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Preparation and Chiroptical Properties of Optically Active Tetracyclic Cage-shaped Hydrocarbons; [*m*.0]Triblattanes and [*m*.1]Triblattanes

Koichiro Naemura,* Tohru Katoh, Rinkō Fukunaga, Hiroaki Chikamatsu,
and Masao Nakazaki
Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560

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Horse liver alcohol dehydrogenase mediated reduction of tetracyclo[4.3.0.$0^{2,5}$.$0^{3,8}$]nonan-9-one ([1.0]triblattan-9-one) (**17**) gave (+)-**17** and (−)-tetracyclo[4.3.0.$0^{2,5}$.$0^{3,8}$]nonan-9-ol (**18**). Hydrogenolysis of (+)-**17** with 5% rhodium-alumina to (+)-(1*R*,3*R*,6R8*R*)-twist-brendan-9-ol with known absolute rotation allowed us to assign the 1*S*,2*S*,3*R*,5*R*,6*R*,8*R* absolute configuration to (+)-**17** and to calculate the absolute rotation of (+)**17**. Wolff-Kishner reduction of (+)-**17** gave (+)-[1.0]triblattane. BF_3-Catalyzed diazomethane ring expansion of (+)-**17** was followed by Wolff-Kishner reduction to afford optically active [*m*.0]triblattanes. (+)-Tetracyclo-[5.2.$1^{2,6}$.$0^{4,8}$]decan-5-one ([1.1]triblattan-5-one) with known absolute configuration and absolute rotation was transformed to optically active [*m*.1]triblattanes by diazomethane ring expansion with BF_3 etherate followed by Wolff-Kishner reduction. The known optical purities of our starting materials permitted calculation of the absolute molecular rotations of [*m*.0]triblattanes and [*m*.1]triblattanes. The chiroptical properties of triblattanes are discussed.

The C2–C8 diagonal bridging of D_3-twisted bicyclo[2.2.2]octane (**1**) with a polymethylene bridge provides a tricyclic cage-shaped hydrocarbon **2**, and further C3–C6 diagonal bridging of the chiral molecule with a polymethylene bridge gives a tetracyclic hydrocarbon **3**. Final C5–C7 diagonal bridging furnishes a pentacyclic hydrocarbon **4**.

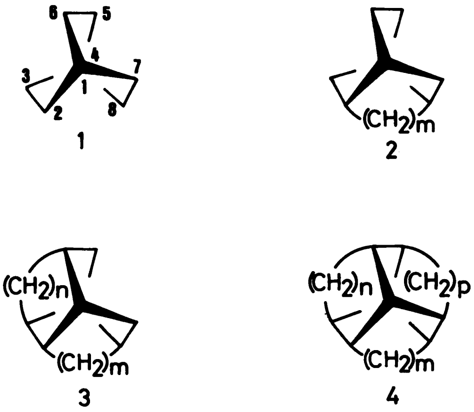


Chart 1.

We have coined for these hydrocarbons **2**, **3**, and **4** the generic names [*m*], [*m*.*n*], and [*m*.*n*.*p*]triblattane, respectively. Since our first preparation of twistane ([2]triblattane) in an optically active form,[1] we have been interested in the preparation, stereochemistry, and biological transformation of triblattanes.

Figure 1 shows the correlation between bridge span (*m*) and absolute molecular rotation ($[M]_{D\,abs.}$) in triblattanes[2,3] which have been prepared in optically active modification in our laboratory, except for [0]triblattane.[4] Inspection of the Fig. 1 reveals the interesting chiroptical features, (a) all dextrorotatory enantiomers possess a central core, D_3-twisted bicyclo[2.2.2]octane framework, fixed in a P-helical conformation, (b) however, triblattanes having two long diagonal bridges are levorotatory in spite of possessing the central core with P-helicity as shown in a se-

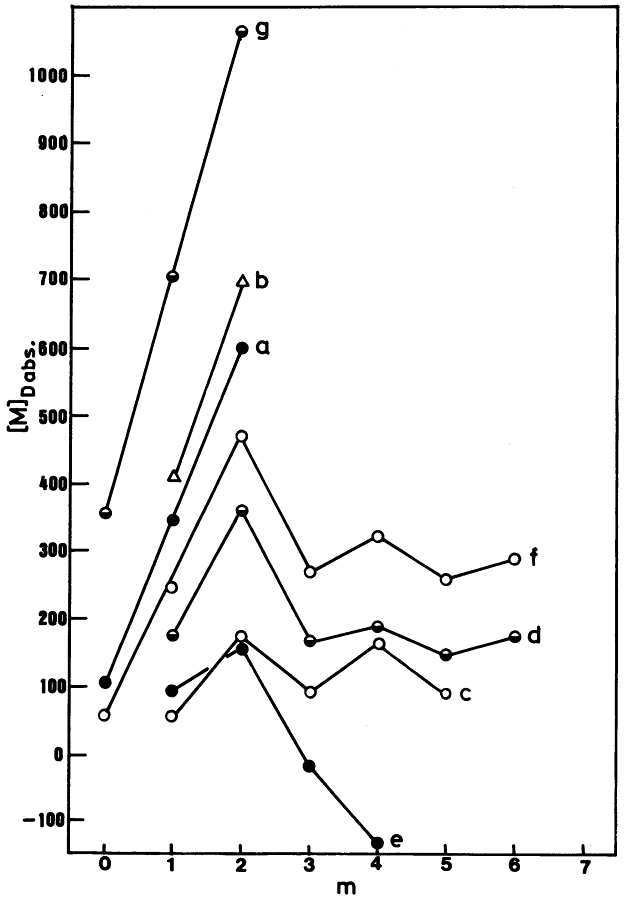
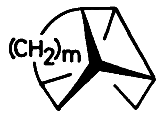


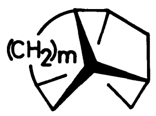
Fig. 1. Correlation between bridge span (*m*) and absolute molecular rotation ($[M]_{D\,abs.}$); a: [*m*]triblattane (**2**), b: [*m*.1]triblattane (**3**, *n*=1), c: [*m*.1.0]triblattane (**4**, *n*=1 *p*=0), d: [*m*.2.0]triblattane (**4**, *n*=2 *p*=0), e: [*m*.3.0]triblattane (**4**, *n*=3 *p*=0), f: [*m*.1.1]triblattane (**4**, *n*=*p*=1), g: [*m*.2.2]triblattane (**4**, *n*=*p*=2).

ries of [*m*.3.0]triblattanes ($m \geqq 3$), (c) for all series of triblattanes, the values of molecular rotations increase linearly with bridge span (*m*) to $m=2$, (d) the values drop abruptly on going from $m=2$ to $m=3$ and then remain almost constant.

Natural extension of these studies led us to investigate chiroptical properties of series of tetracyclic triblattanes. In this paper, we wish to report the preparation of series of optically active [*m*.0]triblattanes (**5**—**8**) and [*m*.1]triblattanes (**9**—**15**) with known absolute configuration and discuss their chiroptical properties.



(+)-5 m=1
(+)-6 m=2
(+)-7 m=3
(−)-8 m=4

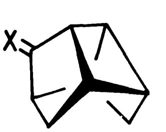


(+)-9 m=1 (+)-13 m=5
(+)-10 m=2 (+)-14 m=6
(+)-11 m=3 (+)-15 m=7
(+)-12 m=4

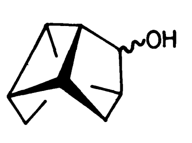
Chart 2.

Results and Discussion

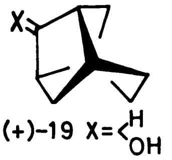
Optical Resolution of [1.0]Triblattan-9-one. The diagonal bridging between C3 and C6 positions of [0]triblattane (**2**, $m=0$), being the smallest triblattane, furnishes a series of [*m*.0]triblattanes (**3**, $n=0$). The first task is optical resolution of (±)-[1.0]triblattan-9-one (**17**), being the starting material for the preparation of [*m*.0]triblattanes. Acid hydrolysis of 9,9-ethylenedioxytetracyclo[$4.3.0.0^{2,5}.0^{3,8}$]nonane (**16**), prepared according to Toyne's procedure,[5] gave (±)-**17** which was resolved by horse liver alcohol dehydrogenase (HLADH) mediated reduction. The ketone (±)-**17** was incubated for 5 min at 25 °C with NAD^+ and HLADH in 1/15 M (1 M=1 mol dm^{-3}) Sϕrensen phosphate buffer solution (pH 7.0). GLC analysis of the ether-extracted metabolite revealed the presence of the recovered ketone **17** (51%) and a 4:1 mixture of diastereomeric alcohols (49%). Column chromatography of the metabolite on alumina furnished (+)-**17**, mp 96—98 °C (in a sealed tube) $[\alpha]_D$ +46.3°, and the major alcohol (−)-**18**, mp 118—120 °C (in a sealed tube) $[\alpha]_D$ −67.7°, but attempts to purify the minor alcohol were unsuccessful. The mixture of metabolite alcohols was oxidized with chromium trioxide in acetone gave (−)-**17**, $[\alpha]_D$ −33.0°, as a sole product.



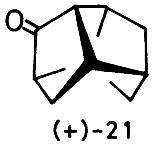
16 X=$<^{O}_{O}]$
(+)-17 X=O



(−)-18



(+)-19 X=$<^{H}_{OH}$
20 X=$<^{O}_{O}]$



(+)-21

Chart 3.

Our next task is determination of the absolute configuration of (+)-**17** and (−)-**18**. Circular dichroism (CD) spectra of cage-shaped ketones,[2] prepared from intermediates of known absolute configuration, indicate that the sign of CD curve due to n-π^* transition can be predicted by applying the octant rule to the "outer ring"[6] in the projection formula which holds the carbonyl group at the "point of twist".[7] Applying this generalization to the projection formula **22** of the ketone (+)-**17** with negative Cotton effect, we obtain the 1*S*,2*S*,3*R*,5*R*,6*S*,8*R* absolute configuration for (+)-**17**. In other words, (+)-**17** possess the D_3-twisted bicyclo[2.2.2]octane framework fixed in a P-helical conformation.

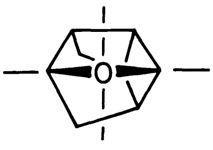


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Chart 4.

This conclusion was unambiguously confirmed by the chemical conversion of (+)-**17** to (+)-twistbrendan-9-ol (**19**), whose absolute configuration and absolute rotation have been determined in our laboratory.[8] Hydrogenolysis of 9,9-ethylenedioxytetracyclo[$4.3.0.0^{2,5}.0^{3,8}$]nonane (**16**) with 5% rhodium–alumina to 9,9-ethylenedioxytwistbrendane (**20**) has been reported by Toyne.[5] The ketone (+)-**17**, $[\alpha]_D$ +46.3°, was hydrogenolyzed with 5% rhodium–alumina in cyclohexane to yield (+)-(1*R*,3*R*,6*R*,8*R*)-twistbrendan-9-ol (**19**), $[\alpha]_D$ +122° (46.5% optical purity).[8] The result permitted us to confirm the absolute configuration and calculate the absolute rotation of (+)-**17** ($[\alpha]_{D\,abs.}$ +99.6°). Jones oxidation of the major alcohol (−)-**18**, $[\alpha]_D$ −67.7°, to (−)-**17**, $[\alpha]_D$ −55.7° (55.9% o.p.), possessing the central core of M-helicity, allowed us to calculate the optical purity of the metabolite alcohol (−)-**18** and to prove the central core of (−)-**18** to be fixed in a M-helical conformation. However, the configuration of the hydroxyl group is unknown.

*Preparation of [*m*.0]Triblattanes.* The ketone (+)-**17**, $[\alpha]_D$ +46.3°, was reduced by Wolff-Kishner reduction and the product was chromatographed on alumina to give [1.0]triblattane (**5**), mp 103—105 °C (in a sealed tube) $[\alpha]_D$ +48.9°. In a previous paper,[3,9] we reported our successful preparation of series of pentacyclic triblattanes by diazomethane ring expansion of cage-shaped ketones. Our preliminary experiment utilizing (±)-**17** indicated that when kept at 0 °C for 6 d an ethereal solution of (±)-**17** containing 10 equiv of diazomethane gave a mixture of [1.0]triblattanone and [2.0]triblattanones with unknown location of the carbonyl group in the expanded bridge. The mixture was directly reduced by Wolff-Kishner reduction to yield a 6:4 mixture of [1.0]triblattane (**5**) and [2.0]triblattane (**6**).

Addition of boron trifluoride was found to push the ring expansion further furnishing a product consisting of higher homologs. An ethereal solution of (+)-**17** containing diazomethane and 1 equiv of BF_3 etherate was kept at 0 °C for 30 min. To reveal composition of the ring-expanded product, the product was directly converted to a mixture of hydrocarbons by Wolff-Kishner reduction and the product was analyzed by GLC. The results are given in Table 1.

After these preliminary experiments utilizing (±)-**17**, we carried out the preparative experiment with (+)-**17**. An ethereal solution of (+)-**17**, $[\alpha]_D$ +46.3°, containing of 4 equiv of diazomethane and 1 equiv of BF_3 etherate was kept at 0 °C for 1 h. The mixture of ring-expanded ketones was directly transformed to a mixture of [m.0]triblattanes by Wolff-Kishner reduction. After being analyzed by GLC, the product was separated by preparative GLC to furnish (+)-**6**, (+)-**7**, and (−)-**8**. The structures of these hydrocarbons were confirmed on the basis of their mass spectra and elemental analyses.

*Preparation of [*m*.1]Triblattanes.* The synthesis of a series of [m.1]triblattanes (**3**, n=1) began with tetracyclo[5.2.1.$0^{2,6}$.$0^{4,8}$]decan-5-one ([1.1]triblattan-5-one) (**21**) which has been prepared in an optically active form with known absolute configuration and absolute rotation in our laboratory.[10] Diazomethane ring expansion of (±)-**21** without catalyst gave no ring-expanded product. Treatment of (±)-**21** with excess of diazomethane and 1 equiv of BF_3 etherate followed by Wolff-Kishner reduction yielded a mixture of ring-expanded hydrocarbons. The results are given in Table 2.

We carried out the preparative experiment with (+)-**21**, $[\alpha]_D$ +145° (59.6% o.p.), which was dissolved in an ethereal solution containing of 15 equiv of diazomethane and 1 equiv of BF_3 etherate. After the mixture was kept at 0 °C for 1 h, the resulting mixture of ring-expanded ketones was reduced by Wolff-Kishner reduction to yield a mixture of [m.1]triblattanes which was analyzed by GLC. Preparative GLC separated and purified these hydrocarbons **9**—**15**.

TABLE 1. REACTION OF (±)-**17** AND DIAZOMETHANE WITH BF_3 ETHERATE

CH_2N_2 (equiv)	Product ratio				
	5	**6**	**7**	**8**	Higher homologs
1	65	25	5	4	1
2	35	41	10	11	3
3	13	46	14	20	7
4	7	34	12	26	21

TABLE 2. REACTION OF (±)-**21** AND DIAZOMETHANE WITH BF_3 ETHERATE

CH_2N_2 (equiv)	Temp / °C	Product ratio					
		9	**10**	**11**	**12**	**13**	Higher homologs
2	0	79	17	2	1	1	0
5	0	49	25	8	13	5	0
10	0	36	23	11	20	6	4
10	−78	4	2	4	16	13	61
15	0	9	15	12	27	6	31

*Chiroptical Properties of [*m*.0]Triblattanes and [*m*.1]Triblattanes.* The known optical purities of our starting materials (+)-**17** and (+)-**21** permitted us to calculate the absolute molecular rotations of these new triblattanes (Table 3).

These values are plotted in Fig. 2 together with that of [2.2]-triblattane.[11] A few conspicuous features are worth noting, (a) all [m.1]triblattanes having the central core of P-helicity are dextrorotatory, (b) [m.0]triblattanes possessing a short diagonal bridge (m<4) as well as the central core of P-helicity are dextrorotatory, but [4.0]triblattane, like [m.3.0]triblattanes (m=3,4), is levorotatory in spite of having the central core fixed in a P-helical conformation, (c) the presence of a zero bridge in [m.0]triblattanes is reflected in a markedly decreased molecular rotation relative to [m.1]triblattanes and [m.2]triblattanes.

Experimental

Infrared spectral data were obtained from a Hitachi 260-10 spectrophotometer. Optical rotations were measured with a JASCO-DIP-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

TABLE 3. ABSOLUTE MOLECULAR ROTATIONS ($[M]_{D\ abs.}$) OF [m.0]TRIBLATTANES AND [m.1]TRIBLATTANES

5	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
+74.0°	+129°	+4.9°	−39.0°	+407°	+692°	+376°	+382°	+295°	+382°	+293°

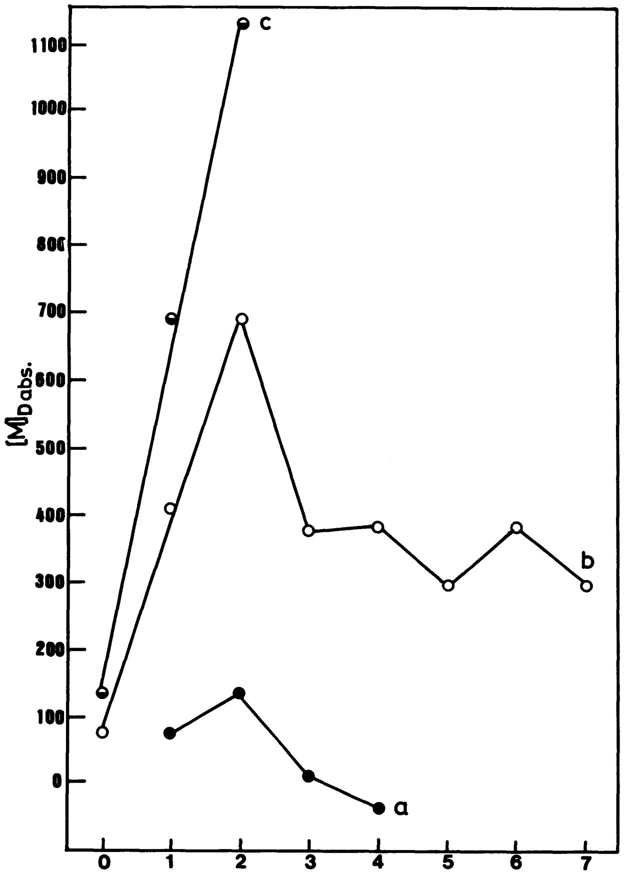

Fig. 2. Correlation between bridge span (m) and absolute molecular rotation ($[M]_{D\ abs.}$) in three series of tetracyclic triblattane; a: [m.0]triblattane, b: [m.1]-triblattane, c: [m.2]triblattane.

Yanagimoto CHN-Corder, Type II. GLC analyses were performed on a JGC-20 K equipped with a FID and using a 1 m×3 mm column of 10% PEG 20 M on UniportHP. Preparative GLC were done on a JGC-20 K equipped with a TCD and using a 2 m×3 mm column of 10% PEG 20 M on UniportHP. HLADH was purchased from Boehringer (Mannheim) as a crystalline suspension in phosphate buffer containing 10% ethanol.

(±)-Tetracyclo[4.3.0.0^{2,5}.0^{3,8}]nonan-9-one (17). 9,9-Ethylenedioxytetracyclo[4.3.0.0^{2,5}.0^{3,8}]nonane (**16**) (670 mg, 3.76 mmol), prepared according to Toyne's procedure,[5] was mixed with 5% sulfuric acid (20 mL) and the mixture was stirred for 2 d at room temperature. After the reaction mixture was extracted with ether, the extract was worked up as usual. The product was chromatographed on alumina and elution with pentane gave a solid which was sublimed at 50—60 °C (20 mmHg (1 mmHg=133.322 Pa)) to yield 216 mg of **17** (43% yield); mp 100—101 °C (in a sealed tube); IR (KBr) 1760 cm^{-1}; Found: C, 80.41; H, 7.53%. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51%.

HLADH-mediated Reduction of (±)-Tetracyclo[4.3.0.0^{2,5}.0^{3,8}]nonan-9-one (17). The ketone (±)-**17** (92.3 mg, 0.690 mmol) was dissolved in 1 L of 1/15 M Sϕrensen phosphate buffer solution (pH 7.0) and then to the solution was added NAD$^+$ (42.6 mg, 0.0594 mmol), ethanol (1 mL), and HLADH (4 mg). After being incubated at 25 °C for 5 min, the mixture was extracted with ether. The extract was washed with water, dried ($MgSO_4$), and concentrated to give a metabolite mixture (81 mg). GLC analysis of the metabolite revealed the presence of **17** (51%) and a 4:1 mixture of diastereomeric alcohols (49%). The product was chromatographed on alumina, and elution with pentane afforded 37 mg of **17**; mp 98—100 °C (in a sealed tube); $[\alpha]_D^{22}$ +46.3° (c 0.220, $CHCl_3$); C.D. (c 4.43×10^{-2} mol dm^{-3}, 2,2,4-trimethylpentane) $[\theta]_{291}$ −3.92×10^2 (sh), $[\theta]_{296}$ −5.59×10^2 (sh), $[\theta]_{300}$ −6.35×10^2, $[\theta]_{303}$ −6.18×10^2 (sh); Found: C, 80.43; H, 7.52%. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51%. Elution with pentane–ether (95:5. v:v) gave 22 mg of **18**; 118—120 °C (in a sealed tube); $[\alpha]_D^{24}$ −67.7° (c 0.200, $CHCl_3$); Found: C, 79.18; H, 8.85%. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88%. Further elution with the same solvent gave 13 mg of a mixture of diastereomeric alcohols.

Oxidation of the Mixture of Diastereomeric Alcohols. To a solution of the 4:1 mixture of alcohols (140 mg, 1.03 mmol) in acetone (2 mL) was added excess of 8 N Jones' reagent.[14] After being stirred for 3 h at room temperature, the reaction mixture was diluted with water (10 mL) and extracted with ether. After a usual workup, the extract was concentrated to give a solid which was chromatographed on alumina (pentane eluent) to furnish 119 mg of (−)-**17** (86% yield); mp 99—101 °C (in a sealed tube); $[\alpha]_D^{23}$ −33.0° (c 0.372, $CHCl_3$); Found: C, 80.39; H, 7.51%. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51%.

Oxidation of the Major Alcohol 18. Oxidation of (−)-**18** (50 mg, 0.37 mmol), $[\alpha]_D$ −67.7°, which 8N Jones' reagent in acetone was carried out by the same procedure described above. Chromatography of the product on alumina followed by sublimation furnished 42 mg of (−)-**17** (85% yield); mp 98—99 °C (in a sealed tube); $[\alpha]_D^{22}$ −55.7° (c 0.250, $CHCl_3$); Found: C, 80.44; H, 7.53%. Calcd for $C_6H_{10}O$: C, 80.56; H, 7.51%.

Hydrogenolysis of (+)-Tetracyclo[4.3.0.0^{2,5}.0^{3,8}]nonan-9-one (17). A mixture of (+)-**17** (79 mg, 0.59 mmol), $[\alpha]_D$ +46.3°, rhodium-alumina (50 mg), and cyclohexane (20 mL) was shaken at room temperature in a hydrogenation flask at 1 atm of hydrogen. After the hydrogen absorption had ceased, the catalyst was filtered off. The filtrate was concentrated to give a solid which was purified by preparative GLC to furnish 42 mg of (+)-**19**; mp 162—164 °C (in a sealed tube) (lit,[8] mp 162—165 °C); $[\alpha]_D^{24}$ +122° (c 0.115, MeOH) (lit,[8] $[\alpha]_D^{23}$ +164° (MeOH)). Spectral comparison with an authentic specimen confirmed its identity.

(+)-Tetracyclo[4.3.0.0^{2,5}.0^{3,8}]nonane (5). A mixture of (+)-**17** (80 mg, 0.60 mmol), $[\alpha]_D$ +46.3°, 100% hydrazine hydrate (0.1 mL), potassium hydroxide (53 mg), and triethylene glycol (2 mL) was heated for 1 h at 110—120 °C and then for an additional 3 h at 190—200 °C. After cooling to room temperature, the reaction mixture was diluted with water and extracted with pentane. The extract was washed with water, dried ($MgSO_4$), and concentrated. The product was chromatographed on alumina (pentane eluent) to give a solid which was sublimed at 50—60 °C (760 mmHg) to yield 27 mg of (+)-**5** (38% yield); mp 103—105 °C (in a sealed tube); $[\alpha]_D^{25}$ +48.9° (c 0.180, $CHCl_3$); MS, m/z 120 (M$^+$); Found: C, 89.84; H, 10.01%. Calcd for C_9H_{12}: C,

89.94; H, 10.06%.

Product Distribution in the Diazomethane Ring Expansion of (±)-Tetracyclo[4.3.0.0^{2,5}.0^{3,8}]nonan-9-one (17). *Without Catalyst*: An ethereal solution of diazomethane (630 mg, 14.9 mmol) was added to an ice cooled solution of (±)-**17** (200 mg, 1.49 mmol) in dry ether (20 mL). The reaction mixture was allowed to stand at 0 °C for 6 d. The product was analyzed by GLC.

With BF_3 etherate Catalyst: The following experimental procedure is typical. An ethereal solution of diazomethane (63 mg, 1.5 mmol) was added to a stirred and chilled (0 °C) solution of (±)-**17** (200 mg, 1.49 mmol) and BF_3 etherate (0.19 mL, 1.5 mmol) in dry ether (20 mL). After the mixture was kept at 0 °C for 30 min, a deposited solid was removed by filtration and the filtrate was washed with aq $NaHCO_3$ solution and water, dried ($MgSO_4$), and concentrated to give an oily product (190 mg). The product was mixed with 100% hydrazine hydrate (0.24 mL), potassium hydroxide (130 mg), and triethylene glycol (2 mL) and then the mixture was heated for 1 h at 110—120 °C and for an additional 4 h at 190—200 °C. After a workup described for the preparation of (+)-**5**, the product (110 mg) was analyzed by GLC.

Preparation of (+)-[2.0]Triblattane (6), (+)-[3.0]Triblattane (7), and (−)-[4.0]Triblattane (8). An ethereal solution of diazomethane (188 mg, 4.47 mmol) was added to a stirred solution of (+)-**17** (150 mg, 1.12 mmol), $[\alpha]_D$ +46.3°, and BF_3 etherate (0.14 mL, 1.1 mmol) in dry ether (15 mL) with ice-cooling. After being stirred for 1 h at 0 °C, the reaction mixture was worked up as described for the reaction of (±)-**17** to yield 145 mg of a mixture of ring expanded ketones, which was without purification used in the next reaction. Wolff-Kishner reduction of the crude product with 100% hydrazine hydrate (0.18 mL), potassium hydroxide (95 mg), and triethylene glycol (2 mL) was carried out by the same procedure as described for the preparation of (+)-**5**. GLC analysis of the product (120 mg) revealed the presence of **5** (3%), **6** (57%), **7** (25%), and **8** (15%). Preparative GLC (at 120 °C) provided specimens of **6** (42 mg); *R*ₜ. 2′48″, **7** (18 mg); *R*ₜ. 5′48″, and **8** (13 mg); *R*ₜ. 11′54″. (+)-[2.0]Triblattane (**6**); mp 123—124 °C (in a sealed tube); $[\alpha]_D^{22}$ +76.1° (*c* 0.325, $CHCl_3$); MS *m/z* 134 (M^+); Found: C, 89.42; H, 10.47%. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51%. (+)-[3.0]Triblattane (**7**); semisolid; $[\alpha]_D^{22}$ +2.60° (*c* 0.153, $CHCl_3$); MS *m/z* 148 (M^+); Found: C, 89.17; H, 10.81%. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88%. (−)-[4.0]Triblattane (**8**); oil; $[\alpha]_D^{22}$ −19.3° (*c* 0.127, $CHCl_3$); MS *m/z* 162 (M^+); Found: C, 88.78; H, 11.15%. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18%.

Product Distribution in the Diazomethane Ring-expansion of (±)-Tetracyclo [5.2.1.0^{2,6}.0^{4,8}]decan-5-one (21). The following experimental procedure is typical. To a chilled (0 °C) solution of (±)-**21** (100 mg, 0.675 mmol) in dry ether (10 mL) was added BF_3 etherate (0.085 mL, 0.68 mmol) and then to the mixture was added an ethereal solution of diazomethane (28 mg, 0.68 mmol). After being stirred for 1 h at 0 °C, the mixture was worked up as described for the reaction of (±)-**17**. Wolff-Kishner reduction of the crude mixture of ring-expanded ketones was carried out by the same procedure as described for the preparation of (+)-**5** and the product was analyzed by GLC.

Preparation of Optically Active [m.1]Triblattanes (9—15). A solution of (+)-**21** (500 mg, 3.37 mmol), $[\alpha]_D^{23}$ +145° ($CHCl_3$) (59.6% o.p.)[10], in dry ether (50 mL) was cooled in an ice bath. To the chilled solution was successively added BF_3 etherate (0.425 mL, 3.37 mmol) and an ethereal solution of diazomethane (2.10 g, 50.0 mmol). After being stirred for 30 min at 0 °C, the reaction mixture was worked up as described for the reaction of (±)-**17** to give 480 mg of a mixture of ketones, which was without purification used in the next reaction. Wolff-Kishner reduction of the crude product was carried out with 100% hydrazine hydrate (0.55 mL), potassium hydroxide (300 mg), and triethylene glycol (10 mL) by the same manner described for the preparation of (+)-**5**. GLC analysis of the product (450 mg) revealed the presence of **9** (9%), **10** (15%), **11** (14%), **12** (25%), **13** (4%), **14** (19%), and **15** (14%). Preparative GLC (at 150 °C) provided specimens of **9** (40 mg); *R*. 2′10″, **10** 56 mg); *R*ₜ. 2′55″, **11** (55 mg); *R*ₜ. 3′48″, **12** (85 mg); *R*ₜ. 8′36″, **13** (20 mg); *R*ₜ. 17′00″, **14** (50 mg), *R*ₜ. 29′06″, and **15** (25 mg), *R*ₜ. 42′06″. (+)-[1.1]Triblattane (**9**); mp 163—164 °C (in a sealed tube) (lit,[10] mp 164.5—165.5 °C); $[\alpha]_D^{23}$ +234° (*c* 0.360, $CHCl_3$); the identity was established by the comparison of its GLC retention time with that of an authentic sample. (+)-[2.1]Triblattane (**10**); mp 138—140 °C (in a sealed tube) (lit,[11] mp 140—141 °C); $[\alpha]_D^{23}$ +276° (*c* 0.330, $CHCl_3$); the identity was established by the comparison of its GLC retention time with that of an authentic sample. (+)-[3.1]Triblattane (**11**); oil; $[\alpha]_D^{23}$ +138° (*c* 0.532, $CHCl_3$); MS *m/z* 162 (M^+); Found: C, 88.58; H, 11.28%. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18%. (+)-[4.1]Triblattane (**12**); oil; $[\alpha]_D^{24}$ +129° (*c* 0.833, $CHCl_3$); MS *m/z* 176 (M^+); Found: C, 88.31; H, 11.46%. Calcd for $C_{13}H_{20}$: C, 88.56, H, 11.44%. (+)-[5.1]Triblattane (**13**); oil; $[\alpha]_D^{24}$ +92.4° (*c* 0.208, $CHCl_3$); MS *m/z* 190 (M^+); Found: C, 88.55; H, 11.54%. Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65%. (+)-[6.1]Triblattane (**14**); oil; $[\alpha]_D^{25}$ +111° (*c* 0.485, $CHCl_3$); MS *m/z* 204 (M^+); Found: C, 87.93; H, 11.80%. Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84%. (+)-[7.1]-Triblattane (**15**); oil; $[\alpha]_D^{25}$ +80.0° (*c* 0.254, $CHCl_3$); MS *m/z* 218 (M^+); Found: C, 87.84; H, 11.88%. Calcd for $C_{16}H_{26}$: C, 88.00; H, 12.00%.

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