References and Notes

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Preparations of Optically Active [8][8]- and [8][10]Paracyclophanes with Known Absolute Configurations[1]

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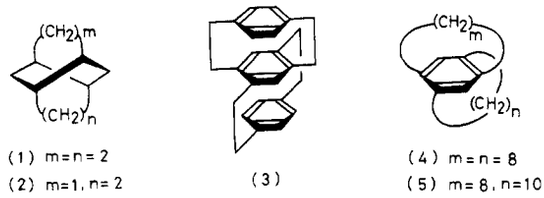
(+)-(*S*)-[8][8]Paracyclophane (**4**) was prepared from (+)-[8]paracyclophane-10-carboxylic acid (**6d**) whose absolute configuration was correlated to (+)-(*S*)-[2.2]paracyclophane-4-carboxylic acid (**20**). Preparations and absolute configurations of (−)-(*R*)-[8][10]paracyclophane (**5**) and related optically active paracyclophane derivatives are also reported.

As part of our continuing efforts to study the chiroptical properties and the biological transformations[2] of high-symmetry chiral (gyrochiral)[3] molecules,[4] the first successful syntheses of (+)-twistane (D_2 symmetry) (**1**),[5] (+)-twistbrendane (C_2 symmetry) (**2**),[3] and (−)-[3]chochin (D_2 symmetry)[6] (**3**), all with known absolute configurations, have been reported from our laboratory (Chart I).

[3]Chochin (**3**) and [*m*][*n*]paracyclophane (**4** and **5**)[7] (D_2 symmetry with $m = n$, and C_2 symmetry with $m \neq n$) bear the twisted central benzene nucleus as a common structural unit, and our preceding papers[8] reported the preparation of unusually strained [8][8]paracyclophane (**4**) and [8][10]paracyclophane (**5**). This contribution reports the preparations of (+)-[8][8]paracyclophane (**4**) and (−)-[8][10]paracyclophane (**5**) together with the determination of their absolute configurations.

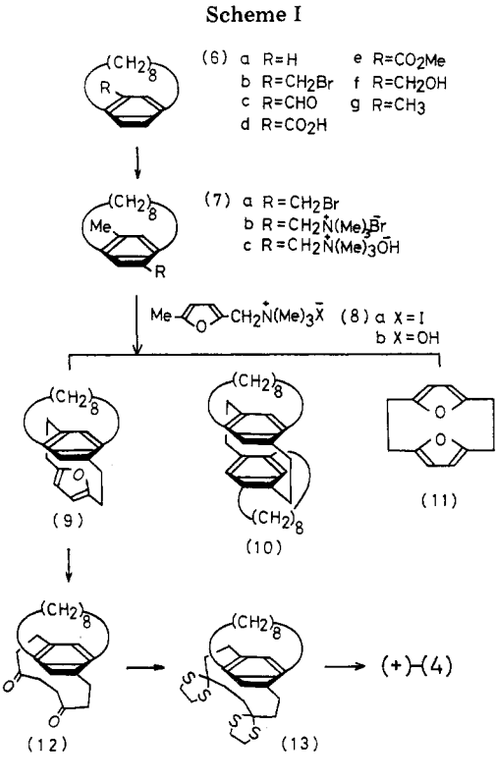
Chart I.



Results and Discussion

Preparation of (+)-[8][8]Paracyclophane (4) (Scheme I).[9] Bromomethylation[10] of [8]paracyclophane (**6a**)[11] afforded the 10-bromomethyl derivative **6b** which was treated with the sodium salt of 2-nitropropane[10] in ethanol to yield the aldehyde **6c.** Permanganate oxidation of the aldehyde **6c** in acetone gave (±)-[8]paracyclophane-10-carboxylic acid (**6d**), the optical resolution of which was accomplished by working with (+)-1-(β-naphthyl)ethylamine as the resolving agent. The (+)-carboxylic acid **6d,** $[\alpha]^{18}_D$ +18°, was converted to the methyl ester **6e** whose hydride reduction afforded the alcohol **6f.** Conversion to the bromide **6b** with phosphorus tribromide followed by reduction with lithium aluminum hydride furnished (+)-10-methyl[8]paracyclophane (**6g**), $[\alpha]^{19}_D$ +4.6°,

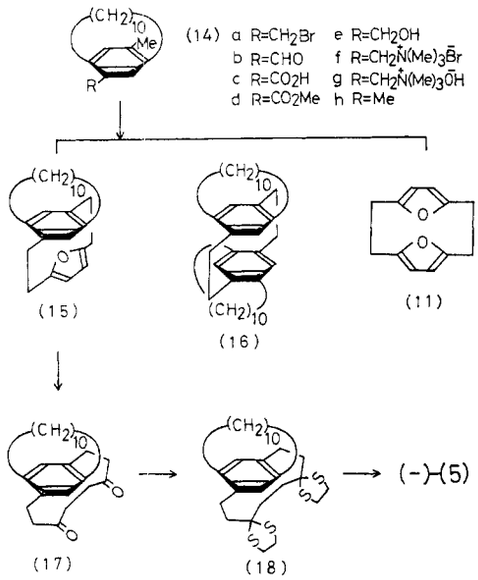
Scheme I



which was further bromomethylated to the bromide **7a.**

Construction of the second [8] bridge was carried out via the benzene–furan "hybrid" [2.2]paracyclophane **9.** The quaternary ammonium bromide **7b** ($[\alpha]^{20}_D$ −5.4°) prepared from the bromide **7a** was mixed with 5-methylfurfuryltrimethylammonium iodide (**8a**),[12] and the mixture was treated with silver hydroxide to give a mixture of Hofmann bases which was pyrolyzed in refluxing toluene. Since a preliminary experiment had revealed the rather labile character of the hybrid [2.2]paracyclophane **9,** the pyrolysate was chromatographed on neutral alumina in a cold room (5 °C). Elution with hexane gave the doubly [8]-bridged [2.2]paracyclophane **10** ($[\alpha]^{20}_D$ −25°, 2.5% yield) which was followed by the hybrid [2.2]par-

Scheme II



acyclophane **9** (9% yield) and [2.2]furanophane (**11**) (16% yield).

The synthetic procedure and the observed optical activity necessitate that the doubly bridged [2.2]paracyclophane possess the staggered structure **10**, and the identity of the IR and mass spectra with those of the previously reported doubly bridged compound[8] from the racemic precursor confirms our previous assumption that formation of the staggered isomer should be preferred on steric grounds.

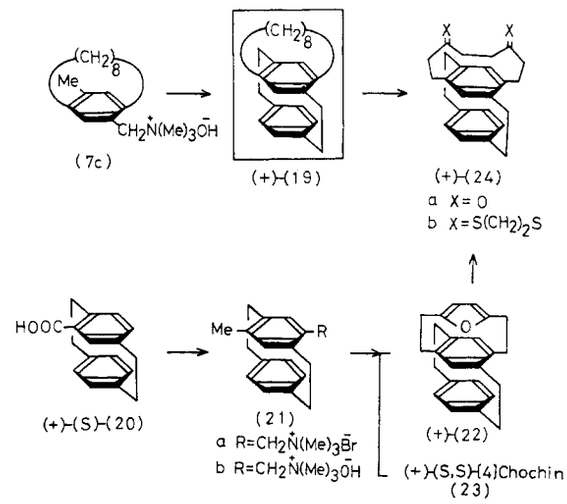
Because of the instability of the hybrid [2.2]paracyclophane **9**, the oily product, without further purification, was directly hydrolyzed with 10% sulfuric acid in acetic acid to afford the 1,4-diketone **12**: mp 149–150 °C, $[\alpha]^{20}_D$ +15°. In order to complete the synthesis, there remained the conversion of the 1,4-diketone bridge to the octamethylene bridge, and this was accomplished by desulfurization with Raney nickel of the bis(dithioketal) **13**. Treatment of the 1,4-diketone **12** with ethanedithiol and boron trifluoride in acetic acid solution yielded the bis(dithioketal) **13** which was heated with Raney nickel in ethyl acetate to afford (+)-[8][8]paracyclophane (**4**): bp 148–150 °C (1.0 mm), $[\alpha]^{20}_D$ +5.4°.

Preparation of (−)-[8][10]Paracyclophane (5) (Scheme II).[9] Optical instability[13] observed in [10]paracyclophane-12-carboxylic acid had warned us that optical resolution in this [10]paracyclophane series of compounds should be carried out on a 12,15-disubstituted [10]paracyclophane intermediate.

(±)-15-Methyl[10]paracyclophane-12-carboxylic acid (**14c**) was prepared from 12-bromomethyl-15-methyl[10]paracyclophane (**14a**) via the aldehyde **14b**, and its optical resolution was accomplished via the brucine salt. Esterification followed by hydride reduction of the levorotatory carboxylic acid **14c**, mp 134–135 °C, $[\alpha]^{21}_D$ −28°, gave the alcohol **14e** which was treated with phosphorus tribromide to furnish (−)-12-bromomethyl-15-methyl[10]paracyclophane (**14a**), $[\alpha]^{22}_D$ −24°.

An equimolar mixture of the quaternary ammonium salt **14f** prepared from the (−)-bromide **14a** and the 5-methylfurfuryltrimethylammonium iodide (**8a**)[12] was treated with silver hydroxide to give a mixture of Hofmann bases which was pyrolyzed in boiling toluene. The mixture was extracted with hexane, and the extract was chromatographed on neutral alumina to afford the following fractions: the doubly bridged [2.2]paracyclophane **16**, mp 219–221 °C, $[\alpha]^{21}_D$ +61° (5%); the benzene–furan hybrid [2.2]paracyclophane **15**, bp 154–156 °C (0.01 mm), $[\alpha]^{22}_D$ −21.3° (10%); and the [2.2]furanophane (**11**) (8%).

Scheme III



The furan moiety of the hybrid [2.2]paracyclophane **15** was modified to the octamethylene bridge as previously described for [8][8]paracyclophane (vide supra). The hybrid **15** was treated with 10% sulfuric acid in acetic acid to give the 1,4-diketone **17**, mp 159–160 °C, $[\alpha]^{21}_D$ −14.8°, which was then converted into the bis(dithioketal) **18**, mp 194–195 °C, $[\alpha]^{24}_D$ −6°, with ethanedithiol and boron trifluoride. Desulfurization with Raney nickel in boiling ethyl acetate converted the bis(dithioketal) **18** into (−)-[8][10]paracyclophane (**5**), bp 184–186 °C (2 mm), $[\alpha]^{25}_D$ −6.3°, the IR and mass spectra of which were found identical with those of the racemic form.[8]

Absolute Configurations (Scheme III). The [8]-bridged [2.2]paracyclophane **19** was selected as our key intermediate which correlates (+)-[8][8]paracyclophane **4** to (+)-(*S*)-[2.2]paracyclophane-4-carboxylic acid (**20**) with known absolute configuration.[14]

The levorotatory quaternary ammonium bromide **7b**, the precursor of (+)-[8][8]paracyclophane (**4**), was mixed with *p*-xylyltrimethylammonium bromide, and pyrolysis of a mixture of their Hofmann bases in boiling toluene afforded, beside [2.2]paracyclophane (8%), the (+)-[8]-bridged [2.2]-paracyclophane **19**, $[\alpha]^{20}_D$ +14.2° (5%).

This same dextrorotatory [8]-bridged [2.2]paracyclophane could also be obtained from (+)-[2.2]paracyclophane-4-carboxylic acid (**20**) to which the *S* absolute configuration had been assigned by Schlögl.[14] When the [2.2]paracyclophane ammonium base **21a**,[6] accessible from the (+)-(*S*)-[2.2]paracyclophane-4-carboxylic acid (**20**), was coupled with 5-methylfurfuryltrimethylammonium hydroxide (**8b**), the furan–benzene hybrid [3]chochin (**22**) (6%), mp 111–112 °C, $[\alpha]^{20}_D$ +137°, and (+)-(*S,S*)-[4]chochin (**23**)[6] (3%), mp 229–231°, $[\alpha]^{20}_D$ +245°, were isolated from the reaction mixture. Following the sequence of reactions described for the conversion of the furan–benzene hybrid [2.2]paracyclophane **9** into [8][8]paracyclophane (**4**), the furan moiety of the furan–benzene hybrid [3]chochin (**22**) was modified to an [8] bridge to give rise to (+)-[8]-bridged [2.2]paracyclophane **19**, mp 135–136 °C, $[\alpha]^{20}_D$ +33.2°. The infrared spectra of the two samples of **19**, prepared from the two different precursors **7** and **21**, were found to be indistinguishable. This configurational correlation enables us to assign the *S* configuration to (+)-[8]paracyclophane-10-carboxylic acid (**6d**), which eventually leads to the *S* configuration of (+)-[8][8]paracyclophane (**4**).

Chiroptical Properties. Figure 1 reproduces the CD spectra of (+)-(*S*)-[8][8]paracyclophane (**4**) and (−)-[8][10]-paracyclophane (**5**), and their antipodal patterns clearly indicate the *R* configuration to (−)-[8][10]paracyclophane. This conclusion is further supported by the more complicated but

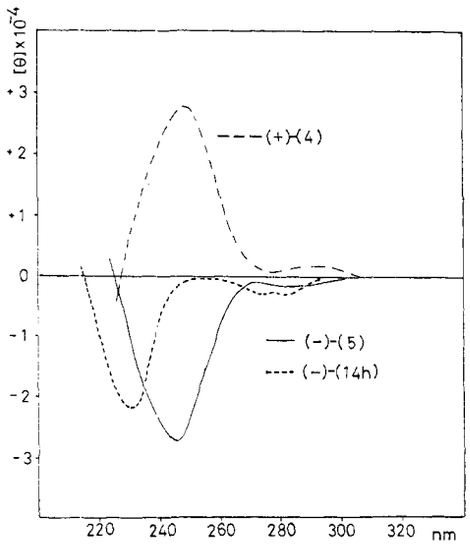


Figure 1. CD spectra of (+)-**4**, (-)-**5**, and (-)-**14h** in isooctane.

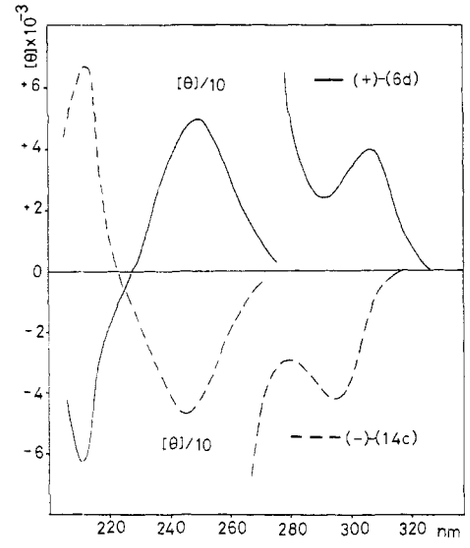


Figure 2. CD spectra of (+)-**6d** and (-)-**14c** in methanol.

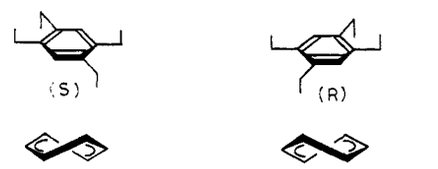


Figure 3. Conformational chirality of D_2-twist benzene and planar chirality of the benzene rings in [*m*][*n*]paracyclophane.

again enantiomeric CD curves shown by their respective precursors (Figure 2): (+)-(*S*)-[8]paracyclophane-10-carboxylic acid (**6d**) and (-)-[10]paracyclophane carboxylic acid (**14c**).

In our preceding paper[6] on optically active multilayered [2.2]paracyclophanes, we extended the Cahn–Ingold–Prelog's nomenclature[15] for conformational chirality to specify the chiralities of the enantiomeric D_2-twist benzene as shown in Figure 3. Inspection of molecular models reveals that the benzene ring in (+)-[8][8]paracyclophene (**4**) with *S*-planar chirality suffers a distortion corresponding to the $(MPM)_2$ D_2-twist benzene ring, whereas (-)-[8][10]paracyclophane (**5**) with *R*-planer chirality is deformed to have the enantiomeric $(PMP)_2$ D_2-twist benzene ring.

From analyses of the CD curves of various D_2-[*n*]chochins, we have drawn the conclusion that the $(PMP)_2$ D_2-twist benzene ring exhibits a (+) Cotton effect at 240–360 nm, and the enantiomeric $(MPM)_2$ D_2-twist benzene ring exhibits a (-) Cotton effect at the same region.

The observed (+) Cotton effect in (+)-(*S*)-[8][8]paracyclophane (**4**) with $(PMP)_2$ D_2-twist benzene confirms this generalization. In Figure 1 is also reproduced the CD curve of (-)-(*R*)-12,15-dimethyl[10]paracyclophane (**14h**) which was prepared by hydride reduction of the (-)-bromide **14a**, and examination of the Cotton curves shown by three paracyclophanes in Figure 1 suggests that the observed bathochromic effect undoubtedly reflects the degree of distortion of the benzene rings in these molecules. Lastly, it would appear to be appropriate to mention here that Schlögl[16] recently suggested the opposite configuration to [*m*][*n*]paracyclophanes based mainly on the theoretical analyses of their CD spectra.

Experimental Section

Melting and boiling points are uncorrected. Infrared spectral data and nuclear magnetic resonance spectra were obtained from a Hitachi EPI-S2 spectrophotometer and a JNM-MH-100 spectrometer, respectively. Ultraviolet spectra were recorded on a Hitachi EPS-3T spectrometer. Circular dichroism data were measured on a JASCO J-20 spectropolarimeter with a CD attachment. Mass spectral data were measured on a Hitachi HMS-4 spectrometer. Elemental analyses were performed by Yanagimoto CHN-Corder Type II.

[8]Paracyclophane-10-carboxaldehyde (6c). 2-Nitropropane (15 g, 0.17 mol) was added to a solution of sodium ethoxide, prepared from sodium (3.4 g-atoms) and absolute ethanol (100 mL). The nitronate salt was brought into solution by the addition of absolute ethanol (190 mL). To this ethanolic solution, the bromide **6b**[6] (41 g, 0.146 mol) was added and the mixture was stirred for 30 h. The reaction mixture was poured into cold water (1 L) and then extracted with ether. The etheral extract was washed with 10% sodium hydroxide solution, water, and then dried. After evaporation of the solvent, the product was distilled to give **6c** (28 g, 89%), bp 126–129 °C (0.3 mm), n^{20}_D 1.5642; IR (film) 1685 cm^{-1} (C=O).

Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.11; H, 9.40.

The 2,4-dinitrophenylhydrazone of the aldehyde **6c** showed mp 224–225 °C after recrystallization from ethanol–benzene.

Anal. Calcd for $C_{21}H_{24}O_4N_4$: C, 63.62; H, 6.10; N, 14.13. Found: C, 63.48; H, 5.93; N, 14.13.

[8]Paracyclophane-10-carboxylic Acid (6d). Powdered potassium permanganate (3 g) was added to a solution of the aldehyde **6c** (28 g) in acetone (400 mL), and the mixture was stirred at 35 °C until the purple color disappeared. To the solution freed from the precipitated manganese dioxide, potassium permanganate (3 g) was added and stirring was continued to give a colorless supernatant. After removal of the manganese dioxide, oxidation was continued with a further 3 g of potassium permanganate until the purple color persisted for several hours. The combined manganese dioxide cakes were extracted with three 100-mL portions of 1% potassium hydroxide solution. The combined extracts were made strongly acidic with concentrated hydrochloric acid to precipitate crystallines which were dried in a vaccum oven (50 °C) and recrystallized from methanol to afford **6d** (18 g, 60%), mp 152–153 °C; IR (KBr) 2980, 2920, 2840, 1670, 1598, 1554, 1483, 1457, 1435, 1394, 1288, 1263, 1207, 922, 910, 777, 705 cm^{-1}; NMR ($CDCl_3$) τ −1.65 (br s, 1 H), 2.03 and 2.95 (AB quartet, J_{ab} = 8 Hz, 2 H), 2.62 (s, 1 H), 6.84 (t, 2 H), 7.42 (t, 2 H), 8.18–8.52 (m, 4 H), 8.60–9.53 (m, 8 H).

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.37; H, 8.66.

Resolution of the Acid 6d. A mixture of **6d** (18 g, 0.077 mol) and (+)-1-(β-naphthyl)ethylamine (13.3 g, 0.077 mol) ($[\alpha]^{18}_D$ +17.5°) in 95% ethanol (100 mL) was warmed to give a clear solution. After standing at room temperature for 24 h, the mixture yielded 3.8 g of a crystalline solid, mp 115–121°. The filtrate was reduced in volume to 50 mL and was kept at room temperature for another 24 h to give 3.6 g of a crystalline solid, mp 112–118 °C. Recrystallization of the

combined crops from 95% ethanol afforded the salt, 6.4 g (20%): mp 141–143 °C; $[\alpha]^{23}_D$ −14.7° (c 0.68, $CHCl_3$). The purified salt was dissolved in chloroform (10 mL), and 5% hydrochloric acid (30 mL) was added with vigorous shaking. The chloroform extract was washed with water and then dried. Evaporation of the solvent afforded a white solid which was recrystallized from methanol–water to give (+)-**6d** (3.5 g): mp 139–140 °C; $[\alpha]^{18}_D$ +18.1° (c 0.52, $CHCl_3$); CD (CH_3OH), $[\theta] \times 10^{-4}$ (nm), −6.38 (212), 0 (228), +4.97 (248), +0.24 (290), +0.41 (305), 0 (327).

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.48; H, 8.65.

(+)-10-Carbomethoxy[8]paracyclophane (6e). To a solution of **6d** (3.4 g, 14.6 mmol) in ether (20 mL) was added diazomethane solution prepared from 6 g of *p*-tosyl-*N*-methyl-*N*-nitrosoamide. After evaporation of the solvent, the residual oil was distilled to give **6e** (3.4 g, 94.5%): bp 135–137 °C (1.0 mm); n^{18}_D 1.5458; $[\alpha]^{18}_D$ +16.8° (c 0.72, $CHCl_3$); IR (film) 1715 cm^{-1} (C=O).

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.10; H, 8.96.

(−)-10-Hydroxymethyl[8]paracyclophane (6f). A solution of (+)-**6e** (3.4 g, 13.8 mmol) in dry tetrahydrofuran (15 mL) was added dropwise to a suspension of lithium aluminum hydride (1.2 g, 32 mmol) in dry tetrahydrofuran (60 mL). The mixture was stirred for 5 h, and the excess reducing reagent was decomposed by addition of ethyl acetate. Dilute hydrochloric acid was added to dissolve the precipitated complex, and the mixture was extracted with ether. The ether solution was washed with 3% sodium bicarbonate solution and water, and then dried. Evaporation of the solvent gave an oil which was distilled to yield **6f** (2.8 g, 93%): bp 141–143 °C (0.8 mm); n^{19}_D 1.5586; $[\alpha]^{21}_D$ −5.8° (c 0.98, $CHCl_3$); IR (film) 3620 cm^{-1} (OH).

Anal. Calcd for $C_{15}H_{22}O$: C, 82.51; H, 10.16. Found: C, 82.41, H, 10.20.

(+)-10-Bromomethyl[8]paracyclophane (6b). To a stirred solution of the alcohol **6f** (2.1 g, 10 mmol) in dry ether (30 mL) was added dropwide a solution of phosphorus tribromide (3.0 g, 11 mmol) in dry ether (20 mL) at room temperature. After the mixture was stirred for 6 h at room temperature, water (150 mL) was slowly added. The separated ether layer was washed with dilute sodium bicarbonate solution and water, and then dried. Removal of the ether afforded an oil which was distilled to give **6b** (2.6 g, 96%): n^{21}_D 1.5793; $[\alpha]^{19}_D$ +5.3° (c 0.86, $CHCl_3$).

Anal. Calcd for $C_{15}H_{21}Br$: C, 64.06; H, 7.53; Br, 28.41. Found: C, 63.92; H, 7.58; Br, 28.49.

(+)-10-Methyl[8]paracyclophane (6g). A solution of (+)-**6b** (2.6 g, 10 mmol) in dry tetrahydrofuran (5 mL) was added dropwise to a suspension of lithium aluminum hydride (0.11 g, 30 mmol) in dry tetrahydrofuran (10 mL). The mixture was refluxed with stirring for 7 h, and the excess reducing reagent was decomposed with ethyl acetate (1 mL). After hydrochloric acid was added to dissolve the precipitated complex, the organic phase was extracted with ether. The ether solution was washed with water, 3% sodium bicarbonate solution, and again with water, and was dried. After evaporation of the solvent, the residual oil was distilled to give **6g** (1.7 g, 91.5%): bp 142–143 °C (0.1 mm); n^{17}_D 1.5418; $[\alpha]^{19}_D$ +4.6° (c 0.96, $CHCl_3$).

Anal. Calcd for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 88.86; H, 10.79.

(−)-10-Trimethylammoniomethyl-13-methyl[8]paracyclophane Bromide (7b). A mixture of **6g** (1.7 g, 8.4 mmol), paraformaldehyde (0.75 g, 16.8 mmol of formaldehyde), acetic acid (7 mL), 85% phosphoric acid (2 mL), and 47% hydrobromic acid (6 mL) was refluxed with stirring for 15 min. The cooled mixture was poured into cold water and extracted with ether. The etheral solution was washed with water, 3% sodium bicarbonate solution, and again water, and was dried. After removal of the solvent, the resulting crude bromide **7a** (2.2 g) was dissolved in ether (20 mL) and then treated with excess anhydrous trimethylamine (5 mL). The resulting salt was collected by filtration, washed with ether, and dried to afford **7b** (2.0 g, 69% from **6g**). An analytical sample was recrystallized from methanol–ether: mp 163–164 °C; $[\alpha]^{20}_D$ −5.4° (c 0.96, $CHCl_3$).

Anal. Calcd for $C_{19}H_{42}NBr$: C, 64.39; H, 9.71; N, 3.95; Br, 22.55. Found: C, 64.47; H, 9.76; N, 3.99; Br, 22.61.

Benzene–Furan Hybrid [2.2]Paracyclophane 9 and (−) Doubly Bridged [2.2]Paracyclophane 10. A mixture of **7b** (2 g, 5.6 mmol) and 5-methylfurfuryltrimethylammonium iodide (**8a**) (2.8 g, 10 mmol) was dissolved in water (100 mL), and freshly prepared silver oxide (from 10 g of silver nitrate) was added. After removal of the precipitate, the resulting hydroxides solution was mixed with toluene (100 mL) containing phenothiazine (20 mg), and the mixture was heated with stirring. Water was removed by azeotropic distillation, and the reaction mixture was refluxed for 3 h. Freed from insoluble polymer by filtration, the solution was concentrated under vacuum. The concentrate was chromatographed on neutral alumina in a cold room (5 °C). Elution with hexane gave (−)-**10** (30 mg, 2.5%), which when recrystallized from ethanol gave mp 204–206 °C; $[\alpha]^{20}_D$ −25° (c 0.31, $CHCl_3$); CD (isooctane), $[\theta] \times 10^{-4}$ (nm), 0 (229), +16.3 (245), 0 (258), −3.88 (284), 0 (356), −1.68 (308).

Anal. Calcd for $C_{32}H_{44}$: C, 89.65; H, 10.35. Found: C, 89.56; H, 10.36.

Elution with hexane–benzene (9:1) produced **9** (0.16 g, 9% based on **7b**) as an oil [MS *m/e* 308 (M^+)] which was found unstable and was converted directly into (+)-3,6-diketo[8][8]paracyclophane (**12**) without further purification. Further elution with hexane–benzene (5:1) gave [2.2]furanophane (**11**) (0.38 g, 16%), mp 180–181 °C.

(+)-3,6-Diketo[8][8]paracyclophane (12). A mixture of **9** (0.16 g, 0.5 mmol), acetic acid (5 mL), water (0.1 mL), and 10% sulfuric acid (0.1 mL) was heated at 65 °C with stirring for 1 h. The reaction mixture was poured into water (20 mL), and the separated organic phase was extracted with chloroform. The extract was washed with water, 3% sodium bicarbonate solution, and again with water, and was dried. After removal of the solvent, the residue was chromatographed on neutral alumina. Elution with dichloromethane afforded **12** (50 mg, 30%), which when recrystallized from hexane gave mp 149–150 °C; $[\alpha]^{20}_D$ +15.4° (c 0.71, $CHCl_3$).

Anal. Calcd for $C_{22}H_{30}O_2$: C, 80.93; H, 9.26. Found: C, 80.82; H, 8.99.

(+)-[8][8]Paracyclophane (4). A solution of **12** (40 mg, 0.12 mmol) in acetic acid (4 mL) was combined with a solution of ethanedithiol (0.1 g, 10 mmol) in acetic acid (2 mL). After 47% boron trifluoride etherate (1 mL) was added, the mixture in a tightly sealed bottle was allowed to stand for 2 days at room temperature. The mixture was poured into water (30 mL), and the product was extracted with chloroform. The extract was washed with 3% sodium bicarbonate solution and water, and then dried. Evaporation of the solvent afforded the crude bis(ethanedithioketal) **13** which was desulfurized directly without further purification. To a solution of the crude bis(dithioketal) **13** (45 mg) in ethyl acetate (6 mL) was added W-5 Raney nickel (0.5 g). The mixture was refluxed for 1 h, cooled, and filtered. After concentration of the filtrate, the oily product was subjected to alumina column chromatography. Elution with hexane gave **4** (15 mg, 42%): bp 148–150 °C (1.0 mm); $[\alpha]^{20}_D$ + 5.4° (c 0.66, $CHCl_3$); CD (isooctane), $[\theta] \times 10^{-4}$ (nm), −2.34 (218), 0 (227.5), +2.84 (247.5), +0.19 (292), 0 (307).

Anal. Calcd for $C_{22}H_{34}$: C, 88.52; H, 11.48. Found: C, 88.47; H, 11.46.

15-Methyl[10]paracyclophane-12-carboxaldehyde (14b). Preparation of the aldehyde **14b** was carried out by the same method described for the preparation of **6c**, utilizing 12-bromomethyl-15-methyl[10]paracyclophane (**14a**) (34 g, 0.105 mol), 2-nitropropane (15 g, 0.17 mol), sodium (2.5 g, 0.11 g-atom), and absolute ethanol (160 mL). Distillation of the product gave **14b** (26 g, 95%): n^{18}_D 1.5536; MS *m/e* 258 (M^+); IR (film) 1686 cm^{-1} (C=O).

Anal. Calcd for $C_{18}H_{26}O$: C, 83.66; H, 10.14. Found: C, 83.56; H, 10.18.

The 2,4-dinitrophenylhydrazone of the aldehyde **14b** showed mp 208–209 °C after recrystallization from ethanol–benzene.

Anal. Calcd for $C_{24}H_{30}O_4N_4$: C, 65.73; H, 6.90; N, 12.78. Found: C, 65.81; H, 6.86; N, 12.73.

15-Methyl[10]paracyclophane-12-carboxylic acid (14c). Oxidation of **14b** (25.9 g, 0.095 mol) was carried out by the same procedure described for the preparation of **6d.** The product was recrystallized from ethanol–water to give **14c** (16.2 g, 59%): mp 168–169 °C; IR (KBr) 2980, 2880, 2830, 1672, 1600, 1550, 1492, 1451, 1402, 1262, 935, 757, 698 cm^{-1}; NMR ($CDCl_3$) τ −1.63 (br s, 1 H), 2.17 (s, 1 H), 3.00 (s, 1 H), 6.05–6.37 (m, 1 H), 6.94–7.23 (m, 1 H), 7.44–7.90 (m, 2 H), 7 65 (s, 3 H), 8.22–8.61 (m, 4 H), 8.72–9.10 (m, 4 H), 9.15–9.72 (m, 8 H).

Anal. Calcd for $C_{18}H_{26}O_2$: C, 78.78; H, 9.55. Found: C, 78.91; H, 9.55.

Resolution of the Acid 14c. A mixture of **14c** (7.9 g, 0.029 mol) and brucine (12.5 g, 0.029 mol) in methanol (200 mL) was warmed until solution was complete. After standing at room temperature for 48 h, the mixture yielded 11.7 g of a solid, mp 93–99 °C; $[\alpha]^{25}_D$ −38.6° (c 0.58, CH_3OH), which was recrystallized from methanol three times to yield 6.4 g of white needles: mp 118–124 °C; $[\alpha]^{26}_D$ −41.4° (c 0.79, CH_3OH). This salt was dissolved in chloroform (80 mL), and 5% hydrochloric acid (70 mL) was added with vigorous shaking. The separated chloroform layer was washed with water and then dried. After evaporation of the solvent, the crude (−)-acid obtained was recrystallized from ethanol–water to give (−)-**14c** (2.9 g): mp 134–135 °C; $[\alpha]^{21}_D$ −28° (c 0.94, CH_3OH); CD (CH_3OH), $[\alpha] \times 10^{-4}$ (nm), +6.82

(213), 0 (224), −3.84 (245), −0.33 (380), −0.43 (294), 0 (315).

Anal. Calcd for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55. Found: C, 78.88; H, 9.51.

(−)-12-Carbomethoxy-15-methyl[10]paracyclophane (14d). The (−)-acid **14c** (1.7 g, 6.2 mmol) was dissolved in ether (20 mL) and esterified with diazomethane. After evaporation of the solvent, the methyl ester was distilled to give **14d** (1.6 g, 90%) as an oil: bp 141–143 °C (0.1 mm); n^{21}_D 1.5386; $[\alpha]^{21}_D$ −20.6° (*c* 0.81, $CHCl_3$); IR (film) 1712 cm^{-1} (C=O).

Anal. Calcd for $C_{19}H_{28}O_2$: C, 72.12; H, 9.79. Found: C, 72.26; H, 9.72.

(+)-12-Hydroxymethyl-15-methyl[10]paracyclophane (14e). A solution of (−)-**14d** (1.6 g, 5.6 mmol) in dry tetrahydrofuran (7 mL) was added dropwise to a suspension of lithium aluminum hydride (0.4 g, 10 mmol) in dry tetrahydrofuran (30 mL). The mixture was heated under reflux for 6 h, and the excess reducing reagent was decomposed with ethyl acetate. The mixture was acidified with dilute hydrochloric acid, and the organic phase was extracted with ether. The ether solution was washed with water, 3% sodium bicarbonate solution, and again with water, and was dried. The solvent was removed to give an oil, which was distilled to give **14e** (1.35 g, 94%): bp 145–147 °C (0.1 mm); n^{22}_D 1.5432; $[\alpha]^{26}_D$ +8.1° (*c* 0.85, $CHCl_3$); IR (film) 3330 cm^{-1} (OH).

Anal. Calcd for $C_{18}H_{28}O$: C, 83.02; H, 10.84. Found: C, 82.91; H, 10.90.

(−)-12-Bromomethyl-15-methyl[10]paracyclophane (14a). To a stirred solution of the alcohol **14e** (1.3 g, 5.0 mmol) in dry ether (15 mL) was added dropwise a solution of phosphorus tribromide (1.4 g, 5.1 mmol) in dry ether (10 mL) at room temperature. After stirring for 3 h at room temperature, the mixture was poured into cold water (50 mL). The separated organic phase was washed with 3% sodium bicarbonate solution and water, and was dried. After removal of the solvent, the residue was distilled to give **14a** (1.4 g, 88%): bp 138–140 °C (0.1 mm); n^{21}_D 1.5669; $[\alpha]^{22}_D$ −24° (0.76, $CHCl_3$); MS *m/e* 323 (M^+).

Anal. Calcd for $C_{18}H_{27}Br$: C, 66.86; H, 8.42; Br, 24.72. Found: C, 66.97; H, 8.51; Br, 24.60.

(+)-12-Trimethylammoniomethyl-15-methyl[10]paracyclophane Bromide (14f). A solution of (−)-**14a** (1.2 g, 3.7 mmol) in ether (30 mL) was treated with excess anhydrous trimethylamine (5 mL). The resulting salt was collected by filtration, washed with ether, and dried to afford **14f** (1.3 g, 91.6%). An analytical sample was recrystallized from methanol–ether: mp 252–254 °C; $[\alpha]^{21}_D$ +14° (*c* 0.84, $CHCl_3$).

Anal. Calcd for $C_{21}H_{36}NBr$: C, 65.95; H, 9.49; N, 3.66; Br, 20.88. Found: C, 66.00; H, 9.53; N, 3.62; Br, 20.83.

(−)-12,15-Dimethyl[10]paracyclophane (14h). A mixture of (−)-**14a** (0.18 g, 0.56 mmol) in dry tetrahydrofuran (5 mL) was added dropwise to a suspension of lithium aluminum hydride (0.2 g, 5.3 mmol) in dry tetrahydrofuran (15 mL). The mixture was heated under reflux for 10 h, and the usual work up furnished the product which was distilled to give **14h** (0.12 g, 88%): bp 174–176 °C (3 mm); n^{25}_D 1.5408; $[\alpha]^{25}_D$ −7.2° (*c* 0.96, $CHCl_3$); CD (isooctane), $[\theta] \times 10^{-4}$ (nm), 0 (217), 2.22 (229), −0.27 (274), −0.29 (282), 0 (294).

Anal. Calcd for $C_{18}H_{28}$: C, 88.45; H, 11.55. Found: C, 88.49; H, 11.51.

(−)-Benzene–Furan Hybrid [2.2]Paracyclophane 15 and (+) Doubly Bridged [2.2]Paracyclophane 16. A solution (70 mL) of the mixed quaternary ammonium hydroxides, **14g** and **8b**, prepared from a mixture of **14f** (1.3 g, 3.4 mmol) and **8a** (1.6 g, 5.7 mmol) in the usual manner, was mixed with toluene (50 mL) containing phenothiazine (10 mg). After pyrolysis, the same procedure described for the [8]paracyclophane series of compound **9** afforded the crude product which was chromatographed on neutral alumina. Elution with hexane afforded **16** (41 mg, 5%), which when recrystallized from hexane gave mp 219–220 °C; $[\alpha]^{21}_D$ +61.3° (*c* 0.77, $CHCl_3$); CD (isooctane), $[\theta] \times 10^{-4}$ (nm), +13.8 (210), 0 (22.5), −19.4 (234.5), 0 (252), +3.68 (273), +1.27 (297), 0 (320).

Anal. Calcd for $C_{36}H_{52}$: C, 89.19; H, 10.81. Found: C, 89.15; H, 10.79.

Elution with hexane–benzene (9:1) produced a colorless oil, which was distilled to give **15** (120 mg, 10% based on **14f**): bp 154–156 °C (0.01 mm); $[\alpha]^{22}_D$ −21° (*c* 0.83, $CHCl_3$); $[\alpha] \times 10^{-4}$ (nm) +1.22 (220), +4.66 (229), 0 (241), −1.57 (257), 0 (290).

Anal. Calcd for $C_{24}H_{32}O$: C, 85.66; H, 9.59. Found: C, 85.25; H, 9.68.

Further elution with hexane–benzene (5:1) gave [2.2]furanophane (**11**) (45 mg, 8%).

(−)-3,6-Diketo[8][10]paracyclophane (17). Ring opening of the furan ring in **15** was carried out by the method described for the preparation of the [8]paracyclophane series of compound **12**, utilizing **15** (120 mg, 0.36 mmol), water (0.1 ml), acetic acid (5 mL), and 10% sulfuric acid (0.1 mL). The resulting product was chromatographed on neutral alumina. Elution with dichloromethane produced **17** (75 mg, 59%), which was recrystallized from hexane to give mp 159–160 °C; $[\alpha]^{21}_D$ −14° (*c* 0.79, $CHCl_3$).

Anal. Calcd for $C_{24}H_{34}O_2$: C, 81.31; H, 9.65. Found: C, 81.12; H, 9.74.

(−)-Bis(ethanedithioketal) (18). A solution of **17** (70 mg, 0.2 mmol) in acetic acid (6 mL) was mixed with a solution of ethanedithiol (3 mL) in acetic acid (4 mL) which contained 47% borontrifluoride etherate (2 mL). After standing for 2 days at room temperature, the reaction mixture was poured into water (20 mL) and extracted with chloroform. The chloroform solution was washed with water and then dried. Removal of the solvent yielded a crystalline solid which on crystallization from ethanol gave **18** (79 mg, 79%): mp 149–150 °C; $[\alpha]^{24}_D$ −6° (*c* 0.75, $CHCl_3$).

Anal. Calcd for $C_{28}H_{42}S_4$: C, 66.34; H, 8.36. Found: C, 66.41; H, 8.35.

(−)-[8][10]Paracyclophane (5). To a solution of **18** (70 mg, 0.173 mmol) in ethyl acetate (5 mL) was added W-5 Raney nickel (1.0 g), and the mixture was refluxed for 1 h. The mixture was freed of Raney nickel and concentrated under vacuum to give an oil which was chromatographed on neutral alumina. Elution with hexane afforded a colorless oil, which was distilled to give **5** (35 mg, 62%): bp 184–186 °C (2 mm): $[\alpha]^{25}_D$ −6.3° (*c* 0.92, $CHCl_3$); MS *m/e* 326 (M^+); CD (isooctane), $[\theta] \times 10^{-4}$ (nm), +6.37 (215), 0 (225), −2.72 (243), −0.17 (285).

Anal. Calcd for $C_{24}H_{38}$: C, 88.27; H, 11.73. Found: C, 88.30; H, 11.69.

(+)-[8]-Bridged [2.2]Paracyclophane 19 (from 7c). A solution (40 mL) of the quaternary ammonium hydroxides prepared from a mixture of **7c** (0.5 g, 1.4 mmol) and *p*-xylyltrimethylammonium bromide (1.0 g, 4.1 mmol) was mixed with toluene (30 mL) containing phenothiazine (5 mg). After pyrolysis, the crude product was chromatographed on neutral alumina. Elution with hexane yielded (+)-**19** (22 mg, 5%), which when recrystallized from hexane–benzene gave mp 138–139 °C; $[\alpha]^{20}_D$ +14.2° (*c* 0.67, $CHCl_3$); MS *m/e* 318 (M^+); IR (KBr) 2980, 2880, 2840, 2820, 1585, 1494, 1431, 1407, 1078, 928, 888, 902, 715 cm^{-1}; UV (isooctane) λ_{max} 220, 280, 325 sh nm (log ϵ 3.83, 3.22, 2.04); CD (isooctane), $[\theta] \times 10^{-4}$ (nm), +1.6 (205), +10.7 (217), 0 (227), −13.7 (242), 0 (256), +4.19 (265), +0.76 (285), +2.21 (302), +0.45 (325 sh), 0 (355); NMR ($CDCl_3$) τ 3.51 (s, 4 H), 3.95 (s, 2 H), 6.55–8.15 (m, 12 H), 8.20–10.06 (m, 10 H), 10.20–10.92 (m, 2 H).

Anal. Calcd for $C_{24}H_{30}$: C, 90.50; H, 9.50. Found: C, 90.41; H, 9.52.

Further elution with hexane–benzene (5:1) gave [2.2]paracyclophane (34 mg, 8%).

(+)-Triple-Layered [2.2]Paracyclophane 22. A solution (60 mL) of the quaternary ammonium hydroxides from a mixture of (+)-(*S*)-4-trimethylammoniomethyl-7-methyl[2.2]paracyclophane bromide (**21a**)[6] (3 g, 8.2 mmol) and **8a** (3 g, 10.7 mmol) was mixed with toluene (100 mL) containing phenothiazine (10 mg). After pyrolysis, the product was chromatographed on neutral alumina. Elution with hexane–benzene (10:1) gave [2.2]furanophane (**11**) (80 mg, 8%). Further elution with hexane–benzene (7:1) produced the (+)-triple-layered compound **22** (188 mg, 6%), which when recrystallized from hexane gave mp 111–112 °C; $[\alpha]^{20}_D$ +137° (*c* 0.58, $CHCl_3$); MS *m/e* 328 (M^+); IR (KBr) 2970, 2880, 2820, 1584, 1532, 1493, 1486, 1452, 1419, 1171, 1128, 1010, 943, 934, 792, 713, 623 cm^{-1}; UV (isooctane) λ_{max} 222, 278, 314, 333 nm (log ϵ 4.09, 3.79, 2.85, 2.80); NMR ($CDCl_3$) τ 3.76 (s, 4 H), 4.27 (s, 2 H), 4.73 (s, 2 H), 6.65–7.85 (m, 16 H); CD (isooctane), $[\theta] \times 10^{-4}$ (nm) 0 (205), +21.0 (217), 0 (234), −25.9 (245.5), 0 (262.5), +3.88 (269), 0 (285.5), −0.56 (288), 0 (291), +3.88 (306), +1.46 (337), 0 (360).

Anal. Calcd for $C_{24}H_{24}O$: C, 87.76; H, 7.36. Found: C, 87.81; H, 7.34.

Elution with hexane–benzene (5:1) gave (+)-(*S,S*)-[4]chochin[6] (57 mg, 3%), which gave mp 229–231 °C after recrystallization from hexane–benzene: $[\alpha]^{20}_D$ +245° (*c* 0.53, $CHCl_3$); MS *m/e* 468 (M^+); UV (isooctane), $[\theta] \times 10^{-4}$ (nm) 0 (211), −31.0 (217.5), −25.9 (232.5), 0 (249), +4.56 (260), +6.23 (272), +3.29 (311), +3.95 (339), +2.60 (355), 0 (385).

Anal. Calcd for $C_{36}H_{36}$: C, 92.26; H, 7.74. Found: C, 92.28; H, 7.73.

(+)-3,6-Diketone 24a. Hydrolysis of **22** was carried out by the method described for the preparation of **12**, utilizing **22** (180 mg, 0.55 mmol), water (5 mL), acetic acid (30 mL), and 10% sulfuric acid (0.5 mL). The resulting product was chromatographed on neutral alumina. Elution with dichloromethane produced **24a** (110 mg, 58%), which

after recrystallization from hexane gave mp 195–197 °C; $[\alpha]^{32}_D$ +17.5° (*c* 0.78, $CHCl_3$); IR (KBr) 2998, 2920, 2830, 1693, 1588, 1423, 1407, 1316, 1141, 1092, 1068, 899, 863, 789, 713 cm^{-1}; NMR ($CDCl_3$) τ 3.58 (s, 4 H), 4.03 (s, 2 H), 6.50–7.97 (m, 16 H), 8.10–8.85 (m, 4 H).

Anal. Calcd for $C_{24}H_{26}O_2$: C, 83.20; H, 7.56. Found: C, 83.57; H, 7.46.

(+)-[8]-Bridged [2.2]Paracyclophane (19) (from 24). The bis(ethanedithiol) **24b** was prepared by the method described for the preparation of **13**, utilizing **24a** (100 mg, 0.29 mmol), acetic acid (15 mL), ethanedithiol (3 mL), and 47% borontrifluoride (1 mL). To a solution of crude **24b** (0.14 g) in ethyl acetate (15 mL) was added W-5 Raney nickel (0.5 g). Refluxing followed by removal of the Raney nickel and concentration gave a solid which was subjected to alumina column chromatography. Elution with hexane–benzene gave **19**: mp 135–136 °C; $[\alpha]^{20}_D$ +33.2° (*c* 0.84, $CHCl_3$).

Anal. Calcd for $C_{24}H_{30}$: C, 90.50; H, 9.50. Found: C, 90.44; H, 8.54.

Registry No.—(*S*)-(+)-**4**, 54059-74-4; (*R*)-(−)-**5**, 36757-10-5; (±)-**6b**, 63534-00-9; (+)-**6b**, 63534-01-0; (±)-**6c**, 63534-02-1; (±)-**6c** DNP, 63534-03-2; (±)-**6d**, 63534-04-3; (*S*)-(+)-**6d**, 63597-46-6; (*S*)-(+)-**6d** (+)-α-(β-naphthylethylamine), 63597-47-7; (+)-**6e**, 63534-05-4; (−)-**6f**, 63534-06-5; (+)-**6g**, 63534-07-6; (±)-**7a**, 63534-08-7; (−)-**7b**, 63534-09-8; **8a**, 1197-60-0; **8b**, 32543-06-9; (±)-**9**, 63534-10-1; (−)-**10**, 63597-48-8; (±)-**11**, 5088-46-0; (+)-**12**, 63534-11-2; (±)-**13**, 63534-12-3; (±)-**14a**, 36659-11-7; (−)-**14a**, 63534-13-4; (±)-**14b**, 36659-12-8; (±)-**14b** DNP, 63534-14-5; (±)-**14c**, 63534-15-6; (−)-**14c**, 36659-13-9; (−)-**14c** brucine, 63534-16-7; (−)-**14d**, 36757-09-2; (+)-**14e**, 36659-14-0; (+)-**14f**, 36659-16-2; (±)-**14g**, 63534-17-8; *R*-(−)-**14h**, 63534-18-9; (−)-**15**, 36659-18-4; (+)-**16**, 63597-49-9; (−)-**17**, 36659-19-5; (−)-**18**, 36659-20-8; (+)-**19**, 63534-19-0; (*S*)-(+)-**21a**, 63534-20-3; (+)-**22**, 63534-21-4; (*S,S*)-(+)-**23**, 36659-04-8; (+)-**24a**, 63534-22-5; (+)-**24b**, 63534-23-6; (+)-α-(β-naphthyl)ethylamine, 3906-16-9; brucine, 357-57-3; *p*-xylyltrimethylammonium bromide, 16814-21-4.

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Synthesis of Methyl *dl*-Jasmonate and Its Related Compounds from Methyl (*E*)- and (*Z*)-4,4-Dimethoxy-2-butenoates

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A synthesis of methyl *dl*-jasmonate (**1b**) and its dehydro derivatives **2b** and **3b** from methyl (*E*)- and (*Z*)-4,4-dimethoxy-2-butenoates (**4**) is described. Dimethyl 2-acetyl-3-dimethoxymethylglutarate (**5**) could be obtained by Michael addition of **4** with methyl acetoacetate in excellent yields. Deacetalization of dimethyl 2-acetyl-3-dimethoxymethyl-2-(2-pentynyl)glutarate (**7a**) followed by cyclization with base after alkylation of **5** (R′ = Me) with 2-pentynyl bromide afforded 5-methoxycarbonyl-4-methoxycarbonylmethyl-5-(2-pentynyl)-2-cyclopentenone (**10a**). Reduction of **10** (R′ = Me) with $NaBH_4$ in MeOH giving 2-methoxycarbonyl-3-methoxycarbonylmethyl-2-(2-pentynyl)cyclopentanol (**13a**) and subsequent oxidation of **13** with chromic acid gave 2-methoxycarbonyl-3-methoxycarbonylmethyl-2-(2-pentynyl)cyclopentanone (**14a**), a precursor of **1b**. Cis hydrogenation of **7a** → **7b**, **10a** → **10b**, **13a** → **13b**, and **14a** → **14b** using Lindlar catalyst proceeded in quantitative yields. Direct demethoxycarbonylation of **10b** (R = 2-*cis*-pentenyl) with Me_2SO–H_2O–NaCl in a sealed tube afforded a mixture of **2b** and **3b**. However, acid-catalyzed de-*tert*-butoxycarbonylation of **10b** (R′ = *t*-Bu), prepared from **5** (R′ = *t*-Bu) by alkylation followed with cyclization, under reflux in benzene gave **2b** as a sole product. Hydrogenation of **10a** with palladium on charcoal afforded **14c** (R = pentyl). The products **2b** and **3b** could be converted into **1b** smoothly.

Our continuing interest in the jasmonoid syntheses[1] has led to discovering an economically significant method in obtaining methyl *dl*-jasmonate (**1b**)[2] and methyl dehydrojasmonates (**2b** and **3b**) without using troublesome reagents. In the course of our efforts to investigate the electrolysis of 2-substituted furans, we have found an effective, one-step preparative way of methyl (*E*)- and (*Z*)-4,4-dimethoxy-2-butenoates (**4**).[3] It should be noted that the butenoates **4** are expected to be a powerful Michael acceptor and they are indeed smoothly obtained in good yield by the simple electrolyses of furfuryl alcohol, furfural, and 2-furoic acid. We now report a straightforword synthesis of the jasmonates **1b**, **2b**, and **3b** from **4** via the intermediates **5**, **7**, **10**, **13**, and **14**.

When the butenoates **4** were allowed to react with methyl acetoacetate using alkali metal carbonates in methanol (Table I, runs 1, 2, and 3), the yield of **5** (R′ = Me) was in the ranges of 0–35% yields along with the formation of **6** (6–11% yields). A successful Michael addition of methyl acetoacetate to **4** was