(17) Gollnick, K.; Schroeter, S.; Ohloff, G.; Schade, G.; Schenck, G. O. *Justus Liebigs Ann. Chem.* **1965**, *687*, 14.
(18) The reported product ratio (Gollnick, K.; Schade, G. *Tetrahedron Lett.* **1966**, 2335) contradicted our rule. Reinvestigation[10] showed that this ratio must be inverted.
(19) Direct structural information is only available in the case of 1-methylcyclobutene (**1**), 3-thujene (**8**), and 3-carene (**13**). In the other cases, we extrapolate from the geometries of the stable conformers of the parent (*Z*)-cycloalkenes which are all known. The stable conformers of cyclobutene[20] and 1-methylcyclobutene[21] are planar. The pairs of allylic C—H bonds on each side of the ring have identical, mirror-symmetric orientations as in A. The stable conformers of cyclopentene, the envelope conformation,[22] and of cycloheptene, the mirror-symmetric chair,[22,23] both have pairs of allylic C—H bonds in identical, mirror-symmetric orientations on either side of the ring; one pair has quasi-axial orientations as in A and the other has quasi-equatorial orientations. The stable conformer of (*Z*)-cyclooctene[22,23] and both stable conformers of (*Z*)-cyclododecene[24] have no symmetry, but have a pair of allylic C—H bonds in nonidentical, quasi-axial orientations on one side of the ring, approximately as in A, and a pair in quasi-equatorial orientations on the other side. In contrast, the stable conformer of cyclohexene, the half-chair,[25] has pairs of allylic C—H bonds with *different* orientations, quasi-axial and quasi-equatorial, on each side of the ring, as in B. 3-Thujene (**8**) is essentially planar[26] and has a pair of allylic C—H bonds in different orientations but approximately as in A on one side of the ring. The geometry of 3-carene (**13**) is not known with certainty; it is either one of the boats[22c,27] or a planar form.[22c,28] The former has a local geometry similar to that of cyclopentene and -heptene, the latter one similar to that of cyclobutene. The geometry of 2-carene (**14**) is unknown.
(20) Bak, B.; Led, J. J.; Nygaard, L.; Rastrup-Anderson, J.; Sørenson, G. O. *J. Mol. Struct.* **1969**, *3*, 369. See also ref 23c.
(21) Huang, Y. S.; Beaudet, R. A. *J. Chem. Phys.* **1970**, *52*, 935.
(22) (a) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 5734, and references cited therein. (b) Ermer, O.; Lifson, S. *Ibid.* **1973**, *95*, 4121, and references cited therein. (c) Günther, H.; Jikeli, G. *Chem. Rev.* **1977**, *77*, 599, and references therein.
(23) Review: Casanova, J.; Waegell, B. *Bull. Soc. Chim. Fr.* **1975**, 911.
(24) Anet, F. A. L.; Rawdah, T. N. *Tetrahedron Lett.* **1979**, 1943.
(25) Eliel, E. L.; Allinger, N. L.; Angyal, S. T.; Morrison, G. A. "Conformational Analysis"; Interscience: New York, 1965.
(26) Abraham, R. J.; Holden, C. M.; Loftus, P.; Whittaker, D. *Org. Magn. Reson.* **1974**, *6*, 184.
(27) (a) Acharya, S. P. *Tetrahedron Lett.* **1966**, 4117. (b) Naumov, V. A.; Bezzubov, V. M. *Dokl. Akad. Nauk SSSR* **1966**, *171*, 634.
(28) Abraham, R. J.; Cooper, M. A.; Whittaker, D. *Org. Magn. Reson.* **1973**, *5*, 515.
(29) This hypothesis is reminiscent of, but different from, the previously established rule that an individual ene addition is favorable when the ground-state geometry of the substrate is such that the (single) C—H bond being broken is roughly perpendicular to the plane of the double bond.[6] This rule is almost solely based on data on half-chair cyclohexenes, which have only one such C—H bond, and are exceptions to our rule.
(30) For recent work, see: (a) Jefford, C. W. *Tetrahedron Lett.* **1979**, 985, and references cited therein. (b) Grdina, B.; Orfanopoulos, M.; Stephenson, L. M. *Ibid.* **1979**, 4351, and references cited therein.
(31) One of us has previously advanced this hypothesis,[2a] on the basis that the constitutional requirement for the PSEA to acyclic substrates appears to be the presence of the element $HC_a—C{=}C—C_bH$ (C_a, C_b cis).
(32) I.e., the Curtin-Hammett principle is applicable: the product composition depends on the relative energies of the transition states and *not* on the populations of the ground-state conformations. The Hammond postulate, however, may also be applicable: the transition states should resemble the reactants (provided that the rate-determining step is strongly exothermic; this may *not* be the case if a perepoxide or some related species is involved).

Karl H. Schulte-Elte,* Valentin Rautenstrauch*
Research Laboratories, Firmenich SA
CH-1211 Geneva 8, Switzerland

Received September 28, 1979

Isolation and Characterization of $[Rh_5(CO)_{10}(\mu_2\text{-}CO)_5]^-$: A Key Product in Rhodium Carbonyl Chemistry

Sir:

The dianion[1] $[Rh_{12}(CO)_{30}]^{2-}$ is known to react reversibly at room temperature with carbon monoxide. This reaction produces a labile species which previously was tentatively formulated as $[Rh_{12}(CO)_{\sim 34}]^{2-}$ on the basis of volumetric measurements of absorbed CO in THF,[2] and which has characteristic IR[2] and ^{13}C NMR[3] spectra. For several years we have tried to clarify the nature of this species because of its relevance both in rhodium carbonyl chemistry[3] and in the catalytic synthesis of ethylene glycol.[4] We now report that we have been able to reformulate the "$[Rh_{12}(CO)_{\sim 34}]^{2-}$ " species as $[Rh_5(CO)_{15}]^-$ and to obtain this pentanuclear cluster starting from $Rh_4(CO)_{12}$ and the $[Rh(CO)_4]^-$ anion.

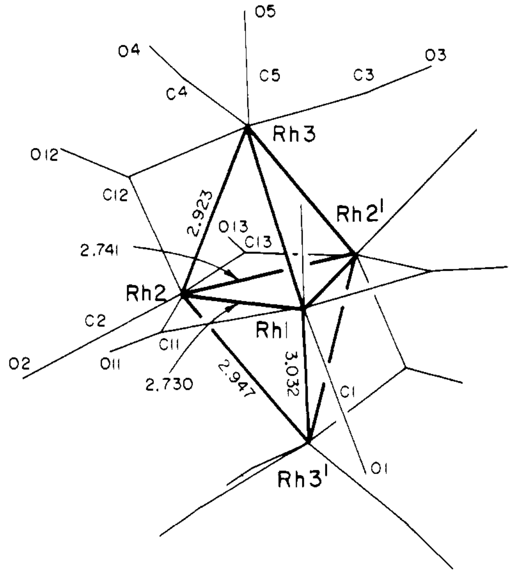

Figure 1. Atomic numbering scheme and Rh–Rh distances. Estimated standard deviations in distances are <0.001 Å.

At low temperature (−78 °C), reaction of $[Rh_{12}(CO)_{30}]^{2-}$ with carbon monoxide (1 atm P) in THF led to slow precipitation of $Rh_6(CO)_{16}$ in such a way that the resultant equilibrium shifted toward formation of the labile species. From the filtered solution maintained under CO at −10 °C, it was possible in fact to obtain red-brown crystals of an extremely reactive anionic species as the bis(triphenylphosphino)iminium (PPN) salt. The precipitation was carried out by means of slow diffusion of 2-propanol saturated with CO. The X-ray structural analysis presented here shows the anionic species to be $[Rh_5(CO)_{15}]^-$. The IR spectrum of this product in THF is identical with that previously reported[2] [2045 (s), 2010 (vs), 1868 (m), 1838 (ms), and 1785 (m) ± 10 cm^{-1}] but this solution is unstable at room temperature under N_2. The same species subsequently was obtained in ~80% yield using the following redox condensation reaction:

$$Rh_4(CO)_{12} + [Rh(CO)_4]^- \xrightarrow[THF]{CO} [Rh_5(CO)_{15}]^- + CO \qquad (1)$$

The $[PPN]^+[Rh_5(CO)_{15}]^-$ salt has been characterized by single-crystal X-ray diffraction techniques. The compound crystallizes in space group $P2/a$, with cell dimensions a = 19.313 (3), b = 9.375 (2), c = 14.804 (2) Å; β = 93.20 (1)°; and Z = 2. Observed and calculated densities are in satisfactory agreement: ρ_{obsd} = 1.81 and ρ_{calcd} = 1.83 g cm^{-3}, assuming a formula weight of 1473. Diffraction data were obtained with an Enraf-Nonius CAD4 diffractometer, using Nb-filtered Mo $K\bar{\alpha}$ (λ = 0.71069 Å) radiation. The structure was solved by standard heavy-atom methods and refined by a full-matrix least-squares procedure to yield an unweighted agreement factor on F^2 of R = 0.050 for 5837 reflections with $(\sin \theta/\lambda) < 0.65$ $Å^{-1}$.[5]

The structure of the $[Rh_5(CO)_{15}]^-$ anion in the crystalline state is illustrated in Figures 1 and 2. The metal atoms form a trigonal bipyramid, and the anion as a whole possesses crystallographic C_2 symmetry. A twofold axis passes through one of the Rh atoms in the equatorial plane [Rh(1)] and a bridging carbonyl ligand [CO(13)].[6] Altogether, there are ten terminal carbonyls [three each on the axial Rh(3) and Rh(3'),

0002-7863/80/1502-1740$01.00/0

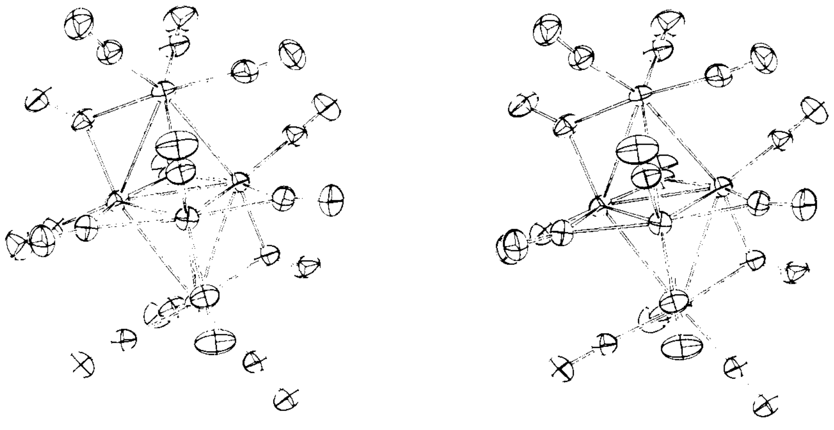

Figure 2. Stereoscopic view of the anion with thermal ellipsoids drawn at the 20% probability level.

two on Rh(1), and one each on Rh(2) and Rh(2′)] and five μ_2-bridging carbonyls, spanning the equatorial Rh—Rh bonds in addition to Rh(2)—Rh(3) and Rh(2′)—Rh(3′). Metal-metal bond distances in the anion are indicated in Figure 1; bond distances involving the carbonyl ligands fall in the following ranges: Rh—C (terminal), 1.896 (7)-1.975 (6); Rh—C (bridging), 1.999 (5)-2.226 (5); C═O (terminal), 1.077 (8)-1.125 (8); C═O (bridging), 1.085 (7)-1.122 (7) Å.

The present structure is an example of a trigonal-bipyramidal cluster with 76 valence electrons. Several other systems of this type are known, i.e. $[Ni_5(CO)_{12}]^{2-}$,[7] $[M_2Ni_3(CO)_{16}]^{2-}$ (M = Cr, Mo, W),[8] $[PtRh_4(CO)_{14}]^{2-}$,[9,10] and $[Rh_5(CO)_{14}I]^{2-}$.[11] In agreement with predictions of extended Hückel molecular orbital calculations,[12] the $[Rh_5(CO)_{15}]^-$ cluster is elongated as is $[Ni_5(CO)_{12}]^{2-}$, in contrast to the situation for the 72-electron system $Os_5(CO)_{16}$ which is found to be more nearly regular.[13] In $[Rh_5(CO)_{15}]^-$ the average of the Rh—Rh bond distances in the equatorial plane is 2.73 Å, while the Rh—Rh distances involving the axial Rh atoms range from Rh(2)—Rh(3) = 2.923 (1) Å, for the edge spanned by the unique bridging carbonyl [CO(12)], to Rh(1)—Rh(3) 3.032 (1) Å. This latter distance corresponds to one of the longest known Rh—Rh bonds.[14] Nevertheless, the degree of elongation in $[Rh_5(CO)_{15}]^-$ is considerably less than that observed in $[Ni_5(CO)_{12}]^{2-}$.[7] In both clusters, terminal M—C bonds involving axial metal atoms are significantly longer than those involving equatorial metals. In $[Rh_5(CO)_{15}]^-$ this trend is also reflected in the asymmetric character of the bridging CO(12) [Rh(2)—C(12) = 1.999 (5) Å; Rh(3)—C(12) = 2.114 (6) Å].[15]

At −80 °C in perdeuterioacetone, the 25- and 90-MHz ^{13}C NMR spectra of the $[Rh_5(CO)_{15}]^-$ anion are identical and are the same as that previously reported[3] for "$[Rh_{12}(CO)_{\sim 34}]^{2-}$". They consist of a triplet[16] at 247.7 ($J_{Rh_a\text{-}C}$ = 32.7 Hz), a doublet of doublets at 207.9 ($J_{Rh_a\text{-}C}$ = 66.9, $J_{Rh_b\text{-}C}$ = 8.3 Hz), and a doublet at 190.6 ppm ($J_{Rh_b\text{-}C}$ = 68.4 Hz) with relative intensities of 2.6:6:6, respectively. Specific ^{103}Rh spin decoupling of the ^{13}C NMR spectrum shows the presence of two different types of rhodium atoms assigned to equatorial (Rh_a) and axial (Rh_b) positions in agreement with the structure of the metallic polyhedron observed in the solid state. Decoupling the equatorial rhodium atoms (δ_{Rh_a} −148.5 ppm)[17] transforms the triplet into a singlet and removes the larger coupling in the doublet of doublets, while decoupling the axial rhodium atoms (δ_{Rh_b} −948.5 ppm)[17] both removes the smaller coupling in the doublet of doublets and collapses the high-field doublet to a singlet. These observations suggest that the anion in solution has a somewhat different arrangement of the carbonyl ligands than that found in the solid. The structure in solution could be D_{3h} and involve six asymmetric bridging carbonyls between Rh_a and Rh_b, leaving the bridging carbonyls between Rh_a's and terminal carbonyls on Rh_b unchanged from the solid-state structure. Alternatively a dynamic situation could occur by means of a rearrangement of the type shown in Figure 3. In the latter case the bridging carbonyls between Rh_a and Rh_b would spend a significantly longer time on Rh_a than Rh_b.

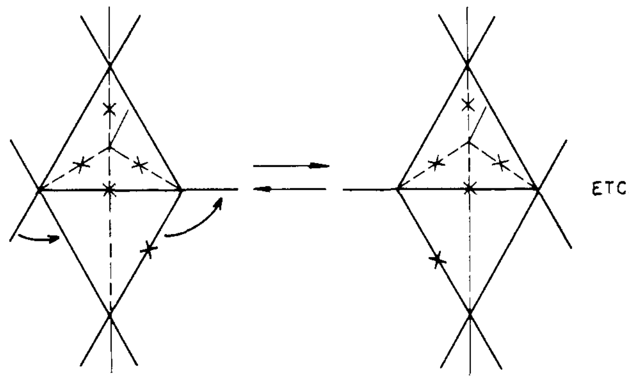

Figure 3. Schematic representation of one of the possible rearrangements of the solid-state structure of $[Rh_5(CO)_{15}]^-$ in solution (X = bridging CO).

Finally, it has been observed that the slow decomposition of $[Rh_5(CO)_{15}]^-$ species in THF solution under nitrogen takes place according to the reversible equilibrium

$$6[Rh_5(CO)_{15}]^- \underset{CO}{\overset{N_2}{\rightleftharpoons}} 2[Rh_{12}(CO)_{30}]^{2-} + [Rh_6(CO)_{15}]^{2-} + 15CO \quad (2)$$

as shown both by IR and ^{13}C NMR spectroscopy, while other as yet unidentified products are formed under prolonged evacuation. At the present moment eq 2 appears to be a key reaction involved in the reported equilibrium between "$[Rh_{12}(CO)_{\sim 34}]^{2-}$" and $[Rh_{12}(CO)_{30}]^{2-}$.[18] In light of the above, the reported instability of $[Rh_6(CO)_{15}]^{2-}$ and $[Rh_7(CO)_{16}]^{3-}$ toward CO at low temperature[19] may now be regarded as resulting from a simple cleavage of one and two Rh atoms respectively, yielding the pentanuclear species together with $[Rh(CO)_4]^-$.

Further work is in progress in order to understand the nature of the other products involved in the complex equilibrium between the anions $[Rh_5(CO)_{15}]^-$ and $[Rh_{12}(CO)_{30}]^{2-}$, as a function of the relative concentration of CO as well as of the temperature.

Acknowledgments. Work at Brookhaven National Laboratory was carried out under contract with the U.S. Department of Energy, Office of Basic Energy Sciences. We (P.C. and B.T.H.) also thank the CNR for a grant and Dr. C. Brown for recording the $^{13}C[^{103}Rh]$ NMR spectra.

Supplementary Material Available: A listing of atomic parameters, complete interatomic bond distance and angles, and structure factor tables (38 pages). Ordering information is given on any current masthead page.

References and Notes

(1) The structure of $[Rh_{12}(CO)_{30}]^{2-}$ consists of two Rh_6 octahedra, joined together by a single Rh—Rh bond and sharing two μ_2-bridging CO ligands: Albano, V. G.; Bellon, P. L. *J. Organomet. Chem.* **1969,** *19*, 405.

(2) Chini, P.; Martinengo, S. *Inorg. Chim. Acta* **1969,** *3*, 299.

(3) Chini, P.; Longoni, G.; Albano, V. G. *Adv. Organomet. Chem.* **1976,** *14*, 285. Values quoted on page 330 from unpublished work of Heaton, B. T.; Chini, P.; Martinengo, S.; McCaffrey, D. J. A.; Fumagalli, A.

(4) (a) Brown, E. S. U.S. Patent 3 929 969, 1975. Kaplan, L. U.S. Patent 3 944 588, 1976; Cawse, J. N. U.S. Patent 3 948 965, 1976; 4 013 700, 1977. Pruett, R. L.; Walker, W. E. U.S. Patent 3 957 857, 1976. (b) Pruett, R. L. *Ann. N.Y. Acad. Sci.* **1977,** *295*, 239.

(5) $R = \sum |F_o^2 - F_c^2| / \sum F_o^2$. Anomalous dispersion corrections were included for P and Rh atoms; positional and anisotropic thermal parameters were varied for all nonhydrogen atoms, while H atoms were not included. The goodness of fit, $S = [\sum w(F_o^2 - F_c^2)^2/(n - m)]^{1/2} = 1.00$, where w is the weight assigned to each reflection, n the number of observations (5837), and m the number of variable parameters (336). Weights were taken as inversely proportional to the estimated variance of each reflection where $\sigma^2(F_o^2) = \sigma_{count}^2 + (C_1 \times F_o^2)^2 + C_2$. The constants C_1 and C_2 were adjusted during the refinement process; final values are $C_1 = 0.007$ and $C_2 = 4486.0$.

(6) An additional twofold axis passes through the N atom of the PPN cation. The cation is bent, with a P–N–P angle of 148.6 (4)°.

(7) Longoni, G.; Chini, P.; Lower, L. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1975,** *97*, 5034.

(8) Ruff, J. K.; White, R. P.; Dahl, L. F. *J. Am. Chem. Soc.* **1971,** *93*, 2159.

(9) Fumagalli, A.; Martinengo, S.; Chini, P.; Albinati, A.; Brückner, S. XIX International Conference on Coordination Chemistry, Prague, 1978, Proceedings II, p 45.

(10) Basically, the structure of $[PtRh_4(CO)_{14}]^{2-}$ is derived from that of $[Rh_5(CO)_{15}]^-$ by replacing Rh(1) and its two terminal carbonyl ligands with a Pt atom terminally bound to one carbonyl.

(11) Martinengo, S.; Ciani, G.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1979,** 1059.

(12) Lauher, J. W. *J. Am. Chem. Soc.* **1978,** *100*, 5305.

(13) Eady, C. R.; Johnson, B. F. G.; Lewis, J.; Reichert, B. E.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1976,** 271.

(14) A Rh—Rh distance of 3.029 (1) Å has been reported in $[Rh_9P(CO)_{21}]^{2-}$, an anion with an interstitial P atom: Vidal, J. L.; Walker, W. E.; Pruett, R. L.; Schoening, R. C. *Inorg. Chem.* **1979,** *18*, 129.

(15) The presence of CO(12) bridging between equatorial and axial metals is responsible for the marked bending of the terminal carbonyl on Rh(2) out of the equatorial Rh_3 plane (the Rh(2)—C(2) bond is inclined 20.4 (2)° to the plane).

(16) The triplet is only found in samples with low (~25%) ^{13}C-isotopic enrichment; at higher levels of enrichment (~80%) the resonance becomes more complex owing to the presence of significant concentrations of isotopomers which exhibit coupling between the edge-bridging CO's in the equatorial plane.

(17) 3.16 MHz = 0 ppm for δ_{Rh} when using a magnetic field such that the protons in Me_4Si resonate at exactly 100 MHz.

(18) As has been noted above, at low temperature (−78 °C) and P(CO) of 1 atm, precipitation of $Rh_6(CO)_{16}$ takes place, and the equilibrium is shifted to the left.

(19) Martinengo, S.; Chini, P. *Gazz. Chim. Ital.* **1972,** *102*, 344.

Alessandro Fumagalli, Thomas F. Koetzle*
Fusao Takusagawa
Chemistry Department, Brookhaven National Laboratory
Upton, New York 11973

Paolo Chini,* Secondo Martinengo
Istituto di Chimica Generale dell'Università e
Centro del CNR per la Sintesi e la Struttura dei Composti
dei Metalli di Transizione nei Bassi Stati di Ossidazione
Via G. Venezian 21, I-20133 Milano, Italy

B. T. Heaton*
University Chemical Laboratory
Canterbury, Kent CT2 7NH, England

Received October 12, 1979

Total Synthesis of (±)-Aphidicolin

Sir:

The tetracyclic diterpene aphidicolin (**1**) is noteworthy both for its intriguing molecular structure and for its biological effect as a potent antiviral and antimitotic agent.[1] We outline herein a synthesis of the racemate of **1** by an approach which includes a number of unique steps. The presently described route is based on a line of analysis which is completely different from that for two syntheses of (±)-**1** which have recently been reported.[2,3]

The oxygenated geranyl bromide **2** was prepared from geranyl acetate by the following sequence: (1) reaction with 1 equiv of selenium dioxide[4] at reflux in 95% ethanol for 1 h followed by brief treatment with sodium borohydride to form the *E,E* 8-hydroxylated derivative (61%), (2) protection of the 8-hydroxyl group as the *tert*-butyldimethylsilyl ether (*tert*-butyldimethylsilyl chloride, 4-dimethylaminopyridine, triethylamine in CH_2Cl_2 at −20 °C),[5] (3) acetate cleavage (potassium carbonate in methanol at 0 °C, 90% over two steps), and (4) conversion of the resulting hydroxy silyl ether into **2** via the mesylate (1 equiv of triethylamine, 1 equiv of CH_3SO_2Cl, in CH_2Cl_2 at −40 °C) by reaction with 2 equiv of lithium bromide in tetrahydrofuran (THF). The solution of the unstable bromide **2** was immediately added to a stirred solution of the lithio-sodio derivative of methyl acetoacetate in THF at 0 °C to give after chromatography on silica gel the keto ester **3**[6-8] (90% overall from 8-*tert*-butyldimethylsilyloxygeraniol).

Treatment of β-keto ester **3** with 1.1 equiv each of sodium hydride and diethyl chlorophosphate[9] in ether at 0 °C afforded the enol phosphate ester **4** which upon reaction with 1 equiv of mercuric trifluoroacetate[10] in nitromethane at 0 °C followed by aqueous sodium chloride produced the mercurated bicyclic keto ester **5** [mp 157–159 °C, IR max 1740, 1710 cm^{-1} ($CHCl_3$)] in 60% yield along with 20% of monocarbocyclic product. Rings A and B were thus established in a single step; the stereochemistry of the product, expected to be as shown from much literature precedent, was established by correlation with intermediates of known constitution produced as described below.

Treatment of **5** with ethylene glycol and a catalytic amount of *p*-toluenesulfonic acid in benzene at reflux gave the corresponding ethylene ketal, mp 160–161 °C (90% yield), which was converted into the keto acetal **6**, mp 127–130 °C, in 58% overall yield by the following sequence: (1) replacement of mercury by hydroxyl by addition to a solution of 2 equiv of sodium borohydride in dimethylformamide (DMF), saturated with oxygen by continuous bubbling at 23 °C, to give a mixture of C-3 epimeric alcohols, (2) oxidation to C-3 ketone using pyridinium dichromate[12] in methylene chloride at 23 °C, (3) desilylation with tetra-*n*-butylammonium fluoride[5] in THF at 0 °C for 30 min, (4) stereospecific reduction of the keto function at C-3 using lithium tri-*sec*-butylborohydride in THF at −78 °C,[13] and (5) acetalization by reaction with 1.2 equiv of pivalaldehyde and 0.15 equiv of *p*-toluenesulfonic acid in CH_2Cl_2 at 0 °C for 30 min. Reduction of **6** using lithium aluminum hydride in ether at 23 °C for 1 h, followed by oxidation of the resulting primary alcohol using 4 equiv of pyridinium chlorochromate in CH_2Cl_2 at 23 °C and deketalization (10:1:1 acetone-water-70% aqueous perchloric acid at 23 °C for 3 h), afforded keto aldehyde **7**, mp 106–108 °C, in 90% overall yield from **6**.

The keto aldehyde **7** was also synthesized by a more conventional route,[14] part of which has been used in recent syntheses of (±)-**1**.[2,3] Keto acetal **8** [made starting from 5,9-dimethyl-5(10)-octalin-1,6-dione][2,3] was converted into its trimethylsilyl enol ether with lithium diisopropylamide (LDA), followed by trimethylsilyl chloride, and epoxidized in CH_2Cl_2 with 1.1 equiv of *m*-chloroperbenzoic acid at −20 °C.[15] Treatment of the crude product with ethanolic KOH, followed by oxidation with 2 equiv of bismuth trioxide in acetic acid-acetone[16] at 135–140 °C in a pressure flask for 1.5 h, gave in quantitative yield the α diketone which was transformed into methyl enol ether **9** [IR max 1685, 1640 cm^{-1} ($CHCl_3$)] in 87–88% yield by reaction with 2.5 equiv of potassium *tert*-

0002-7863/80/1502-1742$01.00/0