(CCl_4) δ 4.28 and 7.45-8.01; mass spectrum *m/e* 270, 268 (M^+), and 189. Anal. Calcd for $C_{15}H_9Br$: C, 66.94; H, 3.37. Found: C, 66.66; H, 3.23.

4-Bromo-4*H*-cyclopenta[*def*]phenanthrene (8). (a). A mixture of 1 (950 mg, 5 mmol) and *N*-bromosuccinimide (890 mg, 5 mmol) in benzene (20 mL) was refluxed for 5 h to afford 1.19 g (89%) of 8: mp 130–132 °C dec (from hexane); NMR (CCl_4) δ 6.25 (1 H, s, CH) and 7.39–7.82 (8 H, m, Ar–H); mass spectrum *m/e* 270, 268 (M^+), and 189. Anal. Calcd for $C_{15}H_9Br$: C, 66.94; H, 3.37. Found: C, 66.67; H, 3.39.

(b). A solution of 4*H*-cyclopenta[*def*]phenanthren-4-ol (9) (600 mg, 2.9 mmol) in HOAc (60 mL) was treated with HBr at 20–23 °C for 1 h to yield 490 mg (63%) of 8 as sublimate and 15 mg (3%) of 4,4′-bis(4*H*-cyclopenta[*def*]phenanthrene) (17): mp 232–233 °C dec (from HOAc) as sublimation residue; NMR of 17 (C_6D_6) δ 5.44 (2 H, s) and 6.99–7.70 (16 H, m). Anal. Calcd for $C_{30}H_{18}$: C, 95.21; H, 4.79. Found: C, 95.22; H, 4.73.

Synthesis and Reactions of 8,9-Dibromo-8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (11). (a). A mixture of 1 (380 mg, 2 mmol) and Br_2 (0.1 mL, 2 mmol) in CCl_4 (4 mL) was placed in a Pyrex test tube and irradiated with a 40-W fluorescent lamp from a distance of 150 cm for 30 s, and then HBr was removed in vacuo. The NMR spectrum of the resulting mixture showed 1 (58%), 8 (8%), and 11 (34%).

Petroleum ether (bp 60–70 °C, 5 mL) was added to the resulting mixture which was cooled at −20 °C to precipitate 125 mg (18%) of 11 as yellowish needles: mp 86 °C dec; NMR (CCl_4) δ 3.90 (2 H, s, CH_2), 5.83 (2 H, s, CH), and 7.22–7.40 (6 H, m, Ar–H); mass spectrum *m/e* 352, 350, 348 (M^+), 270, 268, and 189.

(b). Bromide 11 (80 mg, 0.23 mmol) was heated in a test tube at 90 °C for 15 min to afford 51 mg (83%) of 6, mp 98–99 °C.

(c). A solution of 11 (80 mg) in $CHCl_3$ (5 mL) was stirred with one drop of concentrated H_2SO_4 for 1 min at room temperature to afford 46 mg (75%) of 6. Similarly, treatments of 11 (80 mg) with I_2 (1 mg) and with $AlCl_3$ (1 mg) gave 6 in yields of 53 mg (86%) and 55 mg (89%), respectively.

(d). A solution of 11 (80 mg) in $CHCl_3$ (5 mL) was placed in a Pyrex test tube and irradiated with a 100-W high-pressure mercury lamp for 1 h giving 48 mg (78%) of 8.

Bromination of 8,9-Dihydro-4*H*-cyclopenta[*def*]phenanthrene (2). A solution of Br_2 (0.85 mL, 16.5 mmol) in CCl_4 (30 mL) was added to a solution of 2 (2.88 g, 15 mmol) in CCl_4 (40 mL) with stirring in the dark at 0 °C for 30 min. After being stirred for an additional 2 h, the resulting mixture was treated with aqueous $NaHSO_3$ (1%) and benzene. The organic layer was chromatographed on silica gel, the eluate was evaporated to dryness, and the residue was sublimed in vacuo at 100 °C to give 3.26 g (83%) of 12, mp 93–94 °C.

The residual part was recrystallized from cyclohexane giving 400 mg (8%) of 2,6-dibromo-8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (18): mp 183–184 °C; NMR (C_6D_6) δ 2.44 (4 H, s), 3.11 (2 H, s), 7.02 (2 H, s), and 7.16 (2 H, s); mass spectrum *m/e* 352, 350, 348 (M^+), 271, and 269. Anal. Calcd for $C_{15}H_{10}Br_2$: C, 51.46; H, 2.88. Found: C, 51.76; H, 3.02.

A mixture of 12 (820 mg, 3 mmol) and chloranil (2.0 g) in xylene (30 mL) was refluxed for 45 h to afford 716 mg (88%) of 7, mp 91–92 °C.

Bromination of Cyclopenta[*def*]phenanthren-4-one (3). A solution of 3 (4.00 g, 19.6 mmol) and Br_2 (2.1 mL, 40 mmol) in $CHCl_3$ (240 mL) was stirred for 48 h at room temperature, giving 3.58 g (65%) of 8-bromocyclopenta[*def*]phenanthren-4-one (13), mp 214–215 °C.

1-Bromocyclopenta[*def*]phenanthren-4-one (14). A solution of 4 (135 mg, 0.5 mmol) in benzene (15 mL) was refluxed with activated MnO_2 (5.0 g) for 1 h to give 112 mg (79%) of 14: mp 178–179 °C (from HOEt); IR 1723 cm^{-1} (C=O); mass spectrum *m/e* 284, 282 (M^+), and 203. Anal. Calcd for $C_{15}H_7OBr$: C, 63.63; H, 2.50. Found: C, 63.46; H, 2.37.

2-Bromocyclopenta[*def*]phenanthren-4-one (15) was prepared from 7 in a 59% yield: mp 190.0–190.5 °C (from HOEt); IR 1719 cm^{-1} (C=O); mass spectrum *m/e* 284, 282 (M^+), and 203. Anal. Found: C, 63.89; H, 2.31.

3-Bromocyclopenta[*def*]phenanthren-4-one (16) was also obtained from 5 in a 55% yield: mp 172–173 °C (from HOEt); IR 1714 cm^{-1} (C=O); mass spectrum *m/e* 284, 282 (M^+), and 203. Anal. Found: C, 63.66; H, 2.26.

Registry No. 1, 203-64-5; 2, 27410-55-5; 3, 5737-13-3; 4, 70659-36-8; 5, 70659-37-9; 6, 70659-38-0; 7, 70659-39-1; 8, 70659-40-4; 9, 64884-42-0; 10, 26687-67-2; 11, 70659-41-5; 12, 70659-42-6; 13, 70659-43-7; 14, 70659-44-8; 15, 70659-45-9; 16, 70659-46-0; 17, 70659-47-1; 18, 70659-48-2; 4*H*-cyclopenta[*def*]phenanthren-3-amine HBr, 70659-49-3; 4*H*-cyclopenta[*def*]phenanthren-1-amine, 69706-35-0; 4*H*-cyclopenta[*def*]phenanthren-2-amine, 69706-40-7; 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthren-2-amine, 69706-52-1; 9-bromophenanthrene-4-carboxylic acid, 70659-50-6.

Perhydroazulenes. 2. The 2-*tert*-Butylperhydroazulen-4-one System[1,2]

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After conjugate addition of an allyl group to the enone 5, subsequent hydrobromination and base-induced cyclization formed the cis (1) and trans (2) isomers of the 2-*tert*-butylperhydroazulen-4-one system. Each of these ketones was converted to an appropriate solid derivative, and the structures and conformations of these solid derivatives were established by X-ray crystallography.

Since earlier study[2,3] had developed a route allowing the efficient synthesis of perhydroazulene derivatives, we have been encouraged to prepare several sets of perhydroazulene derivatives with *tert*-butyl or other sterically bulky substituents at selected positions. It is our hope that these perhydroazulene derivatives with bulky substituents will be conformationally homogeneous so that further addition or substitution reactions involving the perhydroazulene ring can be effected with predictable stereochemical outcome. In this paper, we describe the synthesis of the cis (1) and trans (2) isomers (Scheme I) of a 2-*tert*-butylperhydroazulene system and offer evidence concerning the favored conformations of these compounds.

The enone 5 required as a starting material for this synthesis was obtained by the ozonolysis–aldol condensation sequence illustrated in Scheme I. Although this sequence could be run on a sufficient scale to provide adequate amounts of the starting enone 5, the aldol condensation step 4 → 5 formed a relatively complex

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

(2) For the previous paper in this series, see H. O. House, T. S. B. Sayer, and C. C. Yau, *J. Org. Chem.*, **43**, 2153 (1978).

(3) (a) H. O. House, W. V. Phillips, T. S. B. Sayer, and C. C. Yau, *J. Org. Chem.*, **43**, 700 (1978); (b) H. O. House and W. V. Phillips, *ibid.*, **43**, 3851 (1978).

0022-3263/79/1944-3031$01.00/0

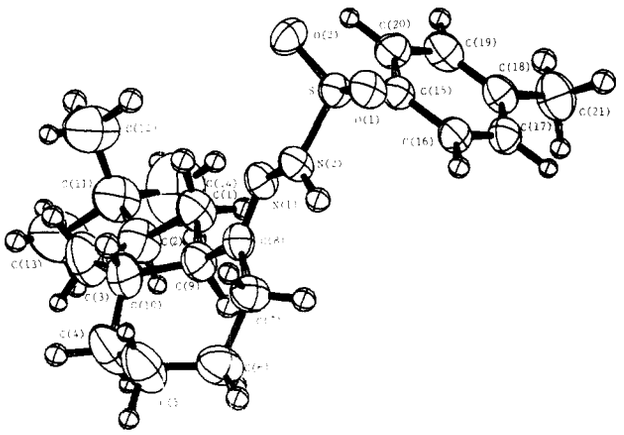


Figure 1. Perspective view of the molecular structure of the trans ketone tosylhydrazone 11 (for clarity, the H atom thermal parameters have been reduced).

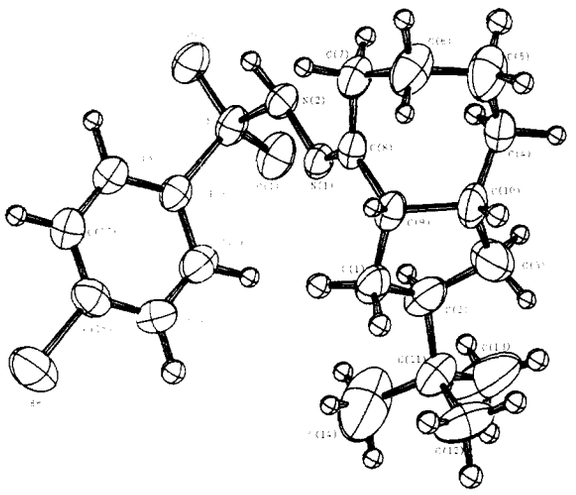


Figure 2. Perspective view of the molecular structure of the cis ketone (*p*-Bromophenyl)sulfonylhydrazone 12. (for clarity, the H atom thermal parameters have been reduced.

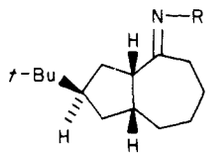
mixture from which the desired enone **5** had to be isolated by liquid chromatography. Our efforts to improve this aldol condensation step have not been fruitful thus far.

The remaining steps, patterned after the synthesis of the parent ketone,[2] proceeded very efficiently to form the mixture of cis and trans ketones **1** and **2**. Since the basic conditions involved in the final cyclization step could interconvert the two ketones **1** and **2**, we did not seek to separate the mixtures of epimeric unsaturated ketones **8** and bromo ketones **9**. It was of interest that reaction of the allylsilane **7** with the enone **5** in the presence of $TiCl_4$[4] produced significant amounts of only two of the four possible diastereoisomers of the unsaturated ketone **8** in which the allyl group was introduced trans to the bulky *tert*-butyl group.

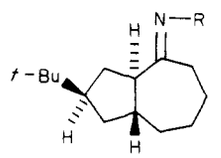
An equilibrium mixture of the two ketones **1** and **2** in MeOH–PhH (1:1 (v/v)) at 25.0 °C contained 88.9% of the trans isomer **2** and 11.1% of the cis ketone **1** corresponding to an equilibrium constant at 25 °C of 8.01 (or $\Delta G = -1.23$ kcal/mol) for the equilibrium **1** ⇄ **2**. The structure and stereochemistry of each ketone was established by X-ray crystallography on an appropriate derivative. The structure of the trans ketone tosylhydrazone **11** (Chart I) is presented in Figure 1 and the bond lengths and angles

(4) (a) A. Hosomi and H. Sakurai, *J. Am. Chem. Soc.*, **99**, 1673 (1977); (b) *Tetrahedron Lett.*, 4041 (1977); (c) *ibid.*, 2589 (1978); (d) A. Hosomi, A. Shirahata, and H. Sakurai, *ibid.*, 3043 (1978); (e) A. Hosomi, M. Endo, and H. Sakurai, *Chem. Lett.*, 499 (1978).

Chart I



10, R = $NHSO_2C_6H_4CH_3$-*p*
12, R = $NHSO_2C_6H_4Br$-*p*



11, R = $NHSO_2C_6H_4CH_3$-*p*
13, R = $NHSO_2C_6H_4Br$-*p*
14, R = OH

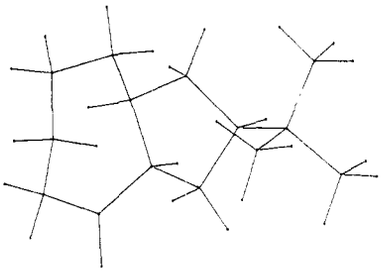


Figure 3. MMI energy-minimized conformation of the trans ketone **2** (calculated steric energy 24.0 kcal/mol).

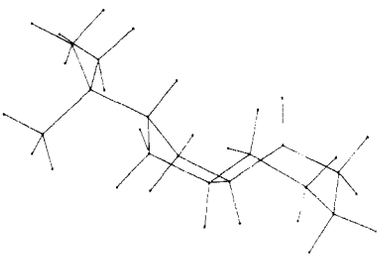


Figure 4. MMI energy-minimized conformation of the cis ketone **1** (calculated steric energy 25.7 kcal/mol).

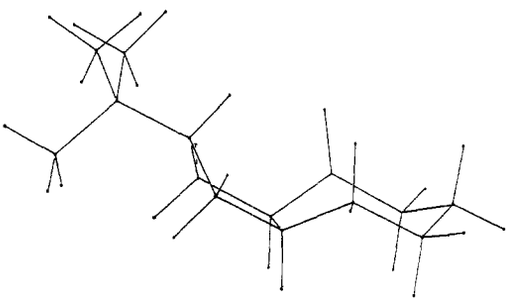


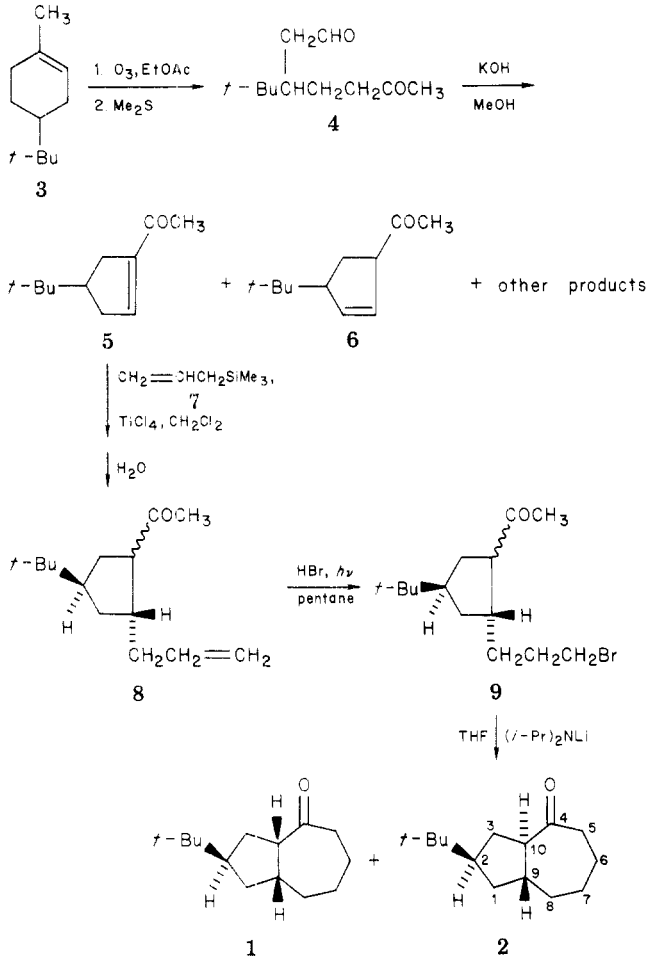
Figure 5. MMI energy-minimized conformation of the cis ketone **1** (calculated steric energy 25.2 kcal/mol).

are provided in Table I. The structure of the cis ketone (*p*-bromophenyl)sulfonylhydrazone **12** is presented in Figure 2 with the corresponding bond lengths and angles listed in Table II.

To obtain evidence concerning whether the conformations of the hydrazones **11** and **12** in the solid state (determined by X-ray crystallography) are also the favored conformations of the corresponding ketones **2** and **1** in solution, we have used the molecular mechanics program of Allinger and co-workers[5] to calculate the steric energies

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

Scheme I



for various conformations of the ketones **1** and **2**. Employing either atomic coordinates derived from models of the trans ketone **2** or coordinates derived from crystallographic data for the trans ketone derivative **11**, we obtained essentially the same minimum energy conformation. This conformation, illustrated in Figure 3,[6] incorporates a twist-chair conformation of the seven-membered ring and has a calculated steric energy of 24.0 kcal/mol. Similar calculations employing either the model coordinates of the cis ketone **1** or crystallographic coordinates of the cis ketone derivative **12** led to a conformer, illustrated in Figure 4,[6] with the seven-membered ring in a twist-boat conformation and a calculated steric energy at 25.7 kcal/mol. A second conformation of the cis ketone **1**, illustrated in Figure 5, with very similar calculated steric energy (25.2 kcal/mol) was also found by employing model coordinates. This conformation (Figure 5) with the seven-membered ring in a chair conformation has a slightly lower calculated steric energy than the conformation actually present (Figure 4) in the crystalline derivative **12**. It will be noted that the difference in calculated steric energies (1.2–1.7 kcal/mol) for the trans ketone **2** (Figure 3) and either of the conformers of the cis ketone **1** (Figures 4 and 5) is in reasonable agreement with the difference in energy for the two ketones (1.23 kcal/mol) derived from equilibration studies.

(6) The plots in these figures are modified ORTEP plots performed on a Calcomp plotter with the CDC Cyber 74 system. The coordinates for these plots were either the final atomic coordinates calculated by the MMI program[5] after energy minimization or the atomic coordinates derived from the X-ray crystal structure determination.

Table I. Molecular Geometry of the Tosylhydrazone 11[a]

A. Bond Lengths (Å)

S-O_1	1.434 (2)	C_6-C_7	1.534 (4)
S-O_2	1.422 (2)	C_7-C_8	1.502 (3)
S-N_2	1.629 (2)	C_8-C_9	1.514 (3)
S-C_{15}	1.760 (2)	C_9-C_{10}	1.548 (4)
N_1-N_2	1.405 (2)	C_{11}-C_{12}	1.525 (6)
N_1-C_8	1.282 (3)	C_{11}-C_{13}	1.549 (5)
C_1-C_2	1.531 (3)	C_{11}-C_{14}	1.514 (6)
C_1-C_9	1.520 (4)	C_{15}-C_{16}	1.388 (3)
C_2-C_3	1.524 (5)	C_{15}-C_{20}	1.386 (3)
C_2-C_{11}	1.529 (4)	C_{16}-C_{17}	1.378 (3)
C_3-C_{10}	1.538 (4)	C_{17}-C_{18}	1.387 (3)
C_4-C_5	1.532 (4)	C_{18}-C_{19}	1.386 (4)
C_4-C_{10}	1.531 (4)	C_{18}-C_{21}	1.520 (4)
C_5-C_6	1.511 (5)	C_{19}-C_{20}	1.385 (4)

B. Bond Angles (deg)

S-N_2-N_1	116.3 (1)	C_3-C_2-C_{11}	116.4 (3)
S-C_{15}-C_{16}	119.2 (2)	C_3-C_{10}-C_4	112.0 (3)
S-C_{15}-C_{20}	120.0 (2)	C_3-C_{10}-C_9	104.6 (2)
O_1-S-O_2	119.6 (1)	C_4-C_5-C_6	115.4 (3)
O_1-S-N_2	103.4 (1)	C_4-C_{10}-C_9	113.8 (3)
O_1-S-C_{15}	108.6 (1)	C_5-C_4-C_{10}	114.1 (3)
O_2-S-N_2	109.2 (1)	C_5-C_6-C_7	114.4 (3)
O_2-S-C_{15}	107.7 (1)	C_6-C_7-C_8	118.0 (2)
N_1-C_8-C_7	123.6 (2)	C_7-C_8-C_9	118.8 (2)
N_1-C_8-C_9	117.6 (2)	C_8-C_9-C_{10}	112.4 (2)
N_2-S-C_{15}	107.9 (1)	C_{12}-C_{11}-C_{13}	107.8 (3)
N_2-N_1-C_8	115.3 (2)	C_{12}-C_{11}-C_{14}	108.3 (4)
C_1-C_2-C_3	101.7 (2)	C_{13}-C_{11}-C_{14}	110.0 (4)
C_1-C_2-C_{11}	118.1 (3)	C_{15}-C_{16}-C_{17}	119.0 (2)
C_1-C_9-C_8	117.4 (2)	C_{15}-C_{20}-C_{19}	119.3 (2)
C_1-C_9-C_{10}	103.3 (2)	C_{16}-C_{15}-C_{20}	120.7 (2)
C_2-C_1-C_9	102.4 (2)	C_{16}-C_{17}-C_{18}	121.2 (2)
C_2-C_3-C_{10}	107.0 (2)	C_{17}-C_{18}-C_{19}	119.0 (2)
C_2-C_{11}-C_{12}	112.6 (3)	C_{17}-C_{18}-C_{21}	119.6 (2)
C_2-C_{11}-C_{13}	109.6 (3)	C_{18}-C_{19}-C_{20}	120.7 (2)
C_2-C_{11}-C_{14}	108.5 (3)	C_{19}-C_{18}-C_{21}	121.4 (2)

[a] Numbers in parentheses indicate estimated standard deviations in the least significant digit.

Preliminary study of the ^{13}C NMR spectra of the two ketones **1** and **2** has failed to provide evidence for the presence of two conformations of either ketone. Thus, neither the spectra of the trans ketone **2** at +35 or at −46 °C nor the spectra of the cis ketone **1** at +35 or at −56 °C provided any indication of the presence of two conformers. We are continuing our study of the ^{13}C NMR spectra of these and other perhydroazulene ketones in an effort to obtain more definitive information on this point. Meanwhile, our present data indicate that Figure 3 is a good conformational representation for the trans ketone **2** and that Figure 4 and, perhaps, Figure 5 are good conformational representations of the cis ketone **1**.[7]

Experimental Section[8]

Preparation of the Enone 5. Previously described procedures[9] were used to convert 4-*tert*-butylcyclohexanone to the olefin **3**: bp 70–73 °C (9–11 mm) [lit.[9] bp 71–72 °C (9 mm)]; $n^{25}D$

(7) For an earlier discussion of conformational analysis in perhydroazulene systems, see J. B. Hendrickson, *Tetrahedron*, **19**, 1387 (1963).

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

(9) H. O. House and M. J. Umen, *J. Org. Chem.*, **38**, 1000 (1973).

Table II. Molecular Geometry of the (*p*-Bromophenyl)sulfonylhydrazone 12[a]

A. Bond Lengths (Å)

$Br-C_{15}$	1.895 (5)	C_5-C_6	1.535 (7)
$S-O_1$	1.417 (3)	C_6-C_7	1.522 (6)
$S-O_2$	1.438 (3)	C_7-C_8	1.507 (6)
$S-N_2$	1.645 (3)	C_8-C_9	1.506 (6)
$S-C_{15}$	1.762 (4)	C_9-C_{10}	1.563 (6)
N_1-N_2	1.430 (4)	$C_{11}-C_{12}$	1.506 (7)
N_1-C_8	1.276 (5)	$C_{11}-C_{13}$	1.507 (8)
C_1-C_2	1.523 (6)	$C_{11}-C_{14}$	1.505 (8)
C_1-C_9	1.525 (6)	$C_{15}-C_{16}$	1.381 (6)
C_2-C_3	1.518 (8)	$C_{15}-C_{20}$	1.393 (6)
C_2-C_{11}	1.544 (7)	$C_{16}-C_{17}$	1.381 (6)
C_3-C_{10}	1.514 (8)	$C_{17}-C_{18}$	1.373 (6)
C_4-C_5	1.530 (7)	$C_{18}-C_{19}$	1.372 (6)
C_4-C_{10}	1.521 (6)	$C_{19}-C_{20}$	1.388 (6)

B. Bond Angles (deg)

$S-N_2-N1$	111.1 (3)	$C_3-C_{10}-C_4$	112.5 (5)
$S-C_{15}-C_{16}$	120.0 (3)	$C_3-C_{10}-C_9$	105.5 (4)
$S-C_{15}-C_{20}$	118.9 (4)	$C_4-C_5-C_6$	114.9 (5)
O_1-S-O_2	119.7 (2)	$C_4-C_{10}-C_9$	115.3 (4)
O_1-S-N_2	109.2 (2)	$C_5-C_4-C_{10}$	116.0 (5)
O_2-S-N_2	104.0 (2)	$C_5-C_6-C_7$	113.5 (4)
O_1-S-C_{15}	108.1 (2)	$C_6-C_7-C_8$	114.6 (4)
O_2-S-C_{15}	108.8 (2)	$C_7-C_8-C_9$	118.8 (4)
N_2-S-C_{15}	106.2 (2)	$C_8-C_9-C_{10}$	112.0 (4)
$C_1-C_2-C_3$	103.2 (5)	$C_{12}-C_{11}-C_{13}$	108.5 (5)
$C_1-C_2-C_{11}$	116.0 (4)	$C_{12}-C_{11}-C_{14}$	108.1 (6)
$C_1-C_9-C_8$	115.6 (4)	$C_{13}-C_{11}-C_{14}$	107.8 (7)
$C_1-C_9-C_{10}$	103.8 (4)	$C_{15}-C_{16}-C_{17}$	119.5 (4)
$C_2-C_1-C_9$	105.8 (4)	$C_{15}-C_{20}-C_{19}$	119.0 (5)
$C_2-C_3-C_{10}$	109.2 (5)	$C_{16}-C_{15}-C_{20}$	120.9 (4)
$C_2-C_{11}-C_{12}$	113.0 (4)	$C_{16}-C_{17}-C_{18}$	119.3 (5)
$C_2-C_{11}-C_{13}$	110.5 (5)	$C_{17}-C_{18}-C_{19}$	121.9 (4)
$C_2-C_{11}-C_{14}$	108.7 (5)	$C_{18}-C_{19}-C_{20}$	119.3 (4)
$C_3-C_2-C_{11}$	114.6 (4)		

[a] Numbers in parentheses indicate estimated standard deviations in the least significant digit.

1.4581–1.4583 (lit.[9] n^{25}_D 1.4588). A stream of O_3 and O_2 was passed through a cold (−72 °C) solution of 24.1 g (160 mmol) of the olefin **3** in 480 mL of EtOAc for 2.75 h at which time GLPC analysis of an aliquot of the reaction mixture indicated that all the olefin had been consumed. The excess O_3 was removed by passing a stream of oxygen through the solution for 10 min. Then the peroxidic components were reduced by adding 100 mL of Me_2S to the cold solution, dropwise and with stirring during 20 min. The resulting mixture was washed with aqueous KI and then dried and concentrated to leave 28.23 g of the crude keto aldehyde **4** as a viscous yellow liquid: IR (CCl_4) 2810, 2700 (aldehyde CH), 1720 (C=O), 1370 (CH_3CO) cm^{-1}. Since attempts to distill this crude product led to a rather complex mixture of products, the crude product was treated with base without further purification. A solution of 20.6 g (100 mmol) of the crude keto aldehyde in 60 mL of MeOH was mixed with a solution of 20 g of KOH in 340 mL of H_2O, and the resulting mixture was stirred at 25 °C for 17 h under an argon atmosphere. The resulting mixture was extracted with pentane, and the organic extract was washed with aqueous NaCl and then dried and concentrated. The residual crude liquid (9.79 g) was distilled to separate 5.005 g of distillate (bp 68–75 °C (0.8 mm)) that contained (GLPC, FFAP on Chromosorb P) the desired enone **5** (retention time 4.2 min) accompanied by several minor impurities. This material was chromatographed on silica gel with an Et_2O–hexane eluent (1:4 (v/v)) to separate 3.098 g of material containing (GLPC) the enone **5** (4.4 min) accompanied by one minor impurity (5.5 min) thought to be the unconjugated isomer **6**. Distillation of this fraction afforded 2.67 g of colorless liquid (bp 69–69.5 °C (0.9 mm), n^{25}_D 1.4721) with the same composition. A collected (GLPC) sample of the pure enone **5** was obtained as a colorless liquid: n^{25}_D 1.4732; IR (CCl_4) 1672 (conjugated C=O), 1620 (conjugated C=C) cm^{-1}; UV λ_{max} (95% EtOH) 249 (ϵ 10 900), 318 nm (ϵ 65); NMR (CCl_4) δ 6.4–6.6 (1 H, m, vinyl CH), 2.1–2.7 (8 H, m, aliphatic CH including a CH_3CO singlet at δ 2.20), 0.89 (9 H, s, *t*-Bu); mass spectrum *m/e* (relative intensity) 166 (M^+, 3), 151 (24), 110 (43), 109 (100), 95 (27), 67 (31), 65 (20), 57 (63), 43 (87), 41 (44).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.92. Found: C, 79.29; H, 10.96.

Preparation of the Unsaturated Ketone 8. A cold (−73 °C) solution of 2.67 g (16.1 mmol) of the enone **5** in 56 mL of CH_2Cl_2 was treated with 3.67 g (19.3 mmol) of $TiCl_4$, and then a solution of 2.63 g (23 mmol) of the silane **7** in 40 mL of CH_2Cl_2 was added, dropwise and with stirring during 85 min while the temperature of the solution was maintained at −71 to −73 °C. After the resulting dark purple solution had been stirred at −71 to −73 °C for 30 min, 30 mL of H_2O was added, dropwise and with stirring during 20 min, and then the solution was allowed to warm to room temperature. During this warming the color of the solution changed from purple to orange (ca. −50 °C) to pale yellow (ca. −30 °C). The reaction mixture was partitioned between Et_2O and aqueous NaCl, and the organic layer was dried and concentrated to leave 3.583 g of pale yellow liquid that contained (GLPC, UNCON 50HB 280X on Chromosorb P) the unsaturated ketone **8** (retention time 10.9 min, epimers not resolved) accompanied by several minor impurities (6.7, 7.3, 8.9, 27.5 min). The crude product was distilled in a short-path still and then chromatographed on silica gel with an Et_2O–hexane eluent (7:93 (v/v)) to separate 418 mg of early fractions containing an unidentified impurity, 37 mg of an intermediate fraction, and 3.069 g (92%) of the ketone **8**. Distillation of this last material afforded 2.172 g of the ketone **8**: bp 71–72 °C (0.25 mm); n^{25}_D 1.4625. A portion of this material was rechromatographed and distilled in a short-path still to separate the pure ketone **8** (a mixture of epimers) as a colorless liquid: n^{25}_D 1.4622; IR (CCl_4) 1712 (C=O), 1640 (C=C), 912 (CH=CH_2) cm^{-1}; NMR (CCl_4) δ 4.7–6.0 (3 H, m, vinyl CH), 1.0–2.4 [12 H, m, aliphatic CH including two CH_3CO singlets for the two stereoisomers at δ 2.06 (major) and 2.10 (minor)], 0.82 and 0.83 (2 s, 9 H, *t*-Bu signals of two stereoisomers); mass spectrum *m/e* (relative intensity) 208 (M^+, 16), 152 (22), 151 (37), 123 (29), 111 (84), 109 (45), 93 (22), 83 (20), 71 (40), 67 (26), 57 (76), 43 (100), 41 (36).

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

Preparation of the Bromo Ketone 9. Following previously described general procedures,[2,3] a stream of anhydrous HBr was passed through a solution of 1.00 g (4.81 mmol) of the unsaturated ketone **8** in 300 mL of anhydrous pentane for 6 min while the solution was irradiated with the light from a Hanovia 450-W medium-pressure Hg lamp. After the resulting solution had been washed successively with aqueous $Na_2S_2O_3$ and with aqueous $NaHCO_3$ and then concentrated, the residual liquid (1.67 g) was distilled in a short-path still to separate 1.123 g (81%) of the bromo ketone **9**: bp 101–105 °C (0.03 mm); n^{25}_D 1.4872–1.4875. This material was chromatographed on silica gel with an Et_2O–hexane eluent (3:7 (v/v)) and redistilled to separate the pure bromo ketone **9** (a mixture of stereoisomers) as a colorless liquid: n^{25}_D 1.4870; IR (CCl_4) 1715 (C=O) cm^{-1}; NMR (CCl_4) δ 3.36 (2 H, t, J = 6 Hz, $BrCH_2$), 1.0–2.7 (14 H, m, aliphatic CH including a CH_3CO singlet at 2.09), 0.83 (9 H, s, *t*-Bu); mass spectrum *m/e* (relative intensity) 290 (M^+, 3), 288 (M^+, 3), 193 (28), 191 (30), 167 (39), 71 (37), 57 (83), 43 (100), 41 (32).

Anal. Calcd for $C_{14}H_{25}BrO$: C, 58.13; H, 8.71; Br, 27.62. Found: C, 58.16; H, 8.71; Br, 27.63.

Cyclization of the Bromo Ketone 9. To a cold (−72 °C) solution of 4.2 mmol of *i*-Pr_2NLi in 8.2 mL of hexane and 40 mL of THF was added, dropwise and with stirring during 10 min, a solution of 894 mg (3.09 mmol) of the bromo ketone **9** in 10 mL of THF. The resulting solution was warmed to boiling during 8 min and then refluxed for 1 h. After the mixture had been partitioned between Et_2O and aqueous NH_4Cl, the organic layer was washed with aqueous NaCl, dried, and concentrated. An 8.7-mg aliquot of the residual crude liquid (634 mg) was mixed with a known weight of *n*-$C_{20}H_{42}$ for GLPC analysis (FFAP on Chromosorb P, apparatus calibrated with known mixtures). The sample contained (GLPC) the cis ketone **1** (retention time 18.5 min), the trans ketone **2** (20.8 min, total yield of **1** + **2**, 78%), *n*-$C_{20}H_{42}$ (32.2 min), the unsaturated ketone **8** (6.5 min, 2% yield), and several minor unidentified components (3.5, 4.4, 13.3 min). The crude point was distilled in a short-path still and a 559-mg aliquot of the distillate (570 mg) was chromatographed on silica gel with an Et_2O–hexane eluent (8:92 (v/v)). After separation

of fractions containing more rapidly eluted impurities, subsequent fractions contained 151 mg (24%) of the cis ketone **1** followed by 305 mg (48%) of the trans ketone **2**. Distillation of appropriate fractions in a short-path still afforded the trans ketone **2** as a colorless liquid (n^{25}_D 1.4818) that solidified on cooling: mp 26.3–27.2 °C; IR (CCl_4) 1700 (C=O) cm^{-1}; UV λ_{max} (95% EtOH) 282 nm (ϵ 37); ^1H NMR (CCl_4) δ 1.0–2.9 (15 H, m, aliphatic CH), 0.83 (9 H, s, *t*-Bu); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 213.0 (s), 58.1 (d), 47.9 (d), 43.8 (t), 43.0 (d), 37.9 (t), 34.9 (t), 31.9 (s), 30.1 (t), 29.0 (t), 27.2 (q, 3 C atoms), 23.4 (t) ppm; mass spectrum *m/e* (relative intensity) 208 (M^+, 8), 152 (13), 151 (13), 111 (100), 67 (12), 57 (34), 55 (10), 41 (16). When the ^{13}C NMR spectrum was redetermined in $CDCl_3$ at −46 °C, no broadening or appearance of additional peaks was observed. At −46 °C, the peak positions were 215.1, 57.9, 47.7, 43.6, 42.3, 37.9, 34.3, 31.8, 29.7, 28.8, 27.2, and 23.1 ppm.

Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.80; H, 11.70.

Appropriate fractions were distilled in a short-path still to separate the cis ketone **1** as a colorless liquid (n^{25}_D 1.4818), that solidified on cooling: mp 29.1–29.3 °C; IR (CCl_4) 1705 (C=O) cm^{-1}; UV λ_{max} (95% EtOH) 285 nm (ϵ 26); ^1H NMR, δ 2.7–3.3 (1 H, m, CHCO), 1.0–2.7 (14 H, m, aliphatic CH), 0.85 (9 H, s, *t*-Bu); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 212.5 (s), 55.4 (d), 47.7 (d), 43.3 (t), 40.6 (d), 37.3 (t), 33.7 (t), 31.6 (s), 29.0 (t), 27.5 (q, 3 C atoms), 26.7 (t), 25.5 (t) ppm; mass spectrum *m/e* (relative intensity) 208 (M^+, 8), 151 (12), 111 (100), 67 (15), 57 (30), 55 (11), 41 (18). When the ^{13}C NMR spectrum was redetermined in $CDCl_3$ at −56 °C, no broadening or appearance of additional peaks was observed. At −56 °C, the peak positions were 215.1, 55.8, 47.0, 43.3, 40.5, 37.3, 33.4, 31.7, 29.5, 27.2, 26.1, and 25.3 ppm.

Anal. Calcd for $C_{14}H_{20}O$: C, 80.71; H, 11.61. Found: C, 80.75; H, 11.67.

A solution of 15.2 mg (0.073 mmol) of the cis ketone **1** and 8.1 mg of *n*-$C_{20}H_{42}$ (an internal standard) in 1.5 mL of PhH was mixed with 1.5 mL of a MeOH solution containing 0.15 mmol of NaOMe and stored in bath at 25.0 °C. Aliquots were removed periodically for GLPC analysis (10% FFAP on Chromosorb P, apparatus calibrated with known mixtures); the retention times were as follows: cis ketone **1**, 14.5 min; trans ketone **2**, 16.3 min; *n*-$C_{20}H_{42}$, 21.0 min. The composition of the mixture became constant after 4 h and contained 11.0% of **1** and 89.0% of **2** (98% recovery of **1** + **2**). Two comparable experiments were performed with mixtures prepared from 15.3 mg (0.074 mmol) of the trans ketone **2**, 8.4 mg of *n*-$C_{20}H_{42}$, 1.5 mL of PhH, and 1.5 mL of 0.1 M NaOMe in MeOH and from 11.9 mg (0.057 mmol) of **2**, 11.0 mg of *n*-$C_{20}H_{42}$, 2.0 mL of PhH, and 2.0 mL of 0.1 M NaOMe in MeOH. The composition of these mixtures became constant after 1–2 h; the mixtures contained 11.1% of **1** and 88.9% of **2** (98–99% recovery of **1** + **2**). Thus, the equilibrium composition at 25.0 °C in PhH–MeOH (1:1 (v/v)) is 11.1 ± 0.3% of the cis ketone **1** and 88.9 ± 0.3% of the trans ketone **2**.

Preparation of the Oxime 14. A solution of 51.9 mg (0.25 mmol) of the trans ketone **2** in 0.75 mL of EtOH was added to a solution of 18.7 mg (0.27 mmol) of $HONH_3Cl$ and 74.6 mg (0.54 mmol) of $NaOAc{\cdot}3H_2O$ in 1 mL of EtOH–H_2O (1:1 (v/v)). The mixture, from which a precipitate began to separate immediately, was allowed to stand for 30 min and then cooled and filtered. The crude oxime (47.8 mg or 86%), mp 172–175 °C, was crystallized from aqueous EtOH to separate 35.1 mg (63%) of the pure oxime **14** as white plates: mp 178–179 °C; IR (CCl_4) 3610 (OH) cm^{-1}; NMR (CCl_4) δ 0.8–3.0 (m, OH and CH including a *t*-Bu singlet at δ 0.85).

Anal. Calcd for $C_{14}H_{25}NO$: C, 75.28; H, 11.28; N, 6.27. Found: C, 75.35; H, 11.26; N, 6.28.

Preparation of the Tosylhydrazones 10 and 11. A solution of 130 mg (0.625 mmol) of the trans ketone **2**, 127 mg (0.688 mmol) of $TsNHNH_2$, and 0.05 mL of HOAc in 4 mL of EtOH was stirred at 25 °C for 45 min and then cooled in an ice bath. The crude tosylhydrazone **11** was collected as 180.7 mg (77%) of white solid; mp 130–132 °C. Recrystallization from MeOH separated 150.3 mg (64%) of the tosylhydrazone **11** as white needles: mp 131–133 °C; IR (CCl_4) 3220 (NH) cm^{-1}; NMR (CCl_4) δ 7.5–8.0 [3 H, m, NH and an aryl CH doublet (J = 8 Hz) at δ 7.90], 7.30 (2 H, d, J = 8 Hz, aryl CH), 0.9–3.0 (18 H, m, aliphatic CH including a CH_3 singlet at δ 2.46), 0.84 (9H, s, *t*-Bu); UV λ_{max} (95% EtOH) 230 (ϵ 10 200), 274 nm (ϵ 965).

Anal. Calcd for $C_{21}H_{32}N_2O_2S$: C, 66.98; H, 8.57; N, 7.44; S, 8.51. Found: C, 66.94; H, 8.62; N, 7.43; S, 8.53.

The same procedure was used with 149.8 mg (0.72 mmol) of the cis ketone **1**, 141.2 mg (0.765 mmol) of $TsNHNH_2$, 0.05 mL of HOAc, and 4 mL of EtOH to yield 209 mg (77%) of the crude tosylhydrazone **10**; mp 132–134 °C. Recrystallization from EtOH afforded 144.4 mg (53%) of the pure tosylhydrazone **10** as white prisms; mp 133–134 °C. A mixture of the cis and trans derivatives **10** and **11** melted at 124–127 °C. The spectral properties of the cis derivative follow: IR (CCl_4) 3230 (NH) cm^{-1}; NMR (CCl_4) δ 7.82 (2 H, d, J = 8 Hz, aryl CH), 7.6 (1 H, broad, NH), 7.24 (2 H, d, J = 8 Hz, aryl CH), 1.0–2.6 (18 H, m, aliphatic CH including a CH_3 singlet at δ 2.82), 0.82 (9 H, s, *t*-Bu); UV λ_{max} (95% EtOH) 226 (ϵ 10 200), 274 nm (ϵ 843).

Anal. Calcd for $C_{21}H_{32}N_2O_2S$: C, 66.98; H, 8.57; N, 7.44; S, 8.51. Found: C, 66.99; H, 8.60; N, 7.44; S, 8.49.

Preparation of the (*p*-Bromophenyl)sulfonylhydrazones 12 and 13. To a solution of 73.1 mg (0.29 mmol) of *p*-$BrC_6H_4SO_2NHNH_2$ and 0.05 mL of HOAc in 1.5 mL of EtOH was added a solution of 51.7 mg (0.25 mmol) of the trans ketone **2** in 0.5 mL of EtOH. After the resulting mixture had been allowed to stand for 24 h, the hydrazone **13** was collected as 64.9 mg (60%) of white needles; mp 152–153 °C. Recrystallization from an EtOH–H_2O mixture afforded the pure hydrazone **13** with no change in melting point: IR ($CHCl_3$) 3300 (NH), 1180 (SO_2) cm^{-1}; UV λ_{max} (95% EtOH) 233 nm (ϵ 12 500); NMR ($CDCl_3$) δ 7.88 (2 H, d, J = 9 Hz, aryl CH), 7.60 (2 H, d, J = 9 Hz, aryl CH), 0.8–2.7 (24 H, m, aliphatic CH including a *t*-Bu singlet at δ 0.85).

Anal. Calcd for $C_{20}H_{29}BrN_2O_2S$: C, 54.42; H, 6.62; Br, 18.10; N, 6.35; S, 7.26. Found: C, 54.41; H, 6.63; Br, 18.09; N, 6.35; S, 7.24.

A comparable reaction was performed with 73.5 mg (0.29 mmol) of *p*-$BrC_6H_4SO_2NHNH_2$, 0.05 mL of HOAc, 46.0 mg (0.22 mmol) of the cis ketone **1**, and 2.0 mL of EtOH. The hydrazone **12** was collected as 40.3 mg (41%) of white needles; mp 147–148 °C. Recrystallization from an EtOH–H_2O mixture did not alter the melting point: IR ($CHCl_3$) 3305 (NH), 1180 (SO_2) cm^{-1}; UV λ_{max} (95% EtOH) 232 nm (ϵ 13 000); NMR ($CDCl_3$) δ 7.90 (2 H, d, J = 9 Hz, aryl CH), 7.63 (2 H, d, J = 9 Hz, aryl CH), 0.7–3.1 (24 H, m, aliphatic CH including a *t*-Bu singlet at δ 0.84).

Anal. Calcd for $C_{20}H_{29}BrN_2O_2S$: C, 54.42; H, 6.62; Br, 18.10; N, 6.35; S, 7.26. Found: C, 54.41; H, 6.66; Br, 18.06; N, 6.33; S, 7.22.

Crystal Structure of the Tosylhydrazone 11. A. Crystallographic Data Collection. A needle-like crystal with approximate dimensions 0.6 × 0.4 × 0.2 mm was mounted on a glass fiber with epoxy cement such that the longest crystal dimension was approximately parallel to the fiber axis. Unit cell parameters and the orientation matrix were determined on a Syntex $P2_1$ four-circle diffractometer equipped with a graphite monochromator (Bragg 2θ angle 12.2°) by using Mo Kα radiation at a takeoff angle of 6.75°. Fifteen reflections whose 2θ values ranged from 7.57 to 16.89° were machine centered and used in least-squares refinement of the lattice parameters and orientation matrix. Unit cell parameters obtained were a = 15.602 (6) Å,[10] b = 6.469 (2) Å, c = 10.588 (4) Å, α = 97.73 (3)°, β = 90.08 (3)°, γ = 92.88 (3)°, and V = 1057.5 (7) Å^3. The calculated density of 1.18 g cm^{-3} for 2 formula units per unit cell agrees with the experimental density of 1.19 g cm^{-3} measured by the flotation method using a mixture of $ZnCl_2$ and H_2O. ω scans of several low 2θ angle reflections gave peak widths at half-height of less than 0.20°, indicating a satisfactory mosaic spread for the crystal.

Axial photographs indicated that the crystal belonged to the triclinic system. Intensity data for the zero and upper levels were collected at a rapid scan rate and the intensities examined carefully for systematic absences. No systematic absences were observed consistent only with space groups $P1$ or $P\bar{1}$ (No. 1 or 2).[11] Successful refinement in $P\bar{1}$ confirmed our initial choice of that space group.

(10) Numbers in parentheses here and elsewhere in this paper indicate estimated standard deviations in the least significant digit(s).

(11) "International Tables for X-Ray Crystallography", Vol. I, Kynoch Press, Birmingham, England, 1952.

Intensity data were collected by using θ–2θ scans with X-ray source and monochromator settings identical with those used for determination of the unit cell parameters. A variable scan rate from 3.91 to 29.3°/min was used and a scan width of 2.0° was sufficient to collect all of the peak intensity. Stationary background counts were measured at the beginning (bgd1) and at the end (bgd2) of each scan with a total background to scan time ratio, TR, of 1.0. No significant fluctuations were observed in the intensities of three standard reflections (003, 500, 020) monitored every 97 reflections. Intensities were calculated from the total scan count (CT) and background counts by the relationship

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

The intensities were assigned standard deviations according to the formula

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

from a total of 3984 reflections collected in a complete hemisphere $\pm h$, $\pm k$, $+l$ of data out to $2\theta = 50°$; 3197 were accepted as statistically above background on the basis that F was greater than $3[\sigma(F)]$. Lorentz and polarization corrections were made in the usual way.

B. Solution and Refinement of the Structure. Computations were performed with standard programs;[12] all computations were carried out on the CDC Cyber 74 System. For structure factor calculations the scattering factors were taken from Cromer and Mann's tabulation.[13] The agreement factors are defined in the usual way as

$$R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$$

and

$$R_w = \frac{[\Sigma(|F_o| - |F_c|)(w^{0.5})]}{[\Sigma(|F_o|)(w^{0.5})]}$$

In all least-squares refinements, the quantity minimized was $w(|F_o| - |F_c|)^2$. A weighting scheme based on counting statistics ($w = 2.53/[\sigma(F)^2 + 0.002F^2]$) was employed for calculating R_w and in least-squares refinement.

The structure was solved by using the automatic centrosymmetric direct methods program of SHELX-76. The total number of parameters varied were 266 for 3197 observations. Parameters varied included a scale factor, coordinates of all atoms except hydrogens, anisotropic thermal parameters for all atoms except H atoms, and isotropic thermal parameters for H atoms. Hydrogen atoms were refined in the riding mode. The full-matrix least-squares refinement converged at $R = 0.0519$ and $R_w = 0.0631$. The final atomic coordinates and thermal parameters are available as supplementary material in Table III.

Crystal Structure of (*p*-Bromophenyl)sulfonylhydrazone 12. A. Crystallographic Data Collection. A crystal of the hydrazone **12** with approximate dimensions 0.3 × 0.3 × 0.4 mm was mounted on a glass fiber with epoxy cement such that the longest crystal dimension (0.4 mm) was approximately parallel to the fiber axis. Unit cell parameters and the orientation matrix were determined on the previously described Syntex $P2_1$ diffractometer by using Mo Kα radiation at a takeoff angle of 6.75°. Fifteen reflections whose 2θ values ranged from 3.76 to 22.10° were machine centered and used in least-squares refinement of the lattice parameters and orientation matrix. Unit cell parameters obtained were $a = 8.928$ (2) Å,[10] $b = 10.873$ (4) Å, $c = 11.404$ (5) Å, $\alpha = 92.85$ (3)°, $\beta = 108.06$ (3)°, $\gamma = 90.08$ (3)°, and $V = 1051.0$ (7) Å^3. The calculated density of 1.395 g cm^{-3} for 2 formula units per unit cell agrees with the experimental density of 1.394 g cm^{-3} measured by the flotation method using a mixture of hexane and CCl_4. ω scans of several low 2θ angle reflections gave peak widths at half-height of less than 0.2°, indicating a satisfactory mosaic spread for the crystal.

Axial photographs indicated that the crystal belonged to the triclinic system. Intensity data for zero and upper levels were collected at a rapid scan rate and the intensities examined carefully for systematic absences. No systematic absences were observed consistent with only space group $P1$ or $P\bar{1}$.[11] Successful refinement in $P\bar{1}$ confirmed our initial choice of that space group.

Intensity data were collected by using θ–2θ scans with X-ray source and monochromator settings identical with those used for determination of the unit cell parameters. A variable scan rate from 3.91 to 29.3°/min was used and a scan width of 2.0° was sufficient to collect all of the peak intensity. Stationary background counts were measured at the beginning (bgd1) and at the end (bgd2) of each scan with a total background to scan time ratio, TR, of 1.0. No significant fluctuations were observed in the intensities of three standard reflections (300, 040, 004) monitored every 97 reflections. Intensities were calculated as previously described. A total of 3723 reflections were collected in a complete hemisphere of data out to $2\theta = 50°$; 2496 were accepted as statistically above background on the basis that F was greater than $3[\sigma(F)]$. Lorentz and polarization corrections were made in the usual way.

B. Solution and Refinement of the Structure. Computations were performed as previously described. A weighting scheme based on counting statistics ($w = 1.86/[\sigma(F)^2 + 0.0002F^2]$) was employed for calculating R_w in the least-squares refinement.

The structure was solved by using the automatic centrosymmetric direct methods program of SHELX-76. The total number of parameters varied were 264 for 2496 observations. Parameters varied included a scale factor, coordinates of all atoms except hydrogens, anisotropic thermal parameters for all atoms except H atoms, and isotropic thermal parameters for H atoms. Hydrogen atoms were refined in the riding mode. The full-matrix least-squares refinement converged at $R = 0.0580$ and $R_w = 0.0491$. The final atomic coordinates and thermal parameters are available as supplementary material in Table IV.

Registry No. **1**, 70775-28-9; **2**, 70775-29-0; **3**, 3419-74-7; **4**, 70775-30-3; **5**, 70775-31-4; **6**, 70775-32-5; **7**, 762-72-1; **8** isomer 1, 70775-33-6; **8** isomer 2, 70812-12-3; **9** isomer 1, 70775-34-7; **9** isomer 2, 70812-13-4; **10**, 70775-35-8; **11**, 70775-36-9; **12**, 70775-37-0; **13**, 70775-37-0; **14**, 70775-38-1.

Supplementary Material Available: Tables of atomic coordinates and thermal parameters (Tables III and IV) (2 pages). Ordering information is given on any current masthead page.

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

(13) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, pp 72–98.