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A Convenient Synthesis of Macrocyclic[2.1.2.1]Paracyclophanes

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Received December 3, 1993

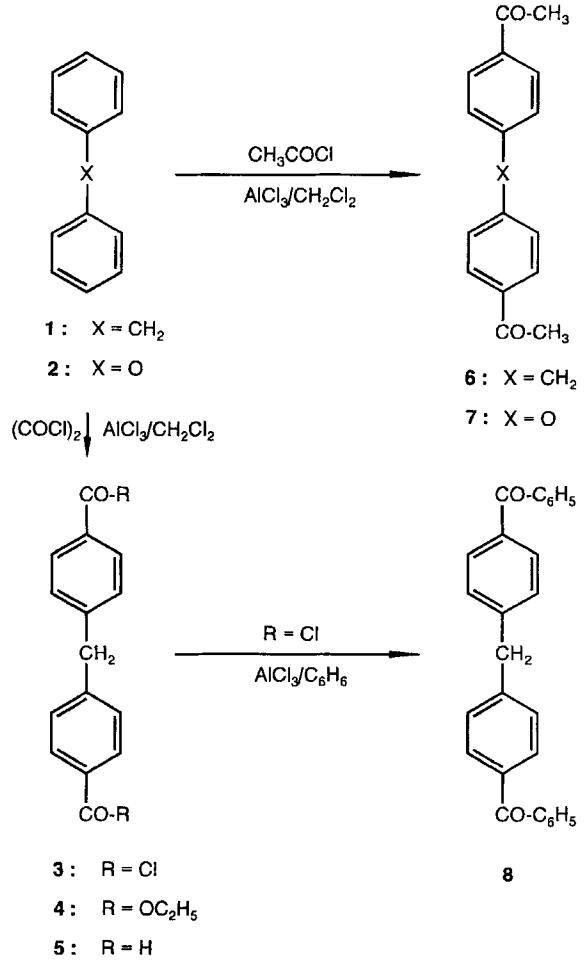
Key Words: Cyclophanes / Coupling reaction / McMurry reaction

The [2.1.2.1]paracyclophanedienes **9**–**11** were prepared in good yields by a McMurry cyclization of the bis(4-acylphenyl)methanes **5** and **6** and of bis(4-acetylphenyl) ether (**7**), respectively.

Macrocyclic cyclophanes are an important class of compounds relevant as host molecules for ions and organic molecules[1,2]. The binding of guests by the host molecules is often strengthened by polar groups used to "dock" certain types of guests by electrostatic or polar host/guest interactions, by hydrogen bonding or even by covalent bonding ("dative bonds"), while secondary interactions determined by the shape of the molecular cavity of the host are responsible for selectivity[3]. Two synthetic strategies can be used to prepare polar host molecules, either by constructing the macrocycle from polar monomers and connecting the monomers by polar groups or by building first a large carbocyclic molecule which is modified eventually by introduction of polar substituents. While most of the host compounds used successfully in complexation studies have been synthesized by the first method, it is nevertheless of interest to follow also the second route. In this connection macrocyclic cyclophanes with olefinic bridges are of special concern because introduction of polar substituents is possible at the aromatic rings as well as at the unsaturated bridges by well-known chemical reactions. Thus, it is of interest to examine whether these macrocycles can be prepared conveniently in sufficient quantities for further synthetic modifications and to study the conformational behavior and the reactivity of these macrocyclic cyclophanes.

In cyclophane chemistry, the reductive coupling of carbonyl compounds by low-valent titanium, the McMurray reaction[4], has been used before by Mitchell et al.[5] to synthesize cyclophanes with glycol units as bridges, by Tanner and Wennerström[6], and recently by Hopf et al.[7] for a cyclization of suitable dialdehydes to yield unsaturated cyclophanes. Recently, we have shown[8] that the McMurry reaction can be used to prepare small [3.2]para- and [3.2]metacyclophan-enes and macrocyclic [3.2.3.2]paracyclophanedienes, respectively, in high yields by adjusting the reaction conditions either to an intramolecular cyclization or to a dimerization of appropriate aromatic aldehydes and ketones. In this paper, we report on the uncomplicated synthesis of [2.1.2.1]paracyclophanedienes by this method. These macrocyclic cyclophanedienes appear to be well suited as precursors of polar host molecules because the diphenylmethane unit and the two etheno bridges form a well-defined cavity[9], and the central methylene groups as well as the aromatic rings of the diphenylmethane unit could be used to introduce polar substituents. An analogous synthetic route starting from diphenyl ether can be used for the easy preparation of an heterocyclic 9,24-dioxa[2.1.2.1]paracyclophanediene.

Scheme 1



The syntheses of [2.1.2.1]paracyclophane-1,16-diene (**9**), 1,2,16,17-tetramethyl[2.1.2.1]paracyclophane-1,16-diene (**10**), and 1,2,16,17-tetramethyl-9,24-dioxa[2.1.2.1]paracyclophane-1,16-diene (**11**) followed the route depicted in Schemes 1 and 2, starting from diphenylmethane (**1**) and diphenyl ether (**2**), respectively. Reaction of

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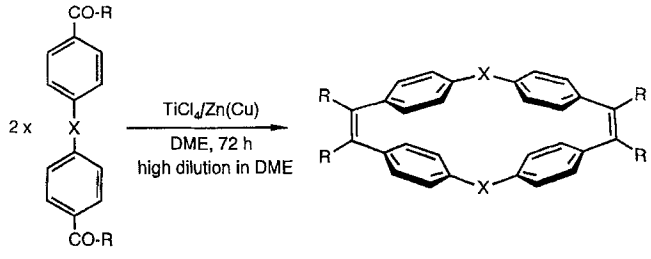
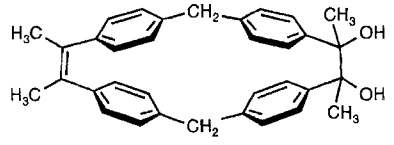
oxalyl chloride with **1** and thermal decarbonylation afforded bis[4-(chlorocarbonyl)phenyl]methane (**3**) which was transformed into the diester **4** without any purification. $LiAlH_4$ reduction of **4** and oxidation of the resulting diol with PCC produced bis(4-formylphenyl)methane (**5**) free of positional isomers (Scheme 1). Analogously, bis(4-acetylphenyl)methane **6**[10,12a] and bis(4-acetylphenyl) ether (**7**)[11] were synthesized by Friedel-Crafts acetylation of **1** and **2**, respectively. Bisacylation of **1** or **2** by a Friedel-Crafts reaction selectively at the two *para*-positions is known[12], but the yield and regioselectivity were improved by a reaction at low temperature in dichloromethane and by using a large excess of the acyl chloride/$AlCl_3$ complex to avoid long reaction times. We also tried to prepare bis(4-benzoylphenyl)methane (**8**)[12c] by this route, but obtained only an intractable mixture of products. Instead, **7** was easily prepared by a Friedel-Crafts reaction of the bisacyl chloride **3** with an excess of benzene.

Scheme 2



	X	R
5	CH_2	H
6	CH_2	CH_3
7	O	CH_3
8	CH_2	C_6H_5

	X	R
9	CH_2	H
10	CH_2	CH_3
11	O	CH_3
12	CH_2	C_6H_5



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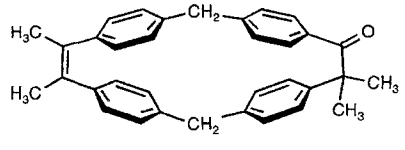

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The bis(4-acylphenyl) derivatives **5**–**8** were subjected to reductive coupling by the McMurry reaction (Scheme 2). Although an intramolecular cyclization of **5**–**8** is sterically not possible, the reaction conditions have to be optimized to circumvent polymerization and formation of oxygenated byproducts. Polymerization can be avoided by using high-dilution techniques and at least a 10fold molar excess of the McMurry reagent. Typically, a diluted solution of about 5 mmol of the dicarbonyl compound has to be added slowly[13] over a period of at least 12 h. Dimethoxyethane as a solvent was superior to THF or 1,4-dioxane. A formation of vicinal diols by the reductive coupling was observed before[5] but depends critically on the preparation of the McMurry reagent. Formation of the diol **13** (Scheme 2) by the McMurry reaction of **6** was observed only if the reduction of $TiCl_4$ during the generation of the McMurry reagent was not complete. In fact, preparation of the McMurry reagent by using deliberately not enough Zn(Cu) resulted in the formation of **13** as the main product in 27% yield (after column chromatography). Compound **13** rearranges easily to the ketone **14** by a pinacol rearrangement when treated with acids.

The best results for the reductive coupling of **5**–**8** were obtained with a reaction time of 32 h and by use of 20 equivalents of the McMurry reagent as a diluted suspension in dimethoxyethane, affording **9**, **10**, and **11** in a yield of 18, 69, and 20%, respectively. However, 1,2,16,17-tetraphenyl[2.1.2.1]paracyclophane-1,16-diene (**12**) was only obtained as a raw material in >50% yield, because this product could not be redissolved in organic solvents for purification by chromatography. Although the mass spectrometric analysis of the reaction product by fractional evaporation in the ion source showed clearly the presence of **12** as the main product, the material contained certainly also polymers and a tetrahydro derivative of **12**, probably the cyclophane with saturated bridges, as byproducts. Presumably, the coupling of **8** is slow and reduction to the benzhydrol analogue of **8** occurs before coupling.

The financial assistance by the *Fonds der Chemischen Industrie* is gratefully acknowledged. We thank Mr. *K.-P. Mester* for the determination of the ^{1}H-NMR spectra and Mrs. *B. Michel* for performing the elemental analysis.

Experimental

^{1}H NMR: Bruker AM 300 (300 MHz), TMS as internal standard. – MS: Finnigan MAT CH5 and Fisons VG AutoSpec, direct insertion and fractional evaporation of the sample. – IR: Perkin Elmer 840, KBr pellet. – Melting points: Büchi 512, uncorrected. – Column chromatography: Merck silica gel 60 (70–230 mesh/0.063–0.200 mm). – DC: Silica gel (Typ 60, Merck F_{254}). – Elemental analyses: Leco CHNS-932, analytical laboratory of the university of Bielefeld.

Bis[4-(ethoxycarbonyl)phenyl]methane (**4**): At −20°C a solution of 71.0 g (56 mmol) of oxalyl chloride in 125 ml of CH_2Cl_2 was added with stirring to a suspension of 75.0 g (56.0 mmol) of $AlCl_3$ in 500 ml of dry CH_2Cl_2 followed at −10°C by slow addition of a solution of 6.64 g of diphenylmethane (**1**) in 250 ml of CH_2Cl_2. After stirring for 4 h at −10°C the reaction mixture was poured onto ice, and the aqueous phase was extracted with several portions of diethyl ether/CH_2Cl_2 (1:1). After drying of the combined extracts and removal of the organic solvents the solid yellow residue was redissolved in dry chlorobenzene and decarbonylated by refluxing for 6 h and subsequent standing at room temp. for 12 h until the gas evolution had stopped. To the crude bis[4-(chlorocarbonyl)phenyl]methane (**3**) was added 5.4 g (79.0) of $NaOC_2H_5$ (in 100 ml of C_2H_5OH), and the mixture was heated for 2 h. Then the solution was washed with 10% $NaHCO_3$, and the aqueous layer was extracted with diethyl ether. 8.32 g (26.6 mmol; 67.5%) of **4** was obtained after removal of the organic solvents and distillation of the residue in vacuo; m.p. 44°C. – IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1}, 2920, 2880, 1702 (C=O), 1602. – ^{1}H NMR ($CDCl_3$): δ = 1.34 (3H, t, CH_2CH_3), 4.05 (2H, s, CH_2), 4.30 (2H, q, OCH_2CH_3), 7.57 (8H, AA'BB', arom. H). – MS (70 eV), *m/z* (%): 312 (58) [M^{+}], 267 (100), 239 (64), 165 (48), 111 (19).

Bis(4-formylphenyl)methane (**5**): 3.00 g of $LiAlH_4$ was suspended in 150 ml of anhydrous THF, and a solution of 5.62 g (18.0 mmol) of **4** was slowly added. The mixture was refluxed for 72 h. Routine workup resulted in 3.50 (17.7 mmol, 85%) of bis [4-(hydroxymethyl)phenyl]methane, which was oxidized without further purification by dissolving it in 15 ml of CH_2Cl_2 and treatment of the obtained

solution with 5.38 g (25.0 mmol) of PCC in 500 ml of CH_2Cl_2. After workup and purification by column chromatography 1.41 g (6.3 mmol, 35%) of **5** was obtained as colorless crystals, m.p. 80°C. – IR (KBr): $\tilde{\nu}$ = 3030 cm^{-1}, 2920, 2865, 1702 (C=O), 1602. – ^1H NMR ($CDCl_3$): δ = 4.14 (2H, s, CH_2), 7.35, 7.83 (8H, AA'BB', J = 8.2 Hz, arom. H), 9.98 (2H, s, CHO). – MS (70 eV), *m/z* (%): 224 (100) [$M^{\cdot+}$], 195 (49), 167 (46), 165 (40), 91 (16).

Bis(4-acetylphenyl)methane (**6**): 24.0 g (180 mmol) of dry $AlCl_3$ was suspended in 240 ml of dry CH_2Cl_2, and at −10°C 13.0 ml (180 mmol) of acetyl chloride was slowly added to the mixture with stirring. This was followed by slow addition of a solution of 3.53 g (21.0 mmol) of diphenylmethane (**1**) in 150 ml of dry CH_2Cl_2. During stirring continuously for additional 3 h the temp. was raised to room temp. After usual workup the product was recrystallized from ethanol/acetone (5:1). 3.70 g (13.9 mmol, 70%) of **6** as colorless crystals, m.p. 91°C (ref.[12] 90–92°C). – IR (KBr): $\tilde{\nu}$ = 3030 cm^{-1}, 2960, 2930, 1671 (C=O), 1450, 1410, 1360. – ^1H NMR ($CDCl_3$): δ = 2.57 (6H, s, CH_3CO), 4.09 (2H, s, CH_2), 7.27, 7.89 (8H, AA'BB', J = 8.2 Hz, arom. H). – MS (70 eV), *m/z* (%): 252 (39) [$M^{\cdot+}$], 237 (100), 165 (13), 111 (10), 43 (66).

Bis(4-acetylphenyl) Ether (**7**): A solution of 4.7 g (60 mmol) of acetyl chloride in 50 ml of CH_2Cl_2 was slowly added at −10°C to a solution of 26.7 g (200 mmol) of $AlCl_3$ and 3.4 g (20 mmol) of diphenyl ether in 100 ml of CH_2Cl_2. The mixture was stirred for 1 h while warming up to room temp. and subsequently at 40°C for 1 h. After standard workup the solid residue was dissolved in benzene and **7** was precipitated from the solution by the addition of petroleum ether. The precipitate was isolated and recrystallized from ethanol to yield 4.0 g (78.4%) of **7** as colorless needles, m.p. 101°C (ref.[11] 100–101°C). R_f 0.64 (ethyl acetate). – IR (KBr): $\tilde{\nu}$ = 1677 cm^{-1}, 1595, 1503, 1357, 1308, 1292, 1269, 1167, 1116, 961, 829. – ^1H NMR ($CDCl_3$): δ = 2.60 (6H, s, CH_3CO), 7.09, 8.00 (8H, AA'BB', J = 8.8 Hz, arom. H). – MS (70 eV), *m/z* (%): 254 (48) [$M^{\cdot+}$], 239 (100), 196 (15), 139 (13), 112 (16), 43 (35).

Bis(4-benzoylphenyl)methane (**8**): A solution of 19.0 g (64.8) of crude **3** in 500 ml of benzene was slowly added to a suspension of 33.8 (25.0 mmol) of dry $AlCl_3$ in 500 ml of dry benzene at 6°C. The mixture was stirred at this temp. for 1 h and for further 20 h at room temp. The product was isolated by pouring the reaction mixture on ice and by extraction of the aqueous phase four times with 100 ml of CH_2Cl_2. The combined organic extracts were dried with Na_2SO_4, and the solvent was removed by evaporation. The residue was purified by flash chromatography (eluant petroleum ether/ethyl acetate, 1:1) and recrystallization from ethyl acetate. Yield: 14.4 g (38.3 mmol, 59%) of **8** as pale yellow crystals, m.p. 143°C (ref.[12c] 142–143°C). – IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 2980, 1650 (C=O), 1590. – ^1H NMR ($CDCl_3$): δ = 4.13 (2H, s, CH_2), 7.32 (4H, d, J = 8.2 Hz, central benzene ring), 7.47 (4H, t, J = 7.7 Hz, terminal phenyl), 7.58 (2H, t, J = 7.5 Hz, terminal phenyl), 7.75–7.80 (8H, 2 d, *o*-H, central and terminal phenyl). – MS (70 eV), *m/z* (%): 376 (15) [$M^{\cdot+}$], 299 (15), 165 (19), 105 (100), 77 (91).

General Procedure for the McMurry Coupling of **5–8**: 10.4 ml (93.2 mmol) of titanium tetrachloride was added at 0°C to 250 ml of dry dimethoxyethane (DME) in a stream of nitrogen by using a high-dilution apparatus. After stirring for 10 min 12.2 g (186 mmol) of a Zn/Cu couple was added in small portions. The blue-violet mixture was refluxed for 2 h, then a solution of 4.6 mmol of the respective bis(4-acylphenyl) derivative **5–8** in 50 ml of dry DME was added continuously within 32 h followed by refluxing of the mixture for additional 12 h. After cooling to room temp. the mixture was treated with 250 ml of 10% $NaHCO_3$. The precipitate formed was separated by filtration and redissolved in dilute HCl. This solution and the filtrate were extracted several times with diethyl ether. The combined organic solutions were washed with water, dried with Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude cyclophanes obtained were purified by chromatography (eluant $CHCl_3$/hexane, 7:3) and recrystallization. By this method the following [2.1.2.1]cyclophanes were synthesized:

[2.1.2.1]Paracyclophane-1,16-diene (**9**): Yield 0.32 g (18%) as colorless crystals from THF/ethanol, m.p. 173–175°C. R_f 0.79 ($CHCl_3$/*n*-hexane, 7:3). – UV (*n*-heptane): λ_{max} (lgε) = 280 nm (3.14). – IR (KBr): $\tilde{\nu}$ = 3055 cm^{-1}, 2860, 1600. – ^1H NMR ($CDCl_3$): δ = 3.87 (4H, s, CH_2), 6.71 (4H, s, −CH=), 6.80, 6.86 (16H, AA'BB', J = 8.1 Hz, arom. H). – MS (70 eV), *m/z* (%): 384 (69) [$M^{\cdot+}$], 206 (100), 191 (52), 178 (31), 115 (24). – $C_{30}H_{24}$ (384.5): calcd. C 93.71, H 6.29; found C 93.61, H 6.60.

1,2,16,17-Tetramethyl[2.1.2.1]paracyclophane-1,16-diene (**10**): Yield 1.40 g (69%) as colorless crystals from THF/ethanol, m.p. 228–230°C. R_f 0.67 ($CHCl_3$/*n*-hexane, 7:3). – UV (*n*-heptane): λ_{max} (lg ε) = 280 (2.72). – IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 2920, 2860, 1606, 812. – ^1H NMR ($CDCl_3$): δ = 2.18 (12H, s, CH_3), 3.74 (4H, s, CH_2), 6.72, 6.80 (16H, AA'BB', J = 8.1 Hz, arom. H). – MS (70 eV), *m/z* (%): 440 (100) [$M^{\cdot+}$], 425 (4), 219 (38), 205 (19). – $C_{34}H_{32}$ (440.6): calcd. C 92.68, H 7.32; found C 92.79, H 7.25.

1,2,16,17-Tetramethyl-9,24-dioxa[2.1.2.1]paracyclophane-1,16-diene (**11**): Yield 0.42 g (20%) as colorless crystals from THF/ethanol, m.p. 275–275. – IR (KBr): $\tilde{\nu}$ = 3036 cm^{-1}, 2916, 2858, 1594, 1495, 1237, 1204 (s), 1166, 1157, 865, 852, 834. – ^1H NMR ($CDCl_3$): δ = 2.19 (12H, s, CH_3), 6.59, 6.77 (16H, AA'BB', J = 8.5 Hz, arom. H). – MS (70 eV), *m/z* (%): 444 (100) [$M^{\cdot+}$], 222 (13), 221 (10), 208 (10), 207 (26), 193 (10), 179 (23), 178 (17). – $C_{32}H_{28}O_2$ (444.6): calcd. C 86.45, H 6.35; found C 86.28, H 6.55.

1,2,16,17-Tetraphenyl[2.1.2.1]paracyclophane-1,16-diene (**12**): Yield 1.55 g (50%) as crude material. – MS (70 eV), *m/z* (%): 688 (100) [$M^{\cdot+}$], 343 (11), 329 (14), 180 (17), 178 (22), 165 (100), 91 (66), 77 (30).

16,17-Dihydroxy-1,2,16,17-tetramethyl[2.1.2.1]paracyclophan-1-ene (**13**): A solution of 1.17 g (4.64 mol) of **6** in 100 ml of dry dimethyoxyethane was added to a refluxing suspension of low-valent titanium in 300 ml of dimethoxyethane prepared from 10.7 ml (92.8 mmol) of $TiCl_4$ and 6.10 g (92.8 mmol) of Zn(Cu) couple over a period of 26 h. The usual workup of the reaction mixture and column chromatography (eluant $CHCl_3$/*n*-hexane, 7:3) afforded in 0.32 g (27.1%) of **13** as colorless crystals, m.p. 201–202°C, R_f 0.51 (petroleum ether/ethyl acetate, 2:1). – IR (KBr): $\tilde{\nu}$ = 3410 cm^{-1} (OH), 3030, 2995, 2914, 1507, 1410. – ^1H NMR ($CDCl_3$): δ = 1.67 (6H, s, CH_3), 2.19 (6H, s, CH_3), 3.83 (4H, s, CH_2), 6.69, 6.84 (16H, AA'BB', J = 8.1 Hz, arom. H). – MS (70 eV), *m/z* (%): 474 (23) [$M^{\cdot+}$], 456 (24) [$M - H_2O]^{\cdot+}$, 354 (35), 133 (21), 121 (19), 105 (14), 91 (25), 43 (100). – $C_{34}H_{34}O_2$ (474.64): calcd. C 86.04, H 7.22; found C 85.45, H 7.18.

1,2,17,17-Tetramethyl-16-oxo[2.1.2.1]paracyclophan-1-ene (**14**): 100 mg (211 μmol) of **13** was heated with dilute sulfuric acid, and the reaction mixture was extracted several times with diethyl ether. The combined organic extracts were dried with Na_2SO_4, and the solvent was evaporated. – IR (KBr): $\tilde{\nu}$ = 3023 cm^{-1}, 1714 (C=O), 1507, 1411. – ^1H NMR ($CDCl_3$): δ = 2.02 (3H, s, CH_3), 2.09 (3H, s, CH_3), 2.35 (6H, s, CH_3), 3.65 (4H, s, CH_2), 6.69, 6.92 (16H, AA'B', J = 8.2 Hz, arom. H). – MS (70 eV), *m/z* (%): 456 (69) [$M^{\cdot+}$], 413 (100), 221 (47), 219 (20), 205 (15), 193 (28), 179 (37), 115 (17), 91 (43).

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[9] Calculations of **9**, **10**, and **12** by means of the MM2 force-field method show a distance of ca. 7.8 Å between the two methylene groups of the diphenylmethane units accross the cavity in the conformation of lowest energy.

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[13] It is important to avoid the formation of droplets during the addition of the solution of the dicarbonyl compound. Instead, the solution has to be infused into the McMurry reagent by using a syringe dipping into the solvent, or one has to use a special high dilution apparatus diluting the original dicarbonyl solution in a cascade of several dilution steps by refluxing the solvent.

[391/93]