

## Synthesis of the Cyclophane Tetramethoxyturriane: a Derivative of the Phenolic Cyclophanes of *Grevillea striata* R. Br.

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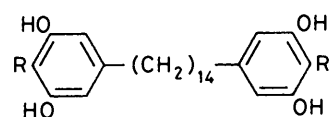
The synthesis of 9,10,11,12,13,14,15,16,17,18,19,20,21,22-tetradecahydro-2,4,6,24-tetramethoxy-5,8-ethenobenzocycloeicosene (tetramethoxyturriane) (9) a derivative of the phenolic cyclophanes extracted from the wood of *Grevillea striata* R.Br., is reported. The key steps in this synthesis were the construction of the biphenyl linkage of the molecule using dihydro-oxazole chemistry and the closure of the macrocycle by oxidative coupling of a diacetylene.

Extraction of the wood of *Grevillea striata* R.Br., yielded a number of 5-alkylresorcinols of obvious polyketide origin. These include striatol (1)<sup>1</sup> and a mixture of phenolic cyclophanes the constituents of which have been shown to have the structures (3)–(8).<sup>2</sup> These structural proposals were based on chemical degradation and spectroscopic methods applied to mixtures of the cyclophanes. All of the cyclophanes on methylation and reduction gave 'tetramethoxyturriane' (9). The cyclophanes (3)–(8) probably owe their biogenesis to C–C phenolic oxidative coupling of a precursor similar in structure to bisdesmethylstriatol (2).<sup>2</sup> In this connection it is pertinent to note that robustol (10)<sup>3,4</sup> a constituent of the leaves of *Grevillea robusta* A.Cunn., would arise by phenolic C–O oxidative coupling of a similar precursor.

Such macrocyclic compounds are rare in Nature and we were attracted to the problem of the total synthesis of tetramethoxyturriane (9) in order to confirm the structural assignment of the skeleton of the *Grevillea striata* cyclophanes. Ridley, Ritchie, and Taylor attempted this total synthesis by the oxidative coupling of the bisdesmethylstriatol (2), and subsequent methylation of the crude product. Although evidence was obtained for the production of traces of cyclic material these proved impossible to isolate.<sup>2</sup> It has been pointed out<sup>3</sup> that since the normal mode of C–C phenolic oxidative coupling of orcinol involves the 4-position and not the 2-position then the cyclic material may have been isomeric with tetramethoxyturriane. A projected synthetic route based on the crossed Ullmann reaction was frustrated by the low yield in this step.<sup>2</sup>

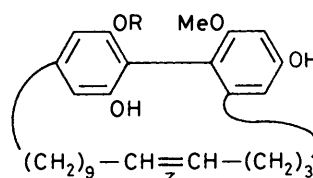
The route we adopted for the synthesis of tetramethoxyturriane (9) depended on the efficient construction of the biphenyl linkage using dihydro-oxazole chemistry. In consequence, an excess of the Grignard reagent (13) derived from the protected aldehyde (12), readily available from the known aldehyde (11),<sup>5</sup> was caused to react with the dihydro-oxazole (14), available from previous work.<sup>6</sup> The methoxy group in the position *ortho* to the dihydro-oxazole entity in compound (14) was smoothly displaced by the Grignard reagent,<sup>7</sup> and a high yield of the required biphenyl (15) was obtained. The dihydro-oxazole entity in the biphenyl (15) was caused to react with methyl iodide and the resultant methiodide was reduced to an oxazolidine with sodium borohydride.<sup>8</sup> Treatment of this intermediate with dilute acid furnished the biphenyldicarbaldehyde (16).

The next step in the synthesis required chain extension by Wittig reaction. Pentane-1,5-diol was therefore converted into the monobenzyl ether (17)<sup>9</sup> which on treatment with thionyl chloride and pyridine provided the chloride (18). This intermediate was converted into the iodide (19) by treatment with sodium iodide in boiling acetone, and thence by reaction with



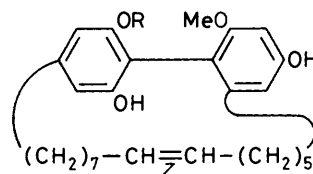
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(2) R = H



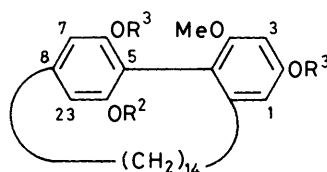
(3) R = H

(4) R = Me



(5) R = H

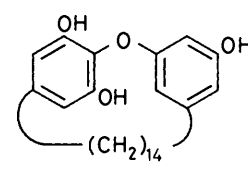
(6) R = Me



(7) R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = H

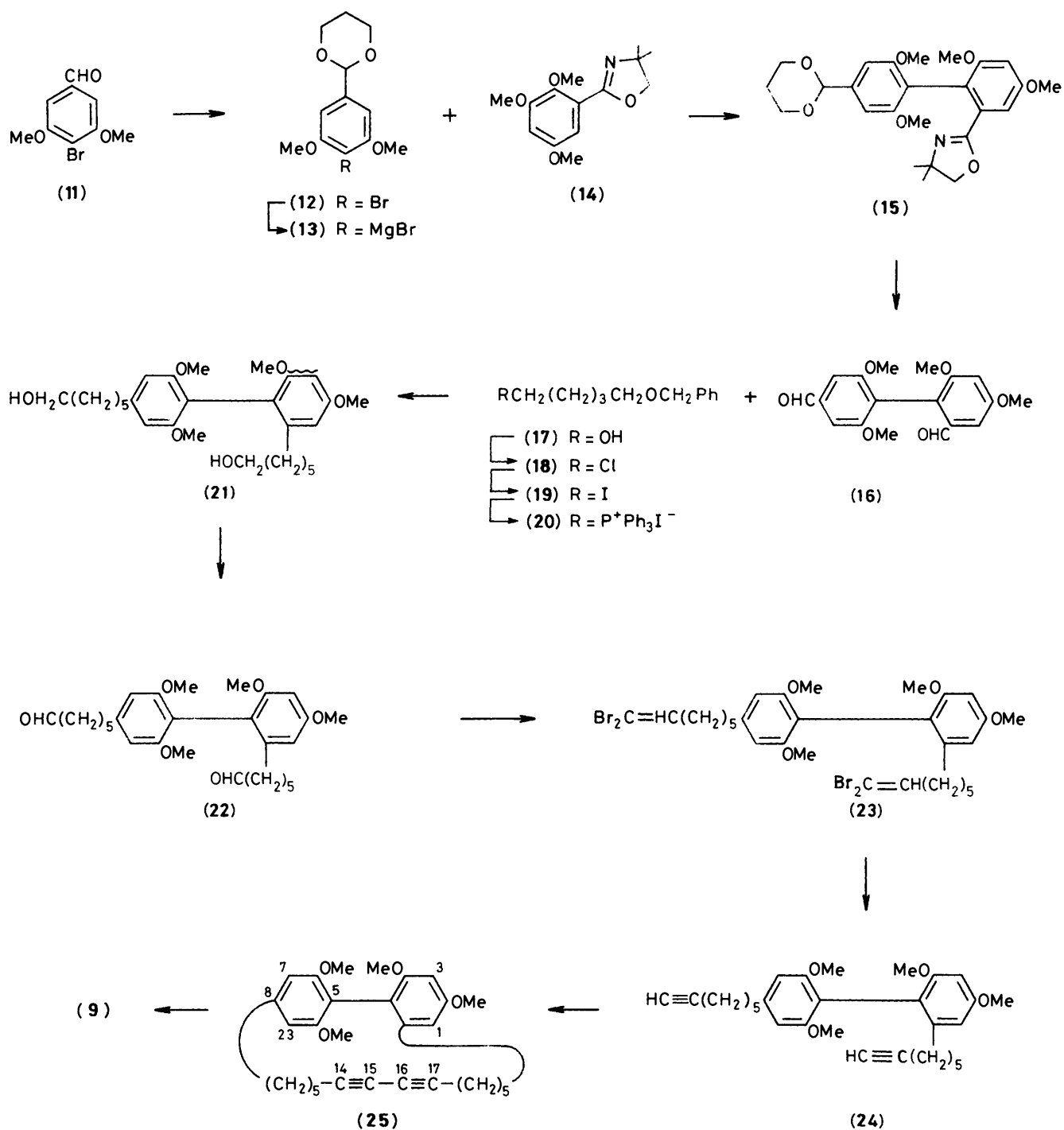
(8) R<sup>1</sup> = R<sup>2</sup> = H, R<sup>3</sup> = Me

(9) R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = Me



(10)

triphenylphosphine into the phosphonium salt (20). The ylide derived from the phosphonium salt (20) was allowed to react with the dialdehyde (16) and catalytic hydrogenation of the stereoisomeric mixture of olefins so produced achieved both



Scheme.

saturation of the double bonds and debenzoylation, and provided the diol (**21**). The diol (**21**) was oxidized by pyridinium chlorochromate to the dialdehyde (**22**) which gave the tetrabromo compound (**23**) on treatment with tetrabromomethane and triphenylphosphine in dichloromethane, after the method of Corey and Fuchs.<sup>10</sup> Sequential treatment of this intermediate with butyl-lithium and water smoothly gave the diyne (**24**).

Oxidative coupling of the diyne (**24**) using anhydrous copper(II) acetate and pyridine under conditions of high dilution gave a high yield of the cyclic diyne (**25**) which on catalytic hydrogenation supplied tetramethoxyturriane (**9**). The

synthetic material proved to be identical with an authentic sample of the natural derivative by all the usual criteria thus proving the structural assignment of the skeleton of the *Grevillea striata* cyclophanes.

### Experimental

General directions have been given previously.<sup>11</sup> Assignments of <sup>13</sup>C n.m.r. spectral signals were assisted by the DEPT technique.

2-(4-Bromo-3,5-dimethoxyphenyl)-1,3-dioxane (**12**).—A solution of 4-bromo-3,5-dimethoxybenzaldehyde (**11**) (7.4 g),<sup>5</sup>

propane-1,3-diol (4.0 ml), and toluene-*p*-sulphonic acid (300 mg) in benzene (230 ml) was stirred and heated under reflux in a Dean-Stark apparatus for 18 h. The cooled solution was poured into saturated aqueous sodium hydrogen carbonate and the organic phase was separated. The aqueous phase was washed with ethyl acetate (2 ×), and the combined extracts were washed with water and with saturated brine. The crude product (9.2 g, 100%) crystallized from ethyl acetate–light petroleum as plates of the *dioxane* (**12**), m.p. 132–133 °C (Found: C, 47.8; H, 4.95; Br, 26.5%;  $M^+$ , 302/304.  $C_{12}H_{15}BrO_4$  requires C, 47.55; H, 5.0; Br, 26.35%;  $M$ , 302/304);  $\delta_H$ (80 MHz) 1.50 (1 H, br d, 5- $H_{eq}$ ), 2.26 (1 H, m, 5- $H_{ax}$ ), 3.92 (6 H, s, 2 × OMe), 4.27 (4 H, m, 4- and 6- $CH_2$ ), 5.46 (1 H, s, 2- $H_{ax}$ ), and 6.73 (2 H, s, ArH).

**4,5-Dihydro-2-[4'-(1,3-dioxan-2-yl)-2',4,6,6'-tetramethoxy-1,1'-biphenyl-2-yl]-4,4-dimethyloxazole (15)**.—The Grignard reagent was prepared under argon in the usual way from the foregoing bromo compound (**12**) (4.60 g), magnesium (410 mg), and anhydrous tetrahydrofuran (40 ml). This reagent was added in a thin stream to a stirred solution of 4,5-dihydro-2-(2,3,5-trimethoxyphenyl)-4,4-dimethyloxazole (**14**) (2.00 g)<sup>6</sup> in anhydrous tetrahydrofuran (40 ml) after which the mixture was first stirred at room temperature for 18 h and then heated under reflux under argon for 24 h. The cooled solution was poured into saturated aqueous ammonium chloride and the crude product was extracted with ethyl acetate. The extract was washed with water and with saturated brine. The crude product was next purified by radial chromatography with 50–70% ethyl acetate–light petroleum as eluant. The *oxazoline* (**15**) (3.04 g, 88.1%) crystallized from ethyl acetate–light petroleum as plates, m.p. 164–165 °C (Found: C, 65.2; H, 7.15; N, 3.4.  $C_{25}H_{31}NO_7$  requires C, 65.65; H, 6.85; N, 3.05%;  $\delta_H$ (300 MHz) 1.29 (6 H, s, Me<sub>2</sub>), 1.48 (1 H, m, 5- $H_{eq}$ ), 2.27 (1 H, m, 5- $H_{ax}$ ), 3.66 (3 H, s, 6-OMe), 3.72 (6 H, s, 2'- and 6'-OMe), 3.76 (2 H, s, 5- $CH_2$ ), 3.90 (3 H, s, 4-OMe), 4.03 (2 H, m, 4- and 6- $H_{ax}$ ), 4.32 (2 H, m, 4- and 6- $H_{eq}$ ), 5.52 (1 H, s, 2- $H_{ax}$ ), 6.65 (1 H, part AB,  $J_{5,3}$  2.4 Hz, 5-H), 6.73 (2 H, s, 3'- and 5'-H), and 7.13 (1 H, br s,  $W_{H/2}$  7 Hz, 3-H).

**2',4,6,6'-Tetramethoxy-1,1'-biphenyl-2,4'-dicarbaldehyde (16)**.—The foregoing oxazoline (**15**) (650 mg) was stirred with iodomethane (1.56 ml) at 60 °C (bath) in nitromethane (12 ml) during 24 h to give the methiodide. The latter, obtained as a gum after removal of the solvent, was dissolved in methanol (10 ml) and the solution stirred at 0 °C during the dropwise addition of sodium borohydride (80 mg) in aqueous sodium hydroxide (5%; 2 ml). The solution was next stirred at room temperature for 45 min and then diluted with water and extracted with ethyl acetate. The extract was washed with water and with saturated brine and evaporated to give the crude product. This was next stirred in tetrahydrofuran (50 ml) and hydrochloric acid (3M; 30 ml) under nitrogen at room temperature for 16 h. After dilution of the reaction mixture with water, the crude product was extracted with ethyl acetate. The extract was washed successively with water, saturated sodium hydrogen carbonate, and with saturated brine and then evaporated to give the *dialdehyde* (**16**) (396.5 mg, 84.4%). This crystallized from dichloromethane–light petroleum as plates, m.p. 189–190 °C (Found: C, 65.4; H, 5.6%  $M^+$ , 330.  $C_{18}H_{18}O_6$  requires C, 65.45; H, 5.5%;  $M$ , 330);  $\delta_H$ (80 MHz) 3.73 (3 H, s, 6-OMe), 3.79 (6 H, s, 2'- and 6'-OMe), 3.90 (3 H, s, 4-OMe), 6.78 and 7.14 (2 H, AB,  $J_{3,5}$  2.5 Hz, 3- and 5-H), 7.17 (2 H, s, 3'- and 5'-H), 9.59 (1 H, s, 2-CHO), and 10.00 (1 H, s, 4'-CHO).

**5-Benzyloxypentan-1-ol (17)**.—A solution of pentane-1,5-diol (25 g) in anhydrous xylene (60 ml) was heated and stirred at 130 °C (bath) during the portionwise addition of sodium (2.07

g). After the sodium had dissolved benzyl chloride (12.66 g) was added dropwise at 120 °C (bath) and the solution was stirred and heated under reflux for 45 min. The cooled solution was diluted with ethyl acetate, washed with water (× 2) and with saturated brine, and then evaporated to give the benzyl compound (**17**). This was distilled under diminished pressure and obtained as an oil (16.1 g, 92.2%), b.p. 115–120 °C (Kugelrohr) at 0.1 mmHg (lit.,<sup>9</sup> 123 °C at 0.4 mmHg).

**5-Benzyloxy-1-chloropentane (18)**.—A solution of the foregoing alcohol (**17**) (4.00 g) and anhydrous pyridine (1.65 ml) in dichloromethane (100 ml) was stirred and treated dropwise with thionyl chloride (2.24 ml). The solution was then stirred at room temperature for 3 h after which it was washed in turn with saturated aqueous sodium hydrogen carbonate, water, and finally with saturated brine. Evaporation of solvent left the *chloro compound* (**18**) which was distilled under reduced pressure and obtained as an oil (4.17 g, 95.3%), b.p. 100–105 °C (Kugelrohr) at 0.08 mmHg (Found: C, 67.7; H, 7.8; Cl, 16.6.  $C_{12}H_{17}ClO$  requires C, 67.75; H, 8.05; Cl, 16.65%;  $\delta_H$ (80 MHz) 1.33–2.00 (6 H, m, 3 ×  $CH_2$ ), 3.48 and 3.53 (each 2 H, t,  $CH_2O$  and  $CH_2Cl$ ), 4.50 (2 H, s,  $CH_2Ph$ ), and 7.32 (5 H, s, Ph).

**5-Benzyloxy-pentyl(triphenyl)phosphonium Iodide (20)**.—A solution of the foregoing chloro compound (**18**) (4.98 g) in anhydrous acetone (100 ml) was stirred and heated under reflux for 18 h with powdered sodium iodide (9.0 g). The cooled solution was poured into water and ice and the crude product was isolated by extraction with ether. The extract was washed in turn with water, dilute aqueous sodium pyrosulphite, water, and finally with saturated brine. Removal of the solvent left 5-benzyloxy-1-iodopentane (**19**) as a light brown oil (6.66 g, 93.5%);  $\delta_H$ (80 MHz) 1.32–2.00 (6 H, m, 3 ×  $CH_2$ ), 3.18 (2 H, t,  $CH_2I$ ), 3.47 (2 H, t,  $CH_2O$ ), 4.49 (2 H, s,  $CH_2Ph$ ), and 7.32 (5 H, s, Ph). This substance (6.6 g) was boiled under reflux in benzene (100 ml) with triphenylphosphine (6.26 g) under nitrogen for 112 h. The benzene was removed under reduced pressure and the residue was boiled with a little ether. The ether was removed by decantation and the residue was triturated with ether. The solid salt, separated by filtration, was washed well with light petroleum. The *hygroscopic salt* (**20**) (11.1 g, 90.3%) crystallized from dichloromethane–ether as plates, m.p. 105–107 °C (Found: C, 62.5; H, 5.9; I, 22.25; P, 5.1.  $C_{30}H_{32}IOP \cdot 0.5H_2O$  requires C, 62.6; H, 5.8; I, 22.05; P, 5.4%).

**2',4,6,6'-Tetramethoxy-1,1'-biphenyl-2,4'-diylidhexanol (21)**.—A solution of butyl-lithium (1.87M) in hexane (1.93 ml) was added by syringe to a stirred solution of the foregoing phosphonium salt (**20**) (2.05 g) in anhydrous tetrahydrofuran (50 ml) under an atmosphere of argon. The solution was stirred at room temperature for 2 h after which a solution of the dialdehyde (**16**) (200 mg) in anhydrous tetrahydrofuran (5 ml) was added. The solution was stirred at room temperature for 16 h and then poured into water and ice. The crude product was isolated by extraction with ethyl acetate and purified by radial chromatography with 10–30% ethyl acetate–light petroleum as eluant. The mixture of olefins, so obtained, was stirred in ethyl acetate (60 ml), containing concentrated hydrochloric acid (2 drops), and palladized charcoal (10%; 200 mg), under an atmosphere of hydrogen. When absorption ceased the catalyst was filtered off and the crude product, obtained by the usual work-up procedure, was purified by radial chromatography with 60% ethyl acetate–light petroleum as eluant. The *diol* (**21**) (154.5 mg, 53.8%) was obtained as an oil (Found: C, 70.95; H, 8.8%;  $M^+$ , 474.  $C_{28}H_{42}O_6$  requires C, 70.85; H, 8.9%;  $M$ , 474);  $\delta_H$ (80 MHz) 1.00–2.00 (18 H, m, 8 ×  $CH_2$  and 2 ×  $D_2O$  exchangeable OH), 2.26 (2 H, t, 2- $CH_2$ ), 2.66 (2 H, t, 4'- $CH_2$ ), 3.58 (4 H, t, 2 ×  $CH_2OH$ ), 3.67 (3 H, s, 6-OMe), 3.68 (6 H, s,

2'- and 6'-OMe), 3.82 (3 H, s, OMe), and 6.44 (4 H, narrow m, ArH).

**2',4,6,6'-Tetramethoxy-1,1'-biphenyl-2,4'-diylidihexanal (22).**—The foregoing diol (**21**) (180 mg) in dichloromethane (5 ml) was added dropwise to a stirred mixture of pyridinium chlorochromate (247 mg) and anhydrous sodium acetate (95 mg) in dichloromethane (10 ml). The mixture was stirred at room temperature for 2 h and then diluted with ether and passed through a short column of silica gel with more ether as eluant. The eluate was washed in turn with water, saturated aqueous sodium hydrogen carbonate, water, and finally with saturated brine. Removal of the solvent gave the dialdehyde (**22**) (165 mg, 92.5%) as an oil which was used immediately;  $\delta_{\text{H}}$ (80 MHz) 1.06—1.91 (12 H, m,  $6 \times \text{CH}_2$ ), 2.11—2.84 (8 H, m, ArCH<sub>2</sub> and CH<sub>2</sub>CHO), 3.67 (3 H, s, 6-OMe), 3.68 (6 H, s, 2'- and 6'-OMe), 3.82 (3 H, s, 4-OMe), 6.44 (4 H, narrow m, ArH), and 9.66 and 9.78 (each 1 H, t, CHO);  $m/z$  470 ( $M^+$ ).

**2,4'-Dihept-6-ynyl-2',4,6,6'-tetramethoxy-1,1'-biphenyl (24).**—The crude dialdehyde (**22**) (160 mg) in dry dichloromethane (5 ml) was added dropwise at 0 °C to a stirred solution of triphenylphosphine (720 mg) and tetrabromomethane (450 mg) in dry dichloromethane (10 ml). After 1 h at 0 °C the reaction mixture was diluted with ice and water and the crude product was isolated by extraction with dichloromethane and purified by radial chromatography. The oily 2,4'-bis(7,7-dibromohept-6-enyl)-2',4,6,6'-tetramethoxy-1,1'-biphenyl (**23**) (150 mg), so obtained, was dissolved in anhydrous tetrahydrofuran (10 ml) and cooled and stirred at -78 °C (bath) under argon. A solution of butyl-lithium (1.87M) in hexane (0.43 ml) was added to the mixture by syringe and the whole then stirred first at -78 °C for 1 h, and then at room temperature for 0.5 h. The solution was next poured into ice and water and the crude product was isolated by extraction with ethyl acetate and purified by radial chromatography with 20% ethyl acetate—light petroleum as eluant. The *diyne* (**24**) (88.0 mg, 58.4%) was obtained as an oil (Found: C, 77.7; H, 8.25%;  $M^+$ , 462.  $\text{C}_{30}\text{H}_{38}\text{O}_4$  requires C, 77.9; H, 8.3%;  $M$ , 462);  $\delta_{\text{H}}$ (300 MHz) 1.20—1.76 (12 H, m,  $6 \times \text{CH}_2$ ), 1.89 and 1.96 (each 1 H, t,  $J_{\text{CH}_2, \text{CH}}$ , 2.6 Hz  $\text{H}=\text{CH}$ ), 2.04 and 2.23 (each 2H, td,  $J_{\text{CH}_2, \text{CH}}$ , 7,  $J_{\text{CH}_2, \text{CH}}$  2.6 Hz,  $\text{CH}_2\text{C}\equiv$ ), 2.26 (2 H, t, 2-CH<sub>2</sub>), 2.65 (2 H, t, 4'-CH<sub>2</sub>), 3.67 (3 H, s, 6-OMe), 3.69 (6 H, s, 2'- and 6'-OMe), 3.82 (3 H, s, OMe), 6.41 and 6.45 (2 H, AB,  $J_{3,5}$  2.4 Hz), and 6.45 (2 H, s, 3'- and 5'-H).

**14,15,16,17-Tetradehydro-9,10,11,12,13,18,19,20,21,22-decahydro-2,4,6,24-tetramethoxy-5,8-ethenobenzocycloecosene (25).**—A high dilution apparatus similar to that described by Cannon and Metcalf<sup>4</sup> was employed. A solution of the *diyne* (**25**) (66.0 mg) in anhydrous pyridine (35 ml) and anhydrous ether (5 ml) was added dropwise, down the condenser, during 10 h to anhydrous copper(II) acetate (580 mg) in a total of anhydrous pyridine (250 ml), anhydrous methanol (72.5 ml), and anhydrous ether (50 ml) contained in the mixing and the reaction flasks. After the addition, heating under reflux was continued for a further 44 h. The contents of the reaction flask were cooled and the bulk of the solvents was removed under reduced pressure. The residue was diluted with ether and the solution was washed in turn with dilute hydrochloric acid, water, saturated aqueous sodium hydrogen carbonate, water, and finally with saturated brine. The crude product was purified by radial chromatography with 20% ethyl acetate—light petroleum as eluant. The *cyclic diyne* (**25**) (51.2 mg, 77.9%) crystallized from dichloromethane—light petroleum as plates, m.p. 152—153 °C (Found: C, 78.15; H, 7.85.  $\text{C}_{30}\text{H}_{36}\text{O}_4$  requires C, 78.25; H, 7.9%);  $\delta_{\text{H}}$ (300 MHz) 1.23—1.87 (12 H, m,  $6 \times \text{CH}_2$ ), 2.18 (2 H, t, 22-CH<sub>2</sub>), 2.32 (4 H, deformed t, 13-

18-CH<sub>2</sub>), 2.71 (2 H, t, 9-CH<sub>2</sub>), 3.67 (3 H, s, 4-OMe), 3.72 (6 H, s, 6- and 24-OMe), 3.82 (3 H, s, 2-OMe), 6.40 and 6.46 (2 H, AB,  $J_{1,3}$  2.4 Hz, 1- and 3-H), and 6.48 (2 H, s, 7- and 23-H);  $m/z$  461 (33%), 460 (100,  $M^+$ ), 445 (17), 429 (16), 361 (21), 329 (10), 327 (10), 296 (10), 285 (14), 283 (15), 282 (14), 281 (12), 277 (10), 271 (22), 270 (12), 269 (29), 268 (25), 267 (14), 257 (13), 256 (13), 255 (25), 254 (13), 253 (17), 252 (10), 243 (12), 242 (15), 241 (12), 240 (10), 239 (23), 238 (11), 237 (12), 231 (12), 229 (27), 227 (22), 226 (12), 225 (24), 215 (15), 213 (15), 212 (13), 211 (10), 202 (12), 197 (11), 195 (10), 191 (10), 189 (14), 179 (12), 177 (11), 165 (16), 152 (12), 151 (27), 145 (15), 131 (19), 129 (11), 121 (13), 117 (28), 105 (14), and 91 (30).

**9,10,11,12,13,14,15,16,17,18,19,20,21,22-Tetradecahydro-2,4,6,24-tetramethoxy-5,8-ethenobenzocycloecosene (Tetramethoxyturriane) (9).**—A solution of the foregoing cyclic *diyne* (**25**) (45.0 mg) in ethyl acetate (10 ml) was stirred under hydrogen with palladized charcoal (10%; 10 mg) until absorption ceased. Work-up of the mixture gave the *turriane* (**9**) (44.0 mg, 96%) which crystallized from pentane as plates, m.p. 60—61.5 °C (lit.<sup>2</sup> 60—62 °C) (Found: C, 77.4; H, 9.9.  $\text{C}_{30}\text{H}_{44}\text{O}_4$  requires C, 76.9; H, 9.45%). It was identical with an authentic sample (mixed m.p.,  $R_{\text{F}}$  values in three different solvent systems, and i.r. and <sup>1</sup>H n.m.r. spectra);  $\delta_{\text{H}}$ (300 MHz) 1.03—1.72 (24 H, m,  $12 \times \text{CH}_2$ ), 2.24 (2 H, m, 22-CH<sub>2</sub>), 2.67 (2 H, t, 9-CH<sub>2</sub>), 3.68 (3 H, s, 4-OMe), 3.70 (6 H, s, 6- and 24-OMe), 3.82 (3 H, s, 2-OMe), 6.40 and 6.46 (2 H, AB,  $J_{1,3}$  2.4 Hz, 1- and 3-H), and 6.45 (2 H, s, 7- and 23-H);  $\delta_{\text{C}}$ (75.5 MHz) 26.77, 27.06, 27.14, 27.50, and 27.58 (each CH<sub>2</sub>), 27.82 (2  $\times$  CH<sub>2</sub>), 28.27, 28.96, 29.69, 30.65, and 31.05 (each CH<sub>2</sub>), 34.01 and 36.27 (9- and 22-C), 55.02 (C-4- or C-2-OMe), 55.85 (C-6- and C-24-OMe), 55.97 (C-4- or C-2-OMe), 96.44, 104.62, and 105.26 (1-, 3-, 7-, and 23-C), 111.97 and 115.57 (5- and 25-C), 143.35 and 144.52 (8- and 26-C), 158.03 (6- and 24-C), and 158.51 and 159.57 (2- and 4-C);  $\nu_{\text{max}}$ (KBr) 2 930s, 2 858m, 1 606m, 1 577s, 1 465m, 1 460m, 1 417m, 1 322m, 1 238m, 1 195m, 1 182w, 1 150m, 1 125s, 1 110w, 1 090m, 1 000m, 942w, 840w, and 810w  $\text{cm}^{-1}$ ;  $m/z$  469 (35%), 468 ( $M^+$ , 100), 453 (3), 437 (6), 315 (3), 314 (2), 313 (3), 303 (2), 302 (11), 301 (4), 297 (4), 296 (3), 289 (3), 288 (2), 287 (12), 286 (3), 285 (5), 284 (6), 283 (8), 282 (4), 281 (3), 273 (3), 272 (3), 271 (11), 270 (7), 269 (12), 268 (3), 267 (3), 257 (6), 256 (6), 255 (9), 243 (3), 242 (4), 241 (6), 240 (4), 239 (6), 227 (3), 226 (2), 225 (4), 213 (2), 211 (2), 191 (2), 165 (6), 152 (6), and 151 (5).

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### References

- 1 M. Rasmussen, D. D. Ridley, E. Ritchie, and W. C. Taylor, *Aust. J. Chem.*, 1968, **21**, 2989.
- 2 D. D. Ridley, E. Ritchie, and W. C. Taylor, *Aust. J. Chem.*, 1970, **23**, 147.
- 3 J. R. Cannon, P. W. Chow, M. W. Fuller, B. H. Hamilton, B. W. Metcalf, and A. J. Power, *Aust. J. Chem.*, 1973, **26**, 2276.
- 4 J. R. Cannon and B. W. Metcalf, *Aust. J. Chem.*, 1973, **26**, 2277.
- 5 I. Kompis and A. Wick, *Helv. Chim. Acta*, 1977, **60**, 3025.
- 6 M. A. Rizzacasa and M. V. Sargent, *J. Chem. Soc., Perkin Trans. 1*, 1988, 2425.
- 7 A. I. Meyers, R. Gabel, and E. D. Mihelich, *J. Org. Chem.*, 1978, **43**, 1372.
- 8 I. C. Nordin, *J. Heterocycl. Chem.*, 1966, **3**, 531.
- 9 G. Eckhardt, *Org. Mass Spectrom.*, 1979, **14**, 31.
- 10 E. J. Corey and P. L. Fuchs, *Tetrahedron Lett.*, 1972, 3769.
- 11 M. V. Sargent, S. Wangchareontrakul, and (in part) A. Jefferson, *J. Chem. Soc., Perkin 1*, 1989, 431.

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