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Enones with Strained Double Bonds. 6. Cycloadditions with the Bicyclo[5.3.1]undecane and Bicyclo[4.3.1]decane Systems[1]

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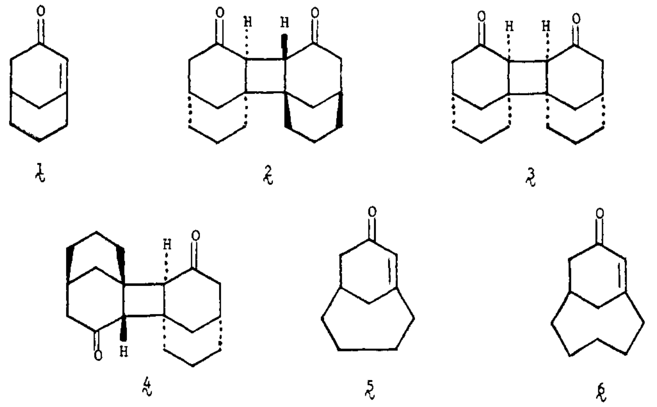
Bicyclo[4.3.1]dec-6-en-8-one (**5**) formed a Diels–Alder adduct **7** with butadiene under conditions where the next higher homologue, bicyclo[5.3.1]undec-7-en-9-one (**6**), failed to react. Both enones **5** and **6** formed dimeric cyclobutane cycloadducts (**9**–**11** from **5** and **14** from **6**) when irradiated with ultraviolet light. The structure of each dimeric product was established by X-ray crystallography.

Earlier study[2] had demonstrated that the bicyclo[3.3.1] enone **1** (Chart I) underwent very rapid Michael addition in the presence of nucleophiles and rapid [2 + 4] cycloaddition (Diels–Alder reaction) in the presence of dienes. In the absence of nucleophiles or dienes, the enone **1** reacted rapidly with itself in a thermal reaction to form the [2 + 2] cycloadducts **2**–**4**. The less strained bicyclic enone **5** also added most nucleophiles in a Michael fashion while the enone **6** underwent conjugate addition only with special reactants (e.g., HOO^-, Me_2CuLi). Neither enone **5** or **6** showed any tendency to undergo a thermal reaction with itself; samples of the unchanged enone **5** were recovered after being heated to 190 °C for 48 h.

In this paper we have explored other possible cycloaddition reactions with the enones **5** and **6**. Neither enone **5** or **6** formed a cycloadduct with refluxing furan (bp 31 °C), indicating that these enones are significantly less reactive dienophiles than the bicyclo[3.3.1] enone **1**. Although the bicyclo[5.3.1] enone **6** failed to form an adduct after being heated to 100 °C with butadiene for 24 h, under the same conditions the more reactive enone **5** was converted to the Diels–Alder adduct **7** (Chart II).

Chart I



When a pentane solution of the enone **6** was irradiated with ultraviolet light by employing a Pyrex glass filter (λ > 290 nm),[3] the three major products isolated were the unconjugated enone **8** (20% yield) and the [2 + 2] cycloadducts **9** (42% yield) and **10** (26% yield). In addition, a small amount of the cycloadduct **11** from enones **6** and **8** was isolated. The structures of each of the cycloadducts were established by X-ray crystallography (see Figures 1–3).

After this work had been completed, another study of the photochemical behavior of the enone **6** in benzene solution was published.[4] this report describes the isolation of enone **8** and cycloadducts **9** and **10** as well as enone **12** (from photoisomerization of **8**) and two cycloadducts considered to be stereoisomers of structure **13**. The structures and stereochemistry assigned cycloadducts **9** and **10** by use of spectral data and chemical transformation correspond to the structures we have determined by X-ray crystallography.

The irradiation of a pentane solution of the enone **5** with ultraviolet light employing a Pyrex glass filter produced

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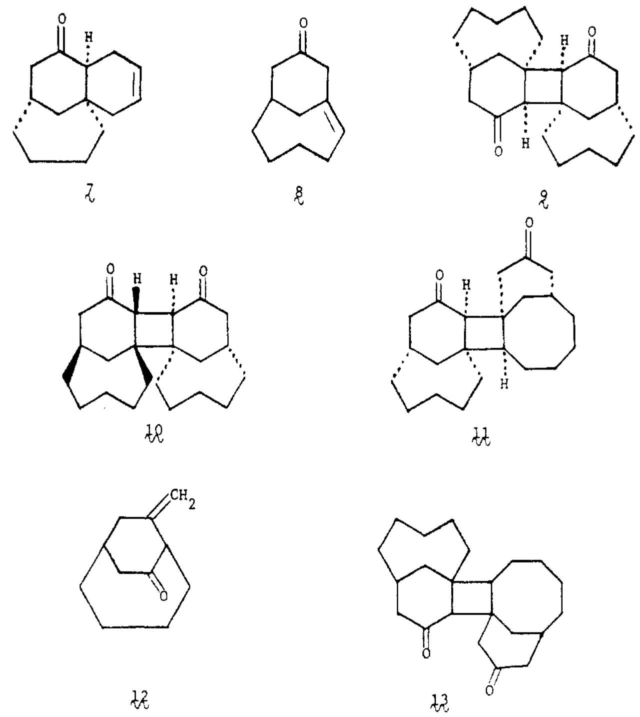
(2) (a) House, H. O.; Lee, T. V. *J. Org. Chem.* **1979**, *44*, 2819. (b) House, H. O.; DeTar, M. B.; VanDerveer, D. *Ibid.* **1979**, *44*, 3793. (c) House, H. O.; Sieloff, R. F.; Lee, T. V.; DeTar, M. B. *Ibid.* **1980**, *45*, 1800.

(3) Irradiations performed in quartz apparatus with a Hanovia medium-pressure Hg lamp led to complex mixtures of reaction products.

(4) Gioia, B.; Ballabio, M.; Beccalli, E. M.; Cecchi, R.; Marchesini, A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 560.

0022-3263/81/1946-4639$01.25/0

Chart II



7 8 9 10 11 12 13

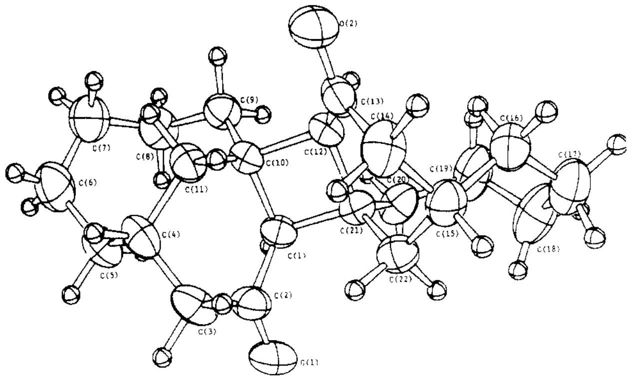


Figure 1. Perspective view of the molecular structure of the dimer **9** from bicyclo[5.3.1]undec-7-en-9-one.

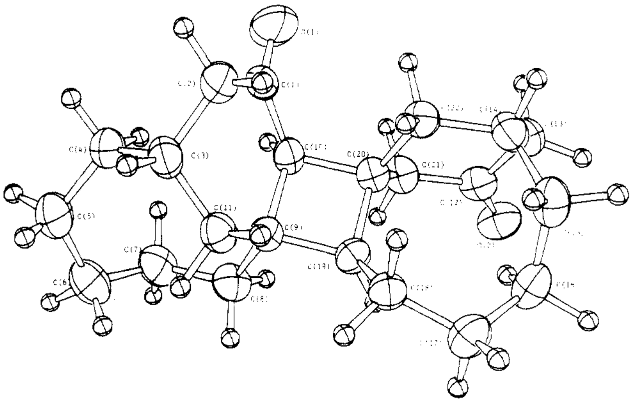


Figure 2. Perspective view of the molecular structure of the dimer **11** from bicyclo[5.3.1]undec-7-en-9-one.

a mixture of a major [2 + 2] cycloadduct **14** (ca. 75% of the mixture) and a minor product thought to be a diastereoisomer of **14** (Chart III). When solutions or samples of this mixture were heated, the minor product was converted to adduct **14**, thwarting our efforts to obtain a pure sample of the minor product. Support for the structure of the cycloadduct **14** was obtained from various spectroscopic measurements (see Experimental Section). The stucture **14** was confirmed by formation of a tosylhydrazone derivative **15**, whose structure was determined by X-ray crystallography (see Figure 4).

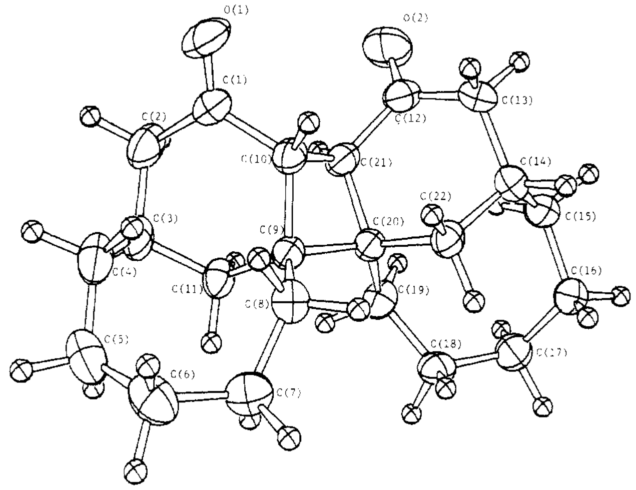


Figure 3. Perspective view of the molecular structure of the dimer **10** from bicyclo[5.3.1]undec-7-en-9-one.

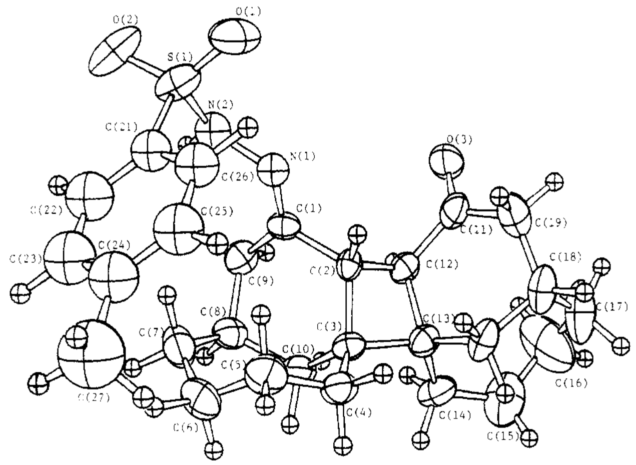
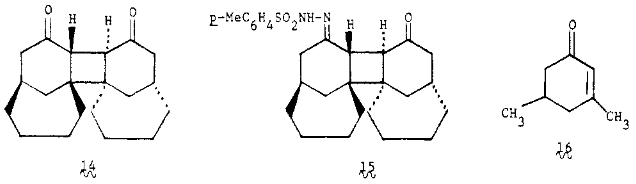


Figure 4. Perspective view of the molecular structure of the dimer tosylhydrazone **15** derived from bicyclo[4.3.1]dec-6-en-8-one.

Chart III



14 15 16

It is clear from these studies that [2 + 2] cycloadducts from enone **5** and **6** are stable isolable compounds. Consequently, the failure to form these [2 + 2] cycloadducts from eneones **5** and **6** in thermal reactions is not attributable to product instability but rather to a marked difference in reactivity between the bicyclo[3.3.1] enone **1** and the less strained enones **5** and **6**.

We also explored the possibility that the polarities of the bicyclic enones **5** and **6** might differ from the polarity of the monocyclic analogue **16** by measuring the dipole moments of the three enones. However, within experimental error the dipole moments of the three enones were all the same value, 3.76 D. Consequently, these dipole moment measurements are a less sensitive measure of molecular distortion than were the reduction potential and UV measurements described earlier.[2c]

Experimental Section[5]

Photochemical Reactions of the Enone 6. A solution of 501 mg (3.06 mmol) of the enone **6** in 30 mL of pentane was purged with a stream of N_2 to remove oxygen and then placed in Pyrex tubes and irradiated for 14 h with the light from a Hanovia 450-W medium-pressure Hg lamp fitted with a Pyrex filter. The resulting solution contained (TLC, silica gel coating with an EtOAc–hexane eluant, 1:9 v/v) the unconjugated enone **8** (R_f 0.40), the dimer **9** (R_f 0.26), and the dimer **10** (R_f 0.18). The material was chromatographed on silica gel with an EtOAc–hexane eluant (1:9 v/v) to separate 116 mg of the crude enone **8**, 215 mg of the crude dimer **9** (mp 125–130 °C), and 138 mg of the crude dimer **10** (mp 154–160 °C).

The dimer **9** was recrystallized from Et_2O to separate 212 mg (42%) of the product as colorless plates: mp 132–134 °C (lit.[4] mp 140 °C); IR (CCl_4) 1690 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.9–3.1 (m, aliphatic CH); mass spectrum, *m/e* (relative intensity), 328 (M^+, 0.8), 166 (20), 165 (90), 164 (100), 122 (31), 121 (69), 108 (26), 95 (27), 82 (52), 79 (20), 41 (32); ^{13}C NMR ($CDCl_3$, multiplicity on off-resonance decoupling) 212.0 (s), 63.0 (d), 48.5 (t), 47.9 (t), 41.0 (s), 33.0 (d), 30.7 (t), 30.5 (t), 26.9 (t), 23.6 (t), and 21.1 ppm (t).

Anal. Calcd for $C_{22}H_{32}O_2$: C, 80.44; H, 9.83. Found: C, 80.46; H, 9.86.

The chromatographic fraction containing the unconjugated enone **8** was distilled [100–103 °C (0.2 mm)] to separate 102 mg (20%) of the enone **8** [n^{25}_D 1.5199 (lit.[2c] n^{25}_D 1.5215)], identified with previously described material[2c] by comparison of IR and NMR spectra. The crude dimer **10** was recrystallized from EtOAc to separate 132 mg (26%) of the material (mp 172–173 °C) that contained mainly the dimer **10** accompanied by two colorless crystals (ca. 0.04 mg) of the dimer **11** that were separated mechanically. This minor dimer **11** [mp 173–174 °C; IR ($CHCl_3$) 1700 cm^{-1} (C=O)] was subjected to X-ray crsytallographic analysis. The remaining material was recrystallized from EtOAc to separate the pure dimer **10** as colorless prisms: mp 172–173 °C (lit.[4] mp 182–183 °C); ^{13}C NMR ($CDCl_3$, multiplicity on off-resonance decoupling) 209.3 (s), 53.4 (d), 47.9 (s), 44.6 (t), 35.3 (d), 33.7 (t), 31.4 (t), 30.6 (t), 27.4 (t), 25.0 (t), 23.3 ppm (t); mass spectrum, *m/e* (relative intensity) 165 (88), 164 (100), 122 (27), 121 (98), 108 (30), 95 (29), 82 (65), 79 (21), 67 (22), 55 (21), 41 (38). When the mass spectrum was repeated with excitation by chemical ionization, the following major peaks were observed: *m/e* (relative intensity), 329 (22, M + 1), 165 (100), 85 (33), 83 (25), 81 (34), 79 (33), 71 (56), 70 (25), 69 (69), 67 (57).

Anal. Calcd for $C_{22}H_{32}O_2$: C, 80.44; H, 9.83. Found: C, 80.37; H, 9.84.

Reactions of the Enones 5 and 6 with Dienes. A solution of 224 mg of the enone **6** in 5 mL of furan was refluxed for 24 h under an N_2 atmosphere. The solution was concentrated and then subjected to liquid chromatography to separate 222 mg (99% recovery) of the starting enone. A cold solution of 20 mL of 1,3-butadiene and 0.25 g (1.52 mmol) of the enone **6** in 10 mL of PhH was sealed in a tube and then heated to 100 °C for 24 h. The resulting mixture was cooled and then concentrated and diluted with pentane. The pentane solution was filtered to remove polymeric material and then concentrated. The residue amounted to 0.20 g (80%) of the starting enone **6** that was identified with an authentic sample by comparison of IR and NMR spectra. Similarly, a solution of 1.00 g (6.09 mmol) of the enone **6** and 0.73 mL (9.1 mmol) of freshly distilled cyclopentadiene in 20 mL of PhH was stirred at 25 °C for 72 h and then concentrated. Chromatography on silica gel with an EtOAc–pentane eluant separated 135 mg (13%) of the enone **8** and 847 mg (85%) of the starting enone **6**.

A solution of 0.34 g of the enone **5** in 10 mL of furan was refluxed for 24 h, concentrated, and distilled. The distillate (0.32 g) contained largely the starting enone **5** (IR and NMR analysis).

A cold solution of 278.6 mg (1.85 mmol) of the enone **5** and 120.6 mg of 2,6-di-*tert*-butylphenol (an inhibitor) in 40 mL of 1,3-butadiene was sealed in a tube and then heated to 100 °C for 46 h. The crude product contained (TLC on silica gel with an EtOAc–hexane eluant, 1:19 v/v) 2,6-di-*tert*-butylphenol (R_f 0.57) and the adduct **7** (R_f 0.20). Chromatography of the crude material on silica gel with an EtOAc–hexane eluant separated the adduct **7**.

The adduct was rechromatographed on alumina and then distilled in a short-path still [bp 80–82 °C (2 mm)] to provide 148 mg (39%) of a pure sample of the adduct **7**: IR (CCl_4) 1710 (C=O), 1653 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 5.4–5.9 (2 H, m, vinyl CH), 0.9–3.0 (18 H, m, aliphatic CH); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 212.0 (s), 125.8 (d), 124.2 (d), 53.6 (d), 47.7 (t), 42.2 (t), 40.8 (t), 40.5 (s), 34.2 (d), 33.3 (t), 32.2 (t), 25.2 (t), 23.8 (t), 21.6 ppm (t); mass spectrum, *m/e* (relative intensity) 204 (M^+, 13), 148 (11), 147 (100), 95 (11), 93 (10), 91 (22), 79 (16), 77 (12), 67 (12), 41 (20).

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.26; H, 9.90.

Photodimerization of the Enone 5. A solution of 745 mg (4.97 mmol) of the enone **5** in 15 mL of pentane was purged with a stream of N_2 for 10 min and then irradiated for 12 h with the light from a Hanovia 450-W medium-pressure Hg lamp fitted with a Pyrex filter. During irradiation the photoproducts separated as a white solid. Rapid recrystallization of the solid from a PhH–hexane mixture separated 745 mg (100%) of white solid (mp 211–212) °C dec) that exhibited only one spot (R_f 0.17) on TLC analysis (silica gel with an EtOAc–hexane eluant, 1:9 v/v).

Anal. Calcd for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39. Found: C, 79.76; H, 9.40.

The ^{13}C NMR spectrum of this sample exhibited two sets of 10 lines, the more intense set (ca. 75% of the mixture) corresponding to the dimer **14** ($CDCl_3$, multiplicity in off-resonance decoupling): 209.3 (s), 54.6 (d), 48.5 (s), 45.1 (t), 35.3 (t), 34.2 (t), 33.4 (d), 30.5 (t), 26.9 (t), 23.6 ppm (t). The minor component in this mixture (ca. 25% of the mixture), also believed to be a dimer with an element of symmetry, exhibited the following 10 lines: 206.4, 57.5, 53.0, 47.3, 38.2, 36.7, 33.3, 29.7, 25.7, 25.1 ppm. In a second experiment a cold (5 °C) solution of 1.021 g of the enone **5** in 10 mL of pentane was irradiated at 5 °C for 16 h. The crystalline product that separated (1.11 g, contains some solvent) was dissolved in $CDCl_3$ for ^{13}C NMR analysis and found to contain about 69% of the dimer **14** and about 31% of the second component. When a sample of this mixture of dimers was sublimed [210 °C (0.5 mm)], recrystallized from boiling cyclohexane, or recrystallized from boiling decane, the recovered product melted in the range 221–223 °C dec to 225–226 °C dec and contained (^{13}C NMR analyses) only 0–4% of the minor product. Thus recrystallization of 231 mg of the mixture of photoproducts from cyclohexane afforded 227 mg (98% recovery) of the pure dimer **14** as colorless needles, mp 224.5–226 °C dec. The sepctral properties of the pure dimer **14** follow: IR ($CHCl_3$) 1700 cm^{-1} (C=O); ^{13}C NMR, listed previously; mass spectrum, *m/e* (relative intensity), 300 (M^+, 13), 151 (100), 150 (78), 122 (85), 95 (39), 91 (37), 82 (59), 79 (40), 67 (41), 55 (30), 41 (77), 39 (39).

Anal. Calcd for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39. Found: C, 79.90; H, 9.40.

The ^1H NMR spectrum of the dimer **14**, measured at 300 MHz in $CDCl_3$ solution, exhibited the following peaks: δ 2.93 (s, 2 H, CHCO), 2.75 (2 H, dd, $J = 6, 15$ Hz, 1 H of CH_2CO), 2.62 (2 H, partially resolved m, bridgehead CH), 2.33 (2 H, dd, $J = 4, 15$ Hz), 2.16 (2 H, dm, $J = 15$ Hz, remaining coupling not resolved, 1 H of CH_2CO), 1.3–2.0 (16 H, m, aliphatic CH), 1.0–1.2 (2 H, m, aliphatic CH). When the sample was measured in a mixture of C_6D_6 and $CDCl_3$ (3:1 v/v), the low-field ^1H NMR peaks observed in $CDCl_3$ underwent the following shifts: δ $2.93 \rightarrow 2.76$, $2.75 \rightarrow 2.48$, $2.62 \rightarrow 2.24$, $2.33 \rightarrow 2.01$, $2.16 \rightarrow 1.98$. To explore the possibility that this dimer may be centrosymmetric, the IR and Raman spectra of $CHCl_3$ solutions of the dimer **14** were compared

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(5) 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 grating. The UV spectra were determined with a Cary Model 14 or a Perkin-Elmer Model 202 recording spectrophotometer. The ^1H NMR spectra were determined at 60 MHz with a Varian Model T-60A NMR spectrometer or at 300 MHz with a Bruker Model WM-300 NMR spectrometer. The ^{13}C NMR spectra were determined at 25 MHz with a JEOL Model PFT-100 NMR spectrometer or at 75 MHz with a Bruker Model WM-300 NMR spectrometer. The chemical shift values are expressed in δ values relative to a Me_4Si as an internal standard. The mass spectra were obtained with either an Hitachi Perkin-Elmer Model RMU-7 or a Varian MAT Model 112S mass spectrometer.

Table I. Crystallographic Information

structure	dimer 9	dimer 11	dimer 10	tosylhydrazone 15
cryst size, mm	0.6 × 0.3 × 0.1	0.9 × 0.2 × 0.1	0.8 × 0.3 × 0.3	0.8 × 0.3 × 0.1
cryst system	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/C$ (No. 14)	$P2_1/C$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/C$ (No. 14)
unit cell parameters a, Å	10.836 (8)	12.526 (6)	13.49 (1)	11.008 (5)
b, Å	21.18 (2)	12.195 (4)	11.200 (8)	20.082 (6)
c, Å	8.078 (6)	14.485 (8)	9.111 (7)	11.296 (4)
α, deg			94.33 (6)	
β, deg	97.69 (5)	125.00 (3)	110.14 (6)	100.26 (3)
γ, deg			129.41 (5)	
V, Å^3	1837 (2)	1812 (1)	913 (1)	2457 (1)
rflctn array, deg	13.53-20.42	15.57-23.98	14.08-26.96	10.72-16.28
density, g cm^{-3}				
calcd	1.192 (4 mole/unit cell)	1.202 (4 mole/unit cell)	1.14 (2 mole/unit cell)	1.265 (4 mole/unit cell)
measd	1.190	1.205	1.14	1.267
total rflctns collected	3238 (quadrant)	3210 (quadrant)	3238 (hemisphere)	4358 (quadrant)
rflctns accepted	2396	2060	2538	1911
std rflctns	700, 080, 004	600, 006, 020	013, 400, 040	104, 150, 061
parameters varied	235	235	235	272
statistic factors A	2.04	2.2	1.0	3.06
B	0.002	0.0004	0.0712	0.00009
final R	0.0612	0.0711	0.0770	0.0855
final R_w	0.0698	0.0626	0.0930	0.0665
atomic coordinates and thermal parameters[a]	Table III	Table IV	Table VII	Table X
bond angles and distances[a]	Table II	Table V	Table VIII	Table XI
calcd and obsd structure factors[b]	Table XIII	Table VI	Table IX	Table XII

[a] Available as supplementary material. [b] Available from the authors.

in the region 800–1900 cm^{-1}.[6] In the following lists of IR and Raman bands, coincident bands (within ±5 cm^{-1}) are disignated with an asterisk: Raman 831, 920,* 981, 1057, 1128,* 1139 (w),* 1151 (w),* 1309 (w), 1418,* 1450,* 1499, 1622 (w), 1636 (w), 1656 (w), 1670, 1700,* 1770, 1806 (w), 1825 (w) cm^{-1}; IR 840, 922 (w),* 945, 965, 1037, 1052, 1065, 1102, 1126 (w),* 1140 (w),* 1156,* 1179, 1217, 1238, 1245, 1257, 1322, 1337, 1350, 1365, 1413,* 1450,* 1459, 1469, 1700,* 1786 cm^{-1}.

Preparation of the Tosylhydrazone 15. A solution of 143 mg (0.47 mmol) of the dimer **14** and 88.7 mg (0.48 mmol) of $TsNHNH_2$ in 35 mL of EtOH was refluxed for 5 min and then concentrated under reduced pressure. The residual solid was chromatographed on silica gel with an EtOAc–hexane eluant (1:4 v/v) to separate 39.5 mg of early fractions containing the dimer **14**. The later fractions (a mixture of $TsNHNH_2$ and the hydrazone **15**) were subjected to preparative TLC on a plate coated with silica gel and eluted with EtOAc–hexane (2:3 v/v) to separate 96.3 mg (88%) of the crude product **15**. Repeated chromatography and subsequent recrystallization from a PhH–hexane mixture separated 86.1 mg (78%) of the tosylhydrazone **15** as a colorless prisms: mp 117–118 °C dec; IR ($CHCl_3$) 1695 cm^{-1} (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.88 (1 H, s, NH), 7.93 (2 H, d, J = 8 Hz, aryl CH), 7.30 (2 H, d, J = 8 Hz, aryl CH), 3.24 (1 H, d, J = 10 Hz, CH—C=N), 2.7–2.85 (1 H, m, aliphatic CH), 2.64 (1 H, d, J = 10 Hz, CH—C=O), 1.0–2.6 (28 H, m, aliphatic CH including a CH_3 singlet at 2.40); mass spectrum (electron impact), m/e (relative intensity), 151 (62), 134 (64), 107 (23), 105 (27), 93 (27), 92 (82), 91 (100), 81 (26), 79 (32), 77 (21), 67 (27), 65 (33), 55 (28), 43 (48), 41 (45), and 39 (22); mol wt + 1 calcd for $C_{27}H_{36}N_2O_3S$ 469.2525, found 469.2533 (mass spectrum with chemical ionization).

Dipole Moment Measurements. Previously described[2c] samples of the enones **5** (n^{25}_D 1.5272), **6** (n^{25}_D 1.5278), and **16** (n^{25}_D 1.4795) were employed as solutions in anhydrous CCl_4. the measurements on the CCl_4 solutions were performed at 38.5 °C with a WTM dipolmeter, Model DM-01. The dipole moment values are as follows: **5**, 3.76 ± 0.02 D; **6**, 3.76 ± 0.02 D; **16**, 3.76 ± 0.01 D.

Crystal Structure Determinations. (A) Data Collection. A crystal was mounted on a glass fiber with epoxy cement such that the longest crystal dimension was approximately parallel to the fiber axis. Unit cell parameters and the orientation matrix were determined on a Syntex $P2_1$ four-circle diffractometer equipped with a graphite monochromator (Bragg 2θ angle 12.2°) and using Mo Kα radiation at a takeoff angle of 6.75%. Fifteen reflections with 2θ values in the range given in Table I were machine-centered and used in least-squares refinement of the lattice parameters and orientation matrix. Unit cell parameters are given in Table I.[7] The experimental density was measured by the flotation method using either a mixture of pentane and CCl_4 or a mixture of $ZnCl_2$ and H_2O. ω scans of several low 2θ angle reflections gave peak widths at half-height of less than 0.24°, indicating a satisfactory mosaic spread for the crystal. Axial photographs identified the crystal system. Intensity data for zero and upper levels were collected at a rapid scan rate and the intensities examined carefully for systematic absences to determine the space group.[8]

Intensity data were collected by using θ-2θ scans with X-ray source and monochromator settings identical with those used for determination of the unit cell parameters. A variable scan rate of from 2.02 to 29.3° was used, and a scan width of 2° was sufficient to collect all of the peak intensity. Stationary background counts were measured at the beginning (bgd1) and at the end (bgd2) of each scan with a total background to scan time ratio (TR) of 1.0. No significant fluctuations were observed in the intensities of three standard reflections monitored every 97 reflections. Intensities were calculated from the total scan count (CT) and background counts by the relationship in eq 1. The

$$I = \mathrm{CT} - \mathrm{TR}(\mathrm{bgd1} + \mathrm{bgd2}) \qquad (1)$$

intensities were assigned standard deviations according to eq 2,

$$\sigma(I) = [\mathrm{CT} + \mathrm{TR}^2(\mathrm{bgd1} + \mathrm{bgd2})]^{1/2} \qquad (2)$$

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[6] For an earlier example of use of this technique, see: Ziffer, H.; Levin, I. W. *J. Org. Chem.* **1969**, *34*, 4056. The Raman spectrum was determined with a Spex monochromator, Model 1401, employing a CR-5 argon laser as a light source. We are grateful to Professor Ronald H. Felton and Mr. Lee Barrow for measuring this spectrum.

[7] Numbers in parantheses here and elsewhere in this paper indicate estimated standard deviations in the least significant digit(s).

[8] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1952; Vol I.

and reflections collected out to $2\theta = 50°$ were accepted as statistically above background on the basis that F was greater than $3\sigma(F)$. Lorentz and polarization corrections were made in the usual way.

(B) Solution and Refinement of the Structure. Computations were performed by using standard programs;[9] all computations were carried out on the CDC Cyber 74 system. For structure factor calculations the scattering factors were taken from Cromer and Mann's tabulation.[10] The agreement factors are defined in the usual way as in eq 3 and 4. In all least-squares

$$R = (\sum||F_o| - |F_c||)/(\sum|F_o|) \quad (3)$$

$$R_w = \sum(|F_o| - |F_c|)w^{0.5}/\sum(|F_o|)w^{0.5} \quad (4)$$

refinements, the quantity minimized was $\sum\omega(|F_o| - |F_c|)^2$. A weighting scheme based on counting statistics ($w = A/[\sigma(F)^2 + BF^2]$; see Table I for factors A and B) was employed for calculating R_w and in least-squares refinement.

The structures were solved by using the automatic centrosymmetric direct methods program of SHELX-76. Parameters varied included a scale factor, coordinates of all atoms except hydrogen, anisotropic thermal parameters for all atoms except H atoms and the C atoms and N atoms of the tosylhydrazone unit in structure **15**, and isotropic thermal parameters for all other atoms. The H atom coordinates were determined by using the routine in SHELX-76 that fixes the C–H distances at 1.08 Å and orients the H atom positions to complete the appropriate coordination about each C atom. The full-matrix least-squares refinement converged to give the R and R_w values listed in Table I. The final atomic coordinates, thermal parameters, bond distances, and bond angles are available as supplementary material. The lists of calculated and observed structure factors are available from the authors.

Registry No. 5, 70562-48-0; **6**, 73274-32-5; **7**, 79135-43-6; **8**, 73274-35-8; **9**, 77188-60-4; **10**, 77188-51-3; **11**, 79199-40-9; **14**, 79135-44-7; **15**, 79135-45-8; 1,3-butadiene, 106-99-0.

Supplementary Material Available: Tables of atomic coordinates and thermal parameters (Tables III, IV, VII, and X) and tables of bond distances and bond angles (Tables II, V, VIII, and XI) (14 pages). Tables VI, IX, XII, and XIII are available from the authors. Ordering information is given on any current masthead page.

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(9) Programs utilized were Sheldrick's SHELX-76 program and Johnson's ORTEP program.

(10) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 72–98.

Selectivity in β-Enamino Ketone Anion Generation and Alkylation

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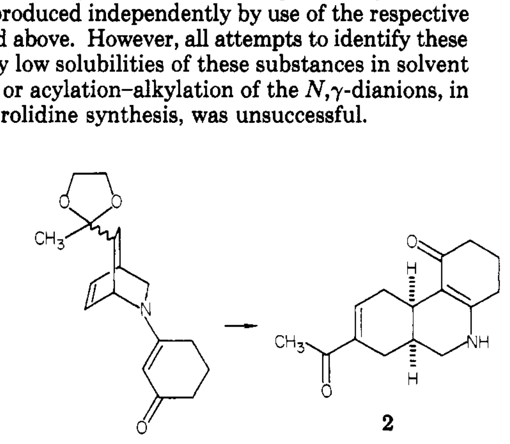
The regioselectivity of anion generation from β-alkoxy- and β-(dialkylamino)-α,β-unsaturated ketones was probed by use of ^{13}C NMR spectroscopy and alkylation techniques. Results indicate that the kinetic anions of these systems can be formed selectively from the parent ketones by using excess lithium diisopropylamide as the base at −78 °C and diethyl ether or tetrahydrofuran as the solvent. The kinetic anion in these systems is the one resulting from deprotonation at the α′-carbon. Alkylation occurs at this center in synthetically useful yields. Equilibration to produce the thermodynamically more stable extended γ-enolate anion occurs when less than 1 equiv of lithium diisopropylamide is present and at elevated temperatures (>−20 °C). The rate of equilibration is sensitive to the solvent employed, occurring much more rapidly in tetrahydrofuran than in diethyl ether. A synthetically more practical method for formation and alkylation of the thermodynamic anions of β-(dialkylamino)-α,β-unsaturated ketones utilizes excess lithium bis(trimethylsilyl)amide as the base in tetrahydrofuran as the solvent at −78 °C followed by quenching with the alkylating agent. Methods for regioselective generation of dianions from β-(alkylamino)-α,β-unsaturated ketones have been explored. Analysis of products produced by methylation suggest that the *N*,α′- and *N*,γ-dianions can be produced independently by use of the respective kinetic and thermodynamic anion-producing conditions described above. However, all attempts to identify these dianions by spectroscopic methods failed due to the exceedingly low solubilities of these substances in solvent systems compatible with the technique. Likewise, dialkylation or acylation–alkylation of the *N*,γ-dianions, in attempts to develop one-step procedures for fused-bicyclic pyrrolidine synthesis, was unsuccessful.

Earlier studies in our laboratory have uncovered an interesting method for the preparation of functionalized hydroisoquinolines and hydrophenanthridines which employs amino-Claisen and related rearrangements of N-vinylisoquinuclidenes in key structural elaboration steps.[2] The utility of this route is exemplified by the six-step sequence for generation of the 1-oxo-decahydrophenanthridine **2** from pyridine via the isoquinuclidine **1**. This methodology appears to be applicable to the synthesis of a variety of naturally occurring materials containing cis-fused hydroisoquinoline and hydrophenanthridine ring systems. One of the targets of our initial efforts to explore



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