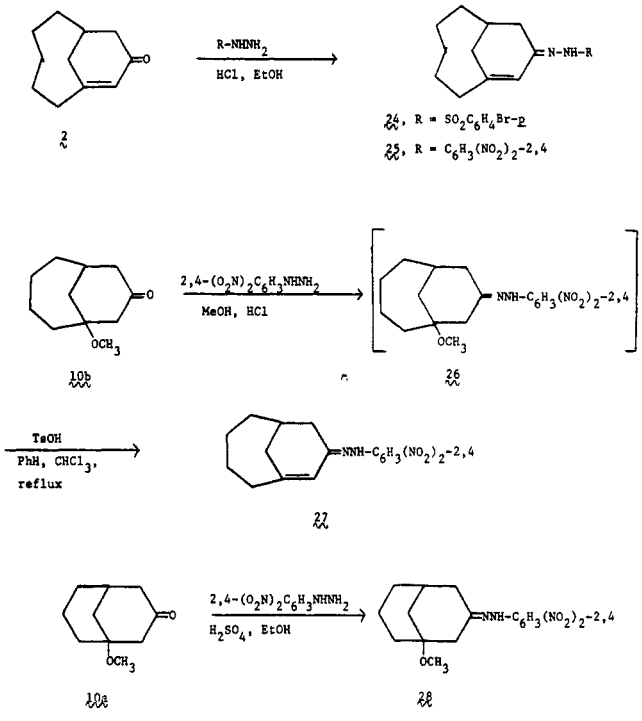


conjugated isomer **8**. The latter product **8** isomerized to the conjugated system **2** on standing. In MeOH solution at 25 °C, the equilibrium composition contains approximately 16% of the unconjugated enone **8** and 84% of the conjugated isomer **2**. We also found an improved synthesis for the previously described enone **3** involving the direct conversion of the methoxy keto ester **9**[2b] to the enone **3** by treatment with a suspension of H_3BO_3 in boiling xylene.

The three bicyclic enones **2–4** exhibit significant differences in their chemical behavior. In the absence of nucleophiles or dienes, the most strained enone **4** undergoes a rapid thermal [2 + 2] cycloaddition with itself to form dimers;[2c] neither of the less strained enones **2** and **3** exhibit this behavior even on prolonged heating.[2b] The enones differ substantially in the ease of conjugate addition of nucleophiles. Thus, generation of the [3.3.1] enone **4** in the presence of MeOH or stirring of the [4.3.1] enone **3** in MeOH with no intentionally added base results in the rapid formation of the methoxy ketone **10a** or **10b**, respectively. By contrast, a solution of the [5.3.1] enone **2** in MeOH containing NaOMe failed to yield the analogous adduct **10c**; instead, an equilibrium mixture of the enones **2** and **8** was formed after prolonged reaction. Conjugate adducts of the [5.3.1] enone **2** could be formed under more favorable conditions. Thus reaction with Me_2CuLi formed the methylated ketone **11** (Scheme II), and reaction with NaOOH formed the epoxy ketone **12**. Comparable reactions with the [4.3.1] enone **3** formed the conjugate adducts **13** and **14**. The enone **3** also formed an unstable conjugate adduct **15** with piperidine that was characterized as its hydrochloride salt **16**.

Samples of the [3.3.1] enone **4**, generated in situ from the bromo ketone **17** (Scheme III), were trapped as the conjugate adducts **18** and **19** when one of the anions CN^- or $(CH_3OOC)_2CH^-$ was present in the reaction solution. Attempts to convert the [3.3.1] enone **4** to an epoxy ketone (analogous to products **12** and **14**) resulted instead in the formation of a mixture of the hydroperoxide **21** and the ketol **22**. When less H_2O_2 was employed in the reaction, the ketol **22** and the symmetrical peroxide **23** were the major products. Failure to form an epoxy ketone in this case presumably reflects the rigidity present in the intermediate **20** that disfavors intramolecular displacement at oxygen to form the epoxy ketone; instead, protonation of the intermediate enolate **20** leads to the hydroperoxide **21**. A comparable result has been observed[4] in attempts to convert certain rigid indenone derivatives to the corresponding epoxy ketones.

Scheme IV



(4) Paquette, L. A.; Carr, R. V. C.; Bellamy, F. *J. Am. Chem. Soc.* **1978**, *100*, 6764.

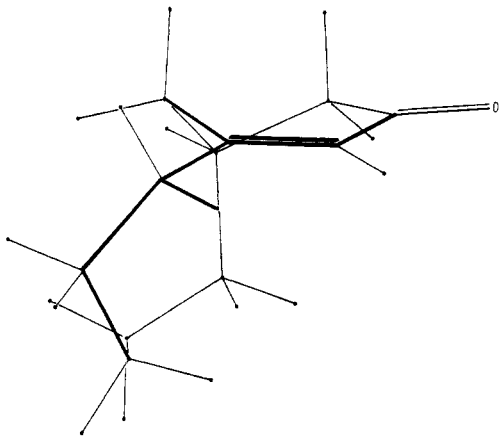


Figure 1. MMPI energy-minimized conformation of the enone **2** (calculated steric energy 23.6 kcal/mol).

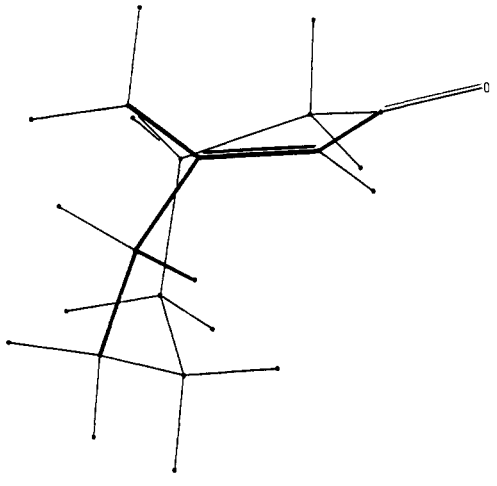


Figure 2. MMPI energy-minimized conformation of the enone **3** (calculated steric energy 22.9 kcal/mol).

The [5.3.1] enone **2** was readily converted to carbonyl derivatives **24** and **25** (Scheme IV) by conventional procedures. Attempts to form analogous derivatives from the [4.3.1] enone **3** produced complex mixtures, suggesting complications from competing conjugate addition to this enone **3**. However, the related methoxy ketone **10b** was converted to the crude, unstable carbonyl derivative **26** that underwent subsequent acid-catalyzed elimination to form the 2,4-dinitrophenylhydrazone, **27**, of enone **3**. Application of the same reaction to the methoxy ketone **10a** formed the corresponding stable carbonyl derivative **28**; we have not yet found conditions that will convert intermediate **28** to a carbonyl derivative of the [3.3.1] enone **4**.

Since the presently available bicyclic enone derivatives have not been satisfactory for X-ray crystallographic analyses, we have sought information about the favored conformations of the enones **1–4** by use of force field calculations employing Allinger's molecular mechanics program for molecules containing conjugated π systems (MMPI).[5,6] The calculated steric energies of the model

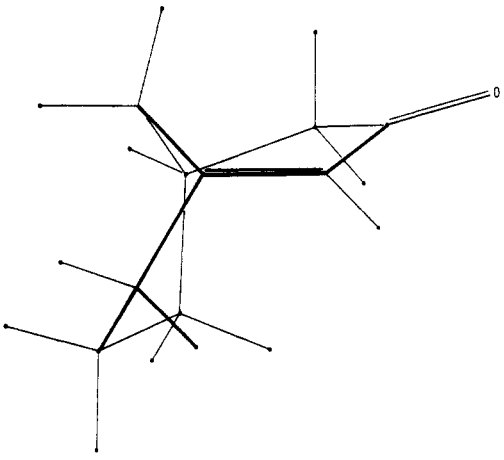
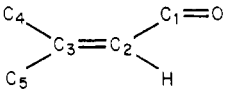


Figure 3. MMPI energy-minimized conformation of the enone **4** (calculated steric energy 25.2 kcal/mol).

Table I. Calculated Geometric Parameters for the Enones 1–4



	1	2	3	4
dihedral angle C_1-C_2-C_3-C_4, deg	1	5	11	12
dihedral angle C_1-C_2-C_3-C_5, deg	177	175	149	131
dihedral angle H-C_2-C_3-C_4, deg	180	178	177	173
dihedral angle H-C_2-C_3-C_5, deg	2	2	18	29
deviation of C_3 from plane of C_2, C_4, and C_5, Å	0.018	0.001	0.149	0.265

Table II. UV Maxima and Reduction Potentials of the Enones 1–3

compd	UV max (CH_3CN), nm (ϵ) $\pi \rightarrow \pi^*$	UV max (CH_3CN), nm (ϵ) $n \rightarrow \pi^*$	$E_{1/2}$ (CH_3CN), V (vs. SCE)
1	232 (13 800)	323 (25)	−2.21
2	240 (14 800)	335 (50)	−2.13
3	250 (5070)	345 (92)	−2.00

monocyclic enone **1** and the [5.3.1] enone **2** could be minimized with a planar enone system. However, for the more strained bicyclic enones **3** and **4**, the calculated steric energies were smaller when the enone systems were distorted from planarity. For [3.3.1] enone **4** the calculated steric energies were 25.2 kcal/mol for the nonplanar conformation and 30.8 kcal/mol for the planar conformer. The corresponding values for the [4.3.1] enone **3** were as follows: nonplanar, 22.9 kcal/mol; planar, 25.6 kcal/mol. Prospective drawings of the calculated conformations of the bicyclic enones are presented in Figures 1–3.[7]

The calculated dihedral angles for the enone systems and the calculated deviations of the enone β-carbon atoms from the plane defined by the three adjacent carbon atoms are presented in Table I. As might be expected, the C=C bond of the enone system is progressively more twisted and progressively more distorted from planarity in the order $1 < 2 < 3 < 4$. Such distortion should be more favorable

(5) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893.
(6) (a) Allinger, N. L.; Tribble, M. T.; Miller, M. A.; Wertz, D. H. *J. Am. Chem. Soc.* **1971**, *93*, 1637. (b) Allinger, N. L.; Sprague, J. T.; Liljefors, T. *Ibid.* **1974**, *96*, 5100. (c) Allinger, N. L.; Wertz, D. H. *Tetrahedron* **1974**, *30*, 1579. A summary of the minimization techniques is given in ref 6a, and force field parameters are listed in ref 6c. Calculations were performed on an IBM 370 system. We are most grateful to Professor Allinger and his associates and to the University of Georgia Computer Center for allowing us to use the current version of the MMPI program for these calculations.

(7) The plots in these figures are modified ORTEP plots performed on a Calcomp plotter with a CDC Cyber 74 computer. The coordinates for these plots are the final atomic coordinates calculated from the MMPI program after energy minimization.

in species where the first antibonding molecular orbital of the enone system (with a node between C_α and C_β) is populated rather than in the ground state of the enone. More specificially, one might expect the energy separating the enone ground state and either the lowest electronically excited state or the enone anion radical state to be lowered by this distortion. We explored this idea for the enones **1–3** that have been isolated by examining their UV spectra and their polarographic reduction potentials. These values are summarized in Table II. It is apparent that both the energies of the $\pi \rightarrow \pi^*$ absorptions and the potential differences required to form the enone anion radicals are diminished as the enone systems become increasingly distorted. Presumably, these effects would be even further accentuated in the more highly distorted enone **4**. The half-lives of the enone anion radicals, estimated by cyclic voltammetry, were comparable for the three compounds examined. Our preliminary efforts to determine the lifetimes of excited states by fluorescence and/or phosphorescence measurements were thwarted when we found no fluorescence for any of the enones **1–3**, only weak phosphorescence for the monocyclic enone **1**, and no phosphorescence for the bicyclic enones **2** and **3**. Since it is apparent that both bicyclic enones **2** and **3** undergo change upon irradiation with ultraviolet light, we are continuing our investigation of various photochemical reactions and thermal cycloaddition reactions of these compounds.

Experimental Section[8]

Improved Preparation of the Enone 3. A direct procedure for the conversion of the previously described[2b] keto ester **9** to the enone **3** in good yield has been found. A suspension of 0.44 g (7 mmol) of H_3BO_3 in 10 mL of xylene containing 2.0 g (7.0 mmol) of the keto ester **9** was heated to 125–130 °C for 1 h and then partitioned between aqueous NaCl and $CHCl_3$. The organic layer was dried, concentrated, and distilled to separate 0.65 g (65%) of the enone **3** [bp 85–90 °C (0.1 mm); n^{25}_D 1.5272 [lit.[2b] bp 85–89 °C (0.08 mm); n^{25}_D 1.5272] that was identified with an authentic sample by comparison of NMR spectra. When the heating period was shortened to only 30 min in a similar reaction, elimination was incomplete, and some methoxy ketone **10b** was detected (NMR analysis) in the crude product.

Reaction of the Enone 3 with $LiCuMe_2$. To a cold (0 °C) colorless solution of $LiCuMe_2$, prepared from 12.4 mmol of MeLi, 1.27 g (6.19 mmol) of Me_2S–CuBr, 10 mL of Me_2S, and 25 mL of Et_2O, was added, dropwise and with stirring, a solution of 0.56 g (3.73 mmol) of the enone **3** in 5 mL of Et_2O. After the resulting yellow suspension had been stirred at 23 °C for 75 min, it was partitioned between Et_2O and aqueous NH_3 plus NH_4Cl (pH 8). The organic layer was dried and concentrated, and the residual liquid (0.61 g) was chromatographed on silica gel with an EtOAc–hexane eluent (1:9 v/v). The pure ketone **13** was collected as 0.51 g (82%) of liquid, n^{25}_D 1.4892, that crystallized as colorless prisms on standing; mp 33.5–35 °C. Recrystallization from pentane did not change the melting point: IR (CCl_4), 1713 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 2.0–2.7 (5 H, m, CH and CH_2CO), 1.2–2.0 (10 H, m, CH_2), 1.05 (3 H, s, CH_3); mass spectrum, *m/e* (relative intensity) 166 (M^+, 11), 109 (100), 81 (33), 67 (39), 55 (33), 41 (45); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 211.8 (s), 54.9 (t), 47.5 (t), 42.0 (t), 39.2 (t or s), 39.1 (s or t), 34.1 (t), 34.0 (t), 33.1 (d), 25.5 (t), 24.8 ppm (q).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.49; H, 10.93.

Preparation of the Epoxy Ketone 14. A solution of NaOOH, from 28.0 mmol of H_2O_2 and 0.94 mmol of NaOH in 4.7 mL of H_2O, was added to a solution of 0.42 g (2.8 mmol) of the enone **3** in 10 mL of CH_2Cl_2. The resulting two-phase mixture was stirred at 25 °C for 120 min and then partitioned between H_2O and CH_2Cl_2. After the organic layer had been dried and concentrated, a 110-mg aliquot of the residual liquid (0.47 g) was distilled. The crude epoxy ketone **14** was collected at 90–93 °C (0.15 mm) as 78 mg (72%) of liquid that solidified as colorless prisms, mp 34.5–35.5 °C. Recrystallization from pentane afforded the pure epoxy ketone **14** as prisms: mp 71.5–73.5 °C; IR (CCl_4) 1718 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 2.53 (1 H, s, CH), 1.0–2.5 (13 H, m, aliphatic CH); mass spectrum, *m/e* (relative intensity) 166 (M^+, 16), 109 (26), 95 (100), 93 (27), 81 (42), 79 (42), 69 (22), 68 (24), 67 (84), 55 (53), 53 (27), 41 (77), 39 (54); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 206.8 (s), 63.0 (d), 54.9 (s), 53.3 (d), 45.7 (t), 35.7 (t), 33.9 (t), 30.1 (t), 26.6 (t), 23.4 ppm (t).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.97; H, 8.52.

Preparation of the Amino Ketone 15. A solution of 0.35 g (2.3 mmol) of the enone **3** and 0.19 g (2.3 mmol) of piperidine in 5 mL of anhydrous hexane was stirred at 25 °C for 90 min and then concentrated under reduced pressure. The residual crude amino ketone **15** remained as 0.45 g (94%) of yellow liquid: IR (CCl_4) 1700 cm^{-1} (C=O); NMR (CCl_4) δ 1.0–3.4 (m, aliphatic CH); mass spectrum, *m/e* (relative intensity) 235 (M^+, 6), 178 (100), 150 (28), 84 (52), 82 (29), 41 (38), 39 (21). Since attempts to purify this product by distillation resulted in conversion of the amino ketone **15** to the starting enone **1** (NMR analysis), the crude amino ketone **15** was converted to its HCl salt for characterization. A solution of 0.45 g (1.9 mmol) of the crude amino ketone **15** in 15 mL of hexane was treated with gaseous HCl, and the salt **16** that separated was collected as 0.43 g (77%) of colorless plates, mp 183–199 °C dec. This crude salt was recrystallized from an absolute EtOH–hexane mixture to separate 0.25 g (48%) of the HCl salt **16** of amino ketone **15** as prisms: mp 190–198 °C dec; IR ($CHCl_3$) 1710 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 11.33 (1 H, br, NH), 3.31 (4 H, t, J = 6 Hz, CH_2N^+), 1.0–3.3 (21 H, m, aliphatic CH); mass spectrum, *m/e* (relative intensity) 235 (16), 192 (24), 178 (100), 150 (22), 84 (30), 82 (46), 69 (45).

Anal. Calcd for $C_{15}H_{26}ClNO$: C, 66.27; H, 9.64; Cl, 13.04; N, 5.15. Found: C, 66.21; H, 9.66; Cl, 13.06; N, 5.14.

Preparation of the Dinitrophenylhydrazone 27. Concentrated aqueous HCl was added, dropwise and with stirring, to a suspension of 0.92 g (4.7 mmol) of 2,4-dinitrophenylhydrazine in 15 mL of boiling MeOH until a solution was obtained. Then a solution of 0.85 g (4.7 mmol) of the methoxy ketone **10b** in a mixture of 5 mL of MeOH and 0.5 mL of CCl_4 was added, and the resulting solution was boiled for 1 min and then cooled. The crude derivative **26**, collected as 0.85 g (50%) of red-orange crystals, mp 95–98 °C, was recrystallized from MeOH to separate 0.51 g (30%) of the crude hydrazone **26** as orange plates: mp 128–130 °C; IR ($CHCl_3$), no absorption in the 6-μm region attributable to a C=O group; ^1H NMR ($CDCl_3$) δ 11.3 (1 H, br, NH), 9.13 (1 H, d, J = 3 Hz, aryl CH), 7.9–8.6 (2 H, m, aryl CH), 3.46 (3 H, s, OCH_3), 0.9–3.2 (15 H, m, aliphatic CH); mass spectrum, *m/e* (relative intensity) 362 (M^+, 13), 330 (85), 181 (28), 180 (58), 151 (21), 148 (27), 125 (100), 107 (31), 93 (56), 91 (53), 79 (55), 77 (44), 67 (34), 55 (35), 41 (70), 39 (38). The mother liquors from this crystallization were chromatographed on silica gel with a $CHCl_3$ eluent to separate 100 mg (5%) of the subsequently described 2,4-dinitrophenylhydrazone **27**, mp 120–122 °C.

A solution of 100 mg (0.27 mmol) of the crude methoxy ketone derivative **26** and 25 mg (0.14 mmol) of *p*-TsOH in a mixture of 5 mL of PhH and 0.5 mL of $CHCl_3$ was refluxed for 1 h and then washed with H_2O, dried, and concentrated. The residual red solid (90 mg) was recrystallized from MeOH to separate 31 mg (34%) of the 2,4-dinitrophenylhydrazone **27** as red plates: mp 120–122 °C; IR ($CHCl_3$), no absorption in the 6-μm region attributable to a C=O group; ^1H NMR ($CDCl_3$) δ 11.61 (1 H, br, NH), 9.10

(8) All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated, $MgSO_4$ was employed as a drying agent. The IR spectra were determined with a Perkin-Elmer Model 257 infrared recording spectrophotometer fitted with a grafting. The UV spectra were determined with a Cary Model 14 or a Perkin-Elmer Model 202 recording spectrophotometer. The proton NMR spectra were determined at 60 MHz with a Varian Model T-60A NMR spectrometer, and the ^{13}C NMR spectra were determined at 25 MHz with a JEOL Fourier transform spectrometer, Model PFT-100. The chemical shift values are expressed in δ values (parts per million) relative to a Me_4Si internal standard. The mass spectra were obtained with either a Hitachi Perkin-Elmer Model RMU-7 or a Varian MAT Model 112S mass spectrometer. All reactions involving strong bases or reactive organometallic intermediates were performed under a nitrogen atmosphere.

(1 H, d, J = 3 Hz, aryl CH), 7.8–8.5 (2 H, m, aryl CH), 6.05 (1 H, s, vinyl CH), 0.8–2.8 (13 H, m, aliphatic CH); mass spectrum, m/e (relative intensity), 331 (31), 330 (M^+, 100), 151 (22), 133 (24), 107 (26), 105 (23), 93 (28), 91 (50), 79 (46), 77 (24), 67 (23), 55 (23), 43 (23), 41 (40).

Anal. Calcd for $C_{16}H_{18}N_4O_4$: C, 58.17; H, 5.49; N, 16.96. Found: C, 57.91; H, 5.63; N, 16.84.

Preparation of Cyclooctenone (5). Following a previously described procedure,[9] we treated a solution of 67.56 g (0.535 mol) of cyclooctanone in 600 mL of ethylene glycol with several drops of Br_2. After the yellow color had been discharged, 85.2 g (0.538 mol) of Br_2 was added, dropwise and with stirring during 20 min, while the mixture was kept at 15 °C. The resulting mixture was poured into a suspension of 125 g of Na_2CO_3 in 900 mL of pentane. After gas evolution ceased, 600 mL of H_2O was added, and the organic layer was separated, dried, and concentrated. Since the residual crude ethylene ketal of 2-bromocyclooctanone [127 g or 95% of yellow liquid: NMR (CCl_4) δ 3.6–4.8 (4 H, m, CH_2O), 1.0–3.0 (13 H, m, aliphatic CH); IR (neat) 1700 cm^{-1} (weak, ketone impurity)] decomposed during attempted distillation, it was dehydrohalogenated without purification. A solution of 127 g (0.509 mol) of the crude bromo ketal and 123.2 g (3.8 mol) of NaOH in 500 mL of MeOH was refluxed for 70 h and then partitioned between pentane and aqueous NaCl. The organic layer was dried, concentrated, and distilled to separate 52.2 g (58%) of the ethylene ketal of 2-cyclooctenone as a colorless liquid: bp 78–79 °C (1 mm) [lit.[9] bp 67–69 °C (1.4 mm)]; n^{25}_D 1.4889; IR (neat) 1655 cm^{-1} (weak, C=C); ^1H NMR (CCl_4) δ 5.1–6.0 (2 H, m, vinyl CH), 3.1–4.3 (4 H, m, CH_2O), 1.0–2.8 (10 H, m, aliphatic CH); mass spectrum, m/e (relative intensity) 168 (M^+, 6), 125 (100), 86 (29), 81 (44), 79 (24), 67 (31), 55 (26), 53 (30), 41 (33), 39 (40).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.17; H, 9.61.

A solution of 8.4 g (50 mmol) of this unsaturated ketal in 50 mL of THF was mixed with 10 mL of aqueous 3% H_2SO_4 and stirred for 1 h, at which time hydrolysis was complete (TLC analysis). The mixture was extracted with Et_2O, and the ethereal extract was washed with aqueous $NaHCO_3$, dried, and concentrated. Distillation afforded 5.14 g (83%) of the enone **5** as a colorless liquid: bp 100–102 °C (0.2 mm); n^{25}_D 1.4942 [lit. bp 82–90 °C (12 mm);[10] n^{25}_D 1.4953[11]];[12] IR (CCl_4) 1685 (sh), 1670, 1660 (sh, conj C=O), 1645 and 1620 cm^{-1} (C=C); ^1H NMR (CCl_4) δ 5.6–6.6 (2 H, m, vinyl CH), 2.1–2.9 (4 H, m, CH_2CO and allylic CH_2), 1.1–2.1 (6 H, m, CH_2); mass spectrum, m/e (relative intensity) 124 (M^+, 17), 81 (100), 80 (70), 68 (32), 67 (30), 55 (25), 54 (22), 53 (35), 41 (21), 39 (30); UV max (95% EtOH) 230 nm (ϵ 13 100), 314 (44).

Various attempts to hydrolyze the unsaturated ketal with aqueous acid in MeOH formed mixtures containing (TLC, silica gel with an EtOAc–pentane eluent, 1:19 v/v) the unsaturated ketal (R_f 0.37), the enone **5** (R_f 0.030), and 3-methoxycyclooctanone (R_f 0.14). A cold (2 °C) solution of 15.84 g (94 mmol) of the unsaturated ketal in 65 mL of MeOH was mixed with 35 mL of cold (2 °C) aqueous 3% H_2SO_4 and then stirred at 2–25 °C for 1 h. After the mixture had been partitioned between Et_2O and H_2O, the organic layer was dried and concentrated. Distillation separated 9.1 g (62%) of the 3-methoxycyclooctanone: bp 99–100 °C (3 mm) [lit.[13] bp 61–63 °C (0.3 mm)]; IR (CCl_4) 1703 cm^{-1} (C=O); NMR (CCl_4) δ 3.30 (3 H, s, OCH_3), 0.8–3.0 (12 H, m, aliphatic CH_2); mass spectrum, m/e (relative intensity) 156 (M^+, 12), 124 (30), 81 (38), 80 (29), 71 (87), 69 (23), 67 (23), 58 (100), 55 (72), 43 (43), 42 (32), 41 (49), 39 (25).

Preparation of the Diketo Ester 6. A solution of 3.87 g (31 mmol) of the enone **5**, 5.0 g (38 mmol) of ethyl acetoacetate, and NaOEt (from 87.5 mg or 3.8 mmol of Na) in 10 mL of EtOH was stirred at 25 °C for 14 h, at which time none of the starting enone **5** was detected (TLC analysis). After the mixture had been partitioned between Et_2O and H_2O, the organic layer was dried, concentrated, and distilled to separate 5.29 g (68%) of the crude diketo ester **6**, bp 156–157 °C (0.8 mm). Redistillation afforded the pure diketo ester **6** (a mixture of diastereoisomers) as a colorless liquid: bp 145–146 °C (0.2 mm); n^{25}_D 1.4775; IR (CCl_4) 1755, 1725, 1710 cm^{-1} (C=O of ester and ketone); ^1H NMR (CCl_4) δ 4.19 (2 H, q, J = 7 Hz), 3.42 (d, J = 3 Hz), 3.26 (d, J = 2 Hz, total 1 H, CH of acetoacetate residue), 1.0–3.0 (19 H, m, aliphatic CH including a CH_3CO singlet at 2.10 and an ethoxy CH_3 triplet at 1.26, J = 7 Hz); mass spectrum, m/e (relative intensity) 208 (4), 165 (13), 82 (17), 81 (16), 55 (38), 45 (27), 43 (100), 41 (28).

Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 66.12; H, 8.75.

Preparation of the Bicyclic Enones 2 and 8. A solution of 12.9 g (51 mmol) of the diketo ester **6** and 12 mL of concentrated H_2SO_4 in a mixture of 85 mL of HOAc and 50 mL of H_2O was refluxed for 5 h and then partitioned between H_2O and pentane. After the organic layer had been washed with aqueous $NaHCO_3$, it was dried and concentrated. The residual liquid (3.8 g) contained (TLC, silica gel coating with an EtOAc–hexane eluent, 1:9 v/v) a mixture of enone **8** (R_f 0.68), enone **2** (R_f 0.41), and the starting ester **6** (R_f 0.13). The material was chromatographed on silica gel with an EtOAc–hexane eluent (1:9 v/v) to separate fractions containing each of the enones **2** and **8**. The earlier fractions were distilled (100–102 °C at 0.2 mm) in a short-path still to separate 1.236 g (15%) of the enone **8** as a colorless liquid: n^{25}_D 1.5215; IR (CCl_4), 1720 (C=O), 1670 cm^{-1} (weak, C=C); ^1H NMR (CCl_4) δ 5.52 (1 H, t, J = 8 Hz, vinyl CH), 0.8–3.4 (15 H, m, aliphatic CH); mass spectrum, m/e (relative intensity) 164 (M^+, 66), 123 (28), 122 (35), 121 (48), 107 (39), 95 (86), 94 (47), 93 (64), 91 (30), 81 (52), 80 (40), 79 (87), 77 (32), 68 (30), 67 (58), 55 (36), 53 (36), 41 (100), 39 (65).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.45; H, 9.85.

When the enone **8** was allowed to stand, its composition changed. The IR and NMR spectra of the resulting sample indicated that the major product was the more stable conjugated enone **2**.

The later chromatographic fractions were distilled (100–102 °C at 0.2 mm) to separate 2.441 g (29%) of the enone **2** as a colorless liquid: n^{25}_D 1.5275; IR (CCl_4) 1673 (C=O), 1655 (sh), 1631 cm^{-1} (C=C); ^1H NMR (CCl_4) δ 5.70 (1 H, br s, vinyl CH), 0.7–3.4 (15 H, m, aliphatic CH); UV max (CH_3CN) 240 nm (ϵ 14 800), 335 (50); mass spectrum, m/e (relative intensity) 164 (M^+, 22), 95 (36), 82 (100), 79 (23), 67 (21), 59 (30), 53 (21), 45 (24), 41 (51), 39 (37); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 198.9 (s), 165.0 (s), 126.4 (d), 45.4 (t), 36.4 (t), 33.0 (d and t, 2 C atoms), 29.7 (t), 28.8 (t, 2 C atoms), 27.3 ppm (t).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.41; H, 9.84.

Several attempts were made to effect the base-catalyzed conjugate addition of MeOH to the enone **2**. In a typical experiment, a solution of NaOMe, from 0.20 g (8.7 mmol) of Na and 15 mL of MeOH, was mixed with 290 mg (1.77 mmol) of the enone **2**, and the mixture was stirred at 25 °C for 48 h. After the resulting solution had been partitioned between H_2O and Et_2O, the ethereal layer was dried and concentrated. The residual liquid containing (TLC) a mixture of the enones **2** and **8** was chromatographed on silica gel to separate 230 mg (79% recovery) of the starting enone **2** and 47 mg (16%) of the unconjugated enone **8**. Each product was identified with previously described samples by comparison of IR and NMR spectra. The results of several similar experiments suggest that the equilibrium mixture of these enones in MeOH at 25 °C contains 16% of the unconjugated isomer **8** and 84% of the conjugated enone **2**.

A solution of 201 mg (1.22 mmol) of the enone **2**, 263 mg (1.33 mmol) of 2,4-dinitrophenylhydrazine, and 0.05 mL of concentrated aqueous HCl in 70 mL of boiling EtOH was allowed to cool. The derivative that precipitated was recrystallized from EtOH to separate 414 mg (98%) of the 2,4-nitrophenylhydrazone **25** as red prisms: mp 157–158 °C; IR ($CDCl_3$), no absorption in the 6-μm region attributable to a C=O group; ^1H NMR ($CDCl_3$) δ 11.18 (1 H, s, NH), 9.10 (1 H, d, J = 2.6 Hz, aryl CH), 8.26 (1 H, dd, J = 2.6, 8.8 Hz), 7.94 (1 H, d, J = 8.8 Hz), 6.2 (1 H, br s, vinyl CH), 0.6–2.8 (15 H, m, aliphatic CH); UV max (95% EtOH) 229

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(11) Cope, A. C.; Kinter, M. R.; Keller, R. T. *J. Am. Chem. Soc.* **1954**, *76*, 2757.
(12) The values for the unconjugated isomer, 3-cyclooctenone, are as follows: bp 80 °C (12 mm);[10] IR 3030, 1700, and 1650 cm^{-1} [10] and 1710 and 1653 cm^{-1} (Paquette, L. A.; Eizember, R. F. *J. Am. Chem. Soc.* **1967**, *89*, 6205).
(13) Cantrell, T. S.; Solomon, J. S. *J. Am. Chem. Soc.* **1970**, *92*, 4656.

Table III. Electrochemical Reduction of Enones

ketone (concn, M × 10^3)	polarography $E_{1/2}$, V (vs. SCE)	n	i_d, μA	cyclic voltammetry $E_{1/2}$, V (vs. SCE)	half-life, s
2 (0.77–1.6)	−2.13	1.1	19–51	−2.15	0.03
3 (2.7–2.9)	−2.00	1.1	65–71	−2.02	0.01
1 (1.0–1.3)	−2.21	1.2	33–44	−2.20	0.01

nm (ε 16 500), 256 (20 600), 288 (sh, 12 000), 386 (25 000); mass spectrum, m/e (relative intensity) 345 (20), 344 (M^+, 100), 165 (16), 91 (23), 79 (19), 41 (19).

Anal. Calcd for $C_{17}H_{20}N_4O_4$: C, 59.29; H, 5.85; N, 16.27. Found: C, 59.18; H, 5.88; N, 16.32.

A boiling solution of 308 mg (1.22 mmol) of *p*-bromophenylsulfonylhydrazine and 0.05 mL of concentrated aqueous HCl in 60 mL of EtOH was treated with 182 mg (1.11 mmol) of the enone **2** and allowed to cool. The derivative that separated was collected and recrystallized from EtOH to give 0.42 g (95%) of the *p*-bromophenylsulfonylhydrazone **24** as colorless plates: mp 181–182 °C dec; IR ($CHCl_3$), no absorption in the 6-μm region attributable to a C=O group; UV max (95% EtOH), 232 nm (ε 28 900), 260 (27 600); mass spectrum, m/e (relative intensity) 398 (M^+, 3.2), 396 (M^+, 3.7), 177 (100), 133 (29), 105 (23), 91 (44), 79 (26), 55 (25), 41 (38).

Anal. Calcd for $C_{17}H_{21}BrN_2O_2S$: C, 51.39; H, 5.32; N, 7.05. Found: C, 51.38; H, 5.37; N, 7.05.

Properties of the Enone 1. A previously described[2a] sample of enone **1** was redistilled to give the enone **1** as a colorless liquid: bp 82–86 °C (10 mm); n^{25}_D 1.4792 [lit.[2a] bp 89–98 °C (16 mm); n^{25}_D 1.4822]; IR (CCl_4) 1671 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 5.73 (1 H, br s, vinyl CH), 1.7–2.6 (8 H, m, aliphatic CH), 0.9–1.2 (3 H, m, CH_3); UV max (CH_3CN) 232 nm (ε 13 800), 323 (25); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 198.8 (s), 161.1 (s), 125.6 (d), 45.0 (t), 39.2 (t), 29.9 (d), 24.2 (q), 21.0 ppm (q).

Electrochemical Measurements. Polarographic and cyclic voltammetry measurements employed a custom-made polarographic module, utilizing solid-state amplifiers, that followed the typical three-electrode design. Descriptions of the cell, working electrodes, reagent purification, and measurement procedures have been published previously.[14] All measurements were performed at 25 °C in anhydrous CH_3CN containing 0.5 M *n*-Bu_4NBF_4 as the supporting electrolyte. The results of these measurements are summarized in Table III.

Examination of the Enones for Phosphorescence and Fluorescence.[15] 2-Methyltetrahydrofuran (freshly distilled from $LiAlH_4$) was used as a solvent for all measurements. In this solvent the long-wavelength maxima for the three enones were as follows: **2**, 344 nm (ε 49); **3**, 355 nm (ε 92); **1**, 337 nm (ε 25). The concentrations used for fluorescence and phosphorescence measurements were as follows: **2**, 7.3×10^{-3} M; **3**, 4.87×10^{-3} M; **1**, 1.87×10^{-2} M. All fluorescence experiments were done in 8.0-mm (i.d.) quartz cells at 25 °C. Phosphorescence spectra were measured at 77 K in the same cells. Samples were not degassed.

Fluorescence and phosphorescence measurements were performed with the following apparatus. The excitation system consisted of a 1000-W xenon arc lamp, a quartz focusing lens, a 10-cm water filter, a Bausch and Lomb high-intensity UV monochromator, and another quartz focusing lens. Emitted light was detected at 90° to the excitation beam, after passing through a quartz focusing lens and a Bausch and Lomb high-intensity UV-visible monochromator, by an RCA 1P28 photomultiplier tube, the output of which was amplified and displayed. For phosphorescence experiments a rotating can chopper was placed around the sample to remove fluorescence and scattered light. The samples were examined for fluorescence with 340-nm exciting light; none of the samples exhibited fluorescence. Phosphorescence measurements were obtained with a band-pass of 3–4 nm (fwhm) for both the excitation and detection monochromators. With 340-nm exciting light neither of the bicyclic enones **2** or **3** exhibited appreciable phosphorescence. The monocyclic enone **1** exhibited a broad phosphorescence band with its maximum at 460 ± 10 nm (uncorrected). The phosphorescence of **1** was quite weak; comparison with a standard benzophenone in EPA sample (phosphorescence quantum yield 0.72[16]) indicated an approximate phosphorescence quantum yield on the order of 0.05 ± 0.03.

Preparation of the Epoxy Ketone 12. To a solution of 456 mg (2.77 mmol) of the enone **2** in 10 mL of CH_2Cl_2 were added 0.90 g (8 mmol) of aqueous 30% H_2O_2 and 6.0 mL (1.2 mmol) of aqueous 0.2 M NaOH. After the two-phase mixture had been stirred vigorously for 2.8 h, an additional 3.80 g (33 mmol) of aqueous 30% H_2O_2 was added, and stirring at 25 °C was continued for an additional 19 h. At this time TLC analysis (silica gel coating with an EtOAc–hexane eluent, 1:19 v/v) indicated the presence of the epoxide **12** (R_f 0.46) but none of the starting enone **2** (R_f 0.25). The mixture was partitioned between H_2O and CH_2Cl_2, and the organic layer was dried and concentrated. The residual liquid was chromatographed on silica gel with an EtOAc–pentane eluent (1:19 v/v) to separate 299 mg (60%) of the epoxide **12** as a colorless semisolid. The epoxide was further purified by distillation in a short-path still (ca. 90 °C at 0.2 mm). The pure epoxide **12** crystallized on standing: mp 62.5–63 °C; IR (CCl_4) 1712 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 2.71 (1 H, s, O—C—CHCO), 0.9–2.6 (15 H, m, aliphatic CH); mass spectrum, m/e (relative intensity) 180 (M^+, 12), 152 (23), 95 (60), 93 (22), 82 (20), 79 (30), 77 (22), 67 (88), 55 (45), 54 (27), 53 (31), 43 (21), 41 (100), 39 (77); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 207.0 (s), 65.1 (s), 59.2 (d), 44.1 (t), 36.0 (t), 34.4 (d), 32.7 (t, two C atoms), 26.9 (t), 25.8 (t), 25.3 ppm (t).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.25; H, 8.97.

Preparation of the Methylated Ketone 11. A cold (0 °C) solution of Me_2CuLi was prepared from 7.3 mmol of MeLi, 752 mg (3.66 mmol) of Me_2S–CuBr, 21.8 mL of Et_2O, and 10 mL of Me_2S. To this solution was added, dropwise and with stirring, a solution of 433 mg (2.64 mmol) of the enone **2** in 6 mL of Et_2O. The cooling bath was removed, and the mixture was stirred and allowed to warm to 25 °C during 4 h. After the reaction mixture had been partitioned between Et_2O and an aqueous solution of NH_4Cl and NH_4OH, the ethereal layer was dried and concentrated. The crude liquid product contained (TLC, silica gel with an EtOAc–hexane eluent, 1:19 v/v) the product ketone **11** (R_f 0.46) but none of the starting enone **2** (R_f 0.25). After the mixture had been chromatographed on silica gel with an EtOAc–pentane eluent (1:19 v/v), the appropriate fractions were combined and distilled (80 °C at 0.2 mm) to separate 316 mg (67%) of the methyl ketone **11** as a colorless liquid: n^{25}_D 1.4941; IR (CCl_4) 1710 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 0.9–2.8 (m, aliphatic CH including a CH_3 singlet at 0.92); mass spectrum, m/e (relative intensity), 180 (M^+, 17), 109 (100), 81 (32), 67 (23), 55 (35), 41 (30); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 210.1 (s), 55.5 (t), 47.2 (t), 38.1 (s), 37.3 (t), 34.9 (q), 33.6 (t), 31.8 (t), 30.9 (t and d, 2 C atoms), 24.8 (t), 22.8 ppm (t).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.23; H, 11.40.

Preparation of the Cyano Ketone 18. A mixture of 1.872 g (8.62 mmol) of the bromo ketone **17**, 472 mg (9.6 mmol) of NaCN, and 25 mL of DMF was heated to 80 °C with stirring for 48 h and then diluted with 10 mL of MeOH. The resulting solution was stirred for an additional 1.5 h, acidified with aqueous 0.1 M HCl, and warmed to 45 °C for 10 min. The resulting solution was cooled and extracted with CH_2Cl_2. After the organic extract had been washed with aqueous NaCl, it was dried and concentrated. Chromatography of the residual solid on silica gel with an EtOAc–CH_2Cl_2 eluent (1:1 v/v) separated 1.257 g (89%) of the crude cyano ketone **18**, mp 148–150 °C (lit.[17] mp 149–151

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(15) We are indebted to our colleague, Professor Raymond F. Borkman, for making the fluorescence and phosphorescence measurements described.

(16) Borkman, R. F.; Kearns, D. R. *J. Chem. Phys.* **1967**, *46*, 2333.

°C). This product was repeatedly crystallized from a CH_2Cl_2–hexane mixture to separate the pure cyano ketone **18** as colorless needles: mp 157–158 °C; IR (CCl_4) 2250 (C≡N), 1721 cm^{-1} (C=O); ^1H NMR (CCl_4), δ 2.66 (2 H, s, CH_2CO), 1.2–2.5 (11 H, m, aliphatic CH); UV max (95% EtOH) 282 nm (ϵ 19); mass spectrum, *m/e* (relative intensity) 163 (M^+, 52), 148 (31), 120 (80), 108 (30), 95 (53), 94 (30), 93 (51), 92 (38), 81 (89), 80 (31), 79 (34), 68 (42), 67 (49), 66 (32), 56 (42), 55 (72), 54 (32), 53 (41), 42 (35), 41 (100), 39 (91); ^{13}C NMR ($CDCl_3$, multiplicity on off-resonance decoupling) 205.9 (s), 123.0 (s), 48.2 (t), 45.6 (t), 35.6 (t), 35.4 (t), 33.3 (s), 30.0 (t), 29.1 (d), 17.5 ppm (t).

Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.53; H, 8.04; N, 8.56.

Preparation of the Keto Diester 19. A mixture of 17.35 g (131 mmol) of dimethyl malonate, 2.179 g (10.0 mmol) of the bromo ketone **17**, and 3.1 mL (22.3 mmol) of Et_3N was stirred at 25 °C for 28 h and then partitioned between CH_2Cl_2 and aqueous NaCl. The organic layer was dried, concentrated, and distilled to separate 2.151 g (80%) of the crude keto malonate **19**, bp 145–148 °C (0.15 mm), that crystallized on standing; mp 54.5–55.5 °C. A 1.616-g sample of the material was chromatographed on silica gel with an EtOAc–hexane eluent (1:4 v/v), and fractions containing the product were combined and distilled in a short-path still (150 °C and 0.2 mm) to separate 987 mg of the keto diester **19**. The product **19** crystallized on standing as colorless plates: mp 56.5–57.5 °C; IR (CCl_4) 1760, 1738 (ester C=O), 1709 cm^{-1} (C=O); UV max (95% EtOH) 275 nm (ϵ 19); ^1H NMR (CCl_4) δ 3.69 (6 H, s, OCH_3), 3.19 (1 H, br, $CH(CO_2R)_2$), 1.2–3.0 (13 H, m, aliphatic CH); mass spectrum, *m/e* (relative intensity) 268 (M^+, 22), 236 (42), 193 (20), 165 (55), 137 (100), 136 (26), 132 (22), 109 (20), 95 (55), 93 (52), 92 (29), 79 (26), 67 (37), 55 (28), 41 (33); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 210.4 (s), 167.2 (s), 166.8 (s), 61.1 (d), 52.0 (q, 2 C atoms), 48.2 (t), 46.0 (t), 38.9 (s), 35.7 (t, 2 C atoms), 31.0 (t), 29.9 (d), 18.6 ppm (t).

Anal. Calcd for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51. Found: C, 62.64; H, 7.54.

Preparation of the 2,4-Dinitrophenylhydrazone 28. A solution of 407 mg (2.06 mmol) of 2,4-dinitrophenylhydrazine in 2.0 mL of concentrated H_2SO_4 was diluted with 10 mL of EtOH and 3.6 mL of H_2O. This solution was added to a solution of 343 mg (2.04 mmol) of the methoxy ketone **10a** in 13 mL of EtOH. The mixture, from which a precipitate began to separate after 15 min, was stirred at 25 °C for 3 h and filtered. The crude derivative **28**, an orange solid melting at 168–172 °C, amounted to 640 mg (90%). Recrystallization from EtOH afforded the pure derivative **28** as orange needles: mp 170.5–173 °C; IR (CCl_4) 3320 cm^{-1} (NH); UV max (95% EtOH) 228 nm (ϵ 17000), 260 (sh, 11700), 360 (25000); ^1H NMR ($CDCl_3$) δ 11.2 (1 H, br, NH), 9.14 (1 H, d, J = 2.5 Hz, aryl CH), 8.37 (1 H, dd, J = 2.5, 8.5 Hz, aryl CH), 7.97 (1 H, d, J = 8.5 Hz, aryl CH), 3.30 (3 H, s, OCH_3), 1.4–3.0 (13 H, aliphatic CH); mass spectrum, *m/e* (relative intensity) 348 (M^+, 5), 166 (12), 111 (100), 79 (15), 41 (15).

Anal. Calcd for $C_{16}H_{20}N_4O_5$: C, 55.16; H, 5.79; N, 16.08. Found: C, 55.16; H, 5.80; N, 16.06.

Preparation of the Peroxide 23 and the Hydroperoxide 21. A solution of 2.14 g (9.85 mmol) of the bromo ketone **17** in 30 mL of THF was treated with a mixture of 0.5 mL (5 mmol) of aqueous 30% H_2O_2 and 8 mL (24 mmol) of aqueous 3 M NaOH. After the resulting mixture had been stirred at 25 °C for 4 h, it was extracted with a PhH–Et_2O mixture (5:12 v/v). This extract was filtered through a column of alumina (activity II) and then concentrated. The residual solid was chromatographed on silica gel with an EtOAc–hexane eluent (2:3 v/v) to separate 474 mg (31%) of early fractions containing the crude peroxide **23**, mp 136–138 °C, and 496 mg (32%) of later fractions containing the crude ketol **22**, mp 228–231 °C. Recrystallization from a CH_2Cl_2–hexane mixture separated 404 mg of the pure peroxide **23** as colorless plates: mp 141–142 °C; IR (CCl_4) 1710 cm^{-1} (C=O); UV max (95% EtOH) 280 nm (ϵ 45); ^1H NMR ($CDCl_3$) δ 1.0–3.0 (m, aliphatic CH); mass spectrum, *m/e* (relative intensity) 306 (M^+, 1.3), 137 (83), 109 (23), 95 (100), 93 (60), 67 (34), 55 (44), 43 (24), 41 (41); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 209.3 (s, 2 C atoms), 80.5 (s, 2 C atoms), 51.0 (t, 2 C atoms), 45.8 (t, 2 C atoms), 36.6 (t, 2 C atoms), 35.4 (t, 2 C atoms), 31.1 (t, 2 C atoms), 30.2 (d, 2 C atoms), 19.5 ppm (t, 2 C atoms).

Anal. Calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found: C, 70.52; H, 8.42.

In a similar experiment where excess H_2O_2 was used, a solution of 2.17 g (10.0 mmol) of the bromo ketone **17** in 30 mL of THF was treated successively with 5.0 mL (50 mmol) of aqueous 30% H_2O_2 and with 5.2 mL (20.8 mmol) of aqueous 4 M NaOH. The resulting two-phase mixture was stirred vigorously for 5 h and then partitioned between Et_2O and aqueous NaCl. The ethereal layer was dried, filtered through a column of alumina (neutral, activity grade III), and then concentrated under reduced pressure. The residue pale yellow liquid contained (TLC, silica gel coating with an EtOAc–hexane eluent, 1:2 v/v) the ketol **22** (R_f 0.08), the hydroperoxide **21** (R_f 0.20), and a minor unidentified component (R_f 0.35). Chromatography on silica gel with an EtOAc–hexane eluent (3:7 v/v) separated later fractions containing 223 mg (14%) of the ketol **22**, mp 229–231 °C, that was identified with an authentic sample by comparison of IR and mass spectra. The early fractions contained 44 mg of an unidentified component, and intermediate fractions contained 946 mg of the crude hydroperoxide **21**, mp 137–141 °C. Recrystallization afforded 863 mg (51%) of the pure hydroperoxide **21** as colorless plates: mp 148–150 °C; IR (CCl_4) 3550 (OH), 1711 cm^{-1} (C=O); UV max (95% EtOH) 274 nm (ϵ 20); ^1H NMR ($CDCl_3$) δ 8.93 (1 H, s, OH), 1.3–3.0 (13 H, m, aliphatic CH); mass spectrum, *m/e* (relative intensity) 154 (3), 111 (20), 97 (68), 43 (25), 41 (18), 32 (100); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 211.7 (s), 81.9 (s), 50.0 (t), 45.7 (t), 35.7 (t), 34.8 (t), 30.9 (t), 30.0 (d), 19.5 ppm (t).

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.57; H, 8.33.

Registry No. **1**, 1123-09-7; **2**, 73274-32-5; **3**, 70562-48-0; **4**, 71370-30-4; **5**, 1728-25-2; **6** (isomer 1), 73274-33-6; **6** (isomer 2), 73274-34-7; **8**, 73274-35-8; **9**, 70562-51-5; **10a**, 66921-79-7; **10b**, 70576-36-2; **11**, 73274-36-9; **12**, 73274-37-0; **13**, 73274-38-1; **14**, 73274-39-2; **15**, 73274-40-5; **16**, 73274-41-6; **17**, 66077-98-3; **18**, 70013-67-1; **19**, 73274-42-7; **21**, 73274-43-8; **22**, 20498-02-6; **23**, 73274-44-9; **24**, 73274-45-0; **25**, 73274-46-1; **26**, 73274-47-2; **27**, 73274-48-3; **28**, 73274-49-4; piperidine, 110-89-4; 2-bromocyclooctanone ethylene ketal, 73274-50-7; 2-cyclooctenone ethylene ketal, 1728-26-3; 3-methoxycyclooctanone, 6925-18-4; $LiCuMe_2$, 15681-48-8; ethyl acetoacetate, 141-97-9; dimethyl malonate, 108-59-8.

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