COCH), 2.14 (2 H, m, aliphatic CH), 1.2–1.9 (11 H, m, aliphatic CH), 1.17 (3 H, s, $CH_3$); mass spectrum, $m/e$ (rel intensity) 166 ($M^+$, 13), 125 (29), 122 (24), 111 (40), 95 (81), 82 (33), 81 (89), 79 (24), 67 (100), 55 (42), 53 (25), 41 (71), 39 (50).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.70; H, 11.19.

**B. Trans Isomer 10.** The same procedure was followed—adding a solution of 939 mg (3.80 mmol) of the crude bromo ketone **19b** in 10 mL of THF to a cold solution of 5.3 mmol of *i*-$Pr_2NLi$ in 10 mL of hexane and 75 mL of THF. The crude liquid product (602 mg) contained (TLC) the unsaturated ketone **18b** ($R_f$ 0.58), the cyclic ketone **10** ($R_f$ 0.49), and several minor unidentified components ($R_f$ 0.91, 0.71, and 0.22–0.05). Chromatography first on silica gel and then on a silica gel–$AgNO_3$ column[15] separated 15 mg (3%) of the unsaturated ketone **18b** and 481 mg (76%) of a product believed to be the cyclic ketone **10** as a colorless liquid: bp 55–57 °C (0.05 mm); $n^{25}_D$ 1.4891. An analytical sample of the ketone **10**, collected from an HPLC column packed with silica gel (10 μm), and eluted with ethyl acetate–hexane (3:97, v/v), was a colorless liquid: $n^{25}_D$ 1.4901; IR ($CCl_4$) 1705 $cm^{-1}$ (C=O); $^1H$ NMR ($CDCl_3$, 300 MHz) δ 0.8–2.0 (18 H, m, aliphatic CH including a $CH_3$ singlet at 1.18); mass spectrum, $m/e$ (rel intensity) 166 ($M^+$, 32), 125 (35), 122 (35), 111 (40), 95 (89), 82 (40), 81 (95), 79 (35), 67 (100), 57 (95), 56 (95), 55 (81), 53 (45), 43 (75), 41 (71), 39 (61).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.59; H, 10.95.

**Preparation of Hydrazone 12.** A solution of 20.0 mg (0.12 mmol) of the cis ketone **11**, 30.2 mg (0.12 mmol) of the bromo hydrazide **6b**, and 1 μL of HOAc in 5 mL of EtOH was stirred at 25 °C for 45 min and then cooled to 0 °C. The crude derivative **12** separated as 35 mg (73%) of colorless solid, mp 175–181 °C. Recrystallization from MeOH afforded 28.1 mg (58%) of the pure hydrazone **12** as colorless prisms: mp 217–218 °C; IR ($CHCl_3$) 3300, 3240 $cm^{-1}$ (NH); $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.6–7.8 (4 H, m, aryl CH), 2.33 (1 H, m, aliphatic CH, 700.3 Hz), 2.0–2.1 (2 H, m, aliphatic CH, 639.3, 628.5, 626.1, 615.3, 612.9, 607.0 Hz), 1.1–1.7 (13 H, m, aliphatic CH), 1.00 (3 H, s, $CH_3$); mass spectrum (chemical ionization), $m/e$ (rel intensity) 401 ($M^+ + 1$, 83), 399 (52), 283 (57), 236 (54), 191 (56), 189 (66), 181 (100).

Anal. Calcd for $C_{17}H_{23}BrN_2O_2S$: C, 51.13; H, 5.80; Br, 20.01; N, 7.02; S, 8.03. Found: C, 51.05; H, 5.79; Br, 20.10; N, 6.99; S, 8.07.

**Registry No.** 1, 5365-37-7; 2, 5365-38-8; 4a, 5365-39-9; 4b, 85318-90-7; 5a, 85318-91-8; 5b, 85318-92-9; 5c, 85318-93-0; (*Z*)-5d, 85354-01-4; (*E*)-5d, 85354-02-5; 6a, 1576-35-8; 6b, 2297-64-5; 6c, 2751-25-9; 8a, 70775-28-9; 9a, 70775-29-0; 10, 85318-94-1; 11, 85318-95-2; 12, 85335-03-1; 13, 16112-10-0; 14, 762-72-1; *cis*-15, 65682-09-9; *trans*-15, 65682-10-2; 16, 74272-08-5; 17, 85318-96-3; 18a, 85318-97-4; 18b, 85318-98-5; 19a, 85318-99-6; 19b, 85335-09-7; *trans*-1-decalone, 21370-71-8; *trans*-1-decalone tosylhydrazone, 85319-00-2; *trans*-1-decalone (*p*-bromophenyl)sulfonylhydrazone, 85319-01-3.

**Supplementary Material Available:** Description of determination of crystal structures for the ketone derivatives **4a**, **5a**, and **12**, including tables of atomic coordinates for each compound (12 pages). Ordering information is given on any current masthead page.

# Perhydroazulenes. 4. The 6-*tert*-Butyl-4-oxoperhydroazulene System[1]

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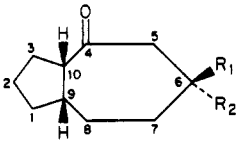
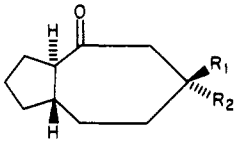
*Received June 14, 1982*

The four diastereoisomeric 6-*tert*-butyl-4-oxoperhydroazulenes (**3–6**) have been prepared and characterized. Molecular mechanics calculations suggest that each of these ketones will exist as one or both of a pair of closely related conformers as follows: **3**, C-3 or TC-7; **4**, TC-1 or TC-2; **5**, B-3 or TB-4; **6**, TC-4 or TC-5. A combination of $^1H$ NMR data and X-ray crystallographic data support the correctness of these predictions.

Our earlier studies[2-4] of the 4-oxoperhydroazulenes indicated that the cis isomer **1** was expected to exist as one





1, $R_1 = R_2 = H$
3, $R_1 = t$-Bu; $R_2 = H$
5, $R_1 = H$; $R_2 = t$-Bu

2, $R_1 = R_2 = H$
4, $R_1 = t$-Bu; $R_2 = H$
6, $R_1 = H$; $R_2 = t$-Bu

or both of two pairs of closely related conformers, either the pair B-3 or TB-4 or the pair C-3 or TC-7.[5] Similarly, the trans isomer **2** was expected to exist either as the conformer TC-1 or as one of the less stable pair of closely related conformers TC-4 or TC-5. In both the cis and the trans series, consideration of these low-energy conformations suggested that introduction of sterically bulky substituent at C-6 with the correct stereochemistry would allow one closely related pair of conformers to be distinctly favored over the other pair.

Support for this idea was gained from calculations that employed Allinger's MM2 molecular mechanics program[7b] to minimize the energies and compute the relative sta-

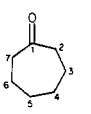
(1) A portion of this research was supported by Public Health Service Grant R01-GM-30735 from the National Institute of General Medical Science. The execution of this research was also aided by Institutional Research Grants from the National Science Foundation for the purchase of a mass spectrometer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

(2) House, H. O.; Sayer, T. S. B.; Yau, C. C. *J. Org. Chem.* **1978**, *43*, 2153.

(3) House, H. O.; Yau, C. C.; VanDerveer, D. *J. Org. Chem.* **1979**, *44*, 3031.

(4) House, H. O.; Gaa, P. C.; VanDerveer, D. *J. Org. Chem.*, preceding paper in this issue.

(5) (a) The conformational designations being used are those suggested by DeClercq[6] on the basis of the earlier cycloheptane designations of Hendrickson.[7a] In this scheme the cycloheptanone ring of the ketoperhydroazulene is numbered as shown below. The number in each conformational designation indicates the atom through which the plane of symmetry [in a chair (C) or boat (B) conformer] or the axis of symmetry [in a twist-chair (TC) or twist-boat (TB) conformer] passes. (b) We arbitrarily designate the stereochemistry of the *t*-Bu group as either syn (e.g., **3**) or anti (e.g., **5**) to the hydrogen atom at C-9.



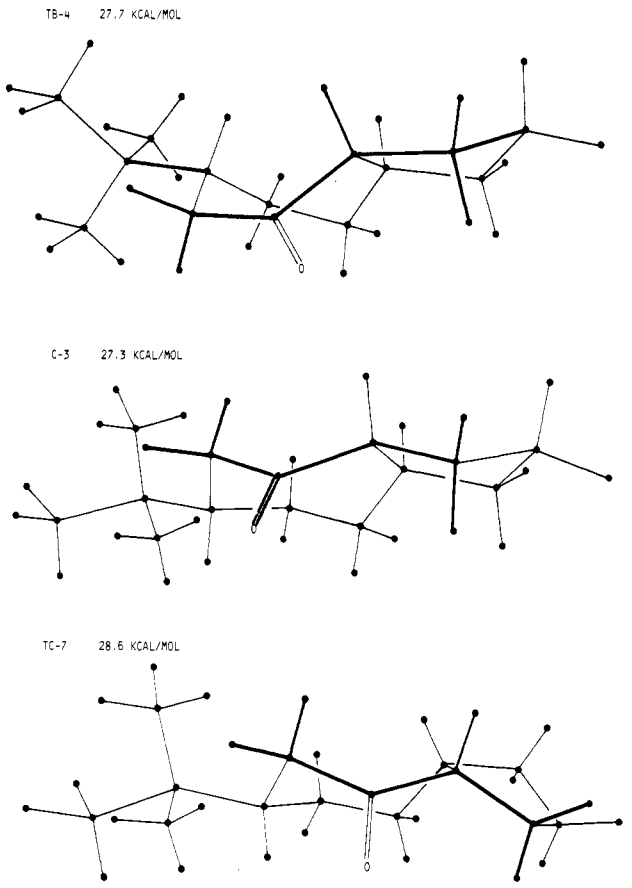



**Figure 1.** Low-energy conformations of the 6-*tert*-butyl-4-oxo-*cis*-perhydroazulenes.

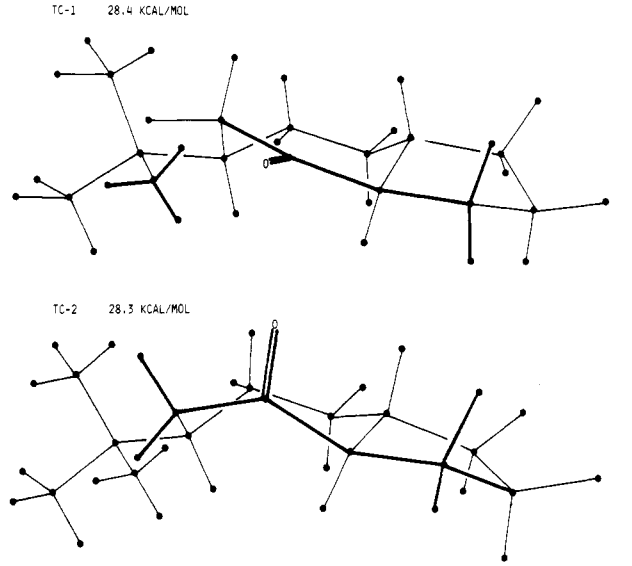



**Figure 2.** Low-energy conformers of 6-*syn-tert*-butyl-4-oxo-*trans*-perhydroazulenes.

bilities of various conformations of each of the 6-*tert*-butyl-4-oxoperhydroazulene diastereoisomers **3**–**6**. The systematic method of DeClercq[6] was used to insure that all reasonable conformations for these ketones **3**–**6** were considered. The low-energy conformers of the *syn-tert*-butyl[5b] cis ketone **3** are the closely related pair of conformers C-3 and TC-7 (Figure 1) and the low-energy conformer of the anti-*tert*-butyl cis ketone **5** is TB-4 (Figure 1), a close relative of the B-3 conformer. Other possible

(6) DeClercq, P. J. *J. Org. Chem.* **1981**, *46*, 667. Also see: DeClercq, P. J. *Tetrahedron* **1981**, *37*, 4277.

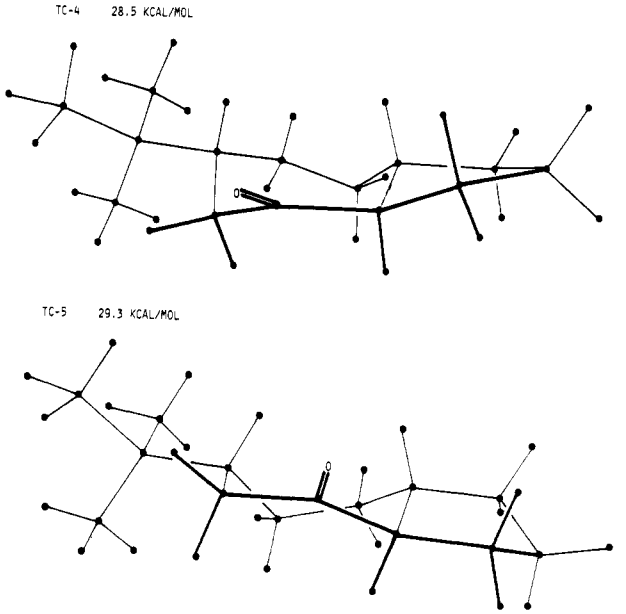
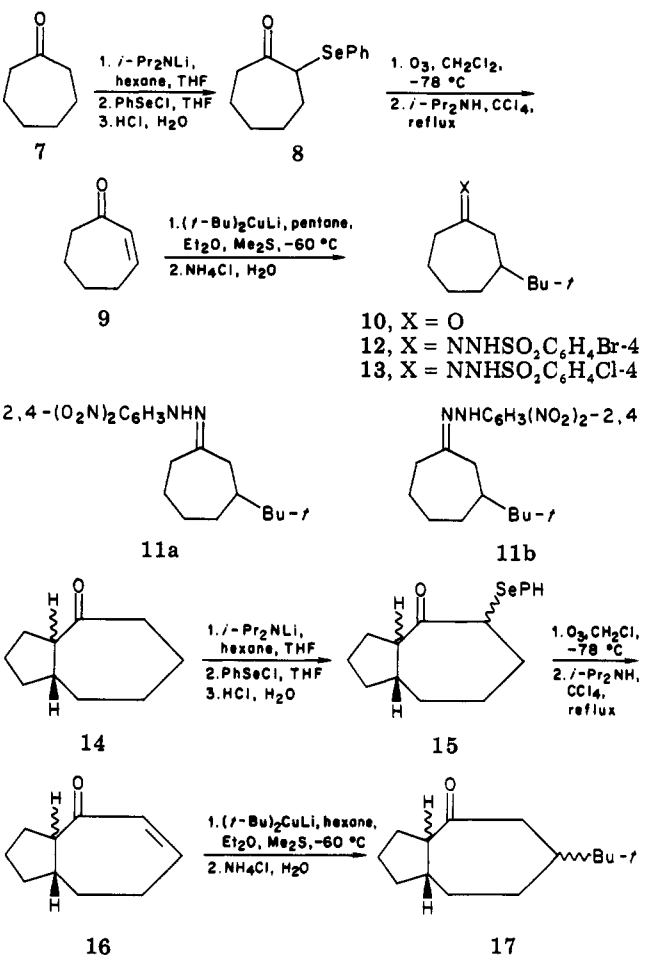


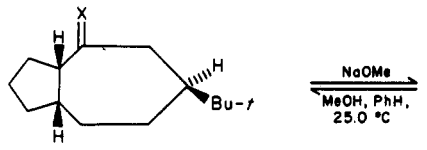

**Figure 3.** Low-energy conformers of 6-*anti-tert*-butyl-4-oxo-*trans*-perhydroazulene.

Scheme I

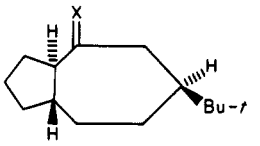



conformers of these cis ketones **3** and **5** were calculated to be at least 3 kcal/mol less stable than the conformers presented in Figure 1. The low-energy conformers of the 6-*syn-tert*-butyl trans ketone **4** are the closely related pair TC-1 and TC-2 (Figure 2), and the analogous conformers for the 6-*anti-tert*-butyl trans ketone **6** are the pair TC-4 and TC-5 (Figure 3). Again other possible conformers of the trans ketones **4** and **6** that were considered had cal-

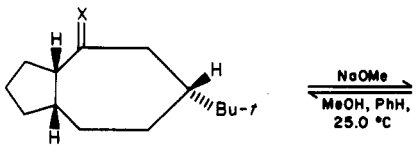
Scheme II



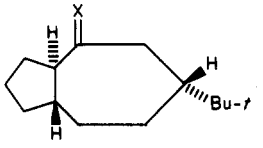

3, X = O (29.7%)
18, X = $NNHC_6H_3(NO_2)_2$-2,4




4, X = O (70.3%)
20, X = $NNHC_6H_3(NO_2)_2$-2,4
21, X = $NNHSO_2C_6H_4Br$-4




5, X = O (2.5%)
22, X = $NNHC_6H_3(NO_2)_2$-2,4




6, X = O (97.5%)
23, X = $NNHC_6H_3(NO_2)_2$-2,4
24, X = $NNHSO_2C_6H_4Br$-4

culated final steric energies at least 2.5 kcal/mol larger than the conformers illustrated in in Figures 2 and 3.

As part of an exploration of synthetic routes to the 6-*tert*-butyl ketones **3–6**, we found that cycloheptanone (**7**) could be efficiently converted to 3-*tert*-butylcycloheptanone (**10**) by the method illustrated in Scheme I. The same procedure served to convert 4-oxoperhydroazulene (**14**, see Scheme I) to a mixture of the four diastereoisomers of 6-*tert*-butyl derivative **17**. The four diastereoisomeric ketones **3–6** (see Scheme II) were at least partially resolved on an HPLC column allowing the separation and characterization of the three ketones **3**, **4**, and **6**. Base-catalyzed equilibration studies for the ketone pairs **3** ⇌ **4** and **5** ⇌ **6** gave the equilibrium compositions indicated in Scheme II.

Other synthetic schemes for the formation of 4-oxoperhydroazulenes with substituents at C-6 or C-7 were also explored briefly. As summarized in Scheme III, intramolecular alkylation of the epoxy ketone **27** formed mainly the perhydroazulene derivative **28** that was characterized as the diketone **30**. The substituted allylsilanes **32** and **36** could also be used to form the intermediate unsaturated ketones **34** and **37**. However, since these synthetic methods were less convenient than the direct reaction of the enone **16** (Scheme I) with lithium di-*tert*-butylcuprate to form ketones **17**, the methods were not pursued further.

The crystal structure of the 3-*tert*-butylcycloheptanone (2,4-dinitrophenyl)hydrazone (**11a**) was determined as illustrated in Figure 4 and detailed in Table I (supplementary material). The ketone moiety in this crystal is present as a C-4 conformer as shown in Figure 5. Since MM2 calculations suggest that a number of conformers (e.g., TC-2, TC-5, TC-7) of 3-*tert*-butylcycloheptanone (**10**)

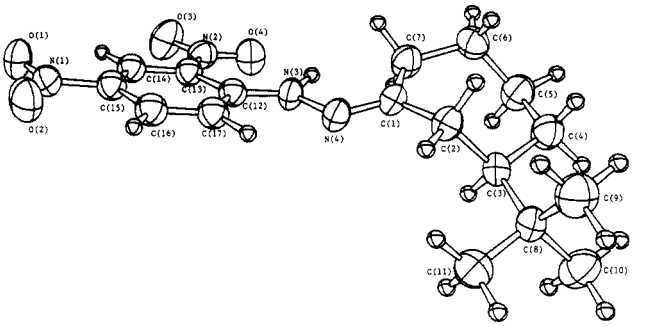



**Figure 4.** Perspective view of the molecular structure of the *anti*-2,4-dinitrophenylhydrazone of 3-*tert*-butylcycloheptanone.

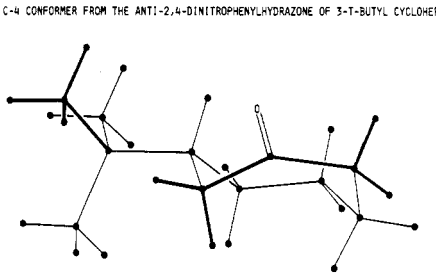



**Figure 5.** Perspective view of the 3-*tert*-butylcycloheptanone conformer present in a crystalline derivative.

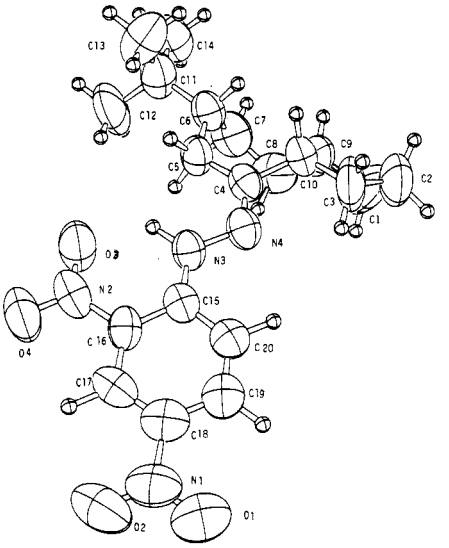



**Figure 6.** Perspective view of the molecular structure of the 2,4-dinitrophenylhydrazone of *anti*-6-*tert*-butyl-*cis*-4-oxoperhydroazulene.

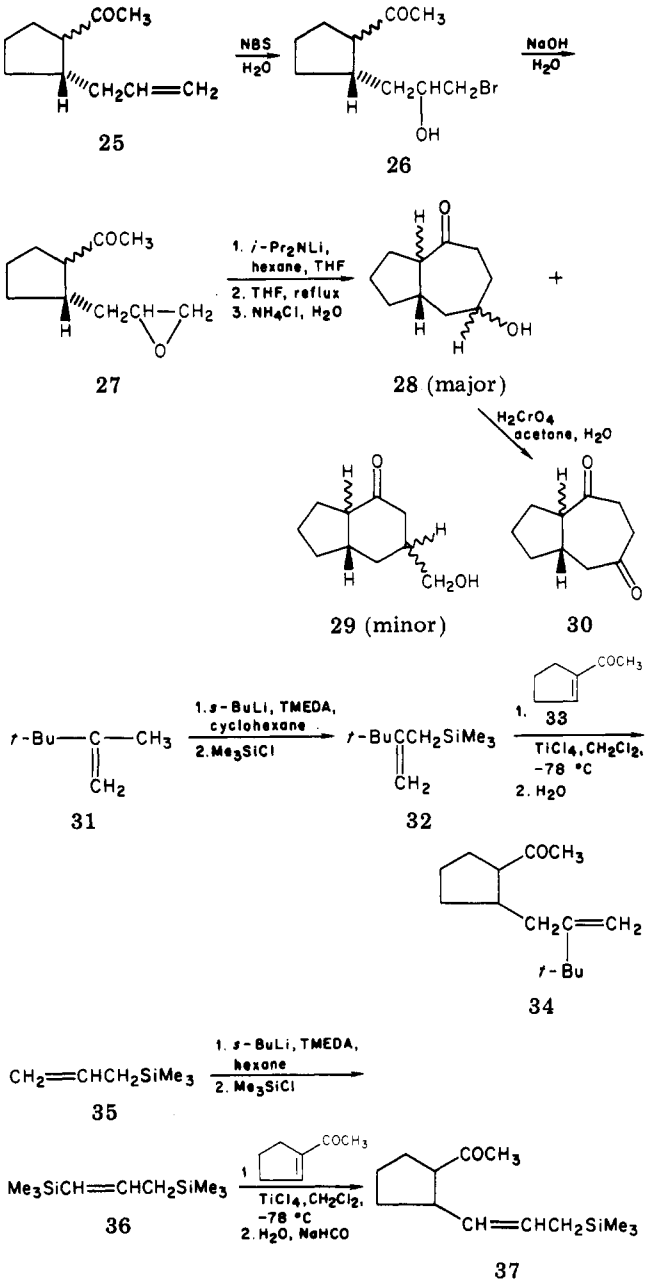
have comparable energies, we presume that solutions of the ketone **10** and its derivatives contain mixtures of several equilibrating conformers.

Crystalline (2,4-dinitrophenyl)hydrazones were prepared from each of the ketones **3–6**, and a crystal structure was obtained for the derivative **22** as illustrated in Figure 6 and in Table II (supplementary material). A perspective view of the ketone conformer present in derivative **22** is shown in Figure 7. The B-3 conformer present in this derivative **22** along with the closely related TB-4 conformer are the expected low-energy conformers for the anti-cis-ketone **5**. Thus far we have been unsuccessful in obtaining crystal structures for various derivatives of ketones **3**, **4**, and **6**. However, we have obtained information about the conformations of these ketones in solution from $^1H$ NMR coupling constant data measured at 300 MHz with appropriate decoupling experiments. Subsequent discussion of coupling constants and dihedral angles employs the

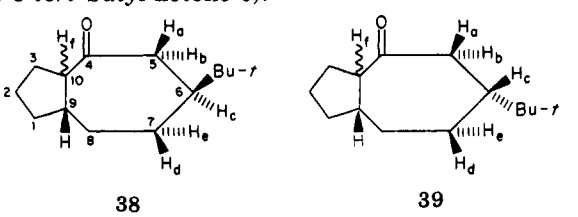
Table III. Measured $^1$H NMR Coupling Constants and Calculated Dihedral Angles for Ketones 3, 4, and 6

| ketone | obsd δ values | | | obsd J values, Hz | | | | | dihedral angle from MM2 calcd, deg | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $H_a$ | $H_b$ | $H_f$ | $J_{ab}$ | $J_{ac}$ | $J_{bc}$ | $J_{be}$ or $J_{ad}$ | conformer | $H_a$–C–C–$H_c$ | $H_b$–C–C–$H_c$ | $H_b$–C–C–$H_e$ or $H_a$–C–C–$H_d$ |
| 3 | 2.15 | 2.40 | 3.23 | 17.6 | 12.9 | 2.4 | 1.5 | C-3 | 170 | 71 | 15 |
| | | | | | | | | TC-7 | 166 | 76 | 29 |
| 4 | 2.18 | 2.53 | 2.83 | 17.3 | 11.8 | 3.7 | 2.3 | TC-1 | 156 | 87 | 17 |
| | | | | | | | | TC-2 | 170 | 52 | 66 |
| 5 | 2.52 | 2.24 | 2.55 | 11.4 | ~0 | 12.8 | ~0 | TC-4 | 90 | 152 | 72 |
| | | | | | | | | TC-5 | 68 | 175 | 38 |

Scheme III




nomenclature conventions illustrated in structures **38** (for the *syn*-6-*tert*-butyl ketones **3** and **4**) and **39** (for the *anti*-6-*tert*-butyl ketone **6**).




B-3 CONFORMER FROM THE 2,4-DINITROPHENYL HYDRAZONE OF ANTI-6-T-BUTYL-CIS-4-KETO PERHYDROAZULENE

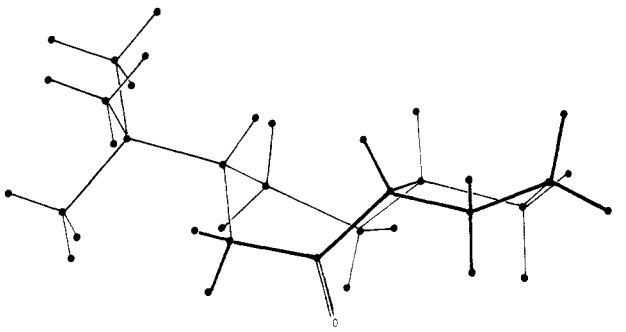
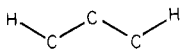


**Figure 7.** Perspective view of the *anti*-6-*tert*-butyl-*cis*-4-oxoperhydroazulene conformer present in a crystalline derivative.

Table III lists certain of the δ values and $J$ values observed for ketones **3**, **4**, and **6**. Table III also lists the corresponding dihedral angles obtained for various low-energy conformers of the ketones by molecular mechanics calculations.[7b] In each case the observed $J_{ac}$ and $J_{bc}$ values are compatible[8] with the calculated dihedral angles $H_a$–C–C–$H_c$ and $H_b$–C–C–$H_c$ for at least one member of a pair of closely related conformers. For ketones **3** and **4** we also observed significant (1.5–2.3 Hz) long-range coupling between a proton at C-5 and some proton other than $H_f$. In each case, we presume that this coupling is of the "W" type,[8] i.e.,



involving coupling of the equatorial proton $H_b$ at C-5 to the equatorial proton $H_e$ at C-7. The best agreements[8] between calculated dihedral angle values and observed coupling constants suggest that the most probable solution conformations are C-3 for ketone **3**, TC-1 or TC-2 for ketone **4**, and TC-4 for ketone **6**.

## Experimental Section[9]

### Preparation of Cycloheptenone 9. A. By Dehydrohalo-

(7) (a) Hendrickson, J. B. *Tetrahedron* **1963**, *19*, 1387. (b) For a review, see: Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1. 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 MM2 program for these calculations.

(8) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: New York, 1969; pp 280–298, 334–341.

(9) 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 $^1$H 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 (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 organometallic intermediates were performed under a nitrogen atmosphere.

**genation.** Following previously published procedures,[10,11] cycloheptanone was converted successively to the α-bromo ketone, the α-bromo ketal, the α,β-unsaturated ketal, and the enone **9**: bp 45–50 °C (2.3 mm), $n^{25}_D$ 1.4958 [lit.[11] bp 49–51 °C (2.3–2.4 mm), $n^{25}_D$ 1.4879].

**B. From the α-Phenylselenyl Ketone 8.** To a cold (−72 °C) solution of 230 mmol of *i*-$Pr_2NLi$ in 200 mL of hexane and 1100 mL of THF was added, dropwise with stirring and cooling during 2 h, a solution of 20.0 g (177 mmol) of cycloheptanone in 20 mL of THF. After the solution had been stirred for 2h, at −72 °C, a solution of 33.0 g (177 mmol) of PhSeCl in 50 mL of THF was added, and the resulting solution was stirred and allowed to warm to 0 °C during a period of 1.5 h. The resulting mixture was partitioned between aqueous 0.5 M HCl and pentane. After the pentane solution had been washed with aqueous $NaHCO_3$ and with aqueous NaCl, it was dried and concentrated. The crude liquid product (38.5 g) contained (TLC, silica gel coating with an diethyl ether–hexane eluent, 1:1, v/v) the keto selenide **8** ($R_f$ 0.56) and some excess PhSeSePh ($R_f$ 0.92) but not the starting cycloheptanone ($R_f$ 0.76). The crude product was chromatographed on silica gel with diethyl ether–hexane eluent (1:9, v/v) to separate 36.8 g (77%) of the liquid keto selenide **8**; $n^{25}_D$ 1.4718; IR ($CCl_4$), 1705 $cm^{-1}$ (C=O); $^1H$ NMR ($CCl_4$) δ 7.0–7.5 (5 H, m, aryl CH), 3.4–3.8 (1 H, m, COCHSeAr), 0.8–3.0 (10 H, m, aliphatic CH).

A stream of $O_3$ and $O_2$ was passed through a cold (−78 °C) solution of the 20.0 g (75 mmol) of the keto selenide **8** in 100 mL of $CH_2Cl_2$. When unchanged $O_3$ appeared in the exit gases, the addition of $O_3$ was stopped and the solution was purged with a stream of $N_2$. The solution was treated with 11.8 mL (84 mmol) of *i*-$Pr_2NH$,[12] and then the solution was transferred into a boiling solution of 5.9 mL (42 mmol) of *i*-$Pr_2NH$ in 400 mL of $CCl_4$. The resulting solution was allowed to cool to 25 °C and then washed with aqueous 10% HCl, with aqueous $NaHCO_3$, with aqueous NaCl and dried. Fractional distillation afforded 7.45 g (90%) of the enone **9**: bp 52–54 °C (2.0 mm); $n^{25}_D$ 1.4881; IR ($CCl_4$) 1690 $cm^{-1}$ (conjugated C=O); UV max (95% EtOH) 225 nm (ε 12 400), 328 (29).

**Preparation of 3-*tert*-Butylcycloheptanone (10).** To a cold (−72 °C) solution of 3.00 g (14.6 mmol) of $Me_2SCuBr$ in 13 mL of $Et_2O$ and 16 mL of $Me_2S$ was added, dropwise with stirring and cooling during 45 min, a solution of 29 mmol of *t*-BuLi in 17.8 mL of pentane. To the resulting cold (−60 °C) orange solution was added, dropwise with stirring and cooling during 10 min, a solution of 1.097 g (10 mmol) of the enone **9** in 3 mL of $Et_2O$. The resulting mixture, from which a red precipitate separated, was stirred at −60 °C for 30 min and then allowed to warm to 0 °C during 20 min (thermal decomposition with separation of a black precipitate began at −25 °C). After the reaction mixture had been partitioned between $Et_2O$ and aqueous $NH_4Cl$, the organic layer was dried, concentrated, and distilled to separate 1.03 g (61%) of the ketone **10** as a colorless liquid: bp 75–80 °C (2.2 mm), $n^{25}_D$ 1.4647 [lit.[13] bp 107–108 °C (12 mm), $n^{20}_D$ 1.4711]; IR ($CCl_4$) 1707 $cm^{-1}$ (C=O); $^1H$ NMR ($CCl_4$) δ 0.8–2.6 (m, aliphatic CH including a *t*-Bu singlet at 0.90); $^{13}C$ NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 214.0 (s), 46.2 (d), 45.8 (t), 43.3 (t), 33.5 (s), 31.3 (t), 29.5 (t), 27.2 (q, 3 C atoms), 25.1 ppm (t); mass spectrum, *m/e* (rel intensity) 168 ($M^+$, 5), 113 (24), 112 (58), 111 (32), 97 (50), 95 (25), 84 (29), 83 (38), 69 (33), 57 (100), 55 (82), 43 (60), 41 (96). The $^{13}C$ NMR spectrum of ketone **10** was determined in a $CDCl_3$–toluene-$d_8$ mixture at +35, at −66, and at −94 °C. The only substantial change in the spectrum as the solution was cooled was a notably broadening of the *t*-Bu $CH_3$ peak at 27.1 ppm. The $^1H$ NMR spectrum of the ketone **10**, determined at 300 MHz in $CDCl_3$, exhibited the following features: δ 2.47 (2 H, m, 768.0, 763.9, 757.7, 755.9, 753.7, 752.6, 749.6, 743.4, 741.6, 740.5, 733.2, 732.7, 728.3, 722.4, 718.4 Hz, CHCO), 2.31 (1 H, m, 707.7, 696.3, 693.4, 682.0 Hz, CHCO), 0.8–2.0 (17 H, m, aliphatic CH).

**Preparation of Sulfonylhydrazones 12 and 13.** After a solution of 0.76 g (3.0 mmol) of *p*-$BrC_6H_4SO_2NHNH_2$, 0.15 mL of HOAc, and 0.51 g (3.0 mmol) of the ketone **10** in 10 mL of EtOH had been stirred at 25 °C for 30 min, the solid that separated amounted to 1.16 g (96%), mp 145–146 °C. Recrystallization from EtOH afforded the hydrazone **12** (a mixture of syn and anti isomers) as colorless prisms: mp 145–146 °C; IR ($CCl_4$) 3300 (NH), 1340, 1172 ($SO_2$); $^1H$ NMR ($CDCl_3$) δ 7.4–8.0 (4 H, m, aryl CH), 0.6–2.6 (20 H, m, aliphatic CH including *t*-Bu singlets for the syn and anti isomers at 0.81 and 0.86).

Anal. Calcd for $C_{17}H_{25}BrN_2O_2S$: C, 50.87; H, 6.28; Br, 19.91; N, 6.98; S, 7.99. Found: C, 50.88; H, 6.29; Br, 19.92; N, 6.98; S, 8.03.

A solution of 478 mg (2.3 mmol) of *p*-$ClC_6H_4SO_2NHNH_2$, 0.05 mL of HOAc, and 353 mg (2.1 mmol) of the ketone **10** in 10 mL of EtOH was stirred at 25 °C for 30 min and then concentrated under a stream of $N_2$. The residual solid was recrystallized from MeOH to separate 728 mg (97%) of the hydrazone **13** (a mixture of syn and anti isomers) as colorless crystals: mp 125–126 °C; $^1H$ NMR ($CDCl_3$) δ 7.3–8.0 (4 H, m, aryl CH), 0.7–2.8 (20 H, m, aliphatic CH including *t*-Bu singlets for the syn and anti isomers at 0.83 and 0.86); mass spectrum, *m/e* (rel intensity) 356 ($M^+$, 0.3), 181 (100), 95 (27), 67 (23), 57 (73), 55 (22), 41 (45).

Anal. Calcd for $C_{17}H_{25}ClN_2O_2S$: C, 57.20; H, 7.06; Cl, 9.93; S, 8.98. Found: C, 57.00; H, 7.07; Cl, 9.83; S, 8.89.

**Preparation of (2,4-Dinitrophenyl)hydrazones 11.** A solution prepared from 124 mg (0.62 mmol) of (2,4-dinitrophenyl)hydrazine, 100 mg (0.60 mmol) of the ketone **10**, 1.0 mL of aqueous 12 M HCl, and 15 mL of MeOH was refluxed for 5 min and cooled. The crystalline 2,4-DNP (**11a** and **11b**) that separated amounted to 198 mg (95%) of red-orange solid, bp 164–165 °C. A 75-mg sample of this material was chromatographed on silica gel with an ethyl acetate–hexane eluent to separate 30 mg of the more rapidly eluted DNP **11a** and 25 mg of the more slowly eluted DNP **11b**. The DNP **11a** crystallized from MeOH–$H_2O$ as orange prisms, mp 168–169 °C; IR ($CCl_4$) 3320 (NH) 1620 $cm^{-1}$ (C=N); UV max (95% EtOH) 231 nm (ε 11 500), 370 (13 100); $^1H$ NMR ($CDCl_3$, 300 mHz) δ 11.06 (1 H, s, NH), 9.10 (1 H, d, *J* = 2 Hz, aryl CH), 8.27 (1 H, dd, *J* = 2, 10 Hz, aryl CH), 7.9 (1 H, d, *J* = 10 Hz), 0.9–2.8 (20 H, m, aliphatic CH including a *t*-Bu singlet at 0.93); $^{13}C$ NMR ($CDCl_3$) 164.1, 145.3, 137.8, 129.9, 129.2, 123.5, 116.5, 49.3, 39.1, 34.0, 30.6, 30.4, 29.7, 27.4 (3 C atoms), 24.3 ppm; mass spectrum, *m/e* (rel intensity) 348 ($M^+$, 16), 291 (35), 109 (23), 108 (28), 95 (94), 93 (22), 91 (28), 81 (60), 79 (27), 69 (32), 67 (36), 57 (96), 55 (48), 43 (31), 41 (100). The solid-state $^{13}C$ NMR spectrum[18] of the (dinitrophenyl)hydrazone **11a** exhibited the following peaks (and differences in ppm from the spectrum in $CDCl_3$ solution): 167.1 (3.0), 136.0 (1.8), 128.4 (0.8), 128.4 (1.5), 123.3 (0.2), 116.2 (0.3), 48.7 (0.6), 39.4 (0.3), 34.2 (0.2), 32.3 (1.7), 30.7 (0.1), 30.7 (0.3), 28.6 (1.2), 28.2 (0.8), 24.2 (0.1) ppm.

Anal. Calcd for $C_{17}H_{24}N_4O_4$: C, 58.60; H, 6.94; N, 16.09. Found: C, 58.55; H, 6.99; N, 16.02.

The DNP **11b** crystallized from MeOH–$H_2O$ as orange plates: mp 165–166 °C; IR ($CCl_4$) 3420 (NH), 1620 $cm^{-1}$ (C=N); UV max (95% EtOH) 230 nm (ε 11 700), 369 (13 200); $^1H$ NMR ($CDCl_3$, 300 MHz) δ 11.01 (1 H, s, NH), 9.06 (1 H, d, *J* = 2 Hz, aryl CH), 8.24 (1 H, d of d, *J* = 2, 9 Hz, aryl CH), 7.92 (1 H, d, *J* = 9 Hz), 3.68 (2 H, m, $CH_2C$=N), 0.9–2.7 (18 H, m, aliphatic CH including a *t*-Bu singlet at 0.88); mass spectrum, *m/e* (rel intensity) 348 ($M^+$, 20), 291 (44), 109 (24), 108 (25), 95 (100), 91 (20), 81 (58), 69 (30), 67 (25), 57 (84), 55 (40), 43 (27), 41 (71).

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(17) If the water was not buffered with $NaHCO_3$, the $Me_3Si$ group was cleaved by the aqueous acid formed to produce the ketone **25**.
(18) The solid-state $^{13}C$ NMR spectrum was determined at 50 MHz by Dr. Paul D. Ellis and his associates at the South Carolina Magnetic Resonance Laboratory, Columbia, SC 29208.

Anal. Calcd for $C_{17}H_{24}N_4O_4$: C, 58.60; H, 6.94; N, 16.09. Found: C, 58.51; H, 6.99; N, 16.02.

**Preparation of α-Phenylselenyl Ketone 15.** To a cold (−72 °C) solution of 8.00 mmol of *i*-$Pr_2NLi$ in 15 mL of hexane and 45 mL of THF was added, dropwise with stirring and cooling during 20 min, a solution of 1.00 g (6.6 mmol) of the ketone **14** (mainly trans-isomer) in 5 mL of THF. After the cold solution had been stirred for 15 min, a solution of 1.26 g (6.6 mmol) of PhSeCl in 5 mL of THF was added, and the mixture was stirred for 2 h while the temperature was allowed to rise to 25 °C. The resulting mixture was partitioned between aqueous 0.5 M HCl and pentane, and the organic layer was washed successively with $H_2O$, with aqueous $NaHCO_3$, and with aqueous NaCl. After the organic layer had been dried and concentrated, the residual brown liquid (1.98 g) was chromatographed on silica gel with diethyl ether–hexane eluent (1:19, v/v). The fractions containing the selenyl ketone **15** were eluted as 1.74 g (86%) of the α-phenylselenyl ketone **15** (a mixture of stereoisomers) as a brown liquid: $n^{25}_D$ 1.4725–1.4738; IR ($CCl_4$), 1700 $cm^{-1}$ (C=O); UV max (95% EtOH) 236 nm (ε 4310), 315 (359); $^1H$ NMR ($CCl_4$) δ 7.0–7.6 (5 H, m, aryl CH), 3.2–4.3 (1 H, m, COCHSePh), 0.7–2.5 (14 H, m, aliphatic CH); 308 ($M^+$, 17), 306 ($M^+$, 12), 151 (25), 95 (30), 91 (31), 81 (100), 79 (33), 78 (25), 77 (39), 69 (20), 67 (89), 55 (64), 53 (25), 51 (23), 43 (37), 41 (83), 39 (40).

Anal. Calcd for $C_{16}H_{20}OSe$: C, 62.54; H, 6.56. Found: C, 62.81; H, 6.68.

**Preparation of Enone 16.** A stream of $O_3$ and $O_2$ was passed through a cold (−78 °C) solution of 6.1 g (20 mmol) of the α-phenylselenyl ketone **15** in 40 mL of $CH_2Cl_2$ until $O_3$ was detected (aqueous KI solution) in the exit gases. The solution was swept with $N_2$ to remove dissolved $O_3$, treated with 3.0 mL (23 mmol) of *i*-$Pr_2NH$,[12] and then siphoned slowly into a refluxing solution of 1.5 mL (11 mmol) of *i*-$Pr_2NH$ in 100 mL of $CCl_4$. The resulting green solution was washed successively with aqueous 10% HCl, with aqueous $NaHCO_3$, and with aqueous NaCl. After the organic solution had been dried and concentrated, distillation of the residual liquid (4.65 g) separated 2.55 g (84%) of the enone **16** as a colorless liquid: bp 44–46 °C (0.2 mm), $n^{25}_D$ 1.5213–1.5220; IR ($CCl_4$) 1682 $cm^{-1}$ (conjugated C=O); $^1H$ NMR ($CCl_4$) δ 5.7–6.8 (2 H, m, vinyl CH), 0.7–3.3 (12 H, m, aliphatic CH); UV max (95% EtOH) 227 nm (ε 12500), 329 (32); mass spectrum, *m/e* (rel intensity) 150 ($M^+$, 18), 109 (22), 93 (27), 82 (20), 81 (50), 80 (35), 79 (46), 68 (100), 67 (47), 54 (20), 53 (30), 41 (36), 39 (45).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.75; H, 9.26.

**Preparation of Epoxy Ketone 27.** A mixture of 2.00 g (13.1 mmol) of the unsaturated ketone **25**, 2.34 g (13.1 mmol) of *N*-bromosuccinimide, and 15 mL of $H_2O$ was stirred at 25 °C for 1 h at which time all of the solid *N*-bromosuccinimide was gone.[14] The mixture was extracted with $Et_2O$, and the ethereal extract was dried and concentrated. The crude liquid bromohydrin **26** (3.20 g or 98%) was used without further purification; IR ($CCl_4$) 3620, 3590, 3400 (OH), 1710 $cm^{-1}$ (C=O).

The bromohydrin **26** (3.20 g or 13.0 mmol) was treated with a solution of 526 mg (13 mmol) of NaOH in 10 mL of $H_2O$, and the mixture was heated to 60 °C with stirring for 1 h. The resulting mixture was extracted with $Et_2O$, and the ethereal extract was dried and concentrated. Distillation of the residual liquid (2.10 g) afforded 1.94 g (88%) of the epoxy ketone **27** (a mixture of stereoisomers) as a colorless liquid: bp 64 °C (1 mm); $n^{25}_D$ 1.4730; IR ($CCl_4$) 1715 $cm^{-1}$ (C=O); $^1H$ NMR ($CCl_4$) δ 2.2–3.8 (3 H, m, $\overset{\frown O \frown}{CH\text{-}CH_2}$), 0.8–2.2 (13 H, m, aliphatic CH including a $CH_3CO$ singlet at 2.10); mass spectrum, *m/e* (rel intensity), 168 ($M^+$, 15), 112 (29), 97 (57), 83 (28), 69 (37), 57 (100), 55 (38), 41 (46). The $^{13}C$ NMR spectrum ($CDCl_3$) suggested that one major stereoisomer of the epoxy ketone **27** was present with the following peaks (multiplicity in off-resonance decoupling): 209.5 (s), 57.7 (d), 51.1 (d), 46.7 (t), 39.4 (q), 38.1 (d), 32.8 (t), 29.9 (t?), 29.2 (t?), 24.7 ppm (t).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.36; H, 9.60.

**Base-Promoted Cyclization of Epoxy Ketone 27.** To a cold (−78 °C) solution of 35.5 mmol of *i*-$Pr_2NLi$ in 67 mL of hexane and 1200 mL of THF was added, dropwise and with stirring during 30 min, a solution of 5.00 g (29.7 mmol) of the epoxy ketone **27** in 300 mL of THF. The resulting solution was heated to reflux during 20 min and then refluxed for 19 h. After the reaction solution had been cooled, it was partitioned between $Et_2O$ and aqueous $NH_4Cl$, and the organic layer was dried and concentrated. The residual orange liquid (4.81 g) was chromatographed on silica gel with an ethyl acetate–hexane eluent (9:11, v/v), and the fraction was analyzed by TLC on silica gel with an ethyl acetate–hexane eluent (9:11, v/v). Early fractions ($R_f$ 0.45–0.52) contained 1.20 g (24%) of the alcohols **28**. Subsequent fractions ($R_f$ 0.30–0.45) contained 3.28 g (65%) of mixtures of alcohols **28** (major) and **29** (minor), and the final fractions ($R_f$ 0.21–0.30) contained 43.5 mg (0.9%) of alcohols **29**. The alcohol **28** was distilled in a short-path still (95 °C and 0.5 mm) to separate 982 mg (20%) of a mixture of stereoisomeric alcohols **28** as a colorless liquid, $n^{25}_D$ 1.4995–1.4999. The material was then fractionally distilled, and a pure sample of the mixture of ketols **28** was collected at 98–100 °C (0.05 mm), $n^{25}_D$ 1.5001; [lit.[19] bp 104–110 °C (0.3 mm)]; IR ($CCl_4$) 3620, 3420 (unassoc and assoc OH), 1710 $cm^{-1}$ (C=O); $^1H$ NMR ($CCl_4$) δ 4.73 (1 H, br, OH), 3.1–4.2 (1 H, m, CHOR), 0.9–3.0 (13 H, m, aliphatic CH); mass spectrum, *m/e* (rel intensity) 168 ($M^+$, 16), 108 (21), 95 (51), 83, (21), 81 (49), 79 (28), 68 (73), 67 (100), 57 (27), 55 (42), 43 (34), 41 (43), 39 (24).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.42; H, 9.70.

A cold (0 °C) solution of 1.83 g (10.9 mmol) of the fractions containing mixtures of alcohols **28** (major) and **29** in 200 mL of acetone was treated with 8.2 mL of aqueous 8 N $H_2CrO_4$ (Jones reagent). After the resulting brown mixture had been stirred at 0 °C for 20 min, it was partitioned between $H_2O$ and $CHCl_3$. The $CHCl_3$ solution was washed successively with aqueous $NaHCO_3$ and with aqueous NaCl and then dried and concentrated. The residual brown liquid (1.54 g) was chromatographed on silica gel with an ethyl acetate–hexane eluent (3:7, v/v) to separate 1.38 g (77%) of the crude diketone **30** as a tan solid, mp 40–46 °C. Distillation of this sample in a short path still (75–80 °C and 0.1 mm) separated 1.18 g (65%) of the diketone **30** (a mixture of stereoisomers) as a white solid, mp 69–70 °C; IR ($CCl_4$) 1700 $cm^{-1}$ (C=O); $^1H$ NMR ($CDCl_3$, 300 MHz) δ 3.28 (1 H, m, CHCO), 2.82 (2 H, m, $CH_2CO$), 2.5–2.7 (4 H, m, $CH_2CO$), 0.9–2.4 (7 H, m, aliphatic CH); mass spectrum, *m/e* (rel intensity) 166 ($M^+$, 9), 138 (19), 111 (22), 109 (21), 99 (74), 98 (38), 95 (35), 81 (24), 68 (45), 67 (100), 56 (30), 55 (24). The $^{13}C$ NMR spectrum exhibited two sets of lines. One set of 10 lines corresponded to the minor isomer (ca. 10% of the mixture), and the second set of 10 lines corresponded to the major isomer of the diketone **30** present (ca. 90% of the mixture, presumably the trans isomer). The positions of the $^{13}C$ NMR lines for the major isomer present follow ($CDCl_3$, multiplicity in off-resonance decoupling): 209.0 (s), 208.3 (s), 52.3 (d), 45.9 (t), 38.3 (d), 38.2 (t), 37.8 (t), 34.0 (t), 25.4 (t), 24.9 ppm (t). The positions of the 10 lines for the minor isomers were 209.3, 207.8, 57.4, 49.6, 40.4, 39.4, 37.8, 35.2, 25.5, and 24.0 ppm.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.30; H, 8.50.

A preliminary attempt to add 1 equiv of *t*-BuLi regioselectively to the presumably less hindered C=O group of the diketone **30** led to a mixture believed to contain comparable amounts of products from attack at each C=O group.

**Preparation of Olefin 31 and Silane 32.** A solution of 30.0 g (299 mmol) of pinacolone in 100 mL of $Et_2O$ was added, dropwise and with stirring, to 1250 mL of a cold (0 °C) $Et_2O$ solution containing 419 mmol of MeLi. After the addition was complete, the resulting solution was stirred and allowed to warm to 25 °C during 6 h. The reaction solution was partitioned between pentane and aqueous $NH_4Cl$, and the organic layer was dried and concentrated by distillation. The residual crude tertiary alcohol was mixed with 30 mL of aqueous 5% $H_2SO_4$ and heated. The olefin **31** distilled from this mixture as 26.7 g (91%) of colorless liquid: bp 78–80 °C, $n^{25}_D$ 1.4001 (lit.[15] bp 77.87 °C, $n^{25}_D$ 1.4004); IR ($CCl_4$) 1640 (C=C), 895 $cm^{-1}$ (C=$CH_2$); $^1H$ NMR ($CCl_4$) δ 4.6–4.8 (2 H, m, vinyl CH), 1.75 (3 H, s), 1.08 (9 H, s); mass spectrum, *m/e* (rel intensity) 98 ($M^+$, 22), 83 (100), 55 (41), 41 (18).

To a cold (−5 °C) solution of 102 mmol of *s*-BuLi in 70.2 mL of cyclohexane was added, dropwise and with stirring during 30

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min, a mixture of 10.0 g (102 mmol) of the olefin **31** and 11.85 g (102 mmol) of tetramethylethylenediamine (TMEDA). The reaction solution, which turned first yellow and then red during the olefin addition, was stirred at 0 °C for 3 h, and then 11.1 g (102 mmol) of $Me_3SiCl$ (freshly distilled from quinoline) was added, dropwise and with stirring during 10 min. The resulting colorless mixture was warmed to 25 °C, washed with aqueous $NH_4Cl$, and then dried and concentrated. Distillation of the residual liquid separated 12.5 g (72%) of the crude silane **32**: bp 168–170 °C; $n^{25}_D$ 1.4350; IR ($CCl_4$) 1622 (C=C), 892 $cm^{-1}$ (C=$CH_2$); $^1H$ NMR (neat) $\delta$ 4.4–4.9 (2 H, m, vinyl CH), 1.51 (2 H, br s, allylic $CH_2$), 1.00 (9 H, s, *t*-Bu), 0.02 (9 H, s, $Me_3Si$); mass spectrum, *m/e* (rel intensity) 170 ($M^+$, 2), 113 (22), 74 (28), 73 (100), 45 (36).

Anal. Calcd for $C_{10}H_{22}Si$: $M_r$, 170.1491. Found: $M_r$, 170.1484 (mass spectrum).

**Preparation of Unsaturated Ketone 34.** A cold (–78 °C) solution of 539 mg (4.9 mmol) of the enone **33** in 15 mL of $CH_2Cl_2$ was treated with 929 mg (4.9 mmol) of $TiCl_4$. To the resulting cold yellow solution was added, dropwise and with stirring, a solution of 1.0 g (5.8 mmol) of the silane **32** in 10 mL of $CH_2Cl_2$. After the resulting purple solution had been stirred at –78 °C for 1 h, 10 mL of $H_2O$ was added and the mixture was allowed to warm to 25 °C. The mixture was partitioned between $Et_2O$ and $H_2O$, and the organic layer was dried and concentrated. The residual brown liquid (981 mg) contained (TLC on a silica gel coating with an ethyl acetate–hexane eluent, 1:19, v/v) the starting silane **32** ($R_f$ 0.90), two stereoisomers of the unsaturated ketone **34** ($R_f$ 0.52 and 0.55), and the starting enone **33** ($R_f$ 0.50). Chromatography on silica gel with an ethyl acetate–hexane eluent (1:19, v/v) separated 638 mg (85%) of the crude unsaturated ketone **34** (both stereoisomers). Distillation of this material in a short-path still (57–60 °C and 0.15 mm) separated 709 mg (70%) of the unsaturated ketone **34** (mainly one stereoisomer, $R_f$ 0.52, presumably the trans isomer) as a colorless liquid: $n^{25}_D$ 1.4590; IR ($CCl_4$), 1715 (C=O), 1635 (C=C), 900 $cm^{-1}$ (C=$CH_2$); $^1H$ NMR ($CDCl_3$) $\delta$ 4.6–5.2 (2 H, m, vinyl CH), 0.9–3.0 (22 H, m, aliphatic CH including a $CH_3CO$ singlet at 2.16 and a *t*-Bu singlet at 1.07); mass spectrum, *m/e* (rel intensity) 208 ($M^+$, 0.8), 152 (31), 151 (32), 111 (25), 109 (69), 95 (22), 83 (31), 67 (29), 57 (22), 43 (100), 41 (34); $^{13}C$ NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 210.2 (s), 155.5 (s), 107.0 (t), 58.4 (d), 40.6 (d), 37.4 (q), 35.9 (t), 32.6 (s), 29.8 (t), 29.2 (3 C atoms, q), 24.8 ppm (t).

Anal. Calcd for $C_{14}H_{24}O$: $M_r$, 208.1821. Found: $M_r$, 208.1813.

**Preparation of Disilane 36 and Ketone 37.** To a cold (–78 °C) solution, prepared from 300 mL of THF and 164 mL of hexane containing 63.8 mmol of *s*-BuLi, was added, dropwise and with stirring during 30 min, a mixture of 7.40 g (63.8 mmol) of tetramethylethylenediamine (TMEDA) and 7.30 g (63.8 mmol) of the silane **35**. The resulting solution was warmed to –40 °C and then stirred at –40 °C for 30 min at which time 7.06 g (65.0 mmol) of $Me_3SiCl$ was added rapidly. After the resulting mixture had been stirred for 10 min, it was partitioned between pentane and aqueous $NH_4Cl$. After the aqueous phase had been washed with $Et_2O$, the combined organic layers were washed with $H_2O$, dried, and concentrated. Distillation separated 10.1 g (85%) of the disilane **36** as a colorless liquid: bp 171 °C, $n^{25}_D$ 1.4289 (lit.[16] bp 171 °C); $^1H$ NMR ($CCl_4$) $\delta$ 6.14 (1 H, d of t, $J$ = 8, 19 Hz, vinyl CH of trans olefin), 5.45 (1 H, d, $J$ = 19 Hz, vinyl CH of trans olefin), 1.66 (2 H, d, $CH_2$, $J$ = 8 Hz), 0.00 (18 H, s, $Me_3Si$); $^{13}C$ NMR ($CDCl_3$) 144.8, 129.4, 30.2, 1.0, 0.0 ppm; mass spectrum, *m/e* (rel intensity) 186 ($M^+$, 4), 171 (10), 98 (72), 83 (12), 73 (100).

Anal. Calcd for $C_9H_{22}Si_2$: $M_r$, 186.126. Found: $M_r$, 186.128.

To a cold (–78 °C) solution of 5.00 g (45.0 mmol) of the enone **33** and 8.60 g (45.0 mmol) of $TiCl_4$ in 100 mL of $CH_2Cl_2$ was added, dropwise and with stirring, a solution of 8.40 g (46.0 mmol) of the disilane **36** in 70 mL of $CH_2Cl_2$. The resulting cold purple solution was stirred for 1 h, treated with 180 mL of saturated aqueous $NaHCO_3$,[17] and allowed to warm to 25 °C. After the mixture had been partitioned between $H_2O$ and $Et_2O$, the organic layer was dried and concentrated to leave 10.5 g of the ketone **37** as a colorless liquid. Chromatography on silica gel with an ethyl acetate–hexane eluent followed by distillation separated 8.60 g (87%) of the ketone **37** (a mixture of stereoisomers) as a colorless liquid: bp 96–100 ° (10 mm); $n^{25}_D$ 1.4693; IR ($CCl_4$) 1710 (C=O), 1655 (C=C), 965 $cm^{-1}$ (trans HC=CH); $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 5.0–5.5 (2 H, m, vinyl CH), 2.55 (1 H, m, CHCO), 1.4–2.1 (10 H, m, aliphatic CH), 1.35 (2 H, m, $CH_2Si$), –0.07 (9 H, s, MeSi); mass spectrum, *m/e* (rel intensity) 224 ($M^+$, 3), 183 (15), 111 (28), 109 (25), 94 (15), 79 (27), 75 (17), 73 (76), 71 (25), 67 (42), 43 (100), 41 (28), 39 (25).

Anal. Calcd for $C_{13}H_{24}OSi$: C, 69.57; H, 10.78. Found: C, 69.70; H, 11.08.

**Preparation of *tert*-Butyl Ketones 17.** To a cold (–72 °C) solution of 5.19 g (25.3 mmol) of $Me_2SCuBr$ in 40 mL of $Et_2O$ and 60 mL of $Me_2S$ was added, dropwise with stirring and cooling during 20 min, 29.7 mL of a hexane solution containing 50 mmol of *t*-BuLi. To the resulting cold (–65 °C), orange solution of $(t\text{-Bu})_2CuLi$ was added, dropwise with stirring and cooling during 10 min, a solution of 2.60 g (17.3 mmol) of the enone **16** in 5 mL of $Et_2O$. During the addition of the enone, the reaction solution turned red and a red precipitate separated. After the resulting mixture had been stirred at –60 °C for 20 min, it was allowed to warm to 0 °C during 25 min and then partitioned between $Et_2O$ and an aqueous solution (pH 6.9) of $NH_4Cl$ and $NH_3$. The organic layer was washed with aqueous NaCl, dried, and concentrated to leave 3.03 g of a pale yellow liquid containing (TLC on silica gel with an ethyl acetate–hexane eluent, 1:9, v/v) a mixture of the *tert*-butyl ketones **17** ($R_f$ 0.62) and the starting enone **16** ($R_f$ 0.50). Chromatography on silica gel with an ethyl acetate–hexane eluent separated 0.75 g (21% recovery) of the enone **16** and 1.91 g (51%) of the mixture of *tert*-butyl ketones **17** as a waxy solid, mp 29–34 °C. Distillation in a short-path still (87–92 °C and 1.0 mm) afforded 1.77 g (49%) of the mixture of ketones **17** as a solid, mp 29–34 °C. GLC analysis (silicone XE-60 on Chromosorb P) of this mixture exhibited two broad peaks at $t_r$ = 26.9 min (smaller peak, a mixture of **3** and **5**) and $t_r$ = 29.8 min (larger peak, a mixture of **4** and **6**). HPLC analysis (10-$\mu$m silica gel with an ethyl acetate–hexane eluent, 3:97, v/v) indicated two minor components **3** ($t_r$ = 65.2 min) and **5** ($t_r$ 70.1 min) and two major components **4** ($t_r$ = 83.5 min) and **6** ($t_r$ = 89.0 min). A 125-mg sample was subjected to preparative HPLC to separate 14 mg (11% of the mixture) of a mixture of **3** and **5**, 56 mg (45% of the mixture) of **4**, and 49 mg (39% of the mixture) of **6**.

The properties of the trans ketone **4** follow: mp 41–43 °C; IR ($CCl_4$) 1700 $cm^{-1}$ (C=O); mass spectrum, *m/e* (rel intensity) 208 ($M^+$, 21), 152 (65), 151 (38), 141 (48), 123 (32), 111 (34), 95 (37), 81 (72), 67 (55), 57 (100), 56 (30), 55 (55), 43 (41), 41 (97), 39 (34); $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 2.81 (1 H, m, 851.2, 843.2, 840.2 Hz, CHCO), 2.60 (1 H, m, 789.4, 787.9, 785.8, 774.5, 771.9, 770.8, 768.2 Hz, CHCO), 2.26 (1 H, m, 692.2, 680.5, 675.0, 663.0 Hz, CHCO), 0.9–2.2 (12 H, m, aliphatic CH), 0.88 (9 H, s, *t*-Bu); $^{13}C$ NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 213.9 (s), 56.7 (d), 47.4 (d), 46.9 (t), 45.4 (d), 36.5 (t), 35.5 (t), 33.5 (s), 30.7 (t), 27.2 (q, 3 C atoms), 26.5 (t), 23.6 ppm (t). When the same spectrum was measured at –59 °C, the peak locations were not notably altered and only the *t*-Bu singlet at 27.2 ppm was appreciably broadened.

Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.69; H, 11.68.

The properties of the trans ketone **6** follow: mp 44–46 °C; IR ($CCl_4$) 1700 $cm^{-1}$ (C=O); mass spectrum, *m/e* (rel intensity) 208 ($M^+$, 25), 152 (81), 151 (35), 123 (34), 95 (36), 81 (94), 69 (31), 67 (65), 57 (100), 55 (44), 43 (76), 41 (79); $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 2.54 (2 H, m, 768.6, 766.0, 760.9, 756.9, 754.7, 753.3 Hz, CHCO), 2.24 (1 H, m, 684.9, 674.3, 672.1, 661.5, 660.4 Hz, CHCO), 0.8–2.1 (21 H, m, aliphatic CH including a *t*-Bu single at 0.87); $^{13}C$ NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 211.7 (s), 57.3 (d), 45.7 (t), 42.8 (d), 41.2 (d), 35.1 (t), 33.8 (s), 30.9 (t), 27.4 (t), 27.0 (q, 3 C atoms), 25.5 (t), 23.8 ppm (t). No notable change was observed when this $^{13}C$ NMR spectrum was determined at –59 °C rather than at 35 °C.

Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.70; H, 11.64.

Since ketones **3** and **5** were not readily separated by HPLC, a sample of ketone **3** was obtained in the following manner. A solution of 102 mg (0.49 mmol) of ketone **4** and 1.0 mmol of NaOMe in 10 mL of MeOH and 5 mL of PhH was stirred at 25 °C for 10 h and then quenched with 10 mL of an aqueous phosphate buffer (pH 6.9). The organic phase was separated and concentrated to leave 96.1 mg (93%) of an equilibrated mixture of ketones **3** and **4**. Separation by HPLC afforded 65.7 mg of

ketone **4** and 28.2 mg of ketone **3**. The properties of the cis ketone **3** follow: mp 34–36 °C; IR ($CCl_4$) 1695 $cm^{-1}$ (C=O); $^1H$ NMR ($CDCl_3$, 300 MHz) δ 3.20 (1 H, m, 977.3, 969.4, 965.9, 961.6, 958.1, 950.2 Hz, CHCO), 2.43 (1 H, m, 730.9, 729.4, 713.1, 712.4, 710.7 Hz, CHCO), 2.15 (3 H, m, 668.7, 667.5, 661.8, 655.9, 654.6, 650.4, 643.0, 637.7, 630.0, 625.4, 612.5 Hz, aliphatic CH), 0.8–2.0 (19 H, m, aliphatic CH including a *t*-Bu singlet at 0.88); $^{13}C$ NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 213.7 (s), 52.2 (d), 43.3 (t), 42.2 (d), 40.8 (d), 34.9 (t), 32.6 (s), 29.8 (t), 27.5 (q, 3 C atoms), 27.1 (t), 26.2 (t), 25.6 (t); mass spectrum, *m/e* (rel intensity) 208 ($M^+$, 8), 152 (46), 151 (34), 123 (32), 111 (33), 110 (38), 109 (28), 95 (63), 81 (100), 69 (37), 67 (76), 57 (68), 55 (58), 41 (97), 39 (33).

Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.80; H, 11.68.

Proton–proton coupling constants for protons at C-5, C-6, and, in some cases, C-7 were measured at 300 MHz in $CDCl_3$ solution for ketones **3**, **4**, and **6**. Each of the $J_{HH}$ values listed in Table III was verified by an appropriate spin-decoupling experiment.

**Equilibration Studies with Ketones 3–6.** Mixtures of the ketones **3–6** were analyzed by GLC by employing a 2-m column packed with silicone fluid XE-60 on Chromosorb P with *n*-$C_{18}H_{38}$ as an internal standard. The GLC retention times were: *n*-$C_{18}H_{38}$, 51.0 min; ketone **3**, 112.0 min; ketone **5**, 121.1 min; ketone **4**, 126.1 min; and ketone **6**, 135.0 min. Response factors were determined for ketones **3**, **4**, and **6** (2.73, 2.68, and 2.69) by chromatography of authentic mixtures. Since the amount of ketone **5** available was insufficient to allow determination of a response factor, this factor was taken to be equal to the factor 2.69 used for ketone **6**.

A solution prepared from 12.7 mg (0.061 mmol) of the ketone **4**, 5.0 mg of *n*-$C_{18}H_{38}$, 0.15 mmol of NaOMe, 1.5 mL of MeOH, and 1.5 mL of benzene was allowed to stand at 25.0 °C. Aliquots of the resulting solution were quenched with an aqueous phosphate buffer (pH 6.9) after 5 h, and after 31 h. The organic layers were separated and analyzed by GLC. After 31 h, the mixture contained 29.9% of ketone **3** and 70.1% of ketone **4** (recovery 97%). From a comparable experiment employing a solution prepared from 2.50 mg (0.012 mmol) of the ketone **3**, 0.10 mmol of NaOMe, 0.31 mg of *n*-$C_{18}H_{38}$, 1.0 mL of MeOH, and 1.0 mL of $C_6H_6$ that was kept at 25.0 °C for 54 h, the product mixture contained (GLC) 29.6% of ketone **3** and 70.4% of ketone **4** (97% recovery).

In a comparable experiment, a solution of 6.70 mg (0.032 mmol) of the ketone **6**, 1.90 mg of *n*-$C_{18}H_{38}$, and 0.15 mmol of NaOMe in 1.5 mL of MeOH and 1.5 mL of $C_6H_6$ was kept at 25.0 °C, and aliquots were removed after 12 h and after 48 h. After 48 h, the mixture contained (GLC) 2.5% of ketone **5** and 97.5% of ketone **6** (97% recovery). A solution was prepared from 2.1 mg (0.01 mmol) of a mixture (ca. 1.1) of ketones **3** and **5**, 0.5 mg of *n*-$C_{18}H_{38}$, 0.10 mmol of NaOMe, 1.0 mL of MeOH, and 1.0 mL of $C_6H_6$ and then allowed to stand at 25.0 °C for 73 h. After the usual quenching procedure, the product contained (HPLC on 10-μm silica gel with an ethyl acetate–hexane eluent, 4:96, v/v) a mixture of ketones **3** (29.2%) and **4** (70.8%) and ketone **6** (>95% of mixture) with <5% of ketone **5** being detected.

To demonstrate that the conditions used with ketone **6** were sufficiently vigorous for equilibration, a solution of 0.22 mmol of NaOMe, 3.0 mg of *n*-$C_{18}H_{38}$, and 15.0 mg of ketone **6** in 2.0 mL of $C_6H_6$ and 2.0 mL of MeOD was kept at 25 °C for 48 h. After the mixture had been quenched with an aqueous phosphate buffer (pH 6.9), the organic layer was dried and concentrated. The crude product contained (GLC) the ketone **6** (more than 95% of the ketones **5** and **6** present, recovery 92%). This sample of ketone **6** contained 0.5% $d_0$ species, 1.5% $d_1$ species, 12.5% $d_2$ species, and 85.5% $d_3$ species (mass spectral analysis); $^1H$ NMR ($CDCl_3$, 300 MHz) δ 2.18 (2 H, m, 662.9, 655.9, 650.4 Hz), 1.0–1.95 (10 H, m, aliphatic CH), 0.89 (9 H, s, *t*-Bu).

The absence of NMR absorption in the region δ 2.2–2.7 confirms our assignment of multiplets at δ 2.25 and 2.56 to the 3 H atoms bound α to the C=O function. In a similar experiment, a 15.0-mg (0.072 mmol) sample of ketone **4** was stirred with 1 mL of MeOD containing 0.5 mmol of NaOMe for 7 days and then quenched with an aqueous phosphate buffer (pH 6.9). The recovered ketone (mainly **4**, 10 mg or 62%) contained 1.6% $d_0$ species, 14.3% $d_2$ species, and 84.1% $d_3$ species (mass spectral analyses). The $^1H$ NMR spectrum ($CDCl_3$, 300 MHz) lacked appreciable absorption in the region δ 2.2–3.0, confirming our assignment of multiplets at δ 2.28, 2.62, and 2.85 to protons to the C=O group.

**Preparation of (2,4-Dinitrophenyl)hydrazones 20 and 23.** A solution of 9.5 mg (0.05 mmol) of (2,4-dinitrophenyl)hydrazine, 1 μL of aqueous 12 M HCl, and 10.0 mg (0.050 mmol) of one of the ketones **4** or **6** in 10 mL of MeOH was stirred at 25 °C for 1 h. Then the crystalline derivatives were collected and washed with MeOH. The crude derivative **20** (18.1 mg or 97%) was recrystallized from EtOAc to separate 13.1 mg (70%) of the hydrazone **20** as yellow prisms: mp 163–164 °C; IR ($CHCl_3$) 3320 $cm^{-1}$ (NH); $^1H$ NMR ($CDCl_3$, 300 MHz) δ 11.05 (1 H, s, NH), 9.14 (1 H, d, $J$ = 2.4 Hz, aryl CH), 8.30 (1 H, d of d, $J$ = 2.4, 9.8 Hz, aryl CH), 8.00 (1 H, d, $J$ = 9.8 Hz), 0.9–3.0 (24 H, m, aliphatic CH including a *t*-Bu singlet at 1.02); mass spectrum, *m/e* (rel intensity) 338 ($M^+$, 100), 331 (68), 81 (33), 79 (34), 67 (35), 57 (54), 55 (35).

Anal. Calcd for $C_{20}H_{28}N_4O_4$: C, 61.84; H, 7.27; N, 14.42. Found: C, 61.85; H, 7.27; N, 14.38.

In examining this crystalline derivative **20**, we found one extraneous crystal, the (2,4-dinitrophenyl)hydrazone **22** as a yellow-orange rectangular prism, that was separated mechanically. This derivative **22** was evidently formed from a small amount of the ketone **5** that contaminated the HPLC fractions containing predominantly ketone **4**. This crystal of derivative **22**, mp 146–147 °C, was used as a seed crystal for a subsequently described experiment.

The crude derivative **23** (17.8 mg or 95%) was recrystallized from EtOAc to separate the hydrazone **23** as 14.0 mg (74%) of orange prisms: mp 157–158 °C; IR ($CHCl_3$) 3320 $cm^{-1}$ (NH); $^1H$ NMR ($CDCl_3$, 300 MHz) δ 11.18 (1 H, s, NH), 9.15 (1 H, d, $J$ = 2.5 Hz, aryl CH), 8.30 (1 H, d of d, $J$ = 2.5, 9.3 Hz, aryl CH), 8.00 (1 H, d, $J$ = 9.3 Hz, aryl CH), 2.52 (1 H, m, 765.1, 748.0 Hz, CHCO), 2.22 (2 H, m, 684.1, 672.9, 661.1, 655.8 Hz, CHCO), 1.1–2.2 (12 H, m, aliphatic CH), 0.98 (9 H, s, *t*-Bu); mass spectrum, *m/e* (rel intensity) 338 ($M^+$, 12), 149 (58), 129 (53), 97 (33), 83 (33), 81 (35), 71 (46), 69 (53), 67 (33), 57 (100), 55 (62), 43 (68), 41 (68), 40 (39).

Anal. Calcd for $C_{20}H_{28}N_4O_4$: C, 61.84; H, 7.27; N, 14.42. Found: C, 61.84; H, 7.30; N, 14.37.

**Preparation of (2,4-Dinitrophenyl)hydrazones 18 and 22.** A solution of 10.0 mg (0.052 mmol) of (2,4-dinitrophenyl)-hydrazine, 11.0 mg (0.050 mmol) of the ketone **3**, and 1 μL of aqueous 12 M HCl in 2 mL of MeOH was stirred at 25 °C for 45 min and then concentrated and filtered. The residue was washed with cold (0 °C) MeOH to leave 17.8 mg of the crude derivative **18**, mp 149–151 °C. Recrystallization from EtOAc separated 17.0 mg (92%) of the pure hydrazone **18** as yellow-orange needles: mp 154–155 °C; $^1H$ NMR ($CDCl_3$, 300 MHz) δ 11.1 (1 H, s, NH), 9.10 (1 H, d, $J$ = 2.5 Hz, aryl CH), 8.28 (1 H, dd, $J$ = 2.5, 9.5 Hz, aryl CH), 7.95 (1 H, d, $J$ = 9.5 Hz, aryl CH), 2.68 (2 H, m, 825.4, 807.9, 805.1, 800.9, 793.9 Hz, CHC=N), 0.8–2.5 (22 H, m, aliphatic CH including a *t*-Bu s at 0.96); mass spectrum, *m/e* (rel intensity) 388 ($M^+$, 25), 331 (36), 131 (22), 121 (26), 95 (30), 93 (25), 91 (27), 81 (38), 79 (33), 69 (27), 67 (39), 57 (100), 55 (38) 43 (23), 41 (70).

Anal. Calcd for $C_{20}H_{28}N_4O_4$: $M_r$, 388.2104. Found: $M_r$, 388.2161.

In another experiment, a solution of 10.0 mg (0.052 mmol) of (2,4-dinitrophenyl)hydrazine, 11.0 mg. (0.05 mmol) of a mixture (ca. 1:1) of ketones **3** and **5**, and 1 μL of aqueous 12 M HCl in 2.0 mL of MeOH was stirred at 25 for 1 h and then concentrated and filtered. After the residue had been washed with MeOH, the residual crude mixture of hydrazones **18** and **22** amounted to 18.1 mg (97%), mp 132–139 °C. Fraction crystallization from EtOAc employing the previously described hydrazone **18** as seed crystals separated 8.4 mg. (46%) of the hydrazone **18**, mp 154–155 °C.

The mother liquors from this fractional crystallization were concentrated and seeded to separate 5.1 mg (28%) of the hydrazone **22** as orange prisms, mp 147–148 °C; $^1H$ NMR ($CDCl_3$, 300 MHz) δ 11.1 (1 H, s, NH), 9.10 (1 H, d, $J$ = 2.5 Hz, aryl CH), 8.28 (1 H, dd, $J$ = 2.5, 9.5 Hz, aryl CH), 7.98 (1 H, d, $J$ = 9.5 Hz, aryl CH), 3.21 (1 Hz, m, 979.0, 970.9, 960.5, 952.3 Hz, CHC=N), 2.50 (1 H, d, $J$ = 16.8 Hz, CHC=N), 0.9–2.3 (19 H, m, aliphatic CH including a *t*-Bu singlet at 0.96); mass spectrum, *m/e* (rel intensity) 388 ($M^+$, 14), 331 (24), 252 (32), 91 (23), 79 (37), 78 (24), 77 (23), 73 (49), 67 (21), 57 (50), 55 (83), 43 (82), 42 (100), 41 (62), 39 (28).

Anal. Calcd. for $C_{20}H_{28}N_4O_4$: $M_r$, 388.2104. Found: $M_r$, 388.2132.

Mixtures of hydrazone **22** with each of the isomeric hydrazones **18**, **20**, and **23** exhibited depressed and broadened melting ranges. The hydrazones were separated by TLC analysis (silica gel coating with an ethyl acetate–hexane eluent, 1:4, v/v) and exhibited the following $R_f$ values: **18**, 0.32; **22**, 0.31; **20**, 0.28, **23**, 0.26. A crystal of the hydrazone **22** was used for X-ray crystallography.

**Preparation of Hydrazones 21 and 24.** Solutions of 18.1 mg (0.072 mmol) of $p$-$BrC_6H_4SO_2NHNH_2$ and 1 μL of HOAc in 5 mL of EtOH were treated with solutions of 15.0 mg (0.072 mmol) of one of the ketones **4** or **6** in 2 mL of EtOH. After the resulting solutions had been stirred at 25 °C for 1 h, they were concentrated and the derivatives were collected on a filter and washed with cold (0 °C) EtOH. The crude derivative **21** (24.1 mg or 77%, mp 141–145 °C) was recrystallized from MeOH to separate 21.0 mg (67%) of the hydrazone **21** as colorless prisms: mp 155–156 °C; IR ($CHCl_3$) 3360, 3300 $cm^{-1}$ (NH); $^1H$ NMR ($CDCl_3$, 300 MHz), δ 9.98 (1 H, s, NH), 7.6–7.8 (4 H, m, aryl CH), 2.55 (1 H, m, 764.3 Hz), 1.2–2.3 (14H, m, aliphatic CH), 0.86 (9 H, s, $t$-Bu).

Anal. Calcd for $C_{20}H_{29}BrN_2O_2S$: C, 54.41; H, 6.62; Br, 18.10; N, 6.35; S, 7.26. Found: C, 54.38; H, 6.62; Br, 18.13; N, 6.35; S, 7.22.

The crude derivative **24** (27.0 mg or 95%, mp 148–151 °C) was recrystallized from MeOH to separate 18.2 mg (56%) of the hydrazone **24** as colorless prisms: mp 152–153 °C; IR ($CHCl_3$) 3200 $cm^{-1}$ (NH); $^1H$ NMR ($CDCl_3$, 300 MHz) δ 7.5–7.8 (4 H, m, aryl CH), 3.24 (1 H, m, 970.8, 959.6 Hz), 2.40 (1 H, m, 730.6, 711.5 Hz), 1.0–2.2 (13 H, m, aliphatic CH), 0.87 (9 H, s, $t$-Bu).

Anal. Calcd for $C_{20}H_{29}BrN_2O_2S$: C, 54.41; H, 6.62; Br, 18.10; N, 6.35; S, 7.26. Found: C, 54.18; H, 6.62; Br, 18.03; N, 6.29; S, 7.15.

**Registry No.** **3**, 85283-13-2; **4**, 85283-14-3; **5**, 85283-15-4; **6**, 85283-16-5; **7**, 120-92-3; **8**, 57205-03-5; **9**, 1121-66-0; **10**, 24301-22-2; **11a**, 85283-17-6; **11b**, 85283-18-7; (*E*)-**12**, 85283-19-8; (*Z*)-**12**, 85283-20-1; (*E*)-**13**, 85283-21-2; (*Z*)-**13**, 85283-22-3; *cis*-**14**, 5365-37-7; *trans*-**14**, 5365-38-8; **15**, 85283-23-4; *cis*-**16**, 85283-24-5; *trans*-**16**, 85283-25-6; **18**, 85283-26-7; **20**, 85283-27-8; **21**, 85283-28-9; **22**, 85283-29-0; **23**, 85283-30-3; **24**, 85283-31-4; **25**, 85283-32-5; **26**, 85283-33-6; **27**, 85283-34-7; **28**, 15144-12-4; **29**, 85283-35-8; *cis*-**30**, 85283-36-9; *trans*-**30**, 85283-37-0; **31**, 594-56-9; **32**, 85283-38-1; **33**, 16112-10-0; *cis*-**34**, 85283-39-2; *trans*-**34**, 85283-40-5; **35**, 762-72-1; **36**, 17891-78-0; **37**, 85283-41-6; phenylselenyl chloride, 5707-04-0; trimethylsilyl chloride, 75-77-4; methyllithium, 917-54-4; pinacolone, 75-97-8.

**Supplementary Material Available:** Descriptions of determination of crystal structures for the ketone derivatives **11a** and **22**, including tables of atomic coordinates for each compound (8 pages). Ordering information is given on any current masthead page.

# Interhalogen-Catalyzed Cleavages of Ethers and Esters with Trimethylsilyl Bromide or Chloride

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The cleavages of various dialkyl ethers, trimethylsilyl alkyl ethers, and alkyl esters by trimethylsilyl bromide are strongly catalyzed by iodine monobromide. This catalyzed cleavage procedure using iodine monobromide makes possible synthetic applications for trimethylsilyl bromide which were previously ruled out by problems with its low reactivity. Cleavages of benzylic and tertiary alkyl ethers and esters by trimethylsilyl chloride are feasible when catalyzed by iodine monochloride. However, other systems are essentially unreactive toward trimethylsilyl chloride even in the presence of iodine monochloride.

We recently reported[1] that small amounts of molecular iodine catalyze the reactions of trimethylsilyl iodide with alkyl chlorides or bromides to give the corresponding alkyl iodides and trimethylsilyl chloride or bromide. The mechanism proposed[1] to explain the catalytic behavior involves initial formation of an alkyl(trimethylsilyl)halonium iodide species in an equilibrium process (Scheme I). The action of the catalyst is to shift this equilibrium to the right by formation of triiodide.

**Scheme I**

$$R\text{-}X + Me_3SiI \rightleftarrows R\text{-}X^+\text{-}SiMe_3 + I^-$$

$$I^- + I_2 \rightleftarrows I_3^-$$

$$R\text{-}X^+\text{-}SiMe_3 + I_3^- \xrightarrow[\text{or } S_N2]{S_N1} R\text{-}I + XSiMe_3 + I_2$$

The present paper reports a brief study of the application of the molecular halogen catalysis to the cleavage of ethers and esters with trimethylsilyl bromide or chloride.[2]

It was envisioned that the halogen catalysis with the ethers and esters would be similar to that given in Scheme I, except involving a (trimethylsilyl)oxonium intermediate. In earlier investigations[3] of uncatalyzed cleavages of ethers and esters with trimethylsilyl bromide, only low to no reactivity was exhibited, depending on the specific substrate being examined.

## Results and Discussion

**Halogen Catalysis of Cleavages with Trimethylsilyl Bromide.** Small-scale reactions of trimethylsilyl bromide with selected ethers and esters were initially carried out to determine if their catalysis by halogens was actually possible. Also, it was of considerable interest to determine

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