The conversion of triflones to ketones was then envisioned as a "one-pot" process (Scheme I) with no intermediate purification of vinyl azide or iminophosphorane. Since the triflone–vinyl azide conversion was well established,[3] we first examined the reaction of vinyl azides, which can also be synthesized from olefins (via iodoazides) by treatment with iodine azide followed by base.[8,9] We found that treatment of vinyl azides with 1 equiv of triethyl phosphite in cyclohexane, followed directly by mild acid hydrolysis, yielded the corresponding ketones in good yield (Table I).

We then examined the direct conversion of triflones to ketones. The results obtained from these reactions, shown in Table II, reveal a very satisfactory "one-pot" operation. This conversion is particularly useful for several reasons. First, the synthesis of vinyl azides from triflones is complementary to the iodine azide method and can be used in cases when the latter method gives mixtures of ketones. With triflones the carbonyl functionality is always produced at the position originally occupied by the CF_3SO_2– group. Second, since triflones are easily obtained from readily available primary alkyl halides, and may be alkylated in high yield,[2,3] they represent useful synthons for the preparation of a wide variety of ketones.

Experimental Section

General. Triflones,[1-3] $TosN_3$,[10] and vinyl azides[8,9] were prepared by known methods. All compounds exhibited physical properties and give IR and NMR spectra consistent with those of known compounds.

Synthesis of Ketones from Vinyl Azides. General Procedure. The vinyl azide (10 mmol) was dissolved in 40 mL of dry cyclohexane. To this was added a solution of $P(OEt)_3$ (1.58 g, 9.50 mmol) in 10 mL of dry cyclohexane (addition time 10 min). The flask warmed during the addition and N_2 gas was evolved. The reaction mixture was then stirred for 18–24 h and then warmed briefly to reflux. After cooling the mixture was poured into a separatory funnel and shaken intermittently for 5 min with an equal volume of 10% HCl. The two phases were then extracted with pentane (3 × 50 mL). The organic extracts were combined, washed with H_2O (2 × 50 mL) and saturated NaCl (2 × 50 mL), dried ($MgSO_4$), and concentrated to give the crude ketone. The product was further purified by crystallization or distillation for comparison with authentic sample.

Synthesis of Ketones from Triflones. General Procedure. To a round-bottom flask was added 57% NaH–oil dispersion (926 mg, 22 mmol). The oil was removed by washing the dispersion with dry hexane (2 × 10 mL). Dry glyme [distilled from Na/benzophenone ketyl (50 mL)] was then added to the flask. To the flask was then added dropwise a solution of the triflone (10 mmol) in 10 mL of dry glyme. After 1 h the flask was cooled to 0 °C and a solution of $TosN_3$ (1.97 g, 10 mmol) in 10 mL of dry glyme was added dropwise over 10 min. The mixture was allowed to warm to room temperature and stirred for 2 h. The reaction mixture was diluted with an equal volume of Et_2O and washed with H_2O (3 × 100 mL) and saturated NaCl (1 × 100 mL). The aqueous washings were combined and extracted with Et_2O (1 × 100 mL). The Et_2O washings were combined, dried ($MgSO_4$), and concentrated to give the crude vinyl azide, which was suspended in 40 mL of dry cyclohexane and the treatment continued as in the procedure above.

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Stereospecific Cyclopentane Synthesis via Intramolecular Nitrone Cycloaddition

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Received March 8, 1977

In 1964 LeBel and co-workers[1] reported an intramolecular nitrone cycloaddition[2] in which 2,6-dimethyl-5-heptenal (melonal) was condensed with *N*-methylhydroxylamine to give a fused cyclopentane derivative. The noteworthy feature of this reaction is the fact that a cyclopentane with three contiguous asymmetric centers is stereospecifically constructed in a single step from an acyclic precursor. We wish to report further examples of this synthetic method in which functionalized cyclopentanes, again with three contiguous asymmetric centers, are prepared in good yield.

The requisite olefinic aldehyde precursors, 2-methyl-2-phenyl-5-hexenal (**3a**) and 2-(methylthio)-2-phenyl-5-hexenal (**3b**), were synthesized according to Scheme I.

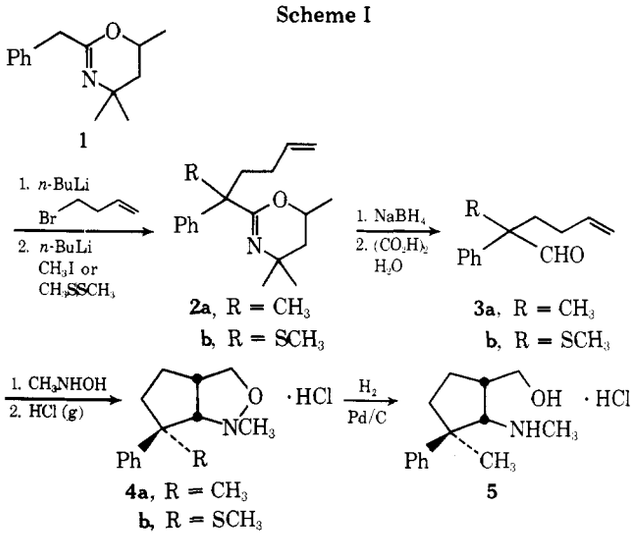
2-Benzyl-4,4,6-trimethyl-5,6-dihydro-1,3(4*H*)-oxazine (1) was sequentially alkylated[3] with 4-bromo-1-butene and then either methyl iodide or dimethyl disulfide. Products **2a,b** were reduced with sodium borohydride and hydrolyzed with aqueous oxalic acid to afford the oily aldehydes **3a,b.** The intramolecular nitrone cycloadditions were carried out by heating **3a,b** at reflux in absolute ethanol containing *N*-methylhydroxylamine hydrochloride and pyridine. Aqueous workup yielded the cycloadducts **4a,b** as oils which were converted to crystalline hydrochloride salts. The 60-MHz ^1H NMR spectrum of the crude free base **4a** indicated the presence of only one isomer.

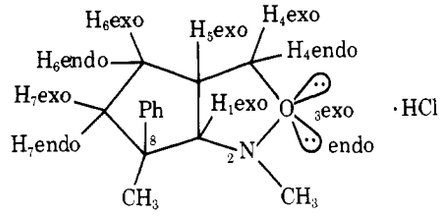
Based on literature precedents,[1] it was anticipated that the ring juncture of **4a** would be cis rather than the more highly strained trans. This hypothesis was verified upon consideration of the 100-MHz ^1H NMR spectrum of **4a**·HCl (see Table I, supplementary material).

First, a long-range W coupling of 1 Hz is observed between H_1exo (δ 4.26) and H_7exo (δ 2.40). A reasonable W (i.e., approximately coplanar arms) exists between these two protons in the cis but not in the trans geometry. Secondly, the signals for the C_7 protons reveal two widely different net coupling patterns with the C_6 protons, an observation more consistent with the flexible cis structure than with the rigid trans.[4]

The assignment of the relative stereochemistry at C_8 was

Scheme I





4a

accomplished by means of paramagnetic shift reagent studies (see Table II, supplementary material). When **4a**·HCl is treated with $Eu(fod)_3$ the exo protons at C_1, C_4, C_5, and C_7 show little or no downfield shift. More significantly, the methyl group at C_8 shows a marked downfield shift while the aromatic region is virtually unchanged. Assuming that the endo lone pair on oxygen is the probable site of complexation of the shift reagent,[5] it thus appears that the C_8 methyl group is endo. As in the case of melonal, the thermodynamically more stable product is formed in which the less bulky group occupies the more sterically congested endo position.

Hydrochloride **4a** was smoothly hydrogenolyzed to **5**, an attractive precursor for a number of further synthetic transformations involving either the alcohol or amine functions.

Experimental Section

Melting points were obtained in a Thomas-Hoover melting point apparatus (uncorrected). Infrared spectra were determined on a Perkin-Elmer Model 521 spectrometer. Proton magnetic resonance spectra were recorded on either a Varian A-60 or a Varian XL-100 spectrometer using Me_4Si as the internal standard. Mass spectra were obtained on an AEI MS 902 mass spectrometer by direct insertion. The following abbreviations are used: (b) broad, (ex) exchangeable with D_2O, (s) singlet, (d) doublet. (t) triplet, (q) quartet, and (m) multiplet.

2-Methyl-2-phenyl-5-hexenal (3a). To a solution of 30.8 g (0.14 mol) of 1 in 270 mL of dry THF at −78 °C under N_2 was added 110 mL (0.165 mol) of 1.5 M *n*-BuLi/hexane. The solution was stirred for 1 h at −78 °C, 20.3 g (0.15 mol) of 4-bromo-1-butene in 30 mL of THF was added, and the mixture was warmed to room temperature. The solution was again cooled to −78 °C, 105 mL (0.16 mol) of 1.5 M *n*-BuLi/hexane was added, the mixture was stirred for 1 h at −78 °C, and 15 mL (0.24 mol) of MeI was added. The solution was warmed to room temperature, stirred overnight, quenched with water, and extracted with ether. The ether extracts were washed with water, dried over Na_2SO_4, and evaporated to give 40 g (~100%) of crude oily **2a** as a diastereomeric mixture.

The above product was dissolved in 140 mL of THF/140 mL of 95% ethanol at −35 to −45 °C. A solution of 5.4 g (0.14 mol) of $NaBH_4$ in 8 mL of water was added dropwise; 9 N HCl was added as needed to maintain pH 6–8. The solution was stirred for 1 h at −35 °C and kept at pH 7. The mixture was poured into 200 mL of water, made basic with 1 N NaOH, and extracted with ether. The ether extracts were washed with brine, dried over Na_2SO_4, and evaporated to give 40 g (~99%) of crude oily product.

The tetrahydrooxazine was heated at reflux for 2 h in 220 mL of water containing 70.6 g of oxalic acid. The solution was extracted with ether, washed with water and saturated $NaHCO_3$ solution, dried over Na_2SO_4, and evaporated to give 17.8 g (68% overall) of **3a** as an oil: bp 72–75 °C (0.20 mm); IR (film) 1721, 1634, 991, 910, 756, 697 cm^{-1}; NMR ($CDCl_3$) δ 1.44 (s, 3 H), 1.95 (m, 4 H), 4.95 (m, 2 H), 5.71 (m, 1 H), 7.27 (s, 5 H), 9.49 (s, 1 H); MS *m/e* 188 (M^+) 159, 144, 105, 91.

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 83.31; H, 8.31.

2-(Methylthio)-2-phenyl-5-hexenal (3b). The procedure described for the preparation of **2a** was carried out on a 0.14-mol scale using 14.1 g (0.15 mol) of dimethyl disulfide in place of MeI to give 44 g (~100%) of crude **2b**. A 0.07-mol sample of **2b** was reduced with $NaBH_4$ and hydrolyzed to give 5.0 g (32% overall) of oily **3b**: bp 86–88 °C (0.28 mm); IR (film) 1703, 1637, 990, 910, 693 cm^{-1}; NMR ($CDCl_3$) δ 1.78 (s, 3 H), 1.91 (m, 4 H), 4.40 (m, 2 H), 5.64 (m, 1 H), 3.33 (s, 5 H), 9.19 (s, 1 H); MS *m/e* 220 (M^+), 205, 191, 143, 103, 91, 77, 41.

The 2,4-dinitrophenylhydrazone was recrystallized from 95% ethanol, mp 108–109 °C.

Anal. Calcd for $C_{19}H_{20}N_4O_4S$: C, 56.98; H, 5.03; N, 13.99. Found: C, 56.97; H, 5,19; N, 14.21.

***cis-trans*-2,8-Dimethyl-8-phenyl-3-oxa-2-azabicyclo-[3.3.0]octane Hydrochloride (4a).** A solution of 17.6 g (0.093 mol) of **3a**, 23.3 g (0.28 mol) of *N*-methylhydroxylamine hydrochloride, 24 mL (0.30 mol) of pyridine, and 300 mL of absolute ethanol was heated at reflux under N_2 for 24 h. The mixture was acidified with 1 N HCl, washed with ether, and made basic with 1 N NaOH. After extraction with CH_2Cl_2, drying over Na_2SO_4, and evaporation of solvent, the cycloadduct was obtained as an orange oil. The crude product was dissolved in ether/acetone at 0 °C and treated with excess HCl gas. Crystalline **4a** was collected by filtration, washed with ether, and dried to give 13.4 g (57%): mp 176–177 °C; IR (Nujol) 2400, 1106, 766, 700 cm^{-1}; NMR ($CDCl_3$) (see Tables I and II and accompanying spectrum); MS *m/e* 217 (M^+), 200, 105.

Anal. Calcd for $C_{14}H_{20}ClNO$: C, 66.26; H, 7.94; N, 5.52. Found: C, 65.89; H, 7.89; N, 5.34.

***cis-trans*-2-Methyl-8-(methylthio)-8-phenyl-3-oxa-2-azabicyclo[3.3.0]octane Hydrochloride (4b).** The procedure described for the preparation of **4a** was followed using 2.5 g (0.011 mol) of **3b** and 3.1 g (0.037 mol) of *N*-methylhydroxylamine hydrochloride. The yield of **4b**·HCl was 1.95 g (62%): mp 177–178 °C; IR (Nujol) 2320, 1139, 981, 722, 698 cm^{-1}; NMR (Me_2SO-d_6) δ 1.60 (s, 3 H, and m, 2 H), 2.44 (m, 2 H), 3.19 (s, 3 H), 3.30 (m, 1 H), 3.88 (m, 1 H), 4.59 (q, 2 H), 7.45 (m, 5 H), 10.8 (b ex, 1 H); MS *m/e* 249 (M^+), 220, 172.

Anal. Calcd for $C_{14}H_{20}ClNOS$: C, 58.82; H, 7.05; N, 4.90. Found: C, 58.97; H, 7.15; N, 4.69.

***N*-Methyl-*cis-trans*-2-hydroxymethyl-5-methyl-5-phenylcyclopentylamine Hydrochloride (5).** A mixture of 13.8 g (0.054 mol) of **4a**·HCl and 2 g of 10% Pd/C in 330 mL of 95% ethanol was hydrogenated at 25 °C and 40 psi until uptake ceased. The mixture was filtered through Celite, concentrated, and crystallized from ether/acetone to give 12.1 g (88%) of **5**: mp 178–180 °C; IR (Nujol) 3346, 2708, 1588, 1068, 1041, 761, 692 cm^{-1}; NMR (Me_2SO-d_6) δ 1.53 (s, 3 H), 1.89 (m, 4 H), 2.46 (s, 3 H, and m, 1 H), 3.77 (m, 1 H), 3.72 (d, 2 H), 7.42 (m, 5 H); MS *m/e* 219 (M^+), 100, 70.

Anal. Calcd for $C_{14}H_{22}ClNO$: C, 65.73; H 8.67; N, 5.48. Found: C, 65.43; H, 8.57; N, 5.27.

Acknowledgment. We wish to acknowledge the support and encouragement of Dr. Neville Finch and the assistance of Ms. Ruth Behnke (NMR), Mr. Michael Hotolski and Ms. Natalie Cahoon (IR), and Mrs. Barbara Warren (MS).

Registry No.—1, 26939-22-0; **2a** epimer 1, 62744-02-9; **2a** epimer 2, 62744-03-0; **2b** epimer 1, 62744-04-1; **2b** epimer 2, 62744-05-2; **3a**, 62744-06-3; **3b**, 62744-07-4; **3b** DNP, 62744-08-5; **4a**, 62744-09-6; **4b**, 62744-10-9; **5**, 62744-11-0; 4-bromo-1-butene, 5162-44-7; *N*-methylhydroxylamine HCl, 4229-44-1.

Supplementary Material Available. The NMR spectrum of **4a**·HCl and LIS data (Tables I and II; 2 pages). Ordering information is given on any current masthead page.

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(4) Examination of molecular models shows the trans compound to be very rigid with the C_6 and C_7 protons held in an approximately cis eclipse relationship. This geometry requires that the coupling patterns for C_6 and C_7 be nearly the same, in contrast to the actual spectral data.

(5) The endo lone pair is the more sterically accessible owing to an unfavorable exo_2, exo_3 interaction.

Organotellurium Chemistry. 2. Dibenzyl Ditelluride: Some Transformations Involving Loss of Tellurium

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Received February 25, 1977

Dibenzyl diselenide (4) has been known for over a century,[1] and its chemistry has been extensively investigated.[2-4] In