($M^+$, 100), 258 (24), 214 (39), 213 (87), 187 (38), 174 (24), 173 (22), 115 (23).

Anal. Calcd for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.52; H, 6.04.

**Conversion of Lactone 44 to Methoxy Ketone 48.** A solution of 404 mg (3.2 mmol) of dimethyl methylphosphonate in 10 mL of THF was added, dropwise and with stirring during 10 min, to a cold (-78 °C) solution of 2.4 mmol of *n*-BuLi in 1.7 mL of hexane. After the resulting suspension 11 had been stirred at -78 °C for 15 min, a solution of 282 mg (0.93 mmol) of the lactone **44** in 60 mL of THF was added, dropwise and with stirring during 45 min. The resulting cold suspension was warmed to 0 °C, and the resultant colorless solution was partitioned between $CHCl_3$ and aqueous HCl. After the organic phase had been washed with aqueous NaCl, it was dried and concentrated to leave a yellow semisolid containing (IR and NMR analysis) a mixture of the starting lactone **44** and the phosphonate **45**. Consequently, a solution of the crude product in 10 mL of DME was added a second time to a cold (-78 °C) slurry of 2.4 mmol of $LiCH_2P(O)(OCH_3)_2$ in 1.7 mL of hexane and 10 mL of DME. After the resulting mixture had been warmed to 0 °C during 3 h, it was subjected to the previously described isolation procedure to separate a pale yellow semisolid. The crude product was chromatographed on silica gel to separate 45 mg of the starting lactone **44** in early fractions eluted with $Et_2O$. Subsequent fractions, eluted with EtOAc, contained 315 mg of the crude phosphonate **45** as a colorless solid. Recrystallization of the phosphonate **45** from a chloroform-hexane mixture afforded 257 mg (68%) of the phosphonate **45** as colorless prisms: mp 177.5-178 °C; IR ($CHCl_3$) 3400 (OH), 1710 $cm^{-1}$ (C=O); $^1H$ NMR ($CDCl_3$) $\delta$ 6.7-7.4 (3 H, m, aryl CH), 3.7-4.7 (13 H, m, ketal $CH_2O$ and $CH_3O$), 1.0-3.6 (10 H, aliphatic CH); mass spectrum, *m/e* (rel intensity) 409 (1), 275 (45), 258 (33), 257 (56), 214 (22), 213 (100), 195 (30), 151 (85), 124 (25), 109 (35), 85 (24), 83 (39), 43 (31), 41 (20). This product was oxidized without further purification or characterization.

A cold (0-5 °C) solution of 240 mg (0.56 mmol) of the crude phosphonate **45** in 75 mL of acetone was treated with 0.20 mL of aqueous 8 N $H_2CrO_4$ (Jones reagent). After the resulting cold solution had been stirred for 15 min, it was partitioned between $H_2O$ and $CHCl_3$. The organic layer was washed with aqueous NaCl, dried, and concentrated to leave 263 mg of viscous yellow liquid. This crude product was chromatographed on silica gel with an EtOAc-$CHCl_3$ eluent to separate 208 mg of the phosphonate **46** as a yellow liquid: IR ($CHCl_3$) 1710 $cm^{-1}$ (C=O); mass spectrum, *m/e* (rel intensity) 424 ($M^+$, 10), 362 (39), 273 (44), 229 (32), 151 (100), 124 (34), 109 (43), 43 (29).

Anal. Calcd for $C_{20}H_{25}O_8P$: $M_r$, 424.1280. Found: $M_r$, 424.1235.

A mixture of 166 mg (0.39 mmol) of the phosphonate **46**, 90 mg (0.85 mmol) of $Na_2CO_3$, and 5 mL of MeOH was stirred at 25 °C. TLC analysis (silica gel coating with an $Et_2O$ eluent) indicated that both the starting phosphonate **46** ($R_f$ 0.04) and the methoxy ketone product **48** ($R_f$ 0.54) were present after 18 h. Therefore this mixture was refluxed for 2 h and then concentrated under reduced pressure. The residual solid was extracted with $CHCl_3$, and the $CHCl_3$ extract was concentrated to leave 159 mg of amber liquid. This material, which solidified on standing, was chromatographed on silica gel with an $Et_2O$ eluent to separate 126 mg of the crude methoxy ketone **48** as a yellow solid. Recrystallization from a $CHCl_3$-$Et_2O$-hexane mixture separated 101 mg (78%) of the methoxy ketone **48** as colorless needles: mp 129-130 °C; IR ($CCl_4$) 1745 $cm^{-1}$ (cyclopentanone C=O); $^1H$ NMR ($CCl_4$) $\delta$ 6.6-7.1 (3 H, m, aryl CH), 3.85-4.3 (4 H, m, ketal $CH_2O$), 3.77 (3 H, s, $ArOCH_3$), 2.5-3.7 (4 H, m, aliphatic CH including a $CH_3O$ singlet at 3.15), 2.3-2.4 (2 H, br, $CH_2CO$), 0.8-2.3 (6 H, m, aliphatic CH); mass spectrum, *m/e* (rel intensity) 330 ($M^+$, 17), 105 (91), 91 (31), 77 (37), 41 (100), 40 (31); UV max (95% EtOH), 219 nm ($\epsilon$ 7660), 290 (2400).

Anal. Calcd for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71; $M_r$, 330.1461. Found: C, 69.05; H, 6.73; $M_r$, 330.1473 (mass spectrum).

**Registry No.** **1**, 73274-32-5; **2**, 70562-48-0; **3**, 71370-30-4; **4**, 84211-62-1; **5**, 85319-15-9; **6**, 497-38-1; **8**, 5724-61-8; **9a**, 37435-80-6; **9b**, 85354-06-9; **10a**, 85319-16-0; **10b**, 85319-17-1; **12**, 85319-18-2; **13**, 85319-19-3; **14**, 85319-20-6; **15**, 85319-21-7; **17**, 75359-72-7; **18a**, 6493-80-7; **18b**, 16646-42-7; **19**, 85319-22-8; **20**, 64326-18-7; **21**, 85319-23-9; **22** (isomer 1), 85319-24-0; **22** (isomer 2), 85319-25-1; **23a**, 85319-26-2; **23b**, 85319-27-3; **24**, 85319-28-4; **25**, 85319-29-5; **26a**, 85319-30-8; **26b**, 85319-31-9; **27** (isomer 1), 85319-32-0; **27** (isomer 2), 85319-33-1; **28**, 85319-34-2; **31a**, 85319-35-3; **31a** 2,4-DNP, 85319-36-4; **31b**, 85404-35-9; **32**, 85319-37-5; **33**, 85319-38-6; **34**, 85319-39-7; **36**, 85319-40-0; **37**, 62015-84-3; **38**, 62015-87-6; **40**, 62015-88-7; **41**, 62015-92-3; **42**, 85319-41-1; **43**, 85319-42-2; **44**, 85319-43-3; **45**, 85319-44-4; **46**, 85319-45-5; **48**, 85319-46-6; **49**, 85319-47-7; **50**, 85319-48-8; CH=CHCH=$CH_2$, 106-99-0; methyl methacrylate, 80-62-6; 3,5-dimethyl-2-cyclohexen-1-one, 1123-09-7.

**Supplementary Material Available:** Descriptions of determination of crystal structures for the adduct **31a** and the cyclobutane **32**, including tables of atomic coordinates for each compound (8 pages). Ordering information is given on any current masthead page.

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# Enones with Strained Double Bonds. 9. The 2-Phenylbicyclo[3.3.1]non-1-en-3-one System[1]

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*Received September 14, 1982*

Reaction of the bromo ketone **2** with $Et_3N$ formed the phenyl-substituted bicyclo[3.3.1]nonenone **1c** that was stable when protected from oxygen, water, or other nucleophiles. The enone **1c** added MeOH to form the methoxy ketone **4** and reacted slowly with $Et_3N$ at 100 °C to form the reduced ketone **3**. The enone **1c** reacted slowly with butadiene at 100 °C to form a mixture of the cycloadducts **13**, **15**, and **16**. Reaction of the enone **1c** with oxygen formed a solid mixture of peroxides (presumably **9** and **11**). These peroxides reacted with $Et_3N$ to form the diol **5** and underwent thermal rearrangement at 50 °C to form the triketone **6**. The reactions with $O_2$ and with butadiene suggest that the enone **1c** tends to react as a diradical species.

Our previous study[2] of bicyclo[3.3.1]nonenone bridgehead enones **1** indicated that the ready reaction of the parent enone **1a** with itself to form 2 + 2 cycloadducts could be markedly retarded by placing a substituent at the

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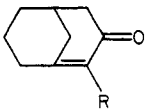


1a, R = H; b, R = $CH_3$;
c, R = $C_6H_5$; d, R = $C(CH_3)_3$

$\alpha$-position of the enone. Estimates of the probable geometries and inherent strain energies for a series of enones **1** were obtained by use of Allinger's MMP1 molecular mechanics program for conjugated systems.[3] Perspective drawings of the probable geometries of chair and twist-boat conformers for the parent enone **1a**, the $\alpha$-methyl enone **1b**, and the $\alpha$-phenyl enone **1c** are presented in Figures 1–3. Estimates of the strain in the C–C double bonds of the enones **1** were obtained by the method of Ermer[4,5] by employing values for twisting distortion and pyramidal distortion obtained from the MMP1 calculations. These values of angular deformation, C=C strain, and inherent strain for the enones **1** are summarized in Table I. It will be noted that the estimated angular deformations and strain energies are comparable for the entire series of enones **1**.

Although the $\alpha$-methyl enone **1b** was resistant to dimerization by 2 + 2 cycloaddition, an alternative side reaction, the ene reaction, rapidly converted the enone **1b** to a dimeric diketone and prevented isolation of the enone **1b**.[2b] Accordingly, we turned our attention to enones with $\alpha$ substituents that possessed no $\alpha$-H atoms such as the phenyl enone **1c** and the *tert*-butyl enone **1d**. Our study of the synthesis of precursors for the enones **1c** and **1d** is described elsewhere.[6] While a suitable precursor for the *tert*-butyl enone **1d** has not yet been obtained, the bromo ketone **2** (Scheme I) could be prepared as a potential precursor for the phenyl enone **1c**.

Reaction of the bromo ketone **2** with $Et_3N$ formed a colorless precipitate ($Et_3NH^+Br^-$) and a yellow solution. Upon addition of MeOH, the yellow color of the solution was discharged and the methoxy ketone **4** was produced. This yellow solution failed to form 2 + 2 or 2 + 4 adducts of the enone **1c** when stirred with furan or heated to 100 °C with vinyl acetate. However, when the yellow solution in $Et_3N$ was heated to 100 °C for prolonged periods, the reduction product **3** was slowly formed in the reaction solution. When a stream of anhydrous $O_2$ was passed through the yellow solution formed from the bromo ketone **2** and $Et_3N$, the major product formed was the crystalline diol **5**. The structure of this product **5** was established by oxidative cleavage with $HIO_4$ to form the triketone **6** and by X-ray crystallographic analysis (see Figure 4). These observations suggested that the relatively stable solutions of the $\alpha$-phenyl enone **1c** in $Et_3N$ were being formed at 25 °C.

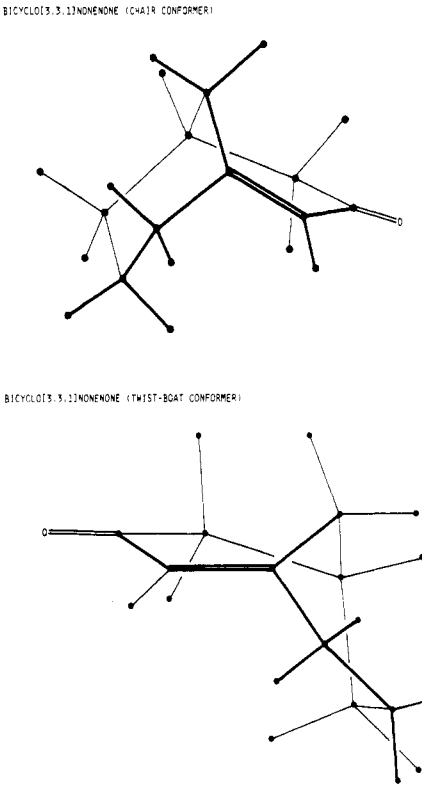



**Figure 1.** Perspective views of the twist-boat chair conformers of bicyclo[3.3.1]nonenone.

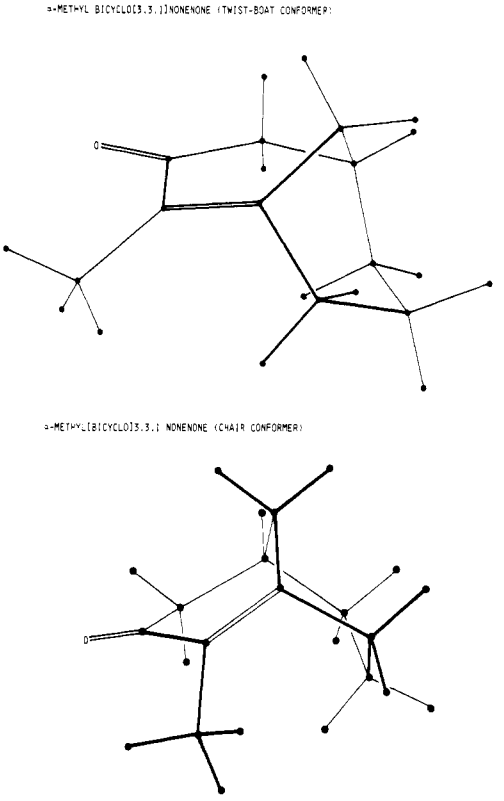



**Figure 2.** Perspective views of the twist-boat and chair conformers of $\alpha$-methylbicyclo[3.3.1]nonenone.

This suggestion has been confirmed by isolating the enone **1c**. A solution of the bromo ketone **2** in oxygen-free $Et_3N$ was stirred at 25 °C for 8 h and then filtered to separate the solid $Et_3NH^+Br^-$. Concentration of the filtrate left a pale yellow liquid with IR, $^1H$ NMR, $^{13}C$ NMR, and mass spectral properties consistent with those of the

(1) A portion of this research was supported by Public Health Service Grant R01-GM-30735 from the National Institute of General Medical Science. The execution of this research was also aided by Institutional Research Grants from the National Science Foundation for the purchase of a mass spectrometer and a NMR spectrometer.

(2) (a) House, H. O.; DeTar, M. B.; VanDerveer, D. *J. Org. Chem.* **1979**, *44*, 3793. (b) House, H. O.; DeTar, M. B.; Sieloff, R. F.; VanDerveer, D. *Ibid.* **1980**, *45*, 3545.

(3) For a review, see: Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1. We are indebted to Professor Allinger and his associates and to the University of Georgia Computer Center for allowing us to use the current versions of the MM2 and MMP1 programs for these calculations.

(4) Ermer, O. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *32B*, 837.

(5) For review and discussion of this and related computation procedures, see: (a) Shea, K. J. *Tetrahedron* **1980**, *36*, 1683. (b) Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1891.

(6) House, H. O.; Outcalt, R. J.; Cliffton, M. D. *J. Org. Chem.* **1982**, *47*, 2413.

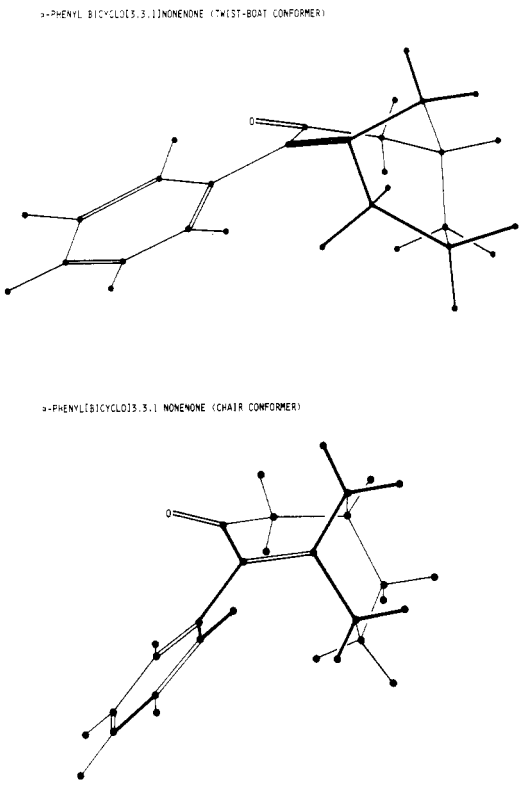
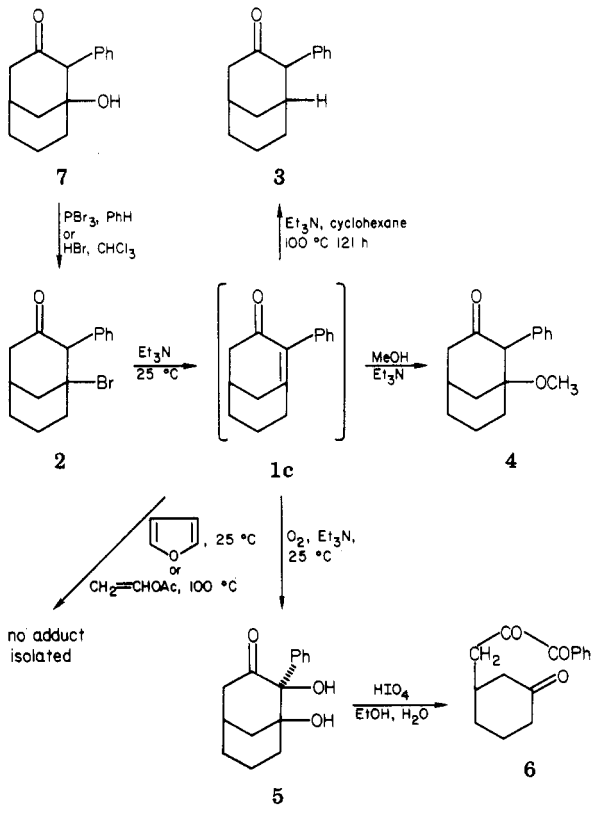



**Figure 3.** Perspective views of the twist-boat and chair conformers of α-phenylbicyclo[3.3.1]nonenone.

Scheme I




bridgehead enone structure **1c** (Scheme II). These spectral data compared favorably with the corresponding data for the model enone **8**. Reaction of the liquid enone **1c** with MeOH formed the methoxy ether **4**, and exposure of the enone **1c** to atmospheric moisture and oxygen resulted in the conversion of the enone **1c** to mixtures of the ketol **7** and the triketone **6**.

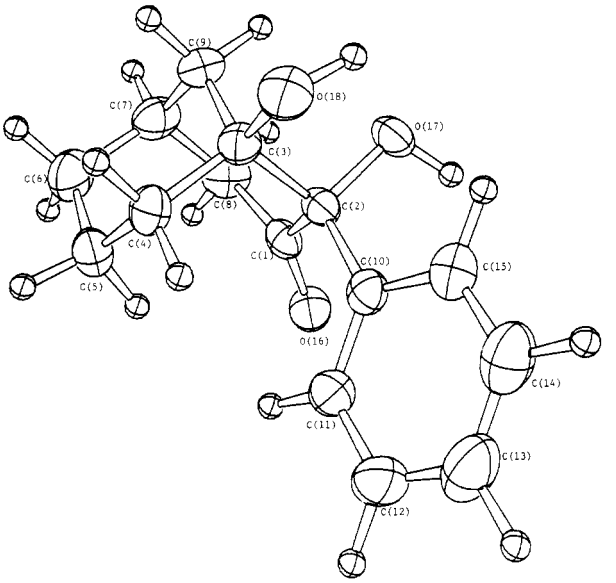



**Figure 4.** Perspective view of the molecular structure of the diol **5**.

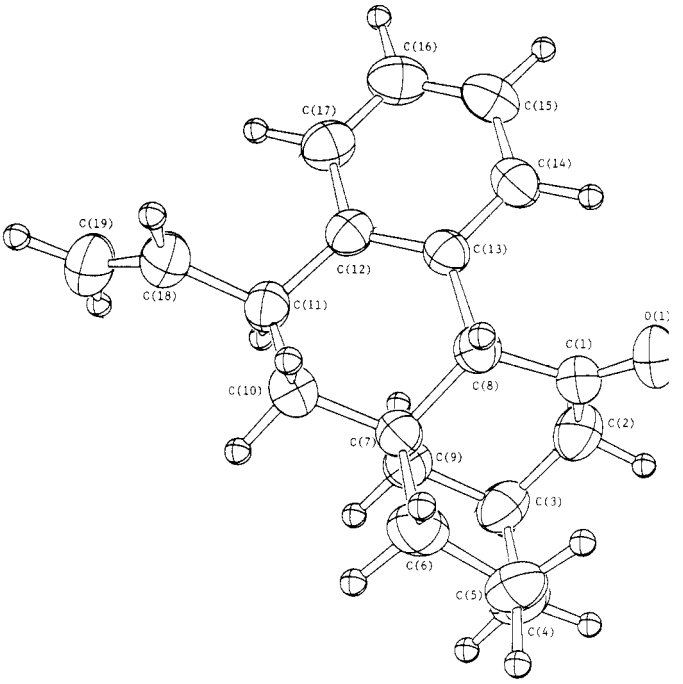
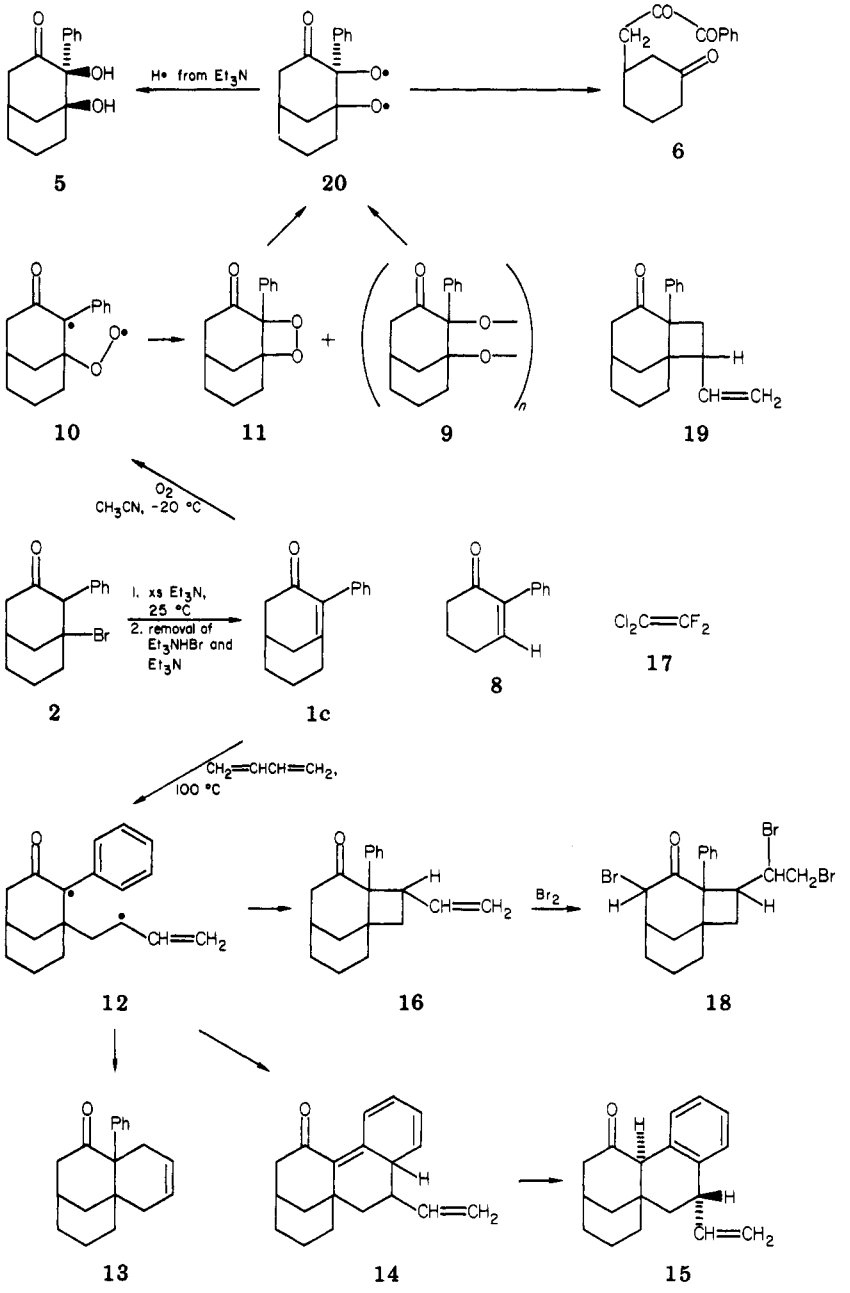



**Figure 5.** Perspective view of the molecular structure of the adduct **15**.

When the enone **1c** (either neat or as a solution in $Et_3N$) was heated to 100 °C with excess 1,3-butadiene for 20 h, a mixture of adducts **13**, **15**, **16** and other minor products was formed. The 2 + 4 cycloadduct **13** was identified by its composition and spectral properties. The corresponding information for adduct **15** accompanied by an X-ray crystal structure (see Figure 5) confirmed the structure of the cycloadduct **15**. This adduct **15** is presumably formed by rearrangement of an H atom in the initial product **14**. The spectral properties of the liquid 2 + 2 cycloadduct indicated that it was a mixture of two diastereoisomers of structure **16**. Since our efforts to separate the diastereoisomers of 2 + 2 cycloadduct **16** were unsuccessful, the mixture was treated with bromine to form a mixture of bromides from which the major product **18** was isolated by fractional recrystallization. The composition and spectral properties of this product provided strong support

Scheme II




for assignment of structure **18** to the tribromide and, consequently, structure **16** to the initial cycloadduct.

The reaction of the enone **1c** with butadiene to form both 2 + 2 and 2 + 4 cycloadducts bears a close resemblance to the reactions of butadiene with the halogenated olefin **17** and related olefins studied by Bartlett.[7] A comparable diradical intermediate **12** seems appropriate to account for the cycloadducts formed from enone **1c**. A related diradical intermediate has also been suggested by Becker[8] to account for the cycloadducts formed from several bridgehead olefins and either the halogenated olefin **17** or diphenyl ketene. Our data do not rigorously exclude the alternative regioisomer **19** as a possible structure for the 2 + 2 cycloadduct. However, the presumed mode of formation of the cycloadduct via a diradical intermediate argues strongly that the correct structure is cycloadduct **16** formed from the most stable diradical intermediate **12**.

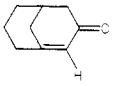
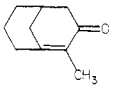
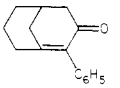
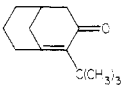
Reaction of a solution of the enone **1c** in $CH_3CN$ with $O_2$ at −20 °C resulted in the separation of a solid that could be washed with more $CH_3CN$ and collected as a pale tan solid, mp 75–80 °C dec. Solutions of this solid in $CHCl_3$ or $CDCl_3$ exhibited IR and $^{13}C$ NMR spectral data compatible with the presence of a mixture of cyclic peroxides **9** and dioxetane **11**.[9]

Heating the $CDCl_3$ solution to 50 °C resulted in complete conversion of these intermediates to the triketone **6**. The $^{13}C$ NMR spectrum of the crude dioxetane–peroxide mixture, measured at −20, at 0, and at 25 °C, exhibited 11 broad peaks attributable to a dioxetane–peroxide mixture accompanied by *sharp* NMR peaks attributable to the solvent $CDCl_3$ and an impurity, $CH_3CN$. Heating this mixture to temperatures above 35 °C is presumed to convert the mixture to a diradical **20** (cf. ref

(7) For a review, see: Bartlett, P. D. *Q. rev., Chem. Soc.* **1970**, *24*, 473.
(8) (a) Becker, K. B.; Hohermuth, M. K. *Helv. Chim. Acta* **1982**, *65*, 229. (b) Becker, K. B.; Hohermuth, M. K.; Rihs, G. *Ibid.* **1982**, *65*, 235.

(9) For reviews of the formation and reaction of 1,2-dioxetanes, see: (a) Adam, W. *Adv. Heterocycl. Chem.* **1977**, *21*, 437. (b) Bartlett, P. D.; Landis, M. E. In "Singlet Oxygen"; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; pp 243–286.

Table I. Calculated C=C Deformation and Strain for the Bridgehead Enones

| compound (conformation) | | average twisting deformation, deg | pyramidal deformations, deg | C=C deformation, kcal/mol | inherent strain, kcal/mol |
|---|---|---|---|---|---|
|  | twist boat | 21 | 19 and 37 | 11.3 | 21.3 |
| | chair | 25 | 25 and 42 | 16.5 | 20.8 |
|  | twist boat | 22 | 18 and 34 | 11.3 | 20.7 |
| | chair | 27 | 23 and 40 | 16.1 | 20.3 |
|  | twist boat | 21 | 13 and 38 | 11.0 | 27.4 |
| | chair | 27 | 17 and 44 | 16.9 | 25.6 |
|  | twist boat | 22 | 13 and 32 | 9.6 | 31.0 |
| | chair | 29 | 17 and 34 | 14.7 | 28.6 |

9) that serves as an intermediate for the formation of the diol **5** or the triketone **6**.

Thus, all of the reactions of the enone **1c** that we have observed appear to be either conjugate additions of nucleophiles (which conceivably could involve an anion radical intermediate) or reactions in which the enone **1c** behaves as a diradical (see Scheme II). The latter reactions can be formulated as processes involving initial thermal conversion of the strained enone **1c** to a triplet diradical that reacts rapidly with butadiene, oxygen, or $Et_3N$ to form products **13**, **15**, **16**, **9**, **11**, or **3**. However, we presently have no experimental evidence demonstrating the thermal conversion of the enone **1c** to a diradical. For example, no line broadening has been observed in the $^{13}C$ NMR spectrum of the enone **1c** measured either at 35 or at 65 °C. Further evidence is being sought concerning the possibility that these strained enones can be converted thermally to diradical intermediates.

## Experimental Section[10]

**Preparation of Methoxy Ketone 4.** A stream of gaseous $N_2$ was passed through a mixture of 10 mL of MeOH and 15 mL of $Et_3N$ for 15 min, and then the mixture was refluxed for 15 min to remove any $O_2$ present. The MeOH–$Et_3N$ mixture was cooled to 18 °C and 464 mg (1.58 mmol) of the bromo ketone **2** was added. After the resulting solution had been stirred at 18–20 °C for 4 h, it was partitioned between $H_2O$ and $CH_2Cl_2$. The organic layer was washed with aqueous $NaHCO_3$, dried, and concentrated to leave 449 mg of pale yellow liquid. Chromatography on silica gel with an ethyl acetate–hexane eluent (2:3, v/v) separated 329 mg (85%) of the crude methyl ether **4**. Distillation in a short-path still (130–150 °C and 0.05 mm) separated 295 mg (76%) of the methyl ether **4** as a colorless liquid: IR ($CCl_4$) 1710 $cm^{-1}$ (C=O); $^1H$ NMR ($CDCl_3$) $\delta$ 7.0–7.6 (5 H, m, aryl CH), 3.78 (1 H, s, benzylic CH), 3.17 (3 H, s, $OCH_3$), 0.8–2.7 (11 H, aliphatic CH); $^{13}C$ NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 208.2 (s), 133.8 (s), 130.5 (d, 2 C atoms), 127.2 (d, 2 C atoms), 126.5 (d), 77.5 (s), 64.4 (d), 48.7 (q), 46.1 (t), 38.1 (t), 32.3 (t), 31.2 (t), 30.0 (d), 20.1 ppm (t); mass spectrum, $m/e$ (rel intensity) 244 ($M^+$, 3), 115 (3), 112 (8), 111 (100), 91 (5), 90 (4), 77 (3), 45 (3), 41 (4), 39 (3).

Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25; $M_r$, 244.1464. Found: C, 78.68; H, 8.25; $M_r$, 244.1462.

**Preparation of Diol 5.** After a 25-mL portion of $Et_3N$ had been saturated with $O_2$, 616 mg (2.10 mmol) of bromo ketone **2** was added. The heterogeneous mixture was stirred at 18–25 °C for 40 min while a stream of anhydrous gaseous $O_2$ was passed through the mixture. During this period, the solid bromo ketone **2** dissolved slowly and a second colorless precipitate ($Et_3NH^+Br^-$) separated. After the flow of oxygen was stopped, the reaction mixture was stirred for an additional hour and then filtered. The filtrate was concentrated under reduced pressure and then partitioned between $CH_2Cl_2$ and aqueous $NaHCO_3$. The organic layer was dried and concentrated, and the residual yellow liquid was chromatographed on silica gel with an ethyl acetate–hexane eluent (2:3, v/v). After the separation of several minor, unidentified, rapidly eluted components, the later fractions contained 334 mg (65%) of the crude diol **5**, mp 110–138 °C dec. Recrystallization from PhH separated 214 mg (41%) of the pure diol **5** as colorless needles: mp 134.5–146.5 °C dec; IR ($CCl_4$) 3580, 3420 (OH), 1715 $cm^{-1}$ (C=O); $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 7.2–7.4 (5 H, m, aryl CH), 3.27 (1 H, s exchange with $D_2O$, OH), 3.08 (1 H, d of d, $J$ = 6.6, 16.9 Hz), 2.54 (1 H, d of m, $J$ = 12.5 Hz), 2.44 (1 H, m), 2.36 (1 H, d of m, $J$ = 16.9 Hz), 2.02 (1 H, s, exchange with $D_2O$, OH), 1.3–1.8 (7 H, m, aliphatic CH); $^{13}C$ NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 207.2 (s), 135.4 (s), 127.9 (d, 2 C atoms), 127.2 (d), 126.7 (d, 2 C atoms), 82.5 (s), 74.1 (s), 42.4 (t), 36.6 (t), 34.9 (t), 30.7 (t), 29.3 (d), 19.8 ppm (t); mass spectrum, $m/e$ (rel intensity) 246 ($M^+$, 14), 151 (28), 150 (100), 105 (26), 97 (91), 77 (27), 43 (30).

Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37. Found: C, 73.17; H, 7.38.

As a control experiment to show that the diol **5** was not formed by oxidation of the ketol **7**, a mixture of 5 mL of $Et_3N$ and 59 mg (0.26 mmol) of the ketol **7** was stirred at 18 °C for 3.5 h while a stream of $O_2$ was passed through the mixture. The mixture was dissolved in $CH_2Cl_2$ and then concentrated under reduced pressure to leave 52 mg (88%) of the crude ketol; mp 136–150 °C. The crude product was chromatographed on silica gel with an ethyl acetate–hexane eluent to separate 42 mg (71%) of the ketol **7**, mp 151.5–154.5 °C. Recrystallization afforded the pure ketol **7**, mp 153.5–156 °C, that was identified with an authentic sample[6]

(10) 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 299 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 $\delta$ values (ppm) 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 organometalic intermediates were performed under a nitrogen atmosphere.

by a mixture-melting-point determination and by comparison of IR, $^1H$ NMR, and mass spectral data.

**Formation of Triketone 6.** A mixture of 15 mL of furan and 5 mL of $Et_3N$ was deoxygenated by passing gaseous $N_2$ through the mixture for 15 min and then refluxing the mixture for 10 min. The mixture was cooled to 25 °C, 304 mg (1.04 mmol) of the bromo ketone **2** was added, and the mixture stirred at 25 °C under an $N_2$ atmosphere for 19 h. During this period a colorless precipitate ($Et_3NH^+Br^-$) separated, and the reaction solution became yellow in color. The mixture was partitioned between $CH_2Cl_2$ and aqueous $NaHCO_3$, and the organic layer was washed successively with aqueous $NH_4Cl$ and with aqueous NaCl. After the solution had been dried and concentrated under reduced pressure, the residual yellow liquid (265 mg) was chromatographed on silica gel with an ethyl acetate–hexane eluent (1:3, v/v) to separate, in order of elution, 17 mg of an unidentified amorphous solid, 17 mg of the bromo ketone **2**, and 82 mg (32%) of the crude triketone **6** as a yellow liquid. This later material was rechromatographed to separate 63 mg (25%) of the triketone **6** as a yellow liquid that solidified on standing. Recrystallization from $Et_2O$ at low temperatures afforded 39 mg (15%) of the pure triketone **6** as yellow prisms: mp 71.5–72.5 °C; IR ($CCl_4$) 1715 (C=O), 1675 $cm^{-1}$ (conjugated C=O); $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 7.99 (2 H, d of m, $J$ = 7.5 Hz, aryl CH), 7.66 (1 H, t of m, $J$ = 7.5 Hz, aryl CH), 7.51 (2 H, t of m, $J$ = 7.7 H z, aryl CH), 2.98 (1 H, d of d, $J$ = 6.8, 17.6 Hz, aliphatic CH), 2.85 (1 H, d of d, $J$ = 6.3, 17.6 Hz, aliphatic CH), 2.55–2.0 (7 H, m, aliphatic CH), 1.68–1.78 (1 H, m, aliphatic CH), 1.41–1.51 (1 H, m, aliphatic CH); $^{13}C$ NMR ($CDCl_3$, multiplicity on off-resonance decoupling) 209.3 (s), 200.3 (s), 190.7 (s), 134.2 (d), 131.2 (s), 129.7 (d, 2 C atoms), 128.4 (d, 2 C atoms), 47.4 (t), 44.6 (t), 41.0 (t), 33.8 (d), 31.0 (t), 24.8 ppm (t); mass spectrum, $m/e$ (rel intensity) 244 ($M^+$, 0.6), 105 (100), 77 (24), 41 (11).

Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.60; H, 6.84.

**Conversion of Diol 5 to Triketone 6.** A solution of 89 mg (0.36 mmol) of the diol **5** in 5 mL of EtOH was added to a solution of 79 mg (0.37 mmol) of $NaIO_4$ in 2 mL of $H_2O$. The resulting colorless solution was stirred at 25 °C for 5 min and then acidified to pH 1 with $H_2SO_4$. After the resulting solution had been warmed to 45 °C for 2 h with development of a yellow color, the reaction mixture was partitioned between $Et_2O$ and aqueous $NaHCO_3$. After the organic layer had been washed with aqueous NaCl, dried, and concentrated, the residual yellow liquid (69 mg) was chromatographed in silica gel with an ethyl acetate–hexane eluent to separate 21 mg (24%) of the triketone **6** as a yellow liquid that was identified with a previously described sample by comparison of IR and NMR spectral data and TLC $R_f$ values.

**Treatment of Bromo Ketone 2 with $Et_3N$ and Vinyl Acetate.** A mixture of 10 mL of $Et_3N$ and 16 mL of $CH_2$=CHOAc was deoxygenated by passing a slow stream of $N_2$ through the mixture for 20 min. This solution was mixed with 1.03 g (3.50 mmol) of the bromo ketone **2** and heated to 100 °C in a sealed tube for 22 h. During this heating the initially colorless solution deposited a colorless precipitate and the supernatant liquid became yellow. The resulting mixture was partitioned between $CH_2Cl_2$ and $H_2O$, and the organic layer was dried and concentrated. The residual orange liquid (949 mg of a complex mixture, TLC analysis) was chromatographed on silica gel. Certain of the earlier fractions contained 67 mg (9%) of the ketone **3** as a colorless solid, mp 92–110 °C. Recrystallization from a hexane–cyclohexane mixture separated 22 mg of the ketone **3** as colorless prisms, mp 112–117 °C. Further recrystallization raised the melting point to 120–122 °C: IR ($CCl_4$) 1716, 1707 (shoulder) $cm^{-1}$ (C=O); $^1H$ NMR ($CDCl_3$) $\delta$ 7.0–7.5 (5 H, m, aryl CH), 3.73 (1 H, d, $J$ = 5 Hz, benzylic CH), 1.0–2.8 (12 H, m, aliphatic CH); $^{13}C$ NMR ($CDCl_3$, multiplicity on off-resonance decoupling) 209.6 (s), 137.4 (s), 129.3 (d, 2 C atoms), 127.6 (d, 2 C atoms), 126.1 (d), 60.9 (d), 47.2 (t), 38.9 (d), 35.1 (t), 32.3 (t), 31.3 (d), 26.7 (t), 18.5 ppm (t); mass spectrum, $m/e$ (rel intensity) 214 ($M^+$, 60), 171 (23), 135 (22), 129 (26), 123 (21), 118 (32), 117 (38), 115 (35), 104 (100), 95 (57), 91 (61), 81 (23), 80 (33), 79 (26), 67 (20), 41 (30).

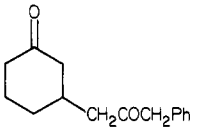
Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47; $M_r$, 214.1358. Found: C, 84.04; H, 8.50; $M_r$, 214.1390.

Certain of the later chromatographic fractions contained (NMR analysis) 80 mg (9%) of the triketone **6**.

**Reaction of Bromo Ketone 2 with $Et_3N$.** After 10 mL of $Et_3N$ had been deoxygenated with a slow stream of $N_2$ for 20 min, 544 mg (1.86 mmol) of the bromo ketone **2** was added, and the resulting mixture was stirred at 25 °C under an $N_2$ atmosphere for 8 h during which time a white precipitate separated and the supernatant liquid became a yellow-green color. The mixture was centrifuged, and the yellow-green supernatant liquid was concentrated under reduced pressure and then treated with 10 mL of deoxygenated MeOH. A 10-mL portion of deoxygenated MeOH was also added to the precipitate. Both solutions were concentrated, and the residual liquids were chromatographed on silica gel with an ethyl acetate–hexane eluent (1:3, v/v). Chromatography fractions from the supernatant liquid contained 306 mg (68%) of the methoxy ketone **4**, and fractions from the precipitate contained 54 mg (12%) of the methoxy ketone **4**. Each methoxy ketone sample **4** was identified with an authentic sample by comparison of IR and NMR spectra. In a second experiment, when the precipitate was washed with a fresh 10-mL portion of $Et_3N$ before MeOH treatment, none of the methoxy ketone **4** was detected (TLC) after treatment of the precipitate with MeOH.

In a related experiment, a solution of 760 mg (2.59 mmol) of the bromo ketone **2** in 7 mL of deoxygenated cyclohexane and 10 mL of deoxygenated $Et_3N$ was heated to 100 °C in a sealed tube for 121 h during which time a colorless precipitate separated and a yellow color formed in the supernatant liquid. After the reaction mixture had been partitioned between $CH_2Cl_2$ and $H_2O$, the organic layer was dried and concentrated. The residual yellow liquid (676 mg) was chromatographed on silica gel with an ethyl acetate–hexane eluent (1:3, v/v) to separate early fractions containing 130 mg (23%) of the previously described ketone **3** as a tan solid, mp 106–115 °C. Recrystallization from a hexane–cyclohexane mixture separated 69 mg of the ketone **3** as colorless prisms, mp 115–120.5 °C. An additional recrystallization from hexane raised the melting point to 120–122 °C.

Subsequent chromatographic fractions contained 73 mg of the crude triketone **6** as a yellow liquid identified by comparison of TLC $R_f$ values and NMR spectra. The final chromatographic fractions contained 115 mg of the crude diketone **21** as a yellow




**21**

liquid that was identified[6] by comparison of NMR spectra and TLC $R_f$ values. This diketone **21** was presumably formed from the ketol **7** during the isolation and chromatography procedures.

**Spectra of 2-Phenylcyclohex-2-enone (8).** An authentic sample of this enone **8** was available from previous work.[11] The spectral properties follow: UV max ($CH_3CN$) 217 nm ($\epsilon$ 10 900), 255 (5200), 328 (53); $^{13}C$ NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 197.4 (s), 147.4 (d), 140.2 (s), 136.5 (s), 128.4 (d, 2 C atoms), 127.8 (d, 2 C atoms), 127.3 (d), 38.9 (t), 26.4 (t), 22.7 ppm (t).

**Preparation and Spectra of Phenyl Enone 1c.** A solution of 350 mg (1.2 mmol) of the bromo ketone **2** and 10 mL of anhydrous $Et_3N$ (oxygen removed by passing a stream of $N_2$ through the sample) was stirred at 25 °C under an $N_2$ atmosphere for 8 h. The resulting suspension was centrifuged, and the supernatant liquid was siphoned into a new vessel and then concentrated under reduced pressure. The crude enone **1c** remained as a pale yellow-green liquid; IR ($CCl_4$) 1680 $cm^{-1}$ (conjugated C=O). When this $CCl_4$ solution was exposed to oxygen of the air, a second C=O peak began to appear at 1710 $cm^{-1}$ (saturated C=O). After the solution had been exposed to the air for 3 h, the 1680-$cm^{-1}$ peak had disappeared and only the 1710-$cm^{-1}$ peak remained. Other spectral properties were as follows: $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 7.0–7.4 (5 H, m, aryl CH), 1.0–2.9 (11 H, m, aliphatic CH); UV max ($CH_3CN$) 242 nm ($\epsilon$ ca. 4600), 350 (ca. 300); $^{13}C$ NMR ($CDCl_3$, multiplicity on off-resonance decoupling) 199.6 (s), 163.5 (s), 137.9

(11) House, H. O.; Huber, L. E.; Umen, M. J. *J. Am. Chem. Soc.* **1972**, *94*, 8471.

(s), 135.7 (s), 129.1 (d, 2 C atoms), 127.8 (d, 2 C atoms), 126.7 (d), 50.3 (t), 36.8 (t), 36.2 (t), 33.3 (d), 29.1 (t), 27.7 ppm (t); mass spectrum, $m/e$ (rel intensity) 212 ($M^+$, 100), 184 (45), 169 (20), 158 (33), 155 (24), 142 (22), 141 (32), 130 (34), 129 (29), 128 (35), 115 (53), 103 (22), 91 (26), 86 (86). When the $^{13}C$ NMR spectrum ($CDCl_3$) of the enone **1c** was repeated at 65 °C rather than at 35 °C, we observed no significant change in the position and line widths of the $^{13}C$ NMR peaks.

**Treatment of Bromo Ketone 2 with $Et_3N$ and Butadiene.** A cold (−78 °C) mixture of 15 mL of $Et_3N$ and 23 mL of liquid butadiene was deoxygenated by passing a slow stream of $N_2$ through the mixture for 15 min. Then this solution was mixed with a solution of 2.011 g (6.86 mmol) of bromo ketone **2** in 4 mL of PhH, and the mixture was sealed in a tube, allowed to stand at 25 °C for 2 h, and then heated to 100 °C for 20 h. After the initially colorless solution had stood at 25 °C for 2 h, a colorless precipitate had separated and the supernatant liquid was yellow. After a 2.5-h heating period the yellow color persisted; but the supernatant liquid had become colorless after the mixture had been heated for 14.5 h. The resulting reaction mixture was concentrated and partitioned between $CH_2Cl_2$ and $H_2O$. After the organic layer had been dried and concentrated, the residual yellow solid (2.084 g) was chromatographed on silica gel with an ethyl acetate–hexane eluent (1:9, v/v). This initial chromatography separated 858 mg (47%) of early fractions containing (NMR analysis and TLC on silica gel with an ethyl acetate–hexane eluent, 1:9, v/v) a mixture of the adduct **15** ($R_f$ 0.63), stereoisomeric adducts **16** ($R_f$ 0.50 and 0.56), and some of the isomeric adduct **13** ($R_f$ 0.40). Later chromatographic fractions contained 753 mg (41%) of the adduct **13** as a colorless solid, mp 132–137.5 °C. Recrystallization from a hexane–cyclohexane mixture afforded 473 mg of the adduct **13** as colorless prisms, mp 137.5–138.5 °C. An additional recrystallization raised the melting point of the adduct **13** to 138–139 °C: IR ($CCl_4$) 1704 (C=O), 1665 $cm^{-1}$ (weak, C=C); $^1H$ NMR ($CDCl_3$, 300 MHz), δ 7.2–7.4 (5 H, m, aryl CH), 5.91 (1 H, m, vinyl CH), 5.77 (1 H, m, vinyl CH), 3.06 (1 H, d of d, $J$ = 6.6, 18.0 Hz, aliphatic CH), 2.56 (1 H, d of m, $J$ = 18.0 Hz, aliphatic CH), 2.2–2.5 (4 H, m, aliphatic CH), 1.2–1.8 (8 H, m, aliphatic CH), 1.0 (1 H, m, aliphatic CH); $^{13}C$ NMR ($CDCl_3$, multiplicity on off-resonance decoupling) 212.0 (s), 139.3 (s), 128.5 (d, 2 C atoms), 126.7 (d, 2 C atoms), 126.0 (d, 2 C atoms), 123.9 (d), 59.1 (s), 42.2 (t), 37.5 (t), 37.2 (t or s, ?), 36.3 (t), 35.8 (t), 35.0 (t or s, ?), 32.9 (t or s, ?), 29.6 (d), 19.3 ppm (t); mass spectrum, $m/e$ (rel intensity) 266 ($M^+$, 57), 223 (81), 205 (35), 188 (47), 145 (80), 144 (34), 141 (40), 129 (51), 128 (51), 115 (47), 91 (100), 77 (37), 41 (49).

Anal. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.33; $M_r$, 266.1672. Found: C, 85.70; H, 8.37; $M_r$, 266.1696.

The early fractions (858 mg) from the first chromatography were rechromatographed on silica gel with an ethyl acetate–hexane eluent (1:9, v/v). The early chromatographic fractions contained 80 mg (4.4%) of the adduct **15** as a colorless solid, mp 105–118 °C. Recrystallization from hexane separated the pure adduct **15** as colorless prisms, mp 121–124 °C; IR ($CCl_4$) 1703 (C=O), 1638 (weak, C=C), 912 $cm^{-1}$ (CH=$CH_2$); $^1H$ NMR ($CDCl_3$, 300 MHz) δ 7.29 (2 H, d, $J$ = 7.7 Hz, aryl CH), 7.1–7.7 (2 H, m, aryl CH), 5.73 (1 H, d of d of d, $J$ = 8.8, 9.8, 16.6 Hz, vinyl CH), 5.23 (1 H, d of d of d, $J$ = 0.6, 1.8, 16.6 Hz, vinyl CH), 5.17 (1 H, d of d, $J$ = 1.8, 9.8 Hz, vinyl CH), 3.60 (1 H, m, aliphatic CH), 3.44 (1 H, m, aliphatic CH), 2.2–2.4 (3 H, m, aliphatic CH), 2.00 (1 H, d of m, $J$ = 13.0 Hz, aliphatic CH), 1.3–1.8 (7 H, m, aliphatic CH); mass spectrum, $m/e$ (rel intensity) 266 ($M^+$, 100), 248 (40), 205 (81), 167 ( 46), 155 (31), 153 (30), 141 (57), 129 (38), 128 (45), 115 (32), 41 (38).

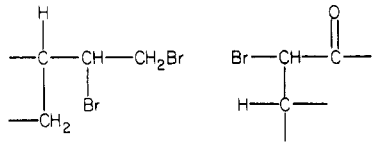
Anal. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.33; $M_r$, 266.1672. Found: C, 85.59; H, 8.38; $M_r$, 266.1680.

Subsequent fractions from the second chromatography afforded 272 mg (15%) of colorless liquid containing a mixture (NMR analysis) of cyclobutanes **16** enriched in one stereoisomer and 201 mg (11%) of colorless liquid fractions containing (NMR analysis) a mixture of isomers **16**. The final chromatographic fractions contained (NMR and TLC analysis) 127 mg (7%) of the crude adduct **13** (total yield 880 mg or 48%) as a colorless solid, mp 119–129 °C.

The spectral properties of this mixture of cycloadducts follow: IR ($CHCl_3$) 1705 $cm^{-1}$ (C=O); $^1H$ NMR ($CDCl_3$, 300 MHz) δ 7.1–7.4 (5 H, m, aryl CH), 6.28 and 5.58 (1 H, 2 multiplets in a ratio of 3:7, vinyl CH), 4.99 (2 H, m, vinyl $CH_2$), 3.62 and 3.30 (1 H, 2 multiplets in a ratio of 7:3, allylic CH), 0.9–2.9 (13 H, m, aliphatic CH); $^{13}C$ NMR of major diastereoisomer ($CDCl_3$, multiplicity on off-resonance decoupling) 219.3 (s), 138.1 (d), 128.4 (d, 2 C atoms), 127.4 (s), 126.9 (d, 2 C atoms), 125.8 (d), 114.1 (t), 63.7 (s, ?), 44.1 (s or t, ?), 43.7 (t), 42.9 (d), 38.8 (t), 36.5 (s or t, ?), 32.9 (s or t, ?), 31.8 (t), 31.4 (t), 18.4 ppm (t); mass spectrum, $m/e$ (rel intensity) 266 ($m^+$, 21), 223 (80), 212 (100), 197 (28), 184 (66), 181 (33), 170 (29), 169 (28), 158 (33), 47 (26), 46 (35), 44 (38), 43 (51), 42 (51).

Anal. Calcd for $C_{19}H_{22}O$: $M_r$, 266.1665. Found: $M_r$, 266.1673.

To a cold (0 °C) solution of 855 mg (3.2 mmol) of the mixture of cycloadducts **16** in 30 mL of $CCl_4$ was added, dropwise and with stirring during 1 h, a solution of 767 mg (4.8 mmol) of $Br_2$ in 15.3 mL of $CCl_4$. The resulting pale orange solution was washed successively with aqueous $Na_2S_2O_3$, with aqueous $NaHCO_3$, and with aqueous NaCl and then dried and concentrated. The residual yellow liquid (1.28 g) was chromatographed on silica gel with an ethyl acetate–hexane eluent (1:9, v/v) to separate later fractions containing 623 mg (39%) of crude brominated product as a colorless liquid that solidified on standing, mp 153–175 °C dec. The $^1H$ NMR spectrum (300 MHz) of the crude product indicated the presence of about 75% of the subsequently described tribromide **18** and two other minor unidentified products that appear to be stereoisomers of tribromide **18**. A series of fractional crystallizations from a $CHCl_3$–EtOAc–hexane mixture separated 87 mg of the pure tribromide **18** (stereochemistry unknown) as colorless crystals: mp 183.5–184 °C dec; IR ($CHCl_3$) 1730 $cm^{-1}$ (C=O with an equatorical α-bromo substituent); $^{13}C$ NMR ($CDCl_3$, multiplicity on off-resonance decoupling) 206.6 (s), 133.9 (s), 128.5 (d, 4 C atoms), 127.7 (d), 62.9 (s), 56.4 (d), 50.0 (d), 47.7 (d), 45.3 (s), 45.1 (d), 38.9 (t), 38.1 (t), 35.7 (t), 32.6 (t), 29.7 (t), 19.2 ppm (t); mass spectrum, $m/e$ (rel intensity) 427 (16), 425 (32), 423 (18), 345 (36), 343 (34), 331 (36), 292 (44), 290 (38), 171 (31), 141 (47), 129 (81), 128 (100), 115 (47), 95 (30), 91 (66), 79 (34), 77 (38), 57 (40), 53 (36), 41 (43), 39 (31). The $^1H$ NMR spectrum ($CDCl_3$, 300 MHz) exhibited the following peaks: δ 7.3–7.4 (5 H, m, aryl CH), 4.79 (1 H, d, $J$ = 2.8 Hz, CHBr–CO), 3.92 (1 H, 5-line pattern, CHBr), 3.67 (2 H, m, $CH_2Br$), 3.48 (1 H, q, $J$ = 9.3 Hz, cyclobutane CH), 2.93 (1 H, d, $J$ = 2.8 Hz, bridgehead CH), 1.8–2.3 (5 H, m, aliphatic CH), 1.3–1.6 (5 H, m, aliphatic CH), 0.92 (1 H, m, aliphatic CH). A series of decoupling experiments demonstrated the presence of part structures **22** and **23** in this



**22** **23**

molecule. Our efforts to obtain a crystal of this tribromide **18** that would be satisfactory for X-ray crystallographic analysis were not successful. Therefore, we have no firm basis for assigning the stereochemistry of this derivative **18**.

Anal. Calcd for $C_{19}H_{21}Br_3O$: C, 45.17; H, 4.20; Br, 47.46. Found: C, 45.02; H, 4.22, Br, 47.39.

**Reaction of Enone 1c with Butadiene.** A sample of the crude enone **1c**, prepared from 2.91 g (9.96 mmol) of the bromo ketone **2** and 60 mL of $Et_3N$, was dissolved in 5 mL of anhydrous oxygen-free benzene. The resulting yellow solution was cooled, 15 mL of liquid butadiene was added, and the resulting solution was heated in a sealed tube for 21 h at which time the initial yellow color of the solution had been discharged. The reaction solution was concentrated and then triturated and extracted with EtOAc to separate soluble material from the butadiene polymer. The EtOAc extract was concentrated and chromatographed on silica gel with an EtOAc–hexane eluent (1:9, v/v). The later chromatographic fractions containing (TLC, silica gel with an EtOAc–hexane eluent, 1:9, v/v) the adduct **13** ($R_f$ 0.40) were combined and recrystallized from hexane to separate 655 mg of the adduct **13** as colorless prisms, mp 138–139 °C, and 270 mg of less pure adduct **13**, mp 136–138 °C. This adduct **13** (total yield 925 mg or 35% based on bromoketone **2**) was identified with the pre-

viously described sample by comparison of IR, $^1$H NMR, and TLC data.

The earlier fractions containing (TLC) a mixture of adducts **15** ($R_f$ 0.64), **16** and other unidentified components was rechromatographed on silica gel to separate early fractions containing the crude cycloadduct **15**. Recrystallization from hexane separated 47 mg (2%) of the adduct **15** as colorless prisms, mp 121-122 °C, that were identified with a previously described sample by comparison of IR, $^1$H NMR, and TLC data.

The middle chromatographic fractions containing (TLC) the adduct **16** and other unidentified materials were chromatographed on silica gel impregnated with $AgNO_3$ by employing an ethyl acetate-hexane eluent (1:1, v/v). The center fractions were collected and rechromatographed on plain silica gel to separate 242 mg (9%) of the crude adduct **16** as a colorless liquid. This sample of the cycloadduct **16** was identified with the previously described sample by comparison of $^1$H NMR spectra and by reaction of this sample with bromine to form the crude tribromide **18**, mp 149-153 °C dec, that was identified with the previously described sample by comparison of $^1$H NMR and mass spectral data.

**Reaction of Enone 1c with Oxygen.** A mixture of 324 mg (1.11 mmol) of the bromo ketone **2** and 20 mL of anhydrous oxygen-free $Et_3N$ was stirred at 25 °C under an $N_2$ atmosphere for 12 h. The resulting slurry was centrifuged, and the supernatant liquid was separated and then concentrated under reduced pressure. The residual enone **1c**, a yellow liquid, was dissolved in 30 mL of anhydrous oxygen-free $CH_3CN$. After the solution had been cooled to -20 °C, a slow stream of anhydrous $O_2$ gas was passed through the cold solution for 1.5 h. The resulting yellow-tan suspension was filtered through a glass frit, and the residual tan solid was washed with two additional portions of cold (0 °C) $CH_3CN$. The residue was dried under reduced pressure to leave 154 mg (54%) of a tan solid, mp 75-80 °C dec, believed to be a mixture of peroxides **9** and **11** mixed with some residual $CH_3CN$. Solutions of this material in $CHCl_3$ or $CDCl_3$ exhibited the following spectral properties: IR ($CHCl_3$) 1725 cm$^{-1}$ (nonconjugated C=O); $^1$H NMR ($CDCl_3$) $\delta$ 6.3-8.2 (br m, ca. 5 H, aryl CH), 0.8-3.4 (br m, ca. 12 H aliphatic CH including a sharp $CH_3CN$ singlet at 1.97); $^{13}$C NMR ($CDCl_3$ at -20 °C) broad peaks at 201.9, 130.8, 130.2, 128.9 (2 C atoms), 126.1 (2 C atoms), 89.5, 85.6, 43.9, 33.5, 30.3 (3 C atoms, ?), 19.6 ppm, accompanied by sharp peaks at 117.0 and 2.1 ppm for $CH_3CN$, at 0.0 ppm for $Me_4Si$, and at 77.6, 77.2, and 76.8 ppm for $CDCl_3$. When the sample was allowed to warm to 25 °C and then the $^{13}$C NMR spectrum determined at 35 °C during a 1-h period, the spectrum exhibited a set of sharp NMR peaks attributable to presence of $CH_3CN$ and ca. 20% of the triketone **6**. In addition, broad peaks attributable to the peroxide **9**-dioxetane **11** mixture were evident at 201.4, 89.8, 85.9, 44.2, 30.5, and 19.7 ppm. After the $CDCl_3$ solution had been heated to 55 °C for 30 min, the $^{13}$C NMR spectrum exhibited a set of sharp signals corresponding to the triketone **6**, and the broad peaks attributable to the peroxide-dioxetane mixture were no longer present. In a comparable experiment, a solution of 140 mg (0.57 mmol) of the crude peroxide **9**-dioxetane **11** mixture in 1.5 mL of $CDCl_3$ was heated to 55 °C for 30 min during which time the solution became bright yellow in color. This solution was concentrated to leave 139 mg of the crude triketone **6**. Chromatography on silica gel followed by recrystallization from $Et_2O$ separated 119 mg (85%) of the triketone **6** as yellow prisms, mp 71.0-72.5 °C, that were identified with an authentic sample by comparison of IR and $^1$H NMR spectral data.

**Registry No.** **1a**, 71370-30-4; **1b**, 74262-53-6; **1c**, 85319-04-6; **1d**, 85319-05-7; **2**, 81408-13-1; **3**, 38259-33-5; **4**, 85319-06-8; **5**, 85335-10-0; **6**, 85319-07-9; **7**, 81408-12-0; **8**, 4556-09-6; **9** (polymer), 85319-13-7; **9** (replating unit), 85319-14-8; **11**, 85319-08-0; **13**, 85319-09-1; **15**, 85319-10-4; **16** (isomer 1), 85319-11-5; **16** (isomer 2), 85354-05-8; **18**, 85319-12-6; **21**, 81408-15-3; $CH_2$=CHCH=$CH_2$, 106-99-0.

**Supplementary Material Available:** Descriptions of determination of crystal structures for the diol **5** and the adduct **15**, including tables of atomic coordinates for each compound (8 pages). Ordering information is given on any current masthead page.

# Perhydroazulenes. 3. Conformations of the 4-Oxoperhydroazulenes[1]

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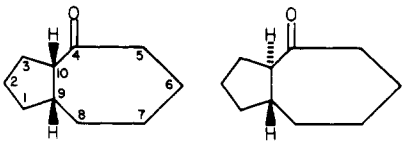
The conformations of cis (**1**) and trans (**2**) 4-oxoperhydroazulenes have been studied by employing data from X-ray crystal structures of solid derivatives, $^1$H NMR spectra, $^{13}$C NMR spectra, and molecular mechanics calculations. Related studies have been performed with the 2-*tert*-butyl-4-oxoperhydroazulenes **8a** and **9a** and the 10-methyl-4-oxoperhydroazulenes **10** and **11**. Those studies suggest that the trans ketone **2** exists in solution as the conformer TC-1 while the cis ketone **1** exists in a solution as a mixture of equilibrating conformers probably including conformer B-3 and the closely related pair of conformers C-3 and TC-7.

In continuing our studies of the synthesis and conformation of perhydroazulene derivatives,[2,3] we wished to determine the probable conformations for cis (**1**) and trans (**2**) 4-oxoperhydroazulenes. To pursue this investigation, we used the procedure recently devised by DeClercq[4] to

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systematize the earlier conformational study of perhydroazulenes by Hendrickson.[5] This procedure allows all reasonable conformations for a perhydroazulene to be considered and provides a system of nomenclature for the

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