The combined mixtures of the isomeric alcohols from two runs (570 mg, endo/exo ratio of 71:29) were chromatographed to afford (a) (−)-*endo*-alcohol **24** [110.7 mg (5.5% yield); mp 162–163 °C (sealed tube); $[\alpha]^{28}_D$ −51.6° (*c* 0.81); op 74%] and (b) (+)-*exo*-alcohol **25** [47.3 mg (2.4% yield); mp 163.5–165.5 °C (sealed tube); $[\alpha]^{25}_D$ +27.4° (*c* 1.3); op 90%].

(C) Catalytic Reduction of (−)-*endo*-Alcohol 24 and (+)-*exo*-Alcohol 25. A solution of 62.6 mg of (−)-**24** ($[\alpha]^{26}_D$ −49.3°, obtained from experiment A) in 3 mL of EtOH was hydrogenated at atmospheric pressure over 15 mg of 5% Pd/C. After filtration and evaporation of the solvent, the residue was sublimed in vacuo to afford 51.8 mg of (+)-bicyclo[2.2.2]octan-2-ol (**4**): mp 212–213 °C (sealed tube); $[\alpha]^{23}_D$ +22.6° (*c* 1.1); op 70.6%. Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.22; H, 11.17.

Hydrogenation of 65 mg of (+)-**25** ($[\alpha]^{26}_D$ +21.0°, obtained from experiment A) in EtOH with 5% Pd/C gave 52.2 mg of (+)-**4**: mp 213–215 °C (sealed tube); $[\alpha]^{23}_D$ +22.0° (*c* 1.08); op 68.8%. Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.17; H, 11.31.

Registry No. 3, 5019-82-9; (+)-(2*S*)-**4**, 40335-86-2; (±)-**5**, 22270-13-9; (+)-**5**, 2630-41-3; (−)-(2*S*)-**6**, 36779-79-0; *exo*-**7**, 497-37-0; (±)-**8**, 51736-74-4; (+)-**8**, 16346-63-7; (−)-(2*S*)-**9**, 16620-80-7; *exo*-**10**, 2890-98-4; (±)-**11**, 74958-72-2; (±)-**11** DNP, 74925-11-4; (+)-**11**, 21159-73-9; (−)-(2*S*)-**12**, 74958-43-3; *exo*-**13**, 13153-47-4; (±)-**14**, 74958-44-4; (±)-**14** DNP, 74925-12-5; (+)-**14**, 29073-66-3; (−)-(2*S*)-**15**, 74958-45-5; (−)-(2*S*)-**15** acetate, 74958-46-6; (+)-(2*S*)-**16**, 74958-47-7; (±)-**17**, 74958-48-8; (−)-**17**, 74958-49-9; (−)-(2*S*)-**18**, 74958-50-2; *exo*-**19**, 16938-87-7; (±)-**20**, 69308-42-5; (+)-**20**, 25225-94-9; (−)-**20**, 74958-51-3; (−)-(4*S*)-**21**, 74958-52-4; (+)-(4*S*)-**22**, 74958-53-5; (±)-**23**, 68908-13-4; (+)-**23**, 16196-15-9; (−)-(2*S*)-**24**, 68069-65-8; (+)-(2*S*)-**25**, 74958-54-6; (−)-**26**, 69308-43-6; (+)-**27**, 68907-11-9; (−)-**28**, 68876-10-8; (−)-**29**, 68926-54-5; (±)-4-protoadamantanone, 74925-13-6; (±)-1-oxo[2.2]metacyclophane, 40143-99-5; 1,10-dioxo[2.2]metacyclophane, 68907-12-0.

Syntheses and Chiroptical Properties of Optically Active C_1-Methanotwistane, C_2-Ditwistane, C_1-Homobasketane, and C_2-3,10-Dehydroditwistane

Masao Nakazaki,* Koichiro Naemura, Yasumasa Kondo, Seiichi Nakahara, and Masaki Hashimoto

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, 560 Japan

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When applied to the tricyclic keto mesylate **23**, a modification of Deslongchamps' 4-twistanone synthesis gave (±)-3-C_2-ditwistanone (**24**, 7% yield) whose Wolff–Kishner reduction afforded (±)-ditwistane (**6**). Diazomethane ring expansion of (+)-C_2-bishomocubane-6,10-dione 6-ethylene ketal (**26**) with known absolute configuration followed by the Wolff–Kishner reduction afforded the (−)-ketal **28** which was converted, via (−)-4-C_1-homobasketanone (**29**), into (−)-C_1-homobasketane (**8**). A similar sequence of transformations converted (−)-**29** into (−)-C_2-3,10-dehydroditwistane (**9**). Hydrogenolysis of (−)-**8** and (−)-**9** gave (−)-C_1-methanotwistane (**5**) and (−)-C_2-ditwistane (**6**), assigning their respective (1*R*,4*S*,7*R*,8*R*) and (1*S*,4*S*,7*R*,8*R*) configurations.

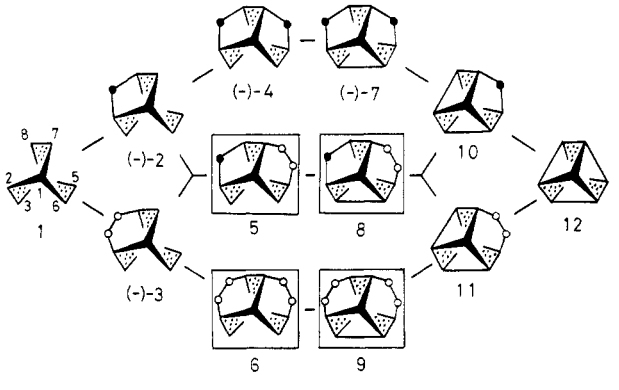
The C2–C8 diagonal bridging of bicyclo[2.2.2]octane (**1**) with methano (the closed circle) and ethano (the two open circles) bridges (Chart I)[1] furnishes two tricyclic cage-shaped hydrocarbons, *twist*-brendane (**2**) (C_2 symmetry) and twistane (**3**, D_2 symmetry), respectively, both with the D_3-twisted molecular framework **1** in a frozen conformation.

Further C5–C7 diagonal bridging of these gyrochiral[2] molecules with methano and ethano bridges gives three tetracyclic cage-shaped hydrocarbons, C_2-di-*twist*-brendane (**4**), C_1-methanotwistane (**5**), and C_2-ditwistane (**6**).

Final C3–C6 diagonal bridging with a single bond provides C_2-bishomocubane (**7**), C_1-homobasketane (**8**), and C_2-3,10-dehydroditwistane (**9**); all can be conceptually constructed, via homocubane (**10**) and basketane (**11**), on the desymmetrization of cubane (**12**) (O_h symmetry) which in turn can be envisaged to be composed of two D_3-twisted bicyclo[2.2.2]octane moieties with opposite chiralities.[3]

Among these chiral cage-shaped hydrocarbons possessing the D_3-twisted bicyclo[2.2.2]octane as a common structural feature, tricyclic *twist*-brendane (**2**)[4] and twistane (**3**)[5] were first synthesized in our laboratory in optically active modifications and their absolute configurations have been determined.[6] Natural extension of these studies led us to explore possible synthetic routes to the optically active gyrochiral tetracyclic **4** and pentacyclic **7** cage-shaped molecules with known absolute configurations, and

Chart I



(1) All structural formulas in this paper with (+) or (−) signs are presented in their absolute configurations.

(2) Nakazaki, M.; Naemura, K.; Kadowaki, H. *J. Org. Chem.* **1976**, *41*, 3725.

(3) Trivial names and symmetries of the pentacyclic hydrocarbons constructed by diagonal bridging of the D_3-twisted bicyclo[2.2.2]octane are listed in: Nakazaki, M.; Naemura, K.; Arashiba, N.; Iwasaki, M. *J. Org. Chem.* **1979**, *44*, 2433.

(4) Naemura, K.; Nakazaki, M. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 888.

(5) Adachi, K.; Naemura, K.; Nakazaki, M. *Tetrahedron Lett.* **1968**, 5467.

(6) Tichy, M. *Tetrahedron Lett.* **1972**, 2001. Nakazaki, M.; Naemura, K.; Harita, S. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1907.

0022-3263/80/1945-4440$01.00/0

Scheme I

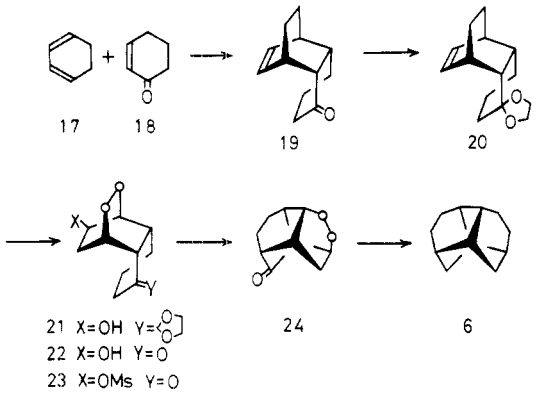
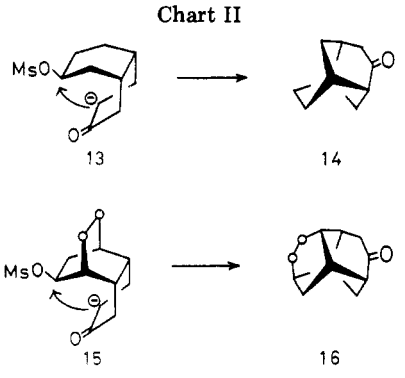


Chart II



our recent papers reported the preparation of (−)-4[7] and (−)-7[8] from the common precursor (+)-25.[9]

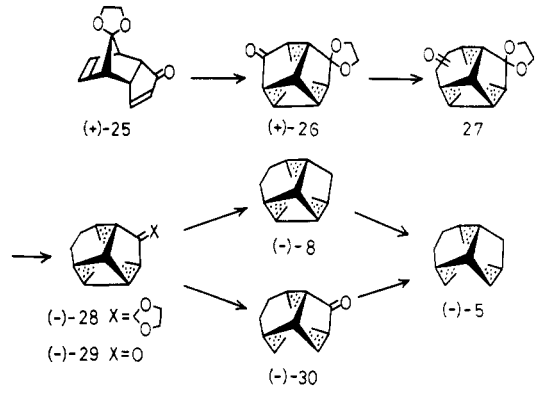
Our continuing interests in the chiroptical properties[10] as well as the microbial stereodifferentiating reactions[11] in gyrochiral cage-shaped molecules prompted us to prepare the remaining two tetracyclic (5 and 6) and two pentacyclic (8 and 9) hydrocarbons in optically active modifications, and this paper reports the successful syntheses of (−)-5, (−)-6, (−)-8, and (−)-9 and their absolute configuration assignment.

Results and Discussion

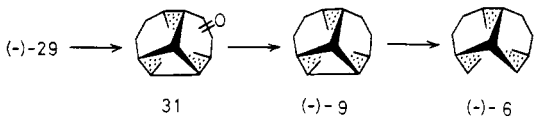
Preparation of (±)-C_2-Ditwistane (6) by Intramolecular Alkylation of the Keto Mesylate 23 (Scheme I). C_2-Ditwistane (6) was first synthesized in a racemic modification by Yonemitsu and co-workers[12] by hydrogenolysis of (±)-3,10-dehydroditwistane (9) which had been prepared through a fairly complicated sequence of reactions comprising photo [$_\pi2_s + {}_\pi2_s$] reaction of the Diels–Alder dimer of a 2,4-cyclohexadienone derivative.

Beside this rather involved synthetic route and inconvenience in preparing the starting material, expected difficulties in finding intermediates suitable for correlating their stereochemistry with compounds of known absolute configurations led us to explore some other synthetic approaches to 6.

Scheme II



Scheme III



We reasoned that Deslongchamps' 4-twistanone synthesis[13] (13 → 14), starting from the tricyclic keto mesylate 15 with the extra ethano bridge (shown with the open circles) should furnish 5-C_2-ditwistanone (16, Chart II).

In actually carrying out this approach, however, we were forced to modify the keto mesylate 15 to 23 because of the expected feasible synthetic route to secure 23 (Scheme I).

The tricyclic Diels–Alder adduct 19[14] between 1,3-cyclohexadiene (17) and 2-cyclohexenone (18) was converted to the ketal 20, whose hydroboration–oxidation followed by removal of the protecting group afforded the keto alcohol 22, mp 87–89 °C (25% yield from 20). The 9-exo stereochemistry was reasonably assumed on account of steric reasons, and this was supported by its eventual conversion to the C_2-ditwistane framework.

When the intramolecular alkylation of the keto mesylate 23 was carried out with sodium hydride in dimethylformamide, there was formed in low yield 3-C_2-ditwistanone (24) which was converted to (±)-C_2-ditwistane (6), mp 115–117 °C, by the Wolff–Kishner reduction.

This reluctance to cyclization observed in 23 lends a conspicuous contrast to the facile reaction (13 → 14) reported by Deslongchamps,[13] and it is tentatively suggested that the introduction of the extra ethano bridge should apparently make the tricyclic 23 more rigid than the bicyclic analogue 13, making the cyclization unfavorable.

Preparation of (−)-C_1-Homobasketane (8) and (−)-C_1-Methanotwistane (5) by Ring Expansion Reaction of (+)-C_2-Bishomocubane-6,10-dione 6-Ethylene Ketal (26) (Scheme II). The poor yield observed in preparing 3-C_2-ditwistanone (24) by intramolecular alkylation discouraged us from pursuing further this approach, and this prompted us to resort to a well-documented path involving diazomethane ring expansion of C_2-bishomocubane-6,10-dione derivatives.[15]

In our synthesis of optically active C_2-bishomocubane (7)[8] and C_2-di-*twist*-brendane (4),[7] we started from (+)-unsaturated keto ketal 25 with known absolute configuration[9] whose photochemical [$_\pi2_s + {}_\pi2_s$] cyclization afforded C_2-bishomocubane framework 26. Removal of the functional groups transformed (+)-26 into (−)-C_2-bishomo-

(7) Nakazaki, M.; Naemura, K.; Arashiba, N. *J. Org. Chem.* **1978**, *43*, 689.
(8) Nakazaki, M.; Naemura, K. *J. Org. Chem.* **1977**, *42*, 2985.
(9) Nakazaki, M.; Naemura, K.; Nakahara, S. *J. Org. Chem.* **1978**, *43*, 4745.
(10) Nakazaki, M.; Naemura, K. *J. Synth. Org. Chem. Jpn.* **1977**, *35*, 883.
(11) Nakazaki, M.; Chikamatsu, H.; Naemura, K.; Nishino, M.; Murakami, H.; Asao, M. *J. Chem. Soc., Chem. Commun.* **1978**, 667. Nakazaki, M.; Chikamatsu, H.; Naemura, K.; Hirose, Y.; Shimizu, T.; Asao, M. *Ibid.* **1978**, 668. Nakazaki, M.; Chikamatsu, H.; Naemura, K.; Nishino, M.; Murakami, H.; Asao, M. *J. Org. Chem.* **1979**, *44*, 4588.
(12) Hirao, K.; Iwakuma, M.; Taniguchi, M.; Abe, E.; Yonemitsu, O.; Date, T.; Kotera, K. *J. Chem. Soc., Chem. Commun.* **1974**, 691.
(13) Belanger, A.; Lambert, Y.; Deslongchamps, P. *Can. J. Chem.* **1969**, *47*, 795.
(14) Hirao, K.; Unno, S.; Yonemitsu, O. *J. Chem. Soc., Chem. Commun.* **1977**, 577.
(15) Hirao, K.; Abe, E.; Yonemitsu, O. *Tetrahedron Lett.* **1975**, 4131.

Table I. Absolute Configurations and IUPAC Names of (−)-5, (−)-6, (−)-8, and (−)-9

compd	trivial name	IUPAC name
(−)-5	(−)-C_1-methanotwistane	(−)-(1*R*,4*S*,7*R*,8*R*)-tetracyclo[6.2.1.0^{2,7}.0^{4,9}]undecane
(−)-6	(−)-C_2-ditwistane	(−)-(1*S*,4*S*,7*R*,8*R*)-tetracyclo[6.2.2.0^{2,7}.0^{4,9}]dodecane
(−)-8	(−)-C_1-homobasketane	(−)-(1*R*,3*S*,5*R*,6*S*,7*S*,9*S*)-pentacyclo[5.4.0.0^{2,6}.0^{3,9}.0^{5,8}]undecane
(−)-9	(−)-C_2-3,10-dehydroditwistane	(−)-(1*R*,3*S*,6*R*,7*S*,8*S*,10*S*)-pentacyclo[6.4.0.0^{2,7}.0^{3,10}.0^{6,9}]dodecane

cubane (7), which in turn was catalytically hydrogenated to open the central single bond of its bicyclo[2.2.0]hexane moiety,[12] affording (−)-C_2-di-*twist*-brendane (4).

A logical combination of this facile hydrogenolysis with the diazomethane ring expansion suggested the designed sequence of steps illustrated in Schemes II and III to lead from the (+)-unsaturated keto ketal **25** to (−)-C_1-homobasketane (8), (−)-C_1-methanotwistane (5), (−)-C_2-3,10-dehydroditwistane (9), and (−)-C_2-ditwistane (6) (Schemes II and III).

Diazomethane ring expansion of (+)-**26**, $[\alpha]_D$ +96.9° (77.4% optical purity),[9] was carried out with 6 mol equiv of diazomethane in an ethereal solution at 0 °C. Monitoring with VPC revealed that after 24 h of standing there remained no starting ketone **26**, and none of higher homologues were detected by mass spectroscopy of the crude product.[16]

The crude mixture of the isomeric ring expansion products **27** was directly treated with hydrazine hydrate and potassium hydroxide in triethylene glycol to provide an 85% yield of the (−)-ketal **28** whose acidic hydrolysis gave (−)-4-C_1-homobasketanone (**29**), mp 126–128 °C. The Wolff–Kishner reduction of (−)-**29** afforded (−)-C_1-homobasketane (8), mp 112–113 °C, which was catalytically hydrogenated in acetic acid with 5% palladium on carbon to furnish a 70% yield of (−)-C_1-methanotwistane (**5**), mp 138–140 °C.

Reversed sequence of these transformations resulted in the formation of (−)-11-C_1-methanotwistanone (**30**), mp 157–159 °C, first, and subsequent Wolff–Kishner reduction converted this to the same (−)-C_1-methanotwistane (**5**, Scheme II).

Preparation of (−)-C_2-3,10-Dehydroditwistane (9) and (−)-C_2-Ditwistane (6) by Ring Expansion Reaction of (−)-4-C_1-Homobasketanone (29) (Scheme III). Monitoring the process with mass spectroscopy indicated that in the diazomethane ring expansion reaction of (−)-4-C_1-homobasketanone (**29**) a considerable amount of doubly expanded products formed, and this finding compeled us to shorten the reaction period to 12 h of standing at 0 °C.

Direct Wolff–Kishner reduction of the crude mixture of the isomeric reaction products **31** gave (−)-3,10-dehydroditwistane (**9**), mp 42–43 °C (73% overall yield from **29**), whose hydrogenolysis in acetic acid with 5% palladium on carbon gave (−)-C_2-ditwistane (**6**), mp 105–106 °C (Scheme III).

Chiroptical Properties. Stereochemical correlation of the starting compound (+)-**25** with (−)-(1*S*,2*S*,4*S*)-*endo*-5-norbornene-2-carboxylic acid has been accomplished in our laboratory,[9] and this combined with the present correlation illustrated in Schemes II and III eventually assigned the absolute configurations summarized in Table I to (−)-C_1-methanotwistane (**5**), (−)-C_2-ditwistane (**6**), (−)-C_1-homobasketane (**8**), and (−)-C_2-3,10-dehydroditwistane (**9**).

Table II records the circular dichroism (CD) spectra of newly prepared (−)-4-C_1-homobasketanone (**29**) and (−)-11-C_1-methanotwistanone (**30**). Examination of the octant projection formula which hold the carbonyl group at the "point of twist"[17] (Chart III) predicts positive Cotton effects for both these compounds which were found to be consistent with their observed CD spectra.

Table II. CD Spectra of 4-C_1-Homobasketanone (29) and (−)-11-C_1-Methanotwistanone (30) (in isooctane and corrected to 100% optical purity)

(−)-29		(−)-30	
nm	[θ]	nm	[θ]
297 sh	+4.84 × 10^3	286 sh	+1.10 × 10^4
301.5	+5.30 × 10^3	290.5	+1.19 × 10^4
304.5	+5.21 × 10^3	293.5 sh	+1.16 × 10^4
311 sh	+4.28 × 10^3	300 sh	+9.57 × 10^3

Table III. Absolute Molecular Rotations ($[M]_{D\ abs}$) of Tetra- and Pentacyclic Hydrocarbons Related to *twist*-Brendane (2) and Twistane (3) (in Chloroform)

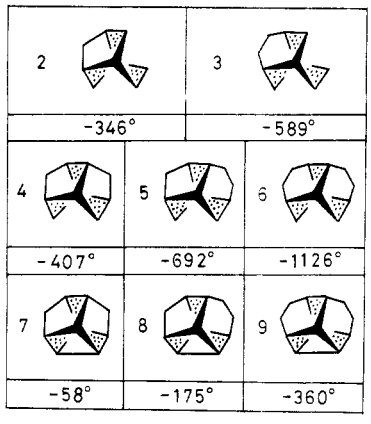


Chart III

(−)-29 (−)-30

Lastly, Table III lists the absolute rotation values of the cage-shaped molecules discussed in this paper together with their absolute configurations. Two conspicuous features are worth noting: (a) all these cage-shaped molecules possessing the D_3-twisted bicyclo[2.2.2]octane moiety with *M*-helicity as a common molecular framework exhibit levorotation, and (b) C_2-ditwistane (**6**) and C_2-bishomocubane (**7**) are outstanding in their unusually large and small rotatory powers, respectively. The latter characteristic undoubtedly reflects their unique molecular structures which deviate most and least from the achiral sphere-like cubane molecular framework with O_h symmetry.

Experimental Section

Infrared spectra were taken with a Hitachi EPI-S2 spectrophotometer. ^{1}H NMR spectra were recorded on a JNM-C-60 HL.

(16) Yonemitsu et al.[14] reported isolation of two isomeric ring expansion products.

(17) Djerassi, C.; Klyne, W. *Proc. Nat. Acad. Sci. U.S.A.* **1962**, *48*, 1093. Snatzke, G.; Werner-Zamojska, F. *Tetrahedron Lett.* **1969**, 3513.

Optical rotations were measured with a JASCO-DIP-SL automatic polarimeter. Circular dichroism data were collected with a JASCO J-40 spectropolarimeter. Mass spectra were taken with a Hitachi RMS-4 spectrometer. Elemental analyses were determined on a Yanagimoto CHN-Corder Type II. All melting and boiling points are uncorrected.

9-Tricyclo[6.2.2.0^{2,7}]dodecen-3-one (19). A mixture of 1,3-cyclohexadiene (17; 129 g, 1.61 mol), 2-cyclohexenone (18; 149 g, 1.55 mol),[18] and hydroquinone (2.0 g) was heated at 170–175 °C for 22 h in an autoclave. Distillation of the crude product gave 25.2 g of dicyclohexadiene (20% yield), bp 120–122 °C (30 mm) [lit.[19] bp 226–229 °C (748 mm)], and 35.3 g of a yellow liquid, bp 103–142 °C (9 mm), which was chromatographed on alumina. The combined fractions eluted with $CHCl_3$ afforded an oil which was distilled to furnish 16.3 g of **19** (6% yield based on **18**); bp 115–117 °C (9 mm); IR (neat film) 1700, 850, 835, 715 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.5–2.6 (m, 13 H), 2.9–3.2 (brs, 1 H), 5.8–6.4 (m, 2 H).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.42; H, 9.14. Semicarbazone: mp 215 °C dec (lit.[14] mp 227–229 °C dec). Anal. Calcd for $C_{13}H_{19}ON_3$: C, 66.92; H, 8.21; N, 18.01. Found: C, 66.86; H, 8.00; N, 17.88.

9-Tricyclo[6.2.2.0^{2,7}]dodecen-3-one Ethylene Ketal (20). The routine procedure of ketalization utilizing **19** (28.2 g, 0.160 mmol), ethylene glycol (20.0 g, 0.320 mmol), *p*-toluenesulfonic acid (150 mg), and benzene (400 mL) afforded a 78% yield of **20** (27.3 g): bp 125–128 °C (4 mm); IR (neat film) 1675, 1140, 1090, 1055, 710 cm^{-1}.

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.30; H, 9.13.

9-*exo*-Hydroxytricyclo[6.2.2.0^{2,7}]dodecan-3-one (22). Diborane, generated from the reaction of borohydride (1.30 g, 34.0 mmol) with boron trifluoride etherate (8.6 mL, 68.1 mmol) in diglyme solution (40 mL), was carried with a slow stream of nitrogen and passed into an ice-cooled solution of **20** (5.00 g, 22.7 mmol) in dry THF (18 mL). After successive addition of water (6 mL), 3 N NaOH solution (6 mL), and 30% hydrogen peroxide (6 mL), the reaction mixture was stirred for 1 h at 30–50 °C, and then saturated NaCl solution (20 mL) was added. The mixture was extracted with ether, and the extract was washed with water and dried ($MgSO_4$). Evaporation of the solvent gave an oily residue which was hydrolyzed by stirring with 10% sulfuric acid (50 mL) for 12 h at room temperature. The ethereal extract was washed with aqueous $NaHCO_3$ solution and water and dried ($MgSO_4$). The solvent was evaporated and the residue was chromatographed on silica gel. Eluates with $CHCl_3$ gave a solid which was recrystallized from ether to furnish 1.05 g of **22** (25% yield based on **20**): mp 87–89 °C; IR (KBr) 3280, 1695 cm^{-1}.

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.98; H, 9.46.

3-C_2-Ditwistanone (24). Methanesulfonyl chloride (1.74 g, 12.9 mmol) was added to a chilled solution of **22** (1.00 g, 5.15 mmol) in dry pyridine (5 mL), and the mixture was stirred for 12 h at room temperature. The reaction mixture was poured into ice–water, made acidic with HCl, and extracted with benzene. The extract was washed successively with 10% HCl solution, aqueous $NaHCO_3$ solution, and water and dried ($MgSO_4$). Evaporation of the solvent gave an oily residue which was dissolved in dimethylformamide (20 mL) and treated with NaH (1.4 g, 57.0 mmol) suspended in dimethylformamide (5 mL). After being stirred at 80–90 °C for 14 h, the mixture was decomposed with ice–water and made acidic with aqueous HCl. Concentration of the pentane extract gave a residue which was chromatographed on neutral alumina (Woelm, activity III). Combined fractions eluted with pentane were sublimed to give 130 mg of **24** (7% yield based on **22**): mp 122–125 °C (in a sealed tube); IR (KBr) 1730, 1255, 1200, 1100, 1070, 1060 cm^{-1}.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.81; H, 9.11.

(±)-C_2-Ditwistane (6). A mixture of **24** (100 mg, 0.568 mmol), 100% hydrazine hydrate (0.1 mL), KOH (55 mg), and triethylene glycol (1 mL) was heated for 1 h at 120 °C in an oil bath. The bath temperature was gradually raised to 190–200 °C and kept for 4 h at this temperature. During this period, a white solid was observed to condense on the inner wall of the condenser. After the mixture cooled, the solid was dissolved in pentane and the pentane solution was washed with water and dried ($MgSO_4$). Removal of the solvent yielded a residue which was chromatographed on silica gel. The combined fractions eluted with pentane were sublimed at 50 °C (30 mm) to afford 41 mg of **6** (45% yield), mp 115–117 °C (in a sealed tube) (lit.[12] mp 117–118 °C).

Comparison of the IR spectrum and GLC with those of an authentic specimen of (−)-C_2-ditwistane (**6**) established its identity.

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.89; H, 10.98.

(−)-4-C_1-Homobasketanone Ethylene Ketal (28). An ethereal solution (45 mL) of diazomethane (ca. 2.7 g, 64 mmol) was added to an ice-cooled solution of (+)-pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-6,10-dione 6-ethylene ketal (**26**), $[\alpha]^{20}_D$ +96.9° (optical purity 77.4%)[9] (2.37 g, 11.1 mmol), and the mixture was allowed to stand for 24 h in a refrigerator (0 °C). After the remaining diazomethane was destroyed with acetic acid, the mixture was washed with aqueous $NaHCO_3$ solution and water and dried ($MgSO_4$). Removal of the solvent afforded a residue which was heated with 100% hydrazine hydrate (1.8 mL) and KOH (1.1 g) in triethylene glycol (20 mL). The procedure described for the Wolff–Kishner reduction of **6** afforded a semisolid product which was distilled to yield 1.93 g of **28** (85% yield based on **26**): bp 70 °C (air-bath temperature, 0.1 mm); $[\alpha]^{20}_D$ −104.5° (*c* 1.43, $CHCl_3$); IR (neat film) 1322, 1085, 1042, 1008, 998, 945, 940 cm^{-1}.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.49; H, 7.94.

(−)-4-C_1-Homobasketanone (29). A mixture of (−)-**28**, $[\alpha]^{20}_D$ −104.5° (1.78 g, 8.71 mmol), and 10% sulfuric acid (60 mL) was stirred for 24 h at room temperature and then extracted with pentane. The extract was washed with aqueous $NaHCO_3$ solution and water and dried ($MgSO_4$). Evaporation of the pentane afforded a white solid which was purified by sublimation at 50 °C (30 mm) to furnish 1.26 g of (−)-**29** (90% yield): mp 126–128 °C (in a sealed tube); $[\alpha]^{20}_D$ −31.2° (*c* 1.13, $CHCl_3$); IR (KBr) 1761, 1135, 865, 839 cm^{-1}; CD (*c* 3.64 × 10^{-2}, isooctane) [θ] (nm) +3.75 × 10^3 (sh, 297), +4.10 × 10^3 (301.5), +4.03 × 10^3 (304.5), +3.31 × 10^3 (sh, 311).

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.58; H, 7.56.

(−)-C_1-Homobasketane (8). Wolff-Kishner reduction of (−)-**29**, $[\alpha]^{20}_D$ −31.2° (300 mg, 1.87 mmol), with 100% hydrazine hydrate (0.3 mL) and KOH (150 mg) in triethylene glycol (3.8 mL) was carried out by following the procedure described for the preparation of (±)-**6**. The product was sublimed at 40 °C (30 mm) to yield 181 mg of (−)-**8** (66% yield): mp 112–113 °C (in a sealed tube); $[\alpha]^{18}_D$ −93.4° (*c* 0.639, $CHCl_3$); IR (KBr) 2935, 2850, 1442, 1318, 1282, 915, 800, 760 cm^{-1}; mass spectrum, *m/e* 146 (M^+), 118.

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.14; H, 9.58.

(−)-11-C_1-Methanotwistanone (30). Catalytic hydrogenation of (−)-**29**, $[\alpha]^{20}_D$ −31.2° (500 mg, 3.12 mmol), was carried out in methanol (50 mL) with 5% palladium on carbon (315 mg) at 1 atm of hydrogen. After 3 days of shaking at room temperature, the reaction mixture freed from the catalyst was concentrated to give a residue which was chromatographed on silica gel. The early pentane eluates which recovered 146 mg of (−)-**29** (29% yield) were followed by the main fractions which after removal of the solvent were sublimed at 50 °C (5 mm) to yield 209 mg of (−)-**30** (41% yield): mp 157–159 °C (in a sealed tube); $[\alpha]^{20}_D$ −268° (*c* 0.418, $CHCl_3$); IR (KBr) 1760, 1160, 1145, 850 cm^{-1}; CD (*c* 4.44 × 10^{-2}, isooctane) [θ] (nm) +8.52 × 10^3 (sh, 286), +9.21 × 10^3 (290.5), +8.99 × 10^3 (sh, 293.5), +7.41 × 10^3 (sh, 300).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.56; H, 8.50.

(−)-C_1-Methanotwistane (5). From (−)-8. A mixture of (−)-**8**, $[\alpha]^{18}_D$ −93.4° (150 mg, 1.03 mmol), and acetic acid (12 mL) was hydrogenated with 5% palladium on carbon (105 mg) at 1 atm of hydrogen. After 30 h of being shaken, the solution freed from the catalyst was diluted with 50 mL of water and neutralized with sodium carbonate followed by extraction with pentane. The extract was washed with water and dried ($MgSO_4$). Removal of

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the solvent gave a solid which was sublimed to afford 107 mg of (-)-**5** (70% yield): mp 140-141 °C (in a sealed tube); $[\alpha]^{17}_D$ -362° (*c* 0.448, $CHCl_3$); IR(KBr) 2935, 2880, 2850, 1470, 1460, 1312, 1280, 945, 938, 920, 895, 835, 805, 750 cm^{-1}; mass spectrum, *m/e* 148 (M^+), 119.

Anal. Calcd for $C_{11}C_{16}$: C, 89.12; H, 10.88. Found: C, 88.96; H, 10.99.

From (-)-30. Wolff-Kishner reduction of (-)-**30**, $[\alpha]^{20}_D$ -268° (122 mg, 0.753 mmol), with 100% hydrazine hydrate (0.12 mL) and KOH (60 mg) in triethylene glycol (1.5 mL) was carried out as described for the preparation of (±)-**6**. A solid obtained from the pentane eluates was sublimed at 50 °C (30 mm) to furnish 45 mg of (-)-**5** (40% yield): mp 138-140 °C (in a sealed tube); $[\alpha]^{18}_D$ -361° (*c* 0.510, $CHCl_3$).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.02; H, 10.65.

(-)-*C*$_2$-3,10-Dehydroditwistane (9). To an ice-cooled solution of (-)-**29**, $[\alpha]^{20}_D$ -31.2° (747 mg, 4.66 mmol), in ether (20 mL) was added an ethereal solution (53 mL) of diazomethane (ca. 1.1 g, 26 mmol) with stirring, and the stirring was continued for 12 h at 0 °C. The procedure described for the ring expansion of (+)-**26** gave a crude oily product which was treated with 100% hydrazine hydrate (0.8 mL) and KOH (450 mg) in triethylene glycol (10 mL). Wolff-Kishner reduction was carried out by following the same procedure described for the preparation of (±)-**6**, and the product was chromatographed on neutral alumina. Combined pentane eluates afforded a solid which was sublimed at 40 °C (5 mm) to give 545 mg of (-)-**9** (73% yield based on **29**): mp 42-43 °C (in a sealed tube); $[\alpha]^{20}_D$ -174° (*c* 0.803, $CHCl_3$); IR (KBr) 2920, 2850, 1455, 1438, 1330, 1285, 1270, 1230, 1158, 982, 940, 925, 870, 832, 780, 770, 748 cm^{-1}; mass spectrum, *m/e* 160 (M^+), 131.

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 90.00; H, 10.02.

(-)-*C*$_2$-Ditwistane (6). Catalytic hydrogenation of (-)-**9**, $[\alpha]^{20}_D$ -174° (200 mg, 1.25 mmol), with 5% palladium on carbon (127 mg) in acetic acid (14 mL) was carried out as described for the preparation of (-)-**5**. The product was sublimed at 40 °C (5 mm) to give 157 mg of (-)-**6** (77% yield): mp 105-106 °C (in a sealed tube); $[\alpha]^{20}_D$ -538° (*c* 0.268, $CHCl_3$); IR (KBr) 2920, 2850, 1465, 1455, 1338, 1282, 1158, 1122, 1040, 918, 878, 845, 805, 740 cm^{-1}; mass spectrum, *m/e* 162 (M^+), 133.

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.73; H, 11.26.

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Registry No. (-)-**5**, 74867-97-3; (-)-**6**, 74867-98-4; (±)-**6**, 74843-75-7; (-)-**8**, 74867-99-5; (-)-**9**, 74868-00-1; **17**, 592-57-4; **18**, 930-68-7; **19**, 64989-29-3; **19** semicarbazone, 65480-54-8; **20**, 74843-76-8; **22**, 74843-77-9; (±)-**24**, 74868-59-0; (+)-**26**, 62928-73-8; (-)-**28**, 74843-78-0; (-)-**29**, 74868-01-2; (-)-**30**, 74843-79-1.

Reactions of α,β-Epoxysilanes with Grignard Reagents. Generation and Trapping of α-Trimethylsilyl Aldehydes and Ketones

Paul F. Hudrlik,*[1] Anne M. Hudrlik,[1] Raj N. Misra,[1a] David Peterson,[1a] Gregory P. Withers,[1a] and Ashok K. Kulkarni[1b]

School of Chemistry, Wright and Rieman Chemistry Laboratories, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903, and Department of Chemistry, Howard University, Washington, DC 20059

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α,β-Epoxysilanes react with Grignard reagents via initial rearrangement to generate α-silyl carbonyl compounds, which are trapped by the Grignard reagent to give β-hydroxysilanes. The reactions of epoxides **8** and **11** take place with very high stereoselectivity to form predominantly erythro β-hydroxysilanes **9** and **12**, respectively, which undergo stereospecific β-elimination reactions to give either cis or trans olefins in 96-98% isomeric purity.

Several years ago we initiated a study of the reactions of α,β-epoxysilanes with organometallic reagents as a possible route to diastereomerically pure β-hydroxysilanes, since we had previously shown that the olefin-forming β-elimination reactions of β-hydroxysilanes were stereospecific.[2] We found that a variety of α,β-epoxysilanes react with organocuprate reagents in a regio- and stereospecific manner at the carbon α to silicon to form diastereomerically pure β-hydroxysilanes.[3] (Stereospecific β-elimination reactions of these β-hydroxysilanes proved that the acid-catalyzed elimination reactions take place in an anti manner and that the base-induced elimination reactions take place in a syn manner.[3]) We also found that (trimethylsilyl)ethylene oxide (1) reacted with organolithium reagents[4] (PrLi, BuLi, *t*-BuLi) to give 2-(trimethylsilyl)-1-alkenes in moderate yield,[6] presumably via initial proton abstraction at the epoxide carbon α to silicon.[7]

The reactions of α,β-epoxysilanes with Grignard reagents[8] were found to give β-hydroxysilanes resulting from

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