In only a few cases are structural data of gold halide complexes in the solid state available.[1] In all cases they compare favorably with our calculated HF values: e.g., the Au–F bond distance in $KAuF_4$ is 1.95 Å,[1] which is in excellent agreement with our value (Table I). The relativistic bond contractions ($\Delta_R r_e = r_e(NR) - r_e(R)$) are much smaller for the Au(III) halide complexes ($\Delta_R r_e < 0.12$ Å) compared to the Au(I) species ($\Delta_R r_e < 0.23$ Å).[3] This is probably due to the larger 5d contributions in the Au(III)–X bond relative to the Au(I)–X bond quenching the effect of the relativistic bond contraction originating from the 6s orbital.[8] In contrast to Au(I) halides[3] a relativistic bond stabilization ($\Delta_R D_e = D_e(NR) - D_e(R) < 0$) is found for Au(III) halides. The dissociation energies (Tables I and II) show that the size of this effect is dependent on the nature of the ligand as well as on the magnitude of the 5d participation in the Au–X bond (at the HF level $\Delta_R D_e$ is 74.5 kJ mol^{-1} for AuF,[3] 3.8 kJ mol^{-1} for AuF_2^-, and −94.1 kJ mol^{-1} for AuF_4^-, and this trend compares with the gross 5d population[8]). Comparing the dissociation energies for both AuX_2^- and AuX_4^-, we obtain the differences in the HF energies ΔU_0 in eq 1. In all cases the nonrelativistic value of ΔU_0 falls in the range −80 to −150 kJ mol^{-1}, indicating that the oxidation state +I is preferred (a negative ΔU_0 favors the right-hand side of eq 1 if entropy effects are neglected). This does not change if we add the HF dissociation energies for the diatomic halides,[9] $D_e(X_2)$. In contrast, the relativistic values of ΔU_0 are positive for fluorine but slightly negative for bromine and iodine (−13 and −39 kJ mol^{-1}, respectively). Furthermore, experimentally AuI_4^- and AuI_2^- were observed to be in equilibrium,[10] which is consistent with the relatively small calculated relativistic value of ΔU_0 shown in Table I. Hence, the nonrelativistic results clearly show a preference for the oxidation state +I in gold. The unusual high thermodynamic stability of the Au(III) halide complexes is therefore a relativistic effect.

Correcting for spin-orbit coupling does not modify this conclusion. The spin-orbit-corrected dissociation energies D_e and the ΔU_0^{SO} values (Table I and II) have been derived from atomic Dirac–Fock calculations[11] by using program MCDF.[12] Also electron correlation is not expected to modify the HF trends because correlation effects in $D_e(NR)$ and $D_e(R)$ would be similar, and the difference $\Delta_R \Delta U_0^{SO} = \Delta U_0(NR) - \Delta U_0^{SO}(R)$ is very large at the HF level (195 kJ mol^{-1} for AuF_4^-). To support this, configuration interaction (CI) calculations with single and double substitutions (CISD) for AuF_2^- and AuF_4^- at the relativistic as well as the nonrelativistic level of the theory have been carried out, the latter only at the calculated HF bond distances given in Table I.[14] At the CISD and the size-consistency corrected level (CISDSC)[6] both the nonrelativistic and relativistic D_e values for AuF_2^- were comparable to the calculated HF values. At the given HF bond distances for AuF_4^- $\Delta_R \Delta U_0 = 137.2$ kJ mol^{-1} at the CISDSC level, which is still significantly large (cf. Table I).

The preference of coordination number two in Au(I) halides is seen if we compare the two dissociation energies D_e^1 and D_e^2 given in Table II. Relativistic and spin-orbit effects increase the preference for this coordination number. Furthermore, the value of D_e for AuF_2^- suggests that this compound, the only example of the AuX_2^- series not currently known, should be a stable species if a suitable synthetic route can be developed.[15] The Au(III) fluorine complex is the most stable found along the halide series. This is consistent with the fact that the only isolated Cu(III) and Ag(III) complexes are the fluorine complexes of the alkali metals, e.g., $CsCuF_4$ and $CsAgF_4$,[16] both of which are more reactive than $CsAuF_4$.[16] Also, AuI_4^- has never been isolated[1] consistent with the negative ΔU_0^{SO} value calculated on the nonrelativistic and relativistic level of the theory. A detailed analyses will be the subject of a further paper in this series.

Acknowledgment. I am indebted to the Alexander von Humboldt-Stiftung for financial support and to IBM New Zealand Ltd. for providing large amounts of computer time. Thanks are due to M. Dolg for providing part of the basis sets and pseudopotentials and to W. H. E. Schwarz, L. P. Aldridge, P. D. W. Boyd, and P. J. Brothers for carefully reading this paper.

Registry No. AuF_4^-, 43739-91-9; $AuCl_4^-$, 14337-12-3; $AuBr_4^-$, 14337-14-5; AuI_4^-, 14349-64-5; AuF_2^-, 55031-54-4; $AuCl_2^-$, 21534-24-7; $AuBr_2^-$, 23000-74-0; AuI_2^-, 23000-72-8.

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[7] For $AuCl_4^-$ a basis set of 260 primitive Gaussians contracted to 157 basis functions was used producing a total number of 28 million two-electron integrals. A HF geometry optimization required about 40 h CPU time on a IBM3081 computer.

[8] Mulliken population analyses show that the gross orbital population of the Au(5d) orbital at the relativistic level in AuF is 9.92, in AuF_2^- 9.67, and in AuF_4^- 8.80.

[9] (a) Schwerdtfeger, P.; Szentpāly, L. v.; Vogel, K.; Silberbach, H.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1985**, *84*, 1606. (b) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986. (c) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797.

[10] Ryan, J. L. *Inorg. Chem.* **1969**, *8*, 2058.

[11] This procedure is justified since the molecular ground-state spin-orbit corrections Δ_M^{SO} are expected to be very small compared to the atomic corrections Δ_A^{SO}.[9,13]

[12] (a) Grant, I. P.; McKenzie, B. J.; Norrington, P. H.; Mayers, D. F.; Pyper, N. C. *Comp. Phys. Commun.* **1980**, *21*, 207. (b) Moore, C. E. Atomic Energy Levels, Natl. Bur. Stand. (U.S.) Circ. No. 467, U.S. GPO Washington, D.C., 1958.

[13] Schwarz, W. H. E. In *Theoretical Models of Chemical Bonding*; Springer: Heidelberg, 1989; Vol. 2.

[14] Configuration interaction calculations are very time consuming for the Au(III) halide complexes. For example, the active CI space has been limited to 103 functions for AuF_4^- including the (5s5p5d) core of gold in the active space (active orbital-energy range −5 to +5 au). A one-point CI calculation required about 50 h CPU time on a IBM3081 computer.

[15] The counterion M^+ in $MAuF_2$ should not have a large M–F dissociation energy to avoid the disproportionation $3MAuF_2 \rightarrow MAuF_4 + 2MF + 2Au$.

[16] (a) Hoppe, R.; Klemm, W. *Z. Anorg. Allg. Chem.* **1952**, *268*, 364. (b) Hoppe, R. *Z. Anorg. Allg. Chem.* **1957**, *292*, 28. (c) Fleischer, T.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1982**, *492*, 76.

[*n*]Staffanes: The Parent Hydrocarbons

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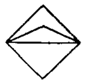
Received April 12, 1989

Doubly end-functionalized [*n*]staffanes, the oligomers of [1.1.1]propellane (**1**), have been proposed for use as elements of a molecular-size "Tinkertoy" construction set.[1] The unsubstituted hydrocarbons [*n*]**1** represent important model compounds for investigations of the structure, vibrations, and electronic properties of these building elements, but only the first two, [1]**1**[2] and [2]**1**,[3] have been known. We report the preparation and characterization of the individual oligomeric hydrocarbons up to $n = 6$ and of a mixture of higher polymers.



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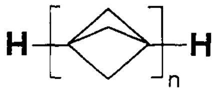

[n]1

[*n*]Staffanes carrying groups X and Y at the bridgehead positions result from radical-induced addition of **1** across single X–Y bonds.[1,3-5] The parent hydrocarbons have now been pre-

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[1] Kaszynski, P.; Michl, J. *J. Am. Chem. Soc.* **1988**, *110*, 5225. Michl, J.; Kaszynski, P.; Friedli, A. C.; Murthy, G. S.; Yang, H.-C.; Robinson, R. E.; McMurdie, N.; Kim, T. In *Strain and Its Implications in Organic Chemistry*; de Meijere, A., Blechert, S., Eds.; NATO ASI Series, Vol. 273; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989; p 463.

[2] Wiberg, K. B.; Connor, D. S. *J. Am. Chem. Soc.* **1966**, *88*, 4437.

[3] Bunz, U.; Polborn, K.; Wagner, H.-U.; Szeimies, G. *Chem. Ber.* **1988**, *121*, 1785.

0002-7863/89/1511-7262$01.50/0

Table I. Structural Parameters of [*n*]**1**

n	*L*(H···H)[a]	*R*(C–C)[a]	*L*(C···C)[a]	*R*[a]	ρ[b]	mp[c]
3	10.44	1.457 (8)	1.866 (9), 1.869 (8)	5.27	1.13	142–144
4	13.74	1.473 (6), 1.498 (8)	1.886 (7), 1.888 (6)	5.36	1.10	240–242

[a] *L*(H···H) is the end-to-end length, *R*(C–C) is the interbridgehead bond length, *L*(C···C) is the interbridgehead separation, and *R* is the axis-to-axis intermolecular separation, all in units of Å. [b] Density in g cm^{-3}. [c] Uncorrected melting points in °C (sealed capillary); the value for [2]**1** is 32–33, for [5]**1**, 290 (dec); [6]**1** starts to decompose at 290 °C.

Table II. ^{1}H and ^{13}C NMR Chemical Shifts of [*n*]**1**[a]

n	CH	CH$_2$[b]		
2	2.360	1.610		
3	2.365	1.588	1.384	
4	2.362	1.583	1.365	
5	2.359	1.579	1.357	1.344
6	2.358	1.577	1.356	1.338

	C$_3$CH	C$_2$CH$_2$[b]			CCC$_3$[b]			
2	26.36	49.75			45.40			
3	26.39	49.08	47.80		45.25	38.14		
4	26.39	49.08	47.73		45.29	38.20	37.96	
5	26.38	49.08	47.72	47.65	45.29	38.19	37.99	38.02

[a] In ppm relative to TMS; accuracy: ^{1}H, ±0.003; ^{13}C, ±0.02. [b] Assignment, from left to right: from the end toward the center of the molecule.

pared by the addition of **1** across the H–H bond. A mixture of Ar and H$_2$ or NH$_3$ (5%) was passed through a microwave discharge[6] and then over a stirred 0.6 M solution of **1**[7,8] in *n*-pentane at −110 °C for 10 h (0.75 L/h) at a pump pressure of 1 Torr. Evaporated volatiles collected in a 77 K trap were periodically returned to the solution. After **1** was consumed, distillation and gradient sublimation yielded almost pure [*n*]staffanes[9] [(*n*, % yield): 2, 13; 3, 9; 4, 6; 5, 2; 6, 0.3] and a 14% yield of a nonvolatile polymer insoluble in common solvents. Its CP-MAS ^{13}C NMR, X-ray diffraction, and thermal behavior were nearly identical with those of the terminally substituted poly([1.1.1]propellane) prepared previously[1] with other free-radical or anionic initiators. Material with the same properties also results from spontaneous polymerization of nearly neat **1**.[10]

Single-crystal X-ray diffraction (Table I) confirmed the anticipated linear molecular shape and staggered conformation. The length increment in the series is 3.3 Å. The interbridgehead C–C bonds are remarkably short, even shorter than in [2]**1**[1,3] and [3]**1**[1,5] carrying one or two bridgehead substituents. This result has been predicted by molecular mechanics,[11] is reproduced by our MINDO/3, MNDO, and AM1 calculations as well as by ab initio SCF/3-21G[12] calculations, and recently has been noted also in bicubyl derivatives.[13] It is understood readily in terms of orbital hybridization (Bent's rules[14]): the small endocyclic CCC valence angles force an increase in the s character of the hybrid AO used for the exocyclic bond. The crystal packing (Figure 1) is of the herringbone type expected[15] for straight rods, with a ~20° inclination that permits neighboring staffs to mesh.

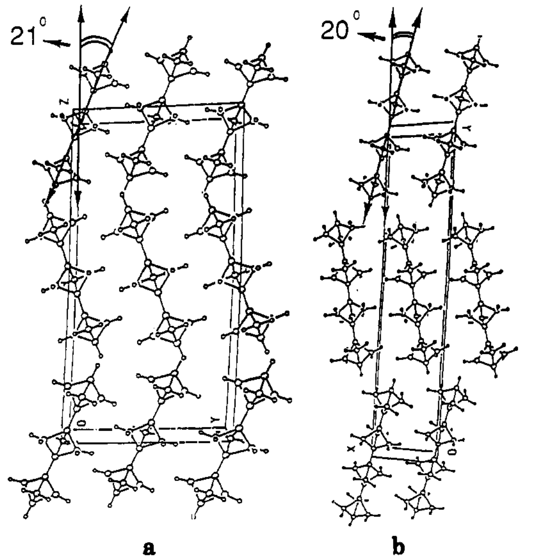

Figure 1. Packing diagrams of (a) [3]**1** projected along the *x* axis and (b) [4]**1** projected along the *z* axis.

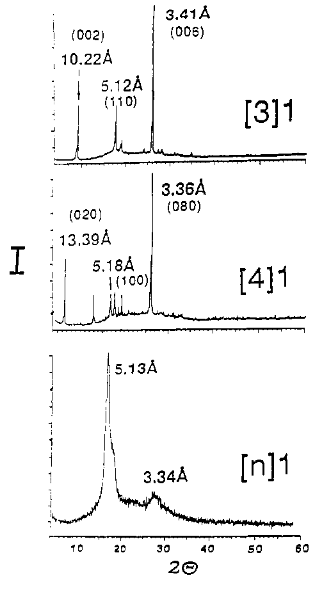

Figure 2. X-ray powder diffraction patterns of [3]**1**, [4]**1**, and polymeric [*n*]**1**. The *d* values and their Miller indices are indicated.

Table II collects the NMR assignments for [*n*]staffanes. Their IR spectra, assigned by using ab initio calculations and polarization measurements,[12] are characterized by three strong CH stretches near 2960, 2905, and 2868 cm^{-1}, CH$_2$ scissors at ~1450 cm^{-1}, a very strong CH$_2$ wag at ~1210 cm^{-1}, and a CH$_2$ rock at ~540 cm^{-1}. Weak accordion-type vibrations have been assigned at the unusually high value of ~1370 cm^{-1}, compatible with the very short interbridgehead C–C single bonds. Very weakly allowed staff bending vibrations are calculated for the far-IR region but have not yet been observed. The calculated barrier to internal rotation is low (<2 kcal/mol).

X-ray powder diffraction patterns of the oligomers extrapolate to that of the polymer (Figure 2). The *d* values of the (002)

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(4) Wiberg, K. B.; Waddell, S. T.; Laidig, K. *Tetrahedron Lett.* **1986**, *27*, 1553.

(5) Friedli, A. C.; Kaszynski, P.; Michl, J. *Tetrahedron Lett.* **1989**, *30*, 455.

(6) KIVA MPG-4M microwave generator, 2450 MHz, 70-W output. This is an adaptation of a technique developed for the reaction of hydrogen atoms with olefins: Beeri, A.; Berman, E.; Viskautsan, R.; Mazur, Y. *J. Am. Chem. Soc.* **1986**, *108*, 6413.

(7) Prepared by the method of: Semmler, K.; Szeimies, G.; Belzner, J. *J. Am. Chem. Soc.* **1985**, *107*, 6410.

(8) See also: Kaszynski, P.; Michl, J. *J. Org. Chem.* **1988**, *53*, 4593.

(9) Analytical samples were obtained by gas chromatography. A mixture of numerous minor side products was also obtained in a total yield of 16%. The mechanism of their formation is under investigation.

(10) Schlüter, A.-D. *Polym. Commun.* **1989**, *30*, 34.

(11) Ermer, O.; Lex, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 447.

(12) Murthy, G. S.; Hassenrück, K.; Balaji, V.; Michl, J., unpublished results.

(13) 4-*tert*-Butylbicubyl, 1.458 (8) Å: Gilardi, R.; Maggini, M.; Eaton, P. E. *J. Am. Chem. Soc.* **1988**, *110*, 7232. 4-Bromobicubyl, 1.473 (5) Å: Hassenrück, K.; Lynch, V. M.; Michl, J., submitted for publication.

(14) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

(15) Slater, J. C. *Introduction to Chemical Physics*: McGraw-Hill: New York; 1939; p 422.

reflection of [3]**1** and (020) of [4]**1** correspond closely to molecular lengths. Absence of diffraction in this region from [*n*]**1** is due to the lack of uniform chain length in the polymer. Reflections (110) of [3]**1** and (100) of [4]**1** reveal a separation of ~5.2 Å between parallel molecular axes. The polymer has a strong peak at this *d* value, indicating that the staffs of varying lengths pack in a similar manner. Reflections (006) of [3]**1** and (080) of [4]**1** arise from intrastaff repetition of the bicyclic cages; in the polymer, $d \simeq 3\ 1/3$ Å. The comparison leaves no doubt that poly([1.1.1]propellane) indeed is a mixture of [*n*]staffanes with larger values of *n*, as deduced originally[1] from the CP-MAS ^{13}C NMR spectrum.

Acknowledgment. This research was supported by the National Science Foundation (Grant DMR 8807701). K.H. is grateful to the Alexander von Humboldt Foundation for a Feodor Lynen fellowship.

Rearrangement Approach to Bridgehead Substitution of 1-Methoxybicyclo[2.2.2]oct-5-en-2-ones

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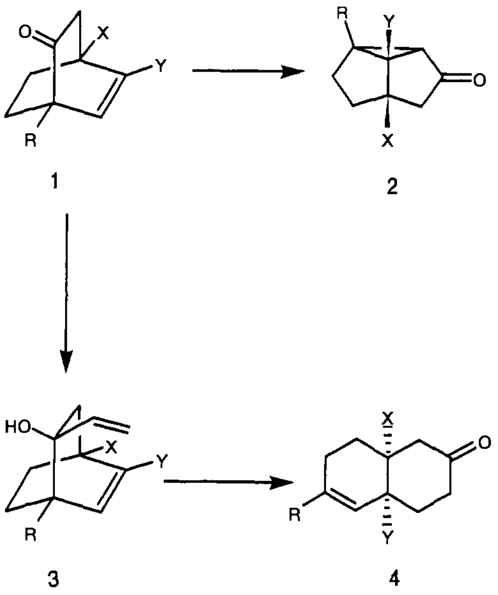
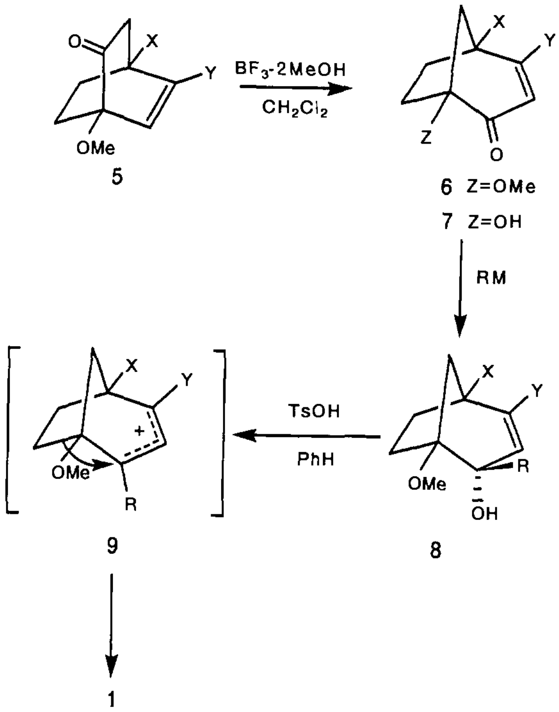
Bicyclo[2.2.2]oct-5-en-2-ones (**1**) are potential compounds which are convertible into [5-5] fused-ring systems (**2**) by the triplet sensitized photochemical process, oxa-di-π-methane rearrangement,[1] and also into [6-6] fused-ring systems (**4**) via vinylation followed by the oxy-Cope rearrangement of the *exo*-alcohols (**3**).[2] In connection with our studies on rearrangement strategies from bridged polycyclic compounds to [*m-n*] fused-ring natural products,[3] we were interested in principal preparation of compounds **1**. Straightforward routes to **1** seem to involve Diels–Alder reaction of 1,3-cyclohexadienes and ketene equivalents.[4] However, selective preparation of even a simply substituted 1,3-cyclohexadiene generally requires many steps.[5] Furthermore, the mode of substituents of the bicyclic ketones, thus obtained, depends upon the regioselectivity of the Diels–Alder reaction that we cannot reverse easily. To compensate these weak points, we must develop a new method for introduction of a substituent at the desired position, including the bridgehead carbon, of the bicyclic system. We wish to report herein formal bridgehead substitution of 1-methoxybicyclo[2.2.2]oct-5-en-2-ones (**5**), derived stereoselectively from anisoles by the Diels–Alder strategy including Birch reduction followed by selective isomerization into 1-methoxy-1,3-cyclohexadienes.[6]

Scheme I



Scheme II



Scheme II shows our rearrangement approach to the bridgehead substitution. The first step is a Lewis-acid-mediated pinacol-type transformation of **5** into the thermally more stable conjugated ketones **6**. When **5a** (X = Me, Y = H) was treated with BF_3–$2CH_3OH$ (1.2 equiv) in dry CH_2Cl_2 at room temperature for 1–2 h, the desired ketone **6a** was obtained in 90% yield along with **7a** (3%) due to ether cleavage.[7] The second step is introduction of a desired bridgehead substituent by treatment with an organometallic reagent (RM) adding in a 1,2-manner. A reaction of **6a** with MeLi gave the *endo*-alcohol **8a** (R = X = Me, Y = H) in 72% yield. The final step is a pinacol-type rearrangement which proceeds stereoselectively. The alcohol **8a** was converted into the bridgehead methyl ketone **1a** in 52% yield by treatment with TsOH (0.1 equiv) in boiling benzene for 5 min. This outcome

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(1) For recent reviews, see: Schaffner, K.; Demuth, M. *Modern Synthetic Method*; Scheffold, R., Ed.; Splinger-Verlag: Berlin, 1986; Vol 4, pp 61–88, pp 89–124.

(2) (a) Berson, J. A.; Jones, M., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 5017–5018, 5019–5021. (b) Gregson, P. G.; Mirrington, R. N. *J. Chem. Soc., Chem. Commun.* **1973**, 598–599. (c) Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765–4766. (d) Gregson, R. P.; Mirrington, R. N. *Aust. J. Chem.* **1976**, *29*, 2037. (e) Evans, D. A.; Golob, A. M.; Mandel, N. S.; Mandel, G. S. *Ibid.* **1978**, *100*, 8170–8174. (f) Hirota, H.; Kitano, M.; Komatsubara, K.; Takahashi, T. *Chem. Lett.* **1987**, 2079–2080.

(3) Uyehara, T.; Yamada, J.; Ogata, K.; Kato, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 211–216. Uyehara, T.; Yamada, J.; Kato, T.; Bohlmann, F. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 861–867. Uyehara, T.; Kabasawa, Y.; Furuta, T.; Kato, T. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 539–543. Uyehara, T.; Kabasawa, Y.; Kato, T. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2521–2528. Uyehara, T.; Yamada, J.; Furuta, T.; Kato, T.; Yamamoto, Y. *Tetrahedron* **1987**, *43*, 5605–5620. Uyehara, T.; Furuta, T.; Kabasawa, Y.; Yamada, J.; Kato, T.; Yamamoto, Y. *J. Org. Chem.* **1988**, *54*, 3669–3673.

(4) For a review, see: Ranganathan, S.; Ranganathan, D.; Mehrotra, A. K. *Synthesis* **1977**, 289–296.

(5) See, for example: reference 2d.

(6) Evans, D. A.; Scott, W. L.; Truesdale, L. K. *Tetrahedron Lett.* **1972**, 121–124. Birch, A. J.; Dastur, K. P. *Tetrahedron Lett.* **1972**, 4195–4198; *J. Chem. Soc., Perkin Trans. 1* **1973**, 1650–1652. Monti, S. A.; Chen, S.-C.; Yang, Y.-L.; Yuan, S.-S.; Bourgeois, O. P. *J. Org. Chem.* **1978**, *43*, 4062–4069.

(7) Similar conversion of a 1-methoxybicyclo[2.2.2]oct-5-en-2-one into a 1-hydroxybicyclo[3.2.1]oct-3-en-2-one, see: Monti, S. A.; Dean, T. R. *J. Org. Chem.* **1982**, *47*, 2679–2681.

0002-7863/89/1511-7264$01.50/0