***o*-Nitrophenyl Benzyl Telluride (2).** To a dry, three-necked flask was added a solution of *o*-nitroiodobenzene (8.98 g, 36 mmol) in THF (freshly distilled from $LiAlH_4$). The mixture was stirred at –100 °C (liquid N_2/Et_2O) under argon while a solution of phenyllithium (19.2 mL of a 1.89 M solution in ether–benzene) was introduced slowly via syringe. The mixture was stirred at –100 °C for 50 min. Further manipulation was conducted in the dark. Benzyl tellurocyanate (8.78 g, 36 mmol) was added quickly, and the mixture was stirred at –100 °C for 4 h and left to warm to 25 °C overnight. The solvent was removed in vacuo, and the residue was partitioned between water and benzene. The aqueous layer was separated and extracted with benzene. The combined organic layers were dried (Na_2SO_4) and removed in vacuo to yield a deep red gum. Column chromatography over neutral alumina (hexane elution) followed by recrystallization from hexane afforded *o*-nitrophenyl benzyl telluride (**2**) as orange needles (8.81 g, 72%): mp 85–86 °C; UV (EtOH) max 210 (16 800), 222 (17 000), 266 nm (9400); IR (KBr) 1580, 1575, 1490, 1250, 1050, 850; NMR ($CDCl_3$) δ 8.35–8.55 (m, 1 H), 7.15–7.92 (m, 9 H), 4.26 (s, 2 H); MS *m/e* 343 (M^+), 252, 106 (base). Anal. Calcd for $C_{13}H_{11}NO_2Te$: C, 45.81; H, 3.25; N, 4.11. Found: C, 45.77; H, 3.33; N, 4.01.

Further elution with hexane yielded red crystals of bis(*o*-nitrophenyl) telluride (**3**) (0.28 g, 2.1%), after recrystallization from hexane, mp 138–142 °C. Recrystallization from hexane afforded an analytical sample: mp 141–142 °C; IR (KBr) 1500, 1310, 1295, 788, 715; MS 374 (M^+), 106 (base). Anal. Calcd for $C_{12}H_{18}N_2O_4Te$: C, 38.74; H, 2.17; N, 7.54; Te, 34.52. Found: C, 38.65; H, 2.05; N, 7.55; Te, 34.07.

When *o*-nitrophenyllithium was generated as above and treated with 1 equiv of *o*-nitrophenyl benzyl telluride (**2**), bis(*o*-nitrophenyl) telluride (**3**) was produced in 20% yield, and **2** was recovered in 68% yield.

(*o*-Nitrophenyl)tellurium Tribromide (5). A solution of **2** (3.43 g, 10 mmol) in carbon tetrachloride was treated dropwise with a solution of bromine (5 g, 31.25 mmol) in carbon tetrachloride. The color of the mixture turned from orange to pale yellow and eventually red. After the solution was warmed for 5 min on a steam bath, hexane was added, and the solution was left to cool. Filtration afforded yellow needles of (*o*-nitrophenyl)tellurium tribromide (4.45 g, 95%): mp 164–165 °C; UV (EtOH) λ_{max} 306 (16 600), 285 (5100); IR (KBr) ν 1580, 1550, 1490, 1470, 1270, 1030, 1100, 850; MS *m/e* (M – Br) 252, 106 (base). Anal. Calcd for $C_6H_4NO_2TeBr_3$: C, 14.72; H, 0.82; N, 2.86; Br, 48.98. Found: C, 14.81; H, 0.85; N, 2.78; Br, 48.85.

Bis(*o*-nitrophenyl telluride) (6). To a stirred solution of sodium bisulfite (1.624 g, 6 mmol) in water at 0 °C was added **5** (0.492 g, 1 mmol). After 3 h at 25 °C, the orange solid which had formed was filtered, dried with suction, washed with hexane, then recrystallized from benzene–hexane to yield reddish-orange needles of bis(*o*-nitrophenyl telluride) (**6**) (0.225 g, 91%): mp 204–206 °C dec; UV (EtOH) λ_{max} 210 (35 000), 245 (16 200); IR (KBr) 1580, 1550, 1470, 1400, 1280, 1160, 850; MS *m/e* 504 (M^+), 252, 234, 106 (base). Anal. Calcd for $C_{12}H_8N_2O_4Te_2$: C, 28.86; H, 1.61; N, 5.61; Te, 51.10. Found: C, 28.98; H, 1.62; N, 5.54; Te, 51.35.

(*o*-Nitrophenyl)tellurenyl Bromide (4). A stirred solution of **6** (0.5 g, 1.0 mmol) in carbon tetrachloride was treated dropwise with a solution of bromine (0.054 mL, 1.0 mmol) in carbon tetrachloride. After the solution was stirred for 30 min, the solvent was removed in vacuo, and the deep red residue was crystallized from petroleum–ether to yield (*o*-nitrophenyl)tellurenyl bromide (**4**) (0.395 g, 90%) as a deep red solid, mp 72–74 °C. Two recrystallizations from ethanol afforded an analytical sample: mp 75–76 °C; IR (KBr) 1590, 1490, 1325; MS *m/e* 330 (M^+), 255 (M – Br, base); exact mass 330.8483 (calcd for $C_6H_4NO_2TeBr$ 330.8492). Anal. Calcd for $C_6H_4NO_2TeBr$: C, 21.86; H, 1.22. Found: C, 22.15; H, 1.14.

Controlled Bromination of *o*-Nitrophenyl Benzyl Telluride. A solution of **2** (0.342 g, 1.0 mmol) in carbon tetrachloride was treated dropwise with a solution of bromine (0.055 mL, 1.0 mmol) in carbon tetrachloride. After the addition was complete, the yellow solution was heated on a steam bath for 20 min. The resultant deep red solution was cooled, and the solvent was removed in vacuo. Column chromatography over silica gel (hexane elution) afforded benzyl bromide (0.12 g; 71%) which was identical (IR) with an authentic sample. Further elution with ether afforded (*o*-nitrophenyl)tellurenyl bromide (**4**) (0.3 g; 90%) indistinguishable from a sample prepared as before from **6**.

Conversion of (*o*-Nitrophenyl)tellurenyl Bromide to *o*-Nitrophenyl Tellurium Tribromide. A solution of **4** (0.059 g, 0.179 mmol) in carbon tetrachloride was treated dropwise with bromine (0.022 mL, 0.4 mmol) in carbon tetrachloride. A yellow solid precipitated immediately, and the slurry was stirred at 25 °C for 3 h. The mixture was diluted with petroleum–ether and suction filtered to yield (*o*-nitrophenyl)tellurium tribromide (**5**) (0.065 g, 75%) as a yellow solid which was identical with a sample prepared as before.

Controlled Reduction of (*o*-Nitrophenyl)tellurium Tribromide. To a stirred suspension of **5** (1.0 g, 3.0 mmol) in water at 0 °C was added solid sodium bisulfite (0.42 g, 6.0 mmol) in small portions over a period of 20 min. The resultant deep red slurry was stirred for 20 min at 0 °C and suction filtered. The red paste was dissolved in CH_2Cl_2, filtered through glass wool, diluted with hexane, and crystallized to yield (*o*-nitrophenyl)tellurenyl bromide (**4**) (0.59 g, 89%) as a deep red solid which was indistinguishable from a sample prepared as before.

Acknowledgment. We thank the National Science Foundation for a grant (CHE 76-83417) in support of this research.

Registry No. 1, 62404-99-3; **2**, 71129-53-8; **3**, 71129-54-9; **4**, 71129-55-0; **5**, 71129-56-1; **6**, 71129-57-2; *o*-nitroiodobenzene, 609-73-4; *o*-nitrophenyllithium, 27329-57-3; benzyl bromide, 100-39-0.

Structure and Stereochemistry of Condensation Products from 1-Morpholino-1-cycloheptene and Methyl Vinyl Ketone

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In order to examine the effect of substituents and ring size on the course of photochemically induced rearrangements of β,γ-unsaturated ketones,[1] we wanted to prepare compound 1. Our projected synthesis paralleled the reported synthesis of 2 and utilized the reaction between 1-morpholino-1-cycloheptene and methyl vinyl ketone.[2] While, however, the reported procedure yields

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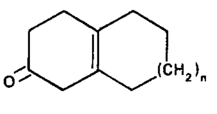
[1] (a) Kenneth Houk, *Chem. Rev.*, **76**, 1 (1976); (b) William G. Dauben, Gerrit Lodder, and Junes Ipaktschi, *Fortschr. Chem. Forsch.*, **54**, 73 (1975); (c) John R. Williams and Herman Ziffer, *Tetrahedron*, **24**, 6725 (1968); (d) Paul S. Engel, Mary A. Schexnayder, Herman Ziffer, and Jeffrey I. Seeman, *J. Am. Chem. Soc.*, **96**, 924 (1974); (e) Beat Winter and Kurt Schaeffner, *ibid.*, **98**, 2022 (1976); (f) Paul S. Engel and Herman Ziffer, *Tetrahedron Lett.*, 5181 (1969); (g) T. Akiyama, David Pedder, J. V. Silverton, Jeffrey I. Seeman, and Herman Ziffer, *J. Org. Chem.*, **40**, 3675 (1975).

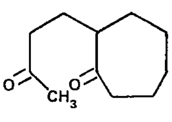
[2] Robert L. Augustin and Joseph A. Caputo, "Organic Syntheses", Collect. Vol. 5, Wiley, New York, 1973, p 869.

Table I. Crystal and Refinement Data

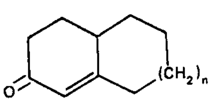
formula: $C_{11}H_{18}O_2$
mol wt: 182.25
habit: monoclinic prismatic, elongation *b*
space group: $P2_1/c$
cell dimens: from LS refinement of $\pm\theta$ data
radiation: Cu Kα, graphite monochromator
a: 12.863 (1) Å
b: 5.703 (1) Å
c: 13.831 (1) Å
β: 98.72 (1)°
D_m: 1.20 (1) g/cm^3
D_x: 1.207 g/cm^3
Z: 4
cryst size: 0.31 × 0.10 × 0.15 mm^3
reflctns: 1715 (449 unobsd, 1σ)
diffractometer: Nonius CAD-4
LS weighting: statistical with error estimate: 0.02*I*
function minimized: $\Sigma w(F_o - F_c)^2$
R (obsd ref only): 0.039



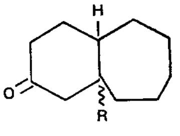
1 n = 2
2 n = 1



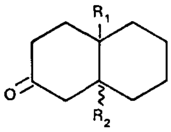
3



4 n = 2
5 n = 1



6 R = β-OH
7 R = α-OH



8 R_1 = H, R_2 = β-OH
9 R_1 = CH_3, R_2 = α-OH

a mixture of 2 and 5, we obtained a mixture of products which, as far as we could determine, did not contain 1. Instead, the mixture consisted of 3 as the major component along with some 4 and a small quantity of a solid ketol. Essentially pure 4 could be prepared in an analogous reaction sequence in which 1-pyrrolidino-1-cycloheptene was substituted for the morpholine enamine. Although the reaction of neither enamine with methyl vinyl ketone yielded the desired ketone 1, isolation of a single solid ketol provided an opportunity to examine the suggestion by Spencer et al.[3] that in the transition state for the reaction of the butanone side chain with the carbonyl, the side chain approaches from the least hindered side; the ketol should thus possess a trans junction. Spencer et al. isolated *cis*-ketols from cyclohexanone derivatives when the substituent at C-2 was a methyl or acetoxyl group, while Marshall and Fanta[4] isolated a *cis*-ketol from the condensation of 2-methylcyclohexanone and methyl vinyl ketone. As the examples studied were all cyclohexanone derivatives and as the reaction of 1-morpholino-1-cycloheptene with methyl vinyl ketone differed from that of the corresponding cyclohexanone derivative, it appeared useful to determine the structure of the ketol isolated.

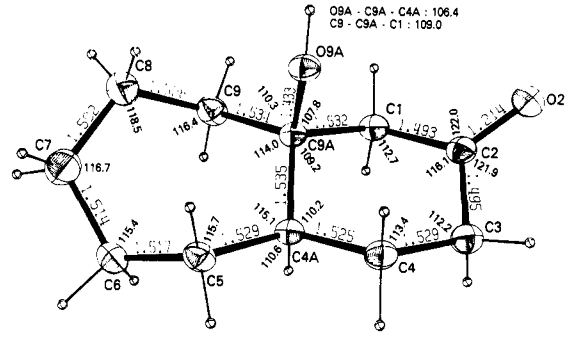


Figure 1. Molecular conformation of the ketol with bond lengths (Å) and angles (deg) as shown.

X-ray data on the final component, the ketol, were collected by standard methods on a Nonius CAD-4-diffractometer. The crystal and refinement data are summarized in Table I and establish the structure and stereochemistry of the ketol as 7. The structure was solved using MULTAN,[5] all heavier atoms being visible in the *E* map. Standard sequences of least-squares refinements and difference maps yielded the complete structure including hydrogen atoms. The final refinement[6] utilized anisotropic thermal parameters for the heavier atoms and isotropic ones for the hydrogen atoms and yielded an *R* factor of 0.039. Atomic parameters are given in Table II. The molecular conformation of the ketol with bond lengths and angles is shown in Figure 1.

The X-ray investigation indicates that the fusion of the two rings is trans (torsion angles −54 and +58°). Consequently, both substituents at the common atoms are axial.[7] The torsion angles in the cycloheptane ring are slightly different from those given by Bucourt[7] for the minimum-energy twist-chair conformation, but this conformation is flexible[8] and could change to accommodate the hydroxyl substituent and the ring fusion. The twist-chair form is predicted as the most stable on the basis of nonbonded H–H repulsions and has been observed in many studies, particularly those of Mc Phail and Sim[8] on sesquiterpenoids. Mc Phail and Sim noted an expansion of the ring carbon valence angles in cycloheptane moieties; a similar effect is also observed in the present study (average angle 116.0°). The ring angles are larger than those predicted by Hendrickson[9] in his theoretical study of seven-membered rings, but the influence of nonbonded H–H repulsions may be somewhat greater than that estimated by Hendrickson, and similarly the C–C bond length used in the theoretical study (1.533 Å) is a little longer than the one actually observed (1.523 Å). Expansion of angles and shortening of bonds could be related, since

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[3] (a) Thomas A. Spencer, Klaus K. Schmiegel, and Kenneth L. Williamson, *J. Am. Chem. Soc.*, **85**, 3785 (1963); (b) Thomas A. Spencer, Hartley S. Nell, David C. Werd, and Kenneth L. Williamson, *J. Org. Chem.*, **31**, 431, (1966).

[4] James A. Marshall and Wayne I. Fanta, *J. Org. Chem.*, **29**, 2501 (1964).

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[6] Programs used in refinement were from James M. Stewart, Gert J. Kruger, Herman L. Ammon, Charles H. Dickinson, and Sidney P. Hall, XRAY-72, TR-192, Computer Science Center, University of Maryland, 1972.

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[8] Andrew T. Mc Phail and George A. Sim, *Tetrahedron*, **29**, 1751 (1973).

[9] James B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961).

Table II. Atomic Parameters[a]

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	3729 (1)	12208 (3)	9514 (1)	50 (1)	36 (1)	41 (1)	1 (1)	−2 (1)	−4 (1)
C(2)	4444 (1)	12646 (3)	8778 (1)	49 (1)	31 (1)	54 (1)	−3 (1)	0 (1)	6 (1)
O(2)	5391 (1)	12790 (2)	9008 (1)	47 (1)	75 (1)	66 (1)	−10 (1)	−4 (1)	20 (1)
C(3)	3925 (2)	12922 (4)	7741 (1)	55 (1)	58 (1)	51 (1)	−6 (1)	1 (1)	16 (1)
C(4)	3073 (2)	11077 (4)	7450 (1)	53 (1)	59 (1)	35 (1)	−4 (1)	1 (1)	6 (1)
C(4A)	2321 (1)	10799 (3)	8196 (1)	41 (1)	37 (1)	36 (1)	5 (1)	1 (1)	−1 (1)
C(5)	1443 (1)	9067 (4)	7825 (1)	47 (1)	55 (1)	40 (1)	−1 (1)	−2 (1)	−5 (1)
C(6)	510 (2)	9058 (4)	8377 (2)	43 (1)	62 (1)	59 (1)	−4 (1)	0 (1)	−2 (1)
C(7)	613 (2)	7454 (5)	9258 (2)	75 (1)	67 (1)	61 (1)	−16 (1)	9 (1)	2 (1)
C(8)	1613 (2)	7631 (5)	9971 (2)	55 (1)	83 (2)	68 (1)	−4 (1)	16 (1)	28 (1)
C(9)	2245 (1)	9906 (4)	10008 (1)	49 (1)	71 (1)	36 (1)	0 (1)	5 (1)	−6 (1)
C(9A)	2938 (1)	10237 (3)	9208 (1)	39 (1)	31 (1)	33 (1)	4 (1)	3 (1)	−3 (1)
O(9A)	3521 (1)	8139 (2)	9095 (1)	47 (1)	32 (1)	44 (1)	9 (1)	2 (1)	0 (1)

atom	x/a	y/b	y/c	U, Å^2	atom	x/a	y/b	y/c	U, Å^2
H(1)	332 (1)	1368 (3)	954 (1)	55 (5)	H(6)	40 (1)	1073 (3)	859 (1)	63 (6)
H(1′)	412 (1)	1177 (3)	1016 (1)	55 (5)	H(6′)	−15 (1)	854 (3)	792 (1)	64 (6)
H(3)	363 (1)	1448 (3)	771 (1)	66 (6)	H(7)	0 (2)	777 (4)	967 (1)	109 (9)
H(3′)	448 (1)	1283 (3)	730 (1)	73 (6)	H(7′)	49 (2)	588 (5)	900 (2)	127 (10)
H(4)	266 (1)	1152 (3)	680 (1)	64 (6)	H(8)	147 (1)	733 (4)	1058 (2)	108 (9)
H(4′)	340 (1)	945 (3)	737 (1)	60 (6)	H(8′)	207 (2)	633 (6)	973 (2)	143 (12)
H(4A)	197 (1)	1232 (2)	826 (1)	40 (4)	H(9)	177 (1)	1126 (3)	1000 (1)	62 (6)
H(5)	120 (1)	950 (3)	713 (1)	62 (5)	H(9′)	272 (1)	996 (3)	1061 (1)	65 (6)
H(5′)	176 (1)	743 (3)	784 (1)	58 (5)	H(9A)	390 (1)	782 (3)	967 (1)	83 (7)

[a] The positional parameters for the heavier atoms have been multiplied by 10 000 and all other parameters by 1000. The anisotropic temperature factor used had the form $\exp[-2\pi^2\Sigma_i\Sigma_j(U_{ij}h_ih_ja^*_ia^*_j)]$.

the expansion might increase the C–C bond overlap in a fashion similar to that observed in sp^2–sp^2 single bonds which can be 0.02 to 0.03 Å shorter than sp^3–sp^3 bonds.

Our observation that a *trans*-ketol forms from the condensation of methyl vinyl ketone and a cycloheptanone derivative is consistent with the suggestion made for cyclohexane derivatives, i.e., the stereochemistry of the ketol isolated is related to the presence or absence of a substituent at C-2 in the intermediate 2-(3′-oxobutyl)-cyclohexanone or -cycloheptanone.

Experimental Section

Melting points were determined by using a hot-stage apparatus; they are uncorrected. Proton magnetic resonance spectra were recorded on a Varian HR 220-MHz instrument in $CDCl_3$ containing tetramethylsilane as an internal standard; coupling constants (J) are reported in hertz. Carbon magnetic resonance spectra were recorded on a JEOL, FX-100 (24-MHz) instrument under noise-modulated decoupling conditions; chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane in $CDCl_3$. Mass spectra were obtained on a LKB Model 9000.

Bicyclo[5.4.0]undec-6(11)-en-7-one (4). To a solution of 1-pyrrolidinoncycloheptene[10] (47 g) in toluene (200 mL) at room temperature was added methyl vinyl ketone (23 g), and the solution was stirred overnight. The reaction mixture was then refluxed for 3–4 h and hydrolyzed by adding 25 mL of acetic acid, 25 mL of water and 12.5 g of sodium acetate[11] and refluxing the mixture for 8 h. The cooled solution was washed with water, dilute HCl, and aqueous $NaHCO_3$, dried, and concentrated. The residue was distilled in vacuo and the fraction boiling at 105–115 °C (1.5 torr) collected (25 g, 53% yield). A comparison of the gas chromatographic behavior (T = 140 °C, 3% OV-17) of the distillate and purified samples of **3**, **4**, and **7** showed it to be almost pure **4**.

The ultraviolet absorption spectrum of a sample of **4**, purified by column chromatography on silica gel, had a λ_{max} of 241 nm (ϵ 13 300) in methanol. The mass spectrum showed a m/e of 164 for the molecular ion. The ^1H NMR spectrum showed a singlet at δ 5.84 in addition to complex absorption in the aliphatic region. The ^{13}C NMR spectrum showed absorptions at 199.1, 171.1, 126.2, 39.9, 37.0, 36.4, 33.1, 31.2, 29.8, 28.0, and 27.2 ppm.

Reaction of 1-Morpholino-1-cycloheptene and Methyl Vinyl Ketone. 1-Morpholino-1-cycloheptene was prepared from the reaction of cycloheptanone, morpholine, and *p*-toluenesulfonic acid in toluene as described for cyclohexanone[12] in 36% yield.

Methyl vinyl ketone (17.3 g) was slowly added to the above enamine (42.4 g) in 230 mL of dioxane, and the mixture was refluxed overnight.[2] The reaction mixture was poured into water (450 mL) and extracted three times with ether (250 mL). The ether phase was washed with dilute HCl, aqueous $NaHCO_3$, and saturated NaCl, dried, and concentrated in vacuo. Distillation [bp 132 °C (1.5 torr)] gave 8.47 g (22%) of a mixture (3:2) of **3** and **4** as determined by GC. A pure sample of **3** was obtained by chromatography on silica gel, and its mass spectrum showed a peak at m/e 182. The proton NMR showed a broadened singlet at δ 2.14 with no absorption above δ 2.60. The ^{13}C NMR spectrum showed absorptions at 214.3, 207.2, 50.9, 42.4, 40.8, 31.3, 29.5, 29.2, 28.2, 25.8, and 24.1 ppm.

The residue from the distillation was chromatographed on silica gel, and in addition to small quantities of **3** and **4** a colorless solid, recrystallized from hexane, mp 120–121 °C, was obtained in 4% yield. The mass spectrum of the solid showed a parent ion at m/e 184. The ^{13}C NMR spectrum showed peaks at 211.5, 76.4, 56.0, 46.7, 43.1, 41.0, 29.9, 29.0, 27.8, 27.1, and 20.6 ppm and suggested a ketol structure, i.e., **6** or **7**. A crystal structure determination of this solid established its structure and stereochemistry as **7**.

Acknowledgment. The authors wish to express their appreciation to Drs. R. J. Highet and H. Yeh for the ^{13}C NMR spectra and to acknowledge assistance from and valuable discussions with Drs. J. I. Seeman and Ken-ichi Kawai.

Registry No. **3**, 26871-79-4; **4**, 19198-29-9; **7**, 40050-41-7; 1-pyrrolidinocycloheptane, 18707-34-1; methyl vinyl ketone, 78-94-4; 1-morpholino-1-cycloheptene, 7182-08-3; cycloheptanone, 502-42-1; morpholine, 110-91-8.

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