of 0.155 g (0.901 mmol) of blastmycinolactol (**46**) and 0.36 mL (0.34 g, 1.8 mmol) of isovaleric anhydride in 15 mL of pyridine was allowed to stand at room temperature for 5 days. The reaction mixture was poured into 30 mL of water and extracted with ether. The ether extracts were washed with saturated aqueous $CuSO_4$, saturated aqueous $NaHCO_3$, and water and then dried over $MgSO_4$. Evaporation of the solvent left 0.324 g of a yellow oil. The crude acylation product was passed through a column of silica and then subjected to chromatography on a Chromatron, eluting with 25% ether/hexane, to give 0.213 g (92%) of (±)-blastmycinone (**47**) as a clear colorless oil. Spectral data for this material are consistent with those published.

Acknowledgment. This work was supported by a grant from the United States Public Health Service (AI-15027). M.C.P. acknowledges the Fannie and John Hertz Foundation for financial assistance in the form of a fellowship.

Registry No. (±)-**7**, 77079-70-0; (±)-**8**, 72507-39-2; (±)-**9**, 77079-71-1; (±)-**10**, 77079-72-2; (±)-**11**, 77079-73-3; (±)-**12**, 77079-74-4; **13a**, 947-91-1; **13b**, 122-78-1; **13c**, 78-84-2; **13d**, 630-19-3; **13e**, 100-52-7; (±)-**14a** (isomer 1), 72523-82-1; (±)-**14a** (isomer 2), 72507-40-5; (±)-**14b** (isomer 1), 72523-83-2; (±)-**14b** (isomer 2), 72507-41-6; (±)-**14c** (isomer 1), 72523-84-3; (±)-**14c** (isomer 2), 72507-42-7; (±)-**14d** (isomer 1), 72523-85-4; (±)-**14d** (isomer 2), 72507-43-8; (±)-**14e** (isomer 1), 72507-44-9; (±)-**14e** (isomer 2), 72523-86-5; (±)-**15a**, 72507-45-0; (±)-**15a** methyl ester, 77079-75-5; (±)-**15b**, 64869-27-8; (±)-**15c**, 64869-26-7; (±)-**15d**, 72507-46-1; (±)-**15e**, 64869-25-6; (±)-**16**, 77079-76-6; (±)-**19a**, 77079-77-7; (±)-**19b**, 77079-78-8; (±)-**19b** free diol, 77079-79-9; (±)-**20a**, 77079-80-2; (±)-**20b**, 77079-81-3; (±)-**20b** free diol, 77079-82-4; (±)-**21**, 34713-70-7; (±)-**22**, 77079-83-5; (±)-**23**, 72523-87-6; (±)-**25**, 66183-63-9; (+)-**25**, 15186-48-8; (±)-**26**, 72507-47-2; (±)-**29**, 41954-96-5; (±)-**30**, 77079-84-6; (±)-**31**, 77122-10-2; (±)-**32**, 77079-85-7; (3*S*,6*S*,7*R*)-**32**, 77097-67-7; (3*S*,6*S*,7*R*)-**32** THP ether, 77079-86-8; (±)-**33**, 77079-87-9; (3*R*,6*S*,7*R*)-**33**, 77079-88-0; (3*R*,6*S*,7*R*)-**33** THP ether, 77079-89-1; (±)-**34**, 77079-90-4; (3*R*,6*R*,7*R*)-**34**, 77079-91-5; (3*R*,6*R*,7*R*)-**34** THP ether, 77079-92-6; (±)-**35**, 77079-93-7; (3*S*,6*R*,7*R*)-**35**, 77079-94-8; (3*S*,6*R*,7*R*)-**35** THP ether, 77079-95-9; **36**, 533-67-5; **37**, 5284-18-4; (±)-**42**, 77079-96-0; (±)-**43**, 77122-11-3; (±)-**44**, 77079-97-1; (±)-**45**, 77079-98-2; (±)-**46**, 53402-76-9; (±)-**47**, 31203-09-5; ethyl vinyl ether, 109-92-2; pivaldehyde, 630-19-3; 5-methyl-4-hexen-3-one, 13905-10-7; propionyl chloride, 79-03-8; isobutylene, 115-11-7; (*E*)-1-methoxypropene, 4188-69-6; (*Z*)-1-methoxypropene, 4188-68-5; 2-pentyl-1,3-dithiane, 21777-32-2; 2-(2,2-dimethyl-1-hydroxypropyl)-2-pentyl-1,3-dithiane, 77079-99-3; sorbitol, 50-70-4; 1,2:5,6-diacetonide sorbitol, 53735-98-1; methyl (±)-2-(benzyloxy)propionate, 41921-90-8.

Synthesis and Absolute Configuration of Optically Active D_3-Tritwistane, the Gyrochiral Prototype of "Twist" Diamond

Masao Nakazaki,* Koichiro Naemura, Hiroaki Chikamatsu, Masami Iwasaki, and Masaki Hashimoto

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

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A modification of Barborak's trishomocubane synthesis, when applied to the higher homologue, afforded 8,12-diacetoxy-C_2-bismethanotwistane (**21**) which was converted into (±)-4-C_2-methanoditwistanone (**29**) by a sequence of conversions involving diazomethane ring expansion of the intermediate keto acetates **24** and **25**. Incubation of the resulting C_2-ketone **29** with *Rhodotorula rubra* yielded a mixture of the (−)-C_2-ketone **29** and the (+)-C_2-alcohol **28** with respective 15% and 33% optical purities. Our proposed microbial C_2-ketone rule coupled with CD analysis assigned the 3*S*,5*S* configuration to the (−)-C_2-ketone **29** whose Wolff–Kishner reduction gave (−)-C_2-methanoditwistane (**9**). Demjanov rearrangement of the amine **31** prepared from the (−)-C_2-ketone **29** followed by removal of the functional group provided (−)-D_3-tritwistane (**10**) ($[M]_{D,abs}$ −1067°), the prototype of "twist" diamond, which was found to be converted into diamantane (congressane, **42**) by aluminum bromide treatment.

Our continuing interests in gyrochiral molecules with twisted π-electron systems have resulted in our reporting the first successful syntheses of [*n*][*m*]paracyclophanes,[1] a series of [*n*]chochins,[2] an anti-Bredt-rule compound,[3] and trans doubly bridged ethylenes[4] all in optically active modifications with known absolute configurations, while our another interests in gyrochiral[5] cage-shaped molecules have led us to expend our efforts to prepare the interesting class of compounds[6] illustrated in Figure 1.

A topological characteristic common to the cage-shaped hydrocarbons **2**–**15** is the D_3-twisted bicyclo[2.2.2]octane moiety (shown with dotting) whose conceptual diagonal bridging with single bond, methano and ethano groups should generate all these compounds with rigid conformation. Since cubane (**16**, O_h symmetry) can be regarded to be composed of two enantiomeric D_3-bicyclo[2.2.2]octane molecular frameworks fused together, the pentacyclic molecules **7**–**15** can also be envisaged to be derived by its dissymmetric homologation with methano and/or ethano bridges.

Reflecting these stereochemistries, these cage-shaped hydrocarbons are chiral except for homocubane (**14**) and basketane (**15**) both belonging to the C_{2v} point group. Among the remaining 12, with exceptions of asymmetric C_1-methanotwistane (**5**) and C_1-homobasketane (**12**), 10 are gyrochiral, belonging to either the C_2, D_2, or D_3 point group.

Little imagination would be required to realize that these rigid cage-shaped compounds with well-defined conformations and symmetries should provide ideal substrates for exploring the stereochemistry around the active sites of redox enzymes, and our efforts in this direction have been rewarded in our finding of the microbial[7] and horse

(1) Nakazaki, M.; Yamamoto, K.; Itoh, M.; Tanaka, S. *J. Org. Chem.* **1977**, *42*, 3468.
(2) Nakazaki, M.; Yamamoto, K.; Tanaka, S.; Kametani, H. *J. Org. Chem.* **1977**, *42*, 287.
(3) Nakazaki, M.; Naemura, K.; Nakahara, S. *J. Org. Chem.* **1979**, *44*, 2438.
(4) Nakazaki, M.; Yamamoto, K.; Maeda, M. *J. Org. Chem.* **1980**, *45*, 3229.
(5) Nakazaki, M.; Naemura, K.; Yoshihara, H. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3278.
(6) A concise summary of our studies in this class of cage-shaped compounds can be found in: Nakazaki M.; Naemura, K. *Yuki Gosei Kagaku Kyokaishi* **1977**, *35*, 883.
(7) Nakazaki, M.; Chikamatsu, H.; Naemura, K.; Nishino, M.; Murakami, H.; Asao, M. *J. Org. Chem.* **1979**, *44*, 4588.

0022-3263/81/1946-2300$01.25/0

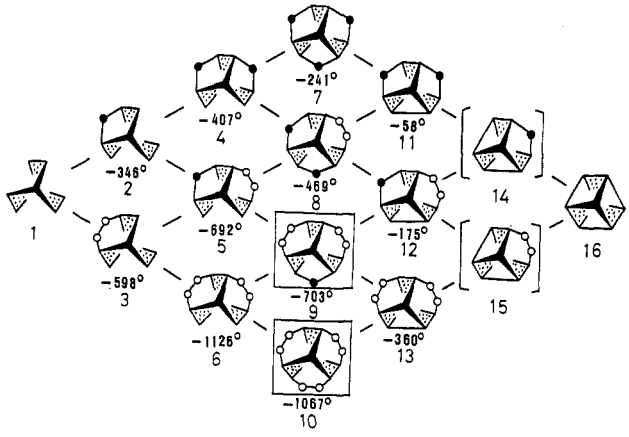
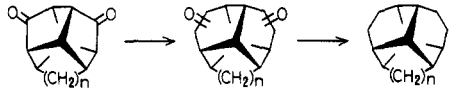


Figure 1. Absolute configurations and absolute molecular rotations ($[M]_{D,abs}$) of the levorotatory tri-, tetra-, and pentacyclic hydrocarbons having D_3-twisted bicyclo[2.2.2]octane molecular framework with *M* helicity.

Scheme I



17 n = 1 19 n = 1 9 n = 1
18 n = 2 20 n = 2 10 n = 2

liver alcohol dehydrogenase (HLADH)[8] C_2-ketone[9] rules. This same unique stereochemistry inherent to these compounds has prompted us to examine their chiroptical properties, and ten compounds[10] (**2**–**8** and **11**–**13**) have been prepared in optically active modifications with known absolute configurations in our laboratory, revealing that the order of optical increment for bridging is invariably ethano > methano > single bond. Their compact sizes with a maximum number of asymmetric carbon atoms might also be utilized to best advantage in construction of a molecule with polyhedral *T* symmetry.[11]

In this paper, we report the preparation of the remaining two gyrochiral molecules in this class, C_2-methanoditwistane (**9**)[12] and D_3-tritwistane (**10**),[13] in optically active forms and discuss their chiroptical properties and their unique topology related to "twist" diamond.

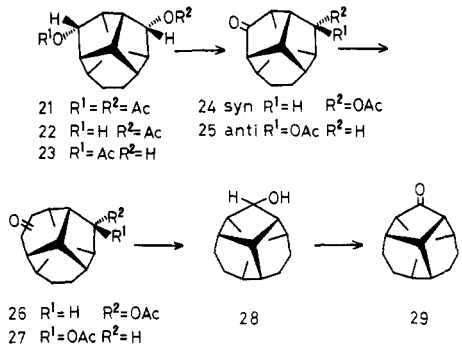
Results and Discussion

In a previous paper,[10f] we reported our successful preparation of (±)-C_2-methanoditwistane (**9**, Scheme I) via the diketone **19** which was obtained by the double diazomethane ring expansion of trishomocubanedione (**17**)[14] and an obvious extension of this approach to the homologous diketone **18** seemed to us a logical strategy to secure the D_3-tritwistane molecular framework.

However, our failure to achieve this double ring expansion of **18** to the diketone **20** with a D_3-tritwistane framework forced us to abandon this approach.[10f]

Guided by our recent experience in preparing C_2-3,10-dehydroditwistane (**13**),[10g] we then initiated an approach which involved (a) initial single ring expansion to the intermediate **29**, a novel C_2-ketone of C_2-methanoditwistane system (Scheme II), (b) biological optical resolution of this C_2-ketone **29** (Scheme III), and (c) final ring expansion of the optically active **29** to the D_3-tritwistane framework **32** (Scheme IV).

Scheme II



21 $R^1 = R^2 = Ac$
22 $R^1 = H$ $R^2 = Ac$
23 $R^1 = Ac$ $R^2 = H$

24 syn $R^1 = H$ $R^2 = OAc$
25 anti $R^1 = OAc$ $R^2 = H$

26 $R^1 = H$ $R^2 = OAc$
27 $R^1 = OAc$ $R^2 = H$

28

29

Scheme III

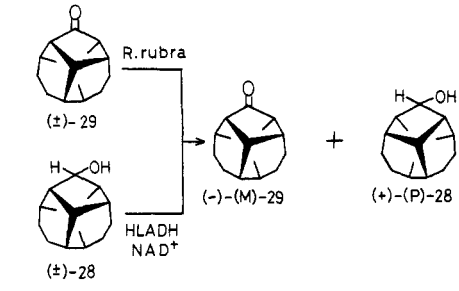
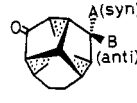


Chart I



	A	B
crystalline syn-keto acetate **24**	$OCOCH_3$ (δ 2.06)	H (δ 4.89)
oily anti-keto acetate **25**	H (δ 4.99)	$OCOCH_3$ (δ 2.03)

Synthesis of (±)-4-C_2-Methanoditwistanone (29, Scheme II). A partial hydrolysate of the diacetate **21** with 1 molar equiv of alkali afforded, besides the recovered diacetate and corresponding diol,[10f] a crystalline monoacetate **22** (mp 118–121 °C, 20% yield) and an oily monoacetate **23** [bp 145 °C (5 mm), 13% yield], providing evidence to support our previous assignment of the cis configuration with C_1 symmetry to **21**. Information on the relative stereochemistry of these monoacetates was secured from the NMR spectra of their oxidation products: crystalline *syn*-keto acetate **24** (mp 99–100 °C) obtained from the crystalline **22** and oily *anti*-keto acetate **25** [bp 142 °C (0.8 mm)] obtained from the oil **23**. Inspection of a molecular model (Chart I) reveals that the syn isomer **24** possessing the acetoxyl group close to the keto group should show the $OCOCH_3$ signal at higher magnetic field than that of the anti isomer **25**, and the opposite should be true for their C(**H**)$OCOCH_3$ signals. Chart I summarizes their NMR data which convincingly assigned their syn–anti relative configuration, automatically giving the structures **22** and **23** to their precursor monoacetates. Ring

(8) Nakazaki, M.; Chikamatsu, H.; Naemura, K.; Sasaki, Y.; Fujii, T. *J. Chem. Soc., Chem. Commun.* **1980**, 626.

(9) In this paper, the ketone which belongs to C_2 point group and has the carbonyl group coincident with the C_2 axis is called a C_2-ketone, and the corresponding alcohol is conveniently called a C_2-alcohol regardless of its symmetry.

(10) (a) Adachi, K.; Naemura, K.; Nakazaki, M. *Tetrahedron Lett.* **1968**, 5467. (b) Naemura, K.; Nakazaki, M. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 888. (c) Nakazaki, M.; Naemura, K.; Harita, S. *Ibid.* **1975**, *45*, 1907. (d) Nakazaki, M.; Naemura, K. *J. Org. Chem.* **1977**, *42*, 2985. (e) Nakazaki, M.; Naemura, K.; Arashiba, N. *Ibid.* **1978**, *43*, 689. (f) Nakazaki, M.; Naemura, K.; Arashiba, N.; Iwasaki, M. *Ibid.* **1979**, *44*, 2433. (g) Nakazaki, M.; Naemura, K.; Kondo, Y.; Nakahara, S.; Hashimoto, M. *Ibid.* **1980**, *45*, 4440.

(11) Nakazaki, M.; Naemura, K. *J. Chem. Soc., Chem. Commun.* **1980**, 911.

(12) The synthesis of the racemic modification has been reported from our laboratory.[10f]

(13) (a) The racemic form was recently prepared; Hirao, K.; Yonemitsu, O. *J. Chem. Soc., Chem. Commun.* **1980**, 423. (b) Our preliminary account on the synthesis and absolute configuration determination of (−)-D_3-tritwistane has appeared in: Nakazaki, M.; Naemura, K.; Chikamatsu, H.; Iwasaki, M.; Hashimoto, M. *Chem. Lett.* **1980**, 1571.

(14) Smith, E. C.; Barborak, J. C. *J. Org. Chem.* **1976**, *41*, 1433.

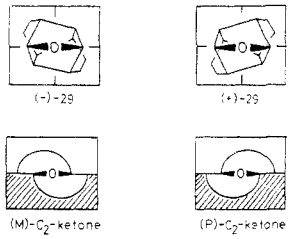


Figure 2. Quadrant orientations for the enantiomeric 4-C_2-methanoditwistanone and the microbial and HLADH C_2-ketone rules.

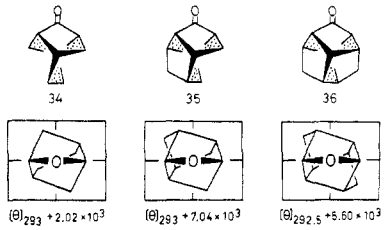


Figure 3. Octant projections of (-)-9-*twist*-brendanone (**34**), (-)-5-di-*twist*-brendanone (**35**), and (-)-D_3-trishomocubanone (**36**) and their Cotton effects (in isooctane, and adjusted to 100% optical purity).

expansion of the crystalline *syn*-keto acetate **24** with 6 molar equiv of diazomethane in ether followed by direct Wolff–Kishner reduction of the crude product **26** gave a 71% overall yield of 4-methanoditwistanol (**28**, mp 101–102 °C) which was also obtained in a comparable yield from the *anti*-keto acetate **27**, via **25**, by the same sequence of conversions.

Finally, Jones oxidation of **28** yielded the desired ring-expanded ketone, 4-methanoditwistanone (**29**): mp 119–120 °C; 71% yield.

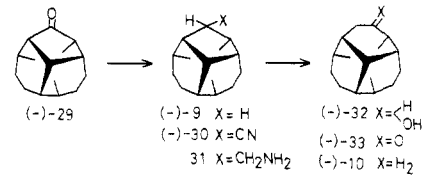
Biological Optical Resolution and Absolute Configuration of 4-C_2-Methanoditwistanone (29, Scheme III). Figure 2 illustrates two possible quadrant orientations for the enantiomeric 4-C_2-methanoditwistanone (**29**), and our proposed microbial C_2-ketone rule[7] predicts that *Rhodotorula rubra* should preferentially reduces the C_2-ketone with *P* helicity ((*P*)-C_2-ketone), leaving the (*M*)-C_2-ketone intact, while the HLADH C_2-ketone rule[8] predicts that HLADH with NAD^+ will preferentially oxidize the (*M*)-C_2-alcohol,[9] leaving the enantiomeric (*P*)-C_2-alcohol unaffected.

Incubation of (±)-**29** with *R. rubra* at 30 °C was terminated after 238 h when GLC monitoring indicated a 63:27 ratio of the C_2-ketone **29** and the C_2-alcohol **28** in the culture solution. Alumina chromatography of the metabolite mixture gave the (-)-ketone **29** (mp 111–112 °C; $[\alpha]_D$ -37.0°; 23% yield) and the (+)-alcohol **28** (mp 99 °C; $[\alpha]_D$ +126°; 10% yield).

HLADH-mediated oxidation[15] of the (±)-C_2-alcohol **28** was also carried out to yield the (+)-C_2-alcohol **28** and the (-)-C_2-ketone **29**, both exhibiting much larger optical rotations, $[\alpha]_D$ +289° and -262°, respectively.

Application of microbial (*P*)-C_2-ketone rule and the HLADH (*M*)-C_2-ketone rule immediately indicates that the (-)-C_2-ketone **29** should be an (*M*)-C_2-ketone with the 3*S*,5*S* configuration around the carbonyl center, and this conclusion was confirmed by the CD spectral analysis of this (-)-C_2-ketone. In Figure 3 are illustrated the octant projections of the closely related tri-, tetra-, and pentacyclic ketones with established absolute configurations: (-)-9-*twist*-brendanone (**34**),[10c] (-)-5-di-*twist*-brendanone (**35**),[10e] and (-)-D_3-trishomocubanone (**36**),[10e] all exhibiting positive Cotton effects in n-π^* regions. The observed positive Cotton effect of (-)-**29** with $[\theta]_{291}$ +9.59 × 10^3 (adjusted to 100% optical purity, vide infra) and comparison of the octant projection (Figure 2) with those in Figure 3 unambiguously indicated that the newly prepared (-)-4-C_2-methanoditwistanone (**29**) should have the 3*S*,5*S* configuration as predicted by the biological experiments.

Scheme IV



It appears pertinent here to divert our attention to the optical purity of these metabolites isolated from the biological experiments. To a CCl_4 solution of the (+)-4-C_2-methanoditwistanol (**28**, $[\alpha]_D$ +126°) obtained from the culture solution of *R. rubra* (vide supra) was added 0.3 molar equiv of Eu(TFC)$_3$, a chiral shift reagent, to split the original CHOH signal centered at δ 3.98 into two peaks located at δ 9.45 and 9.60 and corresponding to the (+) and the (-) enantiomers.

Integration of the peak areas indicated a 33.3% optical purity for this specimen of the (+)-C_2-alcohol **28**, assigning its absolute rotation as $[\alpha]_{D,abs}$ +377°, and this, when coupled with an interconversion experiment between (-)-**29** and (-)-**28** (see Experimental Section), gave $[\alpha]_{D,abs}$ -255° for (-)-C_2-methanoditwistanone (**29**).

Finally, this information enabled us to calculate the optical purity of the metabolites isolated from our biological optical resolutions; the incubation with *R. rubra* afforded the (-)-C_2-ketone **29** and the (+)-C_2-alcohol **28** with respective 15% and 33% optical purities, while the HLADH-mediated oxidation yielded (-)-**29** and (+)-**28** with 100% and 77% optical purity, respectively.

Syntheses of (-)-C_2-Methanoditwistane (9) and (-)-D_3-Tritwistane (10, Scheme IV). Preparation of the optically active C_2-methanoditwistane (**9**) was straightforward, involving Wolff–Kishner reduction of the (-)-C_2-ketone **29** ($[\alpha]_D$ -37.0°, 15% optical purity) to provide a 38% yield of (-)-**9** [mp 108–108.5 °C; $[\alpha]_D$ -58.6° ($CHCl_3$)] whose identification was established by spectral comparison with an authentic racemic specimen.[10f]

Of various synthetic alternatives open to convert the ketone **29** to the D_3-tritwistane system, our choice was the Demjanov ring expansion of an intermediate amine **31** which could be prepared from the nitrile **30**.

The nitrile synthesis by means of tosylmethyl isocyanide proceeded smoothly, converting the (-)-C_2-ketone **29** ($[\alpha]_D$ -113°, 44% optical purity) into the (-)-nitrile **30** (mp 63.5–64 °C) whose $LiAlH_4$ reduction afforded the required primary amine **31**. The Demjanov rearrangement of the amine **31** in acetic acid provided the (-)-alcohol **32** which was directly oxidized with Jones reagent to (-)-4-D_3-tritwistanone (**33**): mp 109–110 °C; $[\alpha]_D$ -204°; 43% overall yield from the nitrile **30**.

Finally the Wolff–Kishner reduction of this (-)-ketone **33** afforded a 57% yield of (-)-D_3-tritwistane (**10**): mp 99–99.5 °C; $[\alpha]_D$ -250° ($CHCl_3$).

Chiroptical Properties. Our assignment of the 3*S*,5*S* absolute configuration to the precursor (-)-C_2-ketone **29** automatically provides information on the absolute configurations of (-)-C_2-methanoditwistane (**9**) and (-)-D_3-tritwistane (**10**) shown in Table I, which also tabulates,

(15) A preliminary note of this HLADH-mediated oxidation was reported elsewhere.[8]

Table I. Trivial and IUPAC Names of the Levorotatory Tri-, Tetra-, and Pentacyclic Cage-Shaped Hydrocarbons Conceptually Constructed by Homologation of Cubane or by Diagonal Bridging of D_3-Twisted Bicyclo[2.2.2]octane

trivial name	IUPAC name	absolute config
twist-brendane (2)	tricyclo[4.3.0.$0^{3,8}$]nonane	1*R*,3*S*,6*S*,8*R*
twistane (3)	tricyclo[4.4.0.$0^{3,8}$]decane	1*R*,3*R*,6*R*,8*R*
di-*twist*-brendane (4)	tetracyclo[5.2.1.$0^{2,6}$.$0^{4,8}$]decane	1*R*,2*R*,4*R*,6*R*,7*R*,8*R*
C_1-methanotwistane (5)	tetracyclo[6.2.1.$0^{2,7}$.$0^{4,9}$]undecane	1*R*,2*R*,4*S*,7*R*,8*S*,9*R*
C_2-ditwistane (6)	tetracyclo[6.2.2.$0^{2,7}$.$0^{4,9}$]dodecane	1*S*,2*S*,4*S*,7*R*,8*R*,9*S*
D_3-trishomocubane (7)	pentacyclo[6.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane	1*S*,3*S*,5*S*,6*S*,8*S*,10*S*
C_2-bismethanotwistane (8)	pentacyclo[7.3.0.$0^{2,7}$.$0^{3,11}$.$0^{6,10}$]dodecane	1*S*,2*R* 3*S*,6*S*,7*S*,9*S*,10*R*,11*S*
C_2-methanoditwistane (9)	pentacyclo[7.4.0.$0^{2,6}$.$0^{3,11}$.$0^{5,10}$]tridecane	1*S*,2*S*,3*S*,5*S*,6*S*,9*S*,10*S*,11*S*
D_3-tritwistane (10)	pentacyclo[8.4.0.$0^{2,7}$.$0^{3,12}$.$0^{6,11}$]tetradecane	1*S*,3*S*,6*S*,7*S*,10*S*,12*S*
C_2-bishomocubane (11)	pentacyclo[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]decane	1*S*,2*S*,3*S*,4*S*,5*R*,7*S*,8*S*,9*R*
C_1-homobasketane (12)	pentacyclo[5.4.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]undecane	1*R*,2*R*,3*S*,5*R*,6*S*,7*S*,8*S*,9*S*
C_2-3,10-dehydroditwistane (13)	pentacyclo[6.4.0.$0^{2,7}$.$0^{3,10}$.$0^{6,9}$]dodecane	1*R*,2*S*,3*S*,6*R*,7*S*,8*S*,9*S*,10*S*

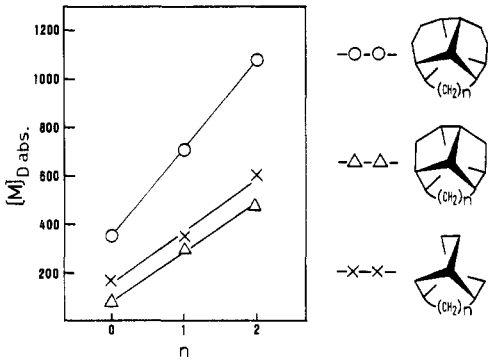


Figure 4. Correlation between bridge span and molecular rotation in three series of gyrochiral cage-shaped molecules.

Chart II

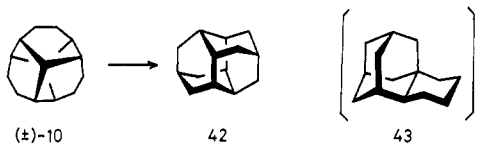
with their *R*,*S* specifications, the trivial and the IUPAC names of the 12 levorotatory cage-shaped molecules (Figure 1) conceptually constructed from D_3-*twist*-bicyclo[2.2.2]-octane of *M* helicity.

The observed optical purity of the precursor C_2-ketone **29** allowed calculation of the absolute rotations of (−)-**9** and (−)-**10**, $[\alpha]_{D,abs}$ −404° and −567°, respectively, the latter being fairly close to our previous estimation (ca. −500°).[10f] Figure 1 summarizes the absolute configuration and absolute molecular rotation of the levorotatory tri-, tetra-, and pentacyclic cage-shaped rigid hydrocarbons with a (*M*)-D_3-*twist*-bicyclo[2.2.2]octane molecular framework, and, as predicted, D_3-tritwistane (**10**) and diwistane (**6**) are conspicuous in their high optical rotatory power among this class of compounds. A casual inspection of Figure 1 would also be enough to notice a symmetrical increase in their molecular rotations on going toward the bottom of the figure, and this marked regularity[16-18] can be seen more clearly within the same series of gyrochiral molecules as illustrated in Figure 4.

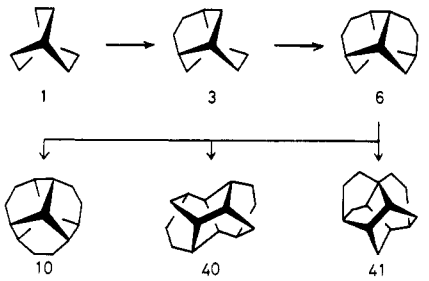
Examination of Figure 4 also enabled us to roughly estimate the increments of molecular rotations corresponding to the bridge span change: single bond → CH_2, +250°; CH_2 → CH_2CH_2, +250°.

When diagonal bridging with a single bond is allowed in desymmetrizing bicyclo[2.2.2]octane, there arises a new series of compounds (Chart II), comprising C_2-bissecocubane (**37**), 2,8-dehydro-*twist*-brendane (**38**), and 2,9-dehydrotwistane (**39**). Although the beautiful linear relationship demonstrated in Figure 4 could not be expected here, we could nevertheless predict **38** and **39** to be levorotatory with confidence and their respective $[M]_{D,abs}$ values, ca. 250° and ca. 500°, with much reservation.

Scheme V



Scheme VI



Topology and Stability of D_3-Tritwistane (10, Schemes V and VI). Basically D_3-tritwistane (**10**) is composed of a twist–boat form of cyclohexane (D_2 symmetry) whose 1,4-diagonal ethano bridging leads to the D_3-twisted bicyclo[2.2.2]octane (**1**, Scheme VI), which in turn can be further bridged to transform into twistane (**3**, D_2 symmetry) which is of rigid conformation. On further diagonal ethano bridging, the D_2 symmetry inherent to the twistane molecule allows only ditwistane (**6**, C_2 symmetry) to emerge as the next member. From this molecule, the route to the higher member diverges, giving three tritwistanes: D_3-tritwistane (**10**), **40** (C_2 symmetry), and **41** (C_2 symmetry). The whole family of compounds constructed by this diagonal ethano bridging starting from the D_2 twist–boat cyclohexane can be represented with molecular formula C_nH_{n+6} ($n = 2p + 6$, where $p = 0, 1, 2...$) and has $n - 5$ D_2 twist–boat cyclohexane units fused together.

Continuation of this bridging process infinitely (on the molecular scale) with simultaneous stripping of surrounding hydrogen atoms ultimately provides us with a giant gyrochiral "twist" diamond network with an infinite number of fused D_2 twist–boat cyclohexane moieties, and

(16) This regularity was first pointed out by us[10f] and was used effectively by Pacquette and co-workers[17] in their estimation of $[M]_{D,abs}$ +125° for C_2-bissecocubane (**37**) for which our experimental work has suggested 270°.[18] Since our estimation was based on an analogy between C_2-bissecocubane and the *twist*-brendane system, our value could be a little higher, and in Figure 4 we adopt $[M]_{D,abs}$ +175° for **37**.

(17) Jenkins, J. A.; Doehner, R. E., Jr.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 2131.

(18) Nakazaki, M.; Naemura, K.; Sugano, Y.; Kataoka, Y. *J. Org. Chem.* **1980**, *45*, 3232.

this new modification of C_∞ molecule presents an interesting contrast to the familiar "regular" diamond whose fundamental ring unit is the chair form of cyclohexane of D_{3d} symmetry.

As the name implies, adamantane has been regarded as the prototype of the "regular" diamond of $Fd3m$ space group (cubic system). By the same token, we could call D_3-tritwistane (**10**) as the prototype of gyrochiral "twist" diamond which belongs to the $P6_3$ space group (hexagonal system). Then, an interesting question which arises is which is more stable, the "regular" diamond or the hypothetical gyrochiral "twist" diamond.

Among ample experimental as well as theoretical evidences which have indicated the higher stability of adamantane over twistane (**3**), none could be more convincing than the observed facile isomerization[19] of twistane (**3**) to adamantane[20,21] with aluminum bromide catalysis.

Although this could be taken as an evidence to suggest the expected high stability of "regular" diamond over the "twist" modification, we tried to demonstrate experimentally isomerization of D_3-tritwistane (**10**), the prototype of "twist" diamond, into diamantane (congressane, **42**) which contains the adamantane system. (±)-D_3-Tritwistane (**10**) was prepared from the racemic modification of C_2-ketone **29**, and allowing its CS_2 solution containing aluminum bromide to stand for 5 h at room temperature was found to be enough to afford a 94% yield of diamantane (**42**),[22] evidence indicating that the "regular" diamond is the sp^3 stabilomer of C_∞ molecules.

Experimental Section

Infrared spectral data were obtained from a Hitachi 260-10 spectrophotometer. ^1H NMR spectra were obtained from a JNM-C-60 and a JNM-FX-100. Chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane. Optical rotations were measured with a JASCO-DPI-140 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 performed on a Yanagimoto CHN-Corder, Type II. All melting and boiling points are uncorrected. The culture of *Rhodotorula rubra* was obtained from the Institute of Fermentation, Osaka, Japan, and was identified by its IFO catalog serial number (IFO 0889).

Hydrolysis of 8,12-Diacetoxypentacyclo[7.3.0.0^{2,7}.0^{3,11}.0^{6,10}]dodecane (21). A solution of (±)-**21**[10f] (22.7 g, 0.0822 mol) and KOH (4.60 g, 0.0822 mol) in 50% aqueous methanol (50 mL) was refluxed for 5 h. After cooling, the reaction mixture was poured into water (100 mL) and extracted with $CHCl_3$. The extract was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. On silica gel column chromatography of the residue, elution with hexane–ether (1:1 v/v) recovered the diacetate **21** (5.62 g), further elution with ether gave a mixture of the monoacetates **22** and **23** (7.80 g), and final elution with ether–methanol (9:1 v/v) yielded the diol[10f] (5.81 g). The monoacetate mixture was rechromatographed (SiO_2), and elution with $CHCl_3$ gave a crystalline monoacetate **22** (3.93 g, 20% yield) followed by an oily monoacetate **23** (2.61 g, 13% yield). The crystalline monoacetate was recrystallized from methanol: mp 118–121 °C; IR (KBr) 3430, 1730, 1240, 1045, 943 cm^{-1}; NMR ($CDCl_3$) δ 1.58 (s, 4 H), 1.95 (s, 3 H), 2.00–2.07 (m, 8 H), 2.75 (s, 1 H), 3.98 (s, 1 H) 4.78 (s, 1 H).

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.66; H, 7.75.

The oily monoacetate was further purified by distillation: bp 145 °C (0.5 mm); IR (neat film) 3430, 1730, 1240, 1055, 958 cm^{-1}; NMR ($CDCl_3$) δ 1.51 (s, 4 H), 1.95 (s, 3 H), 2.10–2.34 (m, 8 H), 2.70 (s, 1 H), 4.01 (s, 1 H), 4.70 (s, 1 H).

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.85; H, 7.71.

***syn*-12-Acetoxypentacyclo[7.3.0.0^{2,7}.0^{3,11}.0^{6,10}]dodecan-8-one (24).** A solution of (±)-**22** (2.48 g, 0.0106 mol) in dry CH_2Cl_2 (20 mL) was added to a suspension of pyridinium chlorochromate (3.40 g, 0.0157 mol) in dry CH_2Cl_2 (20 mL), and the mixture was stirred for 3 h at room temperature. The organic layer was decanted from an inorganic residue, and the residue was thoroughly rinsed with CH_2Cl_2. The combined extracts were washed with water and dried ($MgSO_4$). Removal of the solvent left a residue which was chromatographed on silica gel, and elution with CH_2Cl_2 gave a white solid which was recrystallized from benzene–hexane to afford the keto acetate **24**: 1.48 g (60% yield); mp 99–100 °C; IR (KBr) 1758, 1730, 1360, 1228, 1030 cm^{-1}; NMR ($CDCl_3$) δ 1.5–1.8 (m, 4 H), 1.9–2.2 (m, 3 H), 2.06 (s, 3 H), 2.3–2.5 (m, 4 H), 2.56 (br s, 1 H), 4.89 (s, 1 H).

Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.29; H, 6.92.

***anti*-12-Acetoxypentacyclo[7.3.0.0^{2,7}.0^{3,11}.0^{6,10}]dodecan-8-one (25).** Oxidation of (±)-**23** (2.56 g, 0.0109 mol) with pyridinium chlorochromate (3.53 g, 0.0163 mol) in dry CH_2Cl_2 was carried out in the same manner as described above. Chromatography of the product on silica gel (CH_2Cl_2 as eluent) gave an oily keto acetate which was distilled to afford **25**: 2.31 g (91% yield); bp 142 °C (0.8 mm); IR (neat film) 1758, 1730, 1360, 1230, 1050 cm^{-1}; NMR ($CDCl_3$) δ 1.4–1.7 (m, 4 H), 1.8–2.1 (m, 3 H), 2.03 (s, 3 H), 2.3–2.7 (m, 5 H), 4.99 (s, 1 H).

Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.00; H, 6.99.

4-Pentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]tridecanol (28). From the *syn*-Keto Acetate 24. A freshly prepared ethereal solution (40 mL) of diazomethane[23] (ca. 1 g, 24 mmol) was added dropwise to a chilled (0 °C) solution of **24** (1.00 g, 4.31 mmol) in ether (10 mL), and the mixture was allowed to stand in a refrigerator (5 °C) for 7 days. After the excess diazomethane was destroyed with a small amount of acetic acid, the mixture was successively washed with aqueous $NaHCO_3$ solution and water and dried ($MgSO_4$). Concentration of the mixture left a residue which was heated with a mixture of KOH (0.55 g), 100% hydradine hydrate (0.45 mL), and triethylene glycol (11 mL). The bath temperature was gradually raised to 200 °C during 2 h, and the heating was continued for an additional 3.5 h. After cooling, the reaction mixture was diluted with water and extracted with $CHCl_3$. The extract was washed with water, dried ($MgSO_4$), and concentrated to give a solid. Chromatography of the solid on neutral alumina (activity III, ether–pentane 1:2 v/v as eluent) gave **28** (585 mg, 71% yield) which was further purified by sublimation at 80 °C (5 mm): mp 111–112 °C (in a sealed tube); IR (KBr) 3310, 1455, 1348, 1270, 1212, 1165, 1100, 1073 cm^{-1}; NMR (CCl_4) δ 1.49–2.40 (m, 16 H), 2.58 (br s, 1 H), 3.97 (br s, 1 H).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 81.78; H, 9.45.

From the *anti*-Keto Acetate 25. An ethereal solution (100 mL) of **25** (2.31 g, 9.95 mmol) and diazomethane (ca. 2 g, 48 mmol) was kept in a refrigerator (5 °C) for 7 days and worked up as described above to give a solid (2.15 g). The Wolff–Kishner reduction of the solid (2.15 g) with KOH (1.95 g), 100% hydrazine hydrate (2.46 mL), and triethylene glycol (13 mL) was also carried out in the same manner as described above. Chromatography followed by sublimation of the product furnished **28**: 1.39 g (74% yield); mp 111.5–112 °C (in a sealed tube).

4-Pentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]tridecanone (29). To a solution of (±)-**28** (500 mg, 2.63 mmol) in acetone (7 mL) was added an excess of Jones reagent[24] with ice cooling, and the mixture was

(19) Whitlock, H. W., Jr.; Siefkin, M. W. *J. Am. Chem. Soc.* **1968**, *90*, 4929.

(20) Although D_3-trishomocubane (**7**) shares the D_3 symmetry with D_3-tritwistane (**10**), the former is the stabilomer[21] among pentacyclic $C_{11}H_{14}$ hydrocarbons and cannot be the prototype of any "twist" diamond.

(21) Kent, G. J.; Godleski, S. A.; Osawa, E.; Schleyer, P. v. R. *J. Org. Chem.* **1977**, *42*, 3852.

(22) (a) Cupas, C.; Schleyer, P. v. R.; Trecker, D. J. *J. Am. Chem. Soc.* **1965**, *87*, 917. (b) Gund, T. M.; Williams, V. Z., Jr.; Osawa, E.; Schleyer, P. v. R. *Tetrahedron Lett.* **1970**, 3877. Examination of the mass spectrum of the crude isomerization product failed to detect tetramethyleneadamantane ($C_{14}H_{22}$, **43**), another possible product of the adamantane system.

(23) DeBoer, J.; Backer, H. J. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, p 250.

stirred for 2.5 h at 0–5 °C. After the excess oxidation reagent was destroyed with solid sodium bisulfite (0.3 g), ether (50 mL) was added. The organic layer was decanted from an inorganic residue, and the residue was rinsed with ether. The ether extracts were combined, washed with aqueous $NaHCO_3$ solution and water, and dried ($MgSO_4$). After evaporation of the ether, the residue was chromatographed on neutral alumina (activity III). Elution with pentane gave a white solid which was sublimed at 80 °C (5 mm) to afford **29**: 352 mg (71% yield); mp 119–120 °C (in a sealed tube); IR (KBr) 1752, 1460, 1445, 1322, 1202, 1160, 1148, 825 cm^{-1}.

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.73; H, 8.38.

Incubation of (±)-4-Pentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]tridecanone (29) with *Rhodotorula rubra*. Six growing cultures of *R. rubra* were prepared by inoculating six 25-mL mediums[7] in 100-mL flasks with spores of the microbe followed by a 48-h incubation at 30 °C. The cultures were transfered to six 500-mL flasks each containing 200 mL of the medium, and the incubation was continued for 48 h. After (±)-**29** (80 mg) was added to each culture solution, the incubation was resumed for 238 h. The combined culture mixtures were filtered through a layer of Hyflo-super-cel, and the collected mycelium was washed with ether. The ether extract of the filtrate was combined with this washing, washed with water, dried ($MgSO_4$), and concentrated. A GLC analysis (10% PEG 20M packing) of the residual oil indicated a 63:37 ratio of the recovered ketone **29** and the alcohol **28**. The residue was chromatographed over neutral alumina (activity III). Elution with ether–pentane (1:49 v/v) afforded (−)-**29** (110 mg, 23% yield), and elution with ether yielded (+)-**28** (50 mg, 10% yield).

For (−)-**29**: mp 111–112 °C (in a sealed tube); $[\alpha]^{23}_D$ −37.0° (*c* 0.238, EtOH); CD (*c* 2.49 × 10^{-2} mol/L, isooctane) [θ] (λ, nm) +1.39 × 10^3 (291).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.75; H, 8.45.

For (+)-**28**: mp 99 °C (in a sealed tube); $[\alpha]^{23}_D$ +125.5° (*c* 0.326, EtOH).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 82.07; H, 9.60.

$LiAlH_4$ Reduction of (−)-4-Pentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]tridecanone (29). A solution of (−)-**29** (30 mg, 0.159 mmol; $[\alpha]_D$ −37.0°) in dry ether (10 mL) was added to a suspension of $LiAlH_4$ (8 mg, 0.210 mmol) in dry ether (5 mL), and the mixture was gently refluxed for 4 h. After 10% sulfuric acid was added to the reaction mixture with ice cooling, the ether solution was decanted from an inorganic solid and dried ($MgSO_4$). Evaporation of the ether gave a white solid which was sublimed at 95 °C (20 mm) to afford (−)-**28**: 25 mg (83% yield); mp 110–112 °C (in a sealed tube); $[\alpha]^{25}_D$ −54.7° (*c* 0.250, EtOH).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 82.20; H, 9.50.

(−)-Pentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]tridecane (9). A solution of (−)-**29** (100 mg, 0.532 mmol; $[\alpha]_D$ −37.0°), KOH (40 mg), 80% hydrazine hydrate (0.08 mL), and triethylene glycol (1 mL) was heated for 1 h at 110–120 °C and then for an additional 3 h at 190–200 °C. During this period, a white solid was observed to condense on the inner wall of the condenser. After cooling, the solid was dissolved in pentane, and the pentane solution was washed with water and dried ($MgSO_4$). Evaporation of the pentane gave a solid which was purified through sublimation at 70 °C (20 mm) to yield (−)-**9**: 35 mg (38% yield); mp 108–108.5 °C (in a sealed tube); $[\alpha]^{25}_D$ −58.6° (*c* 0.313, $CHCl_3$); IR (KBr) 2940, 2870, 1460, 1445, 1325, 810 cm^{-1}; mass spectrum, *m/e* 174 (M^+).

Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: 89.55; H, 10.38.

(−)-4-Cyanopentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]tridecane (30). To an ice-cooled solution of (−)-**29** (211 mg, 1.12 mmol; $[\alpha]_D$ −112°, 44% optical purity), tosylmethyl isocyanide (350 mg, 1.80 mmol), absolute ethanol (0.14 mL), and dimethoxyethane (4.2 mL) was added solid potassium *tert*-butoxide (168 mg, 1.50 mmol) at such a rate that the temperature did not exceed 3 °C. After being stirred for 1 h at room temperature, the reaction mixture was heated at 35–40 °C for 30 min. The filtrate freed of the precipitated solid was concentrated under reduced pressure. The residue was chromatographed on neutral alumina (activity III), and elution with pentane afforded a solid which was sublimed at 90 °C (30 mm) to give (−)-**30**: 120 mg (54% yield); mp 63.5–64 °C; $[\alpha]^{27}_D$ −201° (*c* 0.105, EtOH); IR (KBr) 2930, 2855, 2220, 1455, 1440 cm^{-1}.

Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.41; H, 8.36; N, 7.27.

(−)-4-Pentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradecanone (33). A solution of (−)-**30** (108 mg, 0.543 mmol; $[\alpha]_D$ −201°) in dry ether (4 mL) was slowly added to a suspension of $LiAlH_4$ (31 mg, 0.82 mmol) in dry ether (7 mL) with ice cooling. Stirring was continued for 1 h with ice-cooling and then for an additional 1 h at room temperature. The stirred mixture was chilled in an ice bath and was decomposed with successive addition of water (0.2 mL), 20% aqueous NaOH solution (0.15 mL), and water (0.4 mL) to precipitate an inorganic solid which was collected and washed with ether. The combined ether extracts were dried (Na_2SO_4), and removal of the solvent gave an oily residue (0.10 g) which was dissolved in a mixture of acetic acid (0.05 mL) and water (0.5 mL). After addition of a solution of sodium nitrite (74 mg) in water (0.5 mL), the mixture was heated at 100–110 °C for 40 min. Cooling of the mixture was followed by extraction with ether, and the extract was washed with aqueous $NaHCO_3$ solution and water, dried ($MgSO_4$), and concentrated. The residue was chromatographed on neutral alumina (activity III), and elution with ether–pentane (1:19 v/v) afforded (−)-**32** (57 mg, 51% yield) as a white solid, $[\alpha]^{27}_D$ −203° (*c* 0.062, EtOH). The alcohol **32** (52 mg) was dissolved in acetone (2 mL) and treated with excess Jones reagent in a manner similar to that described for the preparation of **29**. After the routine workup, the residue was chromatographed on neutral alumina (activity III). Ether–pentane (3:97 v/v) elution gave a white solid which was sublimed at 70 °C (5 mm) to yield (−)-**33**: 44 mg (85% yield); mp 109–110 °C (in a sealed tube); $[\alpha]^{27}_D$ −204° (*c* 0.143, EtOH); CD (*c* 1.71 × 10^{-2} mol/L, isooctane) [θ] (λ, nm) +254.4 (284 sh), +561.6 (294), +815.7 (303.5), +622.8 (315); IR (KBr) 1722, 1465, 1450, 1230, 1200, 1165 cm^{-1}.

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.93; H, 8.81.

(−)-Pentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradecane (10). A mixture of (−)-**33** (36 mg, 0.178 mmol; $[\alpha]_D$ −204°), KOH (14 mg), 80% hydrazine hydrate (0.03 mL), and triethylene glycol (1 mL) was treated in the same manner as described for the preparation of (−)-**9**. The product was chromatographed over neutral alumina (activity III), and pentane elution afforded a white solid which was sublimed at 70 °C (30 mm) to yield (−)-**10**: 19 mg (57% yield); mp 99–99.5 °C (in a sealed tube); $[\alpha]^{27}_D$ −250° (*c* 0.235, $CHCl_3$); IR(KBr) 2940, 2920, 2870, 1465, 1450, 1270, 1035, 920 cm^{-1}; mass spectrum, *m/e* 188 (M^+).

Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.25; H, 10.71.

4-Cyanopentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]tridecane (30). The (±)-ketone **29** (1.04 g, 5.53 mmol) was treated with TosMIC (1.73 g, 8.86 mmol), potassium *tert*-butoxide (1.93 g, 17.1 mmol) in absolute ethanol (0.7 mL), and dimethoxymethane (21 mL) in the same manner as described for the (−) enantiomer. The crude product was chromatographed over neutral alumina (activity III), and elution with pentane gave the nitrile **30**: 480 mg (44% yield); mp 70–72 °C.

Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.10; H, 8.47; N, 7.10.

4-Pentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradecanone (33). Reduction of (±)-**30** (470 mg, 2.36 mmol) with $LiAlH_4$ (135 mg, 3.54 mmol) and subsequent Demjanov rearrangement were carried out as described for the optically active modification to give the crude (±)-alcohol **32**, 0.35 g, as a solid. The (±)-alcohol **32** (220 mg, 1.08 mmol) was oxidized with an excess of Jones reagent in acetone by following the procedure described for the preparation of (−)-**33**. The crude product was chromatographed over neutral alumina (activity III), and elution with ether–pentane (3:97, v/v) afforded **33** (140 mg, 64% yield) which was sublimed at 80 °C (5 mm); mp 107–108 °C (in a sealed tube).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.20; H, 8.86.

Pentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradecane (10). Wolff–

(24) Meinwald, J.; Crandall, J.; Hymans, W. E. "Organic Syntheses"; Wiley; New York, 1973; Collect Vol. V, p 866.

Kishner reduction of (±)-**33** (109 mg, 0.54 mmol) with 80% hydrazine hydrate (0.07 mL), KOH (40 mg), and triethylene glycol (1 mL) was carried out as described for the preparation of the (-) enantiomer. Chromatography afforded a solid which was sublimed at 50 °C (20 mm) to give **10**: 74 mg (73% yield); mp 100 °C (in a sealed tube) (lit.[13] mp 100–102 °C).

Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.22; H, 10.69.

Aluminum Bromide Catalyzed Isomerization of (±)-10. Aluminum bromide (150 mg) was added to a solution of (±)-**10** (50 mg, 0.266 mmol) in dry carbon disulfide (3 mL), and then the reaction mixture was stirred for 5 h at room temperature. The mixture was poured onto ice and was extracted with ether. The ethereal extract was washed with aqueous $NaHCO_3$ solution and water and dried ($MgSO_4$). Removal of the solvent gave a white solid, whose GLC analysis (5% SE-30 packing) exhibited a single peak. The solid was chromatographed over neutral alumina (activity III), and elution with pentane gave diamantane (**42**): 47 mg (94% yield); mp 238–240 °C (in a sealed tube) (lit.[22a] mp 236–237 °C, lit.[22b] mp 244.0–245.4 °C); mass spectrum, m/e 188 (M^+).

Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.15; H, 10.54.

Registry No. (-)-**9**, 77122-03-3; (±)-**10**, 77079-50-6; (-)-**10**, 77122-04-4; (-)-**21**, 70209-48-2; (±)-**22**, 77079-51-7; (±)-**23**, 77122-05-5; (±)-**24**, 77079-52-8; (±)-**25**, 77122-06-6; (±)-**28**, 77122-78-2; (+)-**28**, 77079-53-9; (-)-**28**, 77122-79-3; (±)-**29**, 77079-54-0; (-)-**29**, 77122-07-7; (±)-**30**, 77079-55-1; (-)-**30**, 77122-08-8; (±)-**32**, 77079-56-2; (±)-**33**, 77079-57-3; (-)-**33**, 77122-09-9; (±)-**42**, 77079-58-4.

Reactions of [(Diphenylphosphino)methyl]lithium with Dimethylfulvene

N. E. Schore* and B. E. LaBelle

Department of Chemistry, University of California, Davis, California 95616

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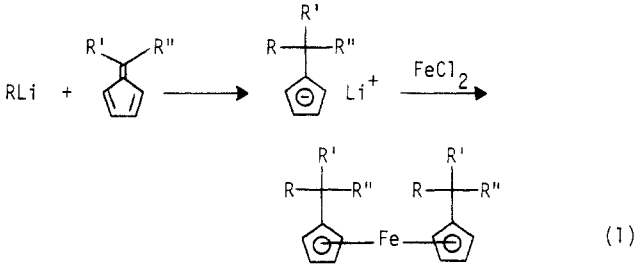
[(Diphenylphosphino)methyl]lithium reacts with dimethylfulvene in ether or THF to yield exclusively lithium isopropenylcyclopentadienide, the product of proton transfer. Neither steric nor electronic effects alone appear sufficient to explain this anomalous result. A similar reaction in petroleum ether gives rise to three major products: lithium [1,1-dimethyl-2-(diphenylphosphino)ethyl]cyclopentadienide and the dilithium salts of 6-(1,3-cyclopentadienyl)-6,8,8-trimethylbicyclo[3.3.0]octa-1,3-diene and 2,4-bis(1,3-cyclopentadienyl)-4-methyl-1-pentene. The latter compound is a new dimethylfulvene dimer whose monoanion had previously been proposed but not observed as an intermediate in the anionic oligomerization of dimethylfulvene.

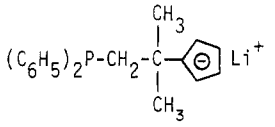
The addition of metal hydrides, Grignard reagents, and alkyllithiums to the C-6 position of fulvenes is a characteristic reaction of these systems and is, perhaps, the most efficient method for generating substituted cyclopentadienides for subsequent attachment to transition metals (eq 1).[1] The reaction proceeds in moderate to very



(1)

high yields for a variety of substituents R, R′, and R″, failing only when steric hindrance to addition is extreme.[2] In the case of dimethylfulvene, the addition reactions of MH, RMgX, and RLi are invariably successful.

We report herein the details of the anomalous reactions of diphenylphosphinomethyllithium, $(C_6H_5)_2PCH_2Li$, with dimethylfulvene, reactions which were originally carried out in the hope that they would result in the efficient generation of the cyclopentadienide system **1**, possessing remote tertiary phosphine functionality.[3]



1

Results

Reactions of $(C_6H_5)_2PCH_2Li$ (2) with Dimethylfulvene in Ethereal Solvents. By use of a procedure slightly modified from that described by Peterson and Hays,[4] the alkyllithium **2** may be isolated as a white powder from the reaction of methyldiphenylphosphine and *n*-butyllithium in diethyl ether. This material is insoluble in petroleum ether and diethyl ether, but it readily dissolves in THF, giving yellow solutions. The NMR spectrum in THF displays a doublet (J_{PCH} = 3.5 Hz) due to the methylene protons at δ -0.34 ppm. Solid **2** is stable for months at room temperature when stored under dry N_2.

The reaction between $(C_6H_5)_2PCH_2Li$ and dimethylfulvene in THF results almost immediately in a nearly colorless solution in which the upfield methylene doublet and the vinyl absorption of the starting materials are no longer visible, and the complex pattern due to the aromatic protons of **2** has been replaced by a narrowed multiplet at δ 7.28. A pair of apparent triplets are present at δ 5.64

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