Compound **31** was obtained from **13b** in the same manner: colorless prisms (hexane); mp 280–282 °C; IR (KBr) 3040, 2980, 1600, 1560, 1465, 1455, 1360, 1245, 1060, 990, 870, 720, 665 cm^{-1}; NMR ($CDCl_3$) δ 1.60 (18 H, s), 8.71 (4 H, s); mass spectrum, *m/e* 452 (M^+). Anal. Calcd for $C_{24}H_{22}Cl_4$: C, 63.74; H, 4.90. Found: C, 63.50; H, 4.88.

Reaction with Iodine. Typical Procedure. A solution of 100 mg (0.289 mmol) of **13a** and 441 mg (1.74 mmol) of iodine in 30 mL benzene was refluxed for 48 h. The reaction mixture was washed with 10% sodium thiosulfate solution and then with water. The benzene solution was dried over Na_2SO_4 and evaporated in vacuo. The residue was chromatographed on silica gel with hexane–benzene 1:1 as eluant. Colorless crystals (79.3 mg, 87.1%) were isolated from the eluate, and the ratio of **28** to **34** was determined to be 60:40 by its NMR spectrum. Similar reactions of **20a–c** afforded **28** in good yield. In the case of **20c**, the reaction mixture was analyzed by GC to detect formation of **38**.

Reaction of the Mixture (28 + 34) with DDQ. A solution of 79.3 mg of the mixture of **28** and **34** and 50 mg of DDQ in 50 mL of toluene was refluxed for 4 h. After the reaction mixture was cooled and concentrated, the residue was extracted and chromatographed on silica gel with hexane:benzene 1:1 as the eluant to give 70 mg (77%) of **28** as colorless prisms. **28**: pale yellow prisms (hexane); mp 210–212 °C; IR (KBr) 3040, 2960, 1600, 1440, 1355, 1220, 920, 875, 800, 715 cm^{-1}; NMR ($CDCl_3$) δ 1.48 (18 H, s), 7.87 (4 H, s), 8.14 (4 H, s); mass spectrum, *m/e* 314 (M^+). Anal. Calcd for $C_{24}H_{26}$: C, 91.67; H, 8.33. Found: C, 91.67; H, 8.41.

Reaction of the Mixture (28 + 34) with Iodine. A solution of 100 mg of the mixture of **28** and **34** and 441 mg (1.74 mmol) of iodine in 30 mL of benzene was refluxed for 48 h. The reaction mixture was treated as described above to give 95 mg (**28** and **34**) of colorless crystals, whose ratio was not exchanged. The GC analysis of the reaction mixture of **20c** with iodine showed the formation of *n*-propyl iodide (**38**). Although **2a** was treated with iodine under the same conditions as described above, no product formed.

Registry No. 2a, 76447-51-3; **2b**, 76466-35-8; **2c**, 76626-78-3; **8b**, 65276-10-0; **9a**, 67691-33-2; **9b**, 81688-07-5; **10a**, 81688-08-6; **10b**, 81688-09-7; **11a**, isomer 1, 81688-10-0; **11a**, isomer 2, 81738-73-0; **11b**, isomer 1, 81688-11-1; **11b**, isomer 2, 81738-74-1; **12a**, isomer 1, 81688-13-3; **12a**, isomer 2, 81738-76-3; **12b**, isomer 1, 81688-15-5; **12b**, isomer 2, 81738-78-5; **13a**, 81688-16-6; **13b**, 81688-17-7; **16a**, 76447-66-0; **16b**, 76447-68-2; **16c**, 76447-69-3; **16d**, 76447-70-6; **17a**, 76446-96-3; **17b**, 76446-97-4; **17c**, 76446-98-5; **17d**, 76466-30-3; **18a**, 81688-84-8; **18b**, 81688-86-0; **18c**, 81688-88-2; **18d**, 81688-90-6; **20a**, 76626-75-0; **20b**, 76626-76-1; **20c**, 76626-77-2; **20d**, 81555-09-1; **27**, 76466-34-7; **28**, 24300-91-2; **29**, 76626-79-4; **30**, 81688-18-8; **31**, 81688-19-9; **34**, 69618-61-7; chloromethyl methyl ether, 107-30-2.

Metacyclophanes and Related Compounds. 7. Preparation and Reduction of [2.2]Metacyclophanequinone[1]

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Abstract: Two preparative methods for [2.2]metacyclophanequinone (**7a**) from 8,16-dimethoxy-5,13-di-*tert*-butyl[2.2]-metacyclophane (**5**) are described. The partially hydrogenated compound 5,8-dihydroxy[2]-(2,6)-benzoquionono[2]metacyclophane (**18**) was prepared from **7a**. It was found that compound **18** is colorless as a solid but is colored in solution. Some discussions of the above phenomena are also included in this paper.

Although many [2.2]paracyclophanequinones[3-9] and [3.3]-metacyclophanequinone[10] have been prepared, [2.2]metacyclophanequinones have not yet been synthesized.

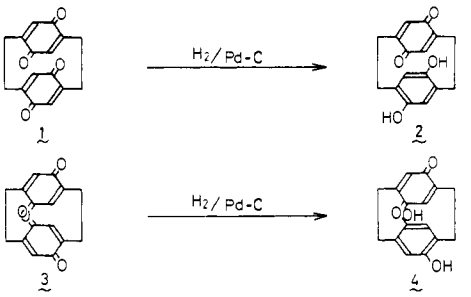
We have previously reported that[11] 8,16-dimethoxy-5,13-di-*tert*-butyl[2.2]metacyclophane (**5**) was easily prepared from anisole in only six steps. This compound (**5**) seems to be a suitable starting material for the preparation of [2.2]metacyclophanequinone.

Staab and Rebafka[6,7] reported that the partial hydrogenation of [2.2]paracyclophanequinones **1** and **3** afforded the interesting intramolecular quinhydrones **2** and **4** as black and dark violet crystals, respectively.

We undertook the present work in order to prepare the title compound and to obtain some information about its chemical nature.

Results and Discussion

When **5** was treated with BBr_3 in benzene at room temperature for 24 h, a mixture of **6a** and **6b** (1:1) was obtained with a total yield of 70%. The separation of **6a** and **6b** could be carried out by fractional recrystallization of the mixture with hexane. However, **6a** was exclusively obtained by the prolonged reaction (155 h) in 86% yield.



Oxidation of **6a** with $Tl(OCOCF_3)_3$[12-14] in CF_3COOH afforded the desired [2.2]metacyclophanequinone (**7a**) in 53% yield. Similar oxidation of **6b** gave 5-*tert*-butyl-8-methoxy[2]-(2,6)-benzoquinono[2]metacyclophane (**7b**) in 70% yield (Scheme I, route A). Another preparative route (route B) of **7a** from **6a** is shown in Scheme II.

We have previously reported that[15] the $AlCl_3$–CH_3NO_2 catalyzed trans-*tert*-butylation of 8,16-dimethyl-5,13-di-*tert*-butyl-[2.2]metacyclophane (**8**) in benzene afforded 8,16-dimethyl-[2.2]metacyclophane (**9c**) together with *tert*-butylbenzene (**10**).

(1) (a) A part of this paper was published as a preliminary communication: Tashiro, M.; Yamato, T. *Chem. Lett.* **1979**, 595. (b) Part 4: Tashiro, M.; Yamato, T. *J. Am. Chem. Soc.*, preceding paper in this issue.
(2) (a) Research Institute of Industrial Sciences. (b) Department of Molecular Science and Technology.
(3) Cram, D. J.; Day, A. C. *J. Org. Chem.* **1966**, *31*, 1227.
(4) Rebafka, W.; Staab, H. A. *Angew. Chem.* **1973**, *85*, 831.
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(8) Vogler, H.; Ege, G.; Staab, H. A. *Tetrahedron* **1975**, *31*, 2441.
(9) Staab, H. A.; Herz, C. P.; Henke, H. W. *Tetrahedron Lett.* **1974**, 4393.
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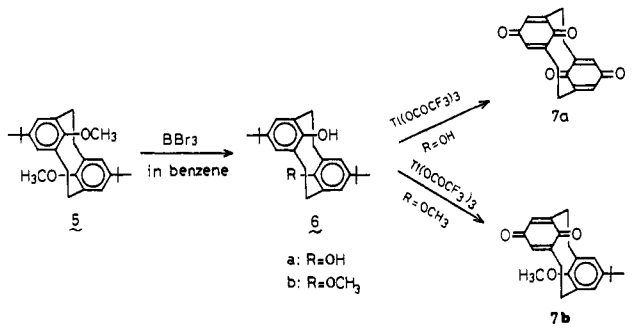
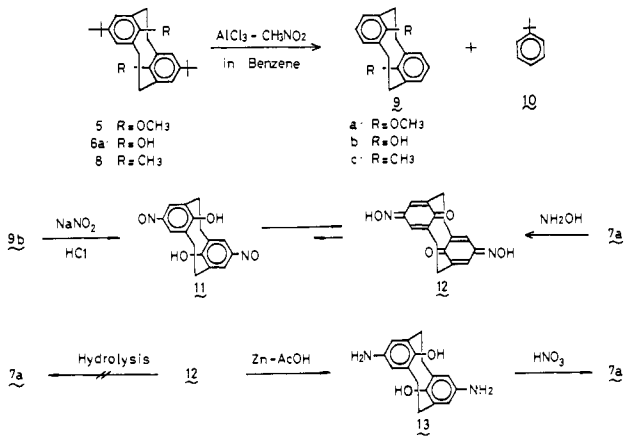
(11) Tashiro, M.; Yamato, T. *Chem. Lett.* **1979**, 595.
(12) McKillop, A.; Fowler, J. S.; Zelesko, M. J.; Hunt, J. D. *Tetrahedron Lett.* **1969**, 2423.
(13) McKillop, A.; Swann, B. P.; Taylor, E. C. *Tetrahedron* **1970**, *26*, 4031.
(14) Shinmyozu, T.; Inazu, T.; Yoshino, T. *Chem. Lett.* **1978**, 1319.
(15) Tashiro, M.; Yamato, T. *Synthesis* **1978**, 435.

0002-7863/82/1504-3707$01.25/0

Scheme I



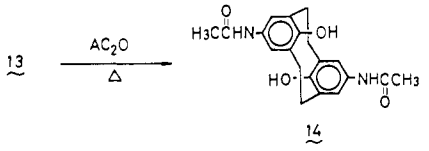
Scheme II



Similar reaction of **6a** gave the expected 8,16-dihydroxy[2.2]-metacyclophane (**9b**) in 70% yield. However, the trans-*tert*-butylation of **5** afforded a complex mixture, but not the expected compound (**9a**).

Treatment of the dihydroxy derivative **9b** with $NaNO_2$ in the usual manner gave the dioxime **12**, which may be produced from the dinitroso derivative (**11**) initially formed. Compound **12** was also obtained by the reaction of **7a** with hydroxylamine.

Although hydrolysis of **12** under various conditions did not give **7a**, oxidation of the diamino derivative (**13**), which was easily obtained by reduction of **12**, afforded **7a** in 69% yield (calculated from **12**). The diamino derivative (**13**) is too unstable to be isolated in pure form. However, the oxidation of **13** could be carried out without purification to give a substantial yield of **7a**. Heating of **13** with acetic anhydride gave the corresponding *N,N'*-diacetate (**14**) as a stable compound.

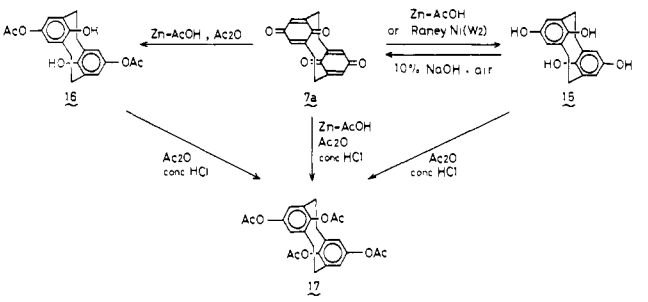


As mentioned above, route B is clearly longer than route A. However, route B seems to be more practical for large-scale investigations, since route A involves $Tl(OCOCF_3)_3$, which is a poisonous and expensive reagent.

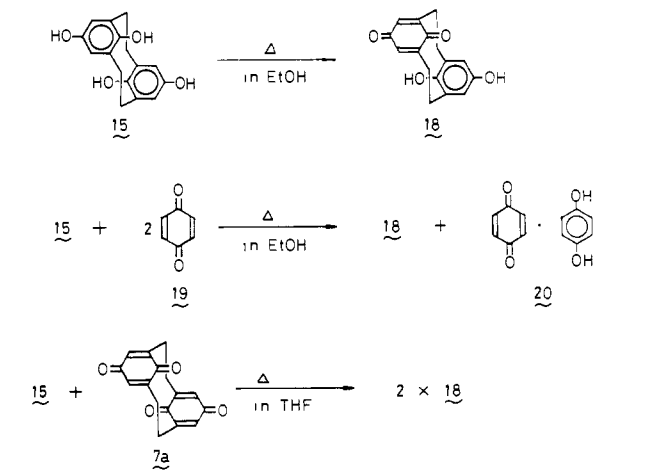
Both Raney Ni catalyzed hydrogenation and reduction of **7a** with Zn powder in acetic acid afforded tetrahydroxy[2.2]metacyclophane (**15**) in 90% yield (Scheme III). However, reduction of **7a** with Zn powder in a mixture of acetic acid and acetic anhydride gave diacetate **16**. When a similar reduction was carried out in the presence of a small amount of concentrated HCl, tetraacetate **17** was produced. It was also obtained by treatment of **16** or **15** with acetic anhydride in the presence of concentrated HCl.

The ^1H NMR spectrum of **15** shows that the protons on the oxygen atoms appear as two singlets at 5.0 and 8.3 ppm. The former signal is assigned to the internal OH groups, since their

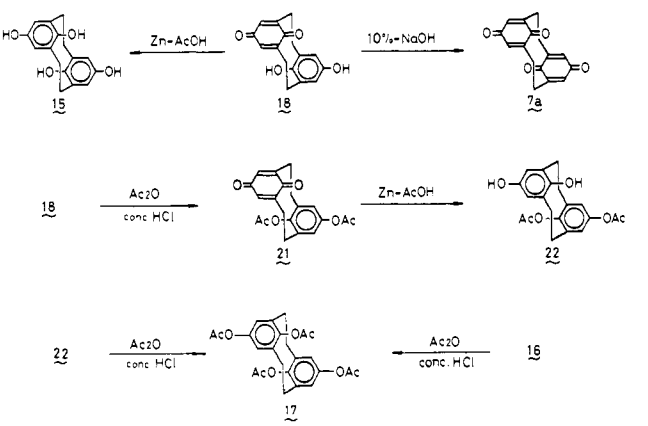
Scheme III



Scheme IV



Scheme V



protons are moved upfield by the ring current of the opposite aromatic ring.

The structure of **16** was confirmed by its elemental analysis, spectral data, and comparison with the isomeric compound **22**, which will be discussed below.

Quinone **7a** was formed immediately when **15** was treated with 10% NaOH solution. However, when a solution of **15** in ethanol was refluxed for a few minutes, quinhydrone **18** was obtained (Scheme IV). This compound (**18**) was also produced by oxidation of **15** with *p*-benzoquionone (**19**) or **7a**. In the latter case, **7a** as well as **15** was converted to **18**.

Treatment of **18** as well as **15** with 10% NaOH solution immediately afforded **7a**. Reduction of **18** with Zn powder in acetic acid gave **15** (Scheme V). Acetylation of **18** with acetic anhydride in the presence of concentrated HCl afforded diacetate **21**, which was easily reduced with Zn powder in acetic acid to give diacetate **22**. As mentioned above, **22** is isomeric to **16**. Acetylation of **22** as well as **16** in the presence of concentrated HCl gave tetraacetate **17**.

Although **18** is colorless in the solid state, its solution in $CHCl_3$, Me_2SO, or ethanol is colored. When the solvent was evaporated,

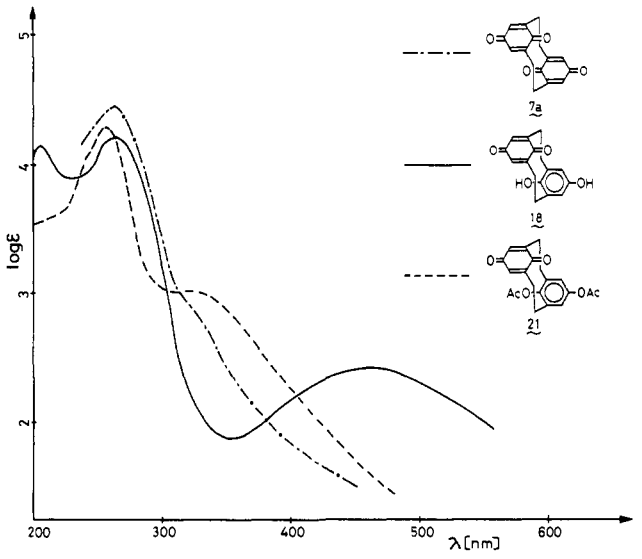
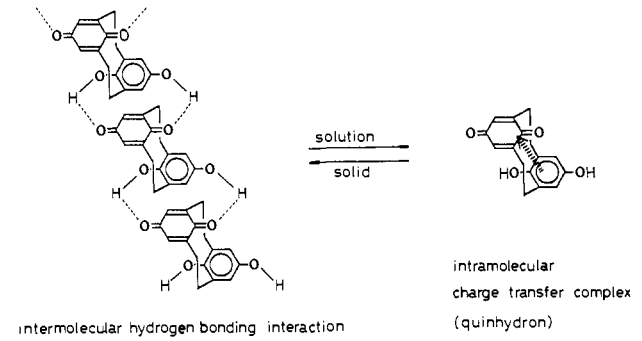


Figure 1. Electronic Spectra of [2.2]metacyclophanequinones: **7a** (in $CHCl_3$); **18** (in EtOH); **21** (in $CHCl_3$).

Scheme VI



compound **18** was obtained again as colorless crystals. The ^1H NMR ($CDCl_3$) spectrum of **18** shows olefinic protons at 6.24 ppm, aromatic protons at 6.32 ppm, and hydroxy protons at 7.80 and 8.80 ppm as singlets.

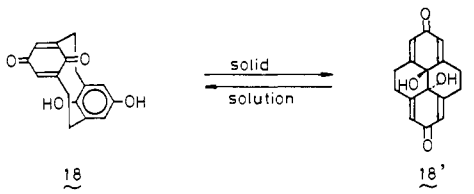
As shown in Figure 1, the absorption band characteristic of a benzoquinone structure appeared in the electronic spectra of **7a** and **21**, but this band was not present in the spectrum of **18**. However, the spectrum of **18** shows a band due to a charge-transfer complex at 459 nm (ϵ 260).

These facts suggest that the electrons in compounds **2** and **4**, reported by Staab and Rebafka, are more mobile than those in **18**, since the overlap between the quinone and hydroquinone rings of the former is larger than that of the latter. In the solid state, compound **18** might have an intermolecular hydrogen-bonded structure with little intramolecular hydrogen bonding. This hydrogen bond might forbid charge transfer from the hydroquinone ring to the quinone ring in **18**. Such intermolecular hydrogen bonding might disturb the n,π^* excitation of the quinone ring of **18**. Thus, in the solid state, **18** might exist as a colorless compound. On the other hand, dissolution of **18** should destroy the intermolecular hydrogen bonding in the solid state, and an intramolecular charge-transfer complex might result (Scheme VI).

An alternative explanation is that compound **18** in the solid state has the bis-dienone structure **18′**, but exists in solution as the charge-transfer complex **18** (Scheme VII). However, the bis-(dienone) structure **18′** can be discounted for the following reasons: (i) compound **18** was easily converted to **7a** by treatment with 10% NaOH solution; (ii) the ^1H NMR spectrum of compound **18** in solution does not give the expected chemical shifts of **18′** (this might mean that there is no such equilibrium); (iii) many dienone compounds are colored.[16]

(16) Boekelheide, V.; Phillips, J. B. *J. Am. Chem. Soc.* **1963**, *85*, 1545.

Scheme VII



18 **18′**

Unequivocal evidence for the structure of compound **18** in the solid state must await X-ray analysis. Unfortunately, a suitable crystal of **18** has not yet been grown.

Experimental Section

All melting and boiling points are uncorrected. NMR spectra were determined at 100 MHz with Nippon Denshi JEOL FT-100 NMR spectrometer with Me_4Si as an internal reference. IR spectra were measured as KBr pellets or liquid films on NaCl plates with a Nippon Bunko IR-A-102 spectrometer. Mass spectra were obtained with a Nippon Denshi, JMS-01SA-2 spectrometer at 75 eV, using a direct-inlet system.

Demethylation of 5. To a solution of 9.0 g (23.7 mmol) of **5** in 640 mL of dry benzene at room temperature was added a solution of 15 mL (158 mmol) of BBr_3 in 100 mL of benzene over a period of 5 h. After the reaction mixture was stirred at room temperature for 155 h, it was washed with water, dried over Na_2SO_4, concentrated in vacuo to leave a residue that after column chromatography (silica gel) afforded crude **6a**. Recrystallization from hexane gave 7.16 g (86%) of **6a**: colorless prisms (hexane); mp 267–268 °C; IR (KBr) 3575, 3040, 2960, 1480, 1360, 1190, 885, 870, 760, 730 cm^{-1}; NMR ($CDCl_3$) δ 1.28 (18 H, s), 2.14 (2 H, s, exchanged by D_2O), 2.76 (8 H, s), 7.08 (4 H, s); mass spectrum, *m/e* 352 (M^+). Anal. Calcd for $C_{24}H_{32}O_2$: C, 81.77; H, 9.15. Found: C, 81.67, H, 9.17.

Preparation of 5,13-Di-*tert*-butyl-8-hydroxy-16-methoxy[2.2]metacyclophane (6b). To a solution of 250 mg (0.66 mmol) of **5** in 30 mL of benzene at room temperature was added a solution of 0.5 mL (5.3 mmol) of BBr_3 in 1 mL of benzene. After the reaction mixture was stirred at room temperature for 24 h, it was treated as described above to give a mixture of **6a** and **6b** (1:1) with a total yield of 70%. The separation of **6a** and **6b** was carried out by fractional recrystallization from hexane. **6b**: colorless prisms (hexane); mp 182–183 °C; IR (KBr) 3550, 3040, 2960, 1480, 1360, 1285, 1190, 1025, 890, 860 cm^{-1}; NMR ($CDCl_3$) δ 1.30 (9 H, s), 1.32 (9 H, s), 1.94 (1 H, s, exchanged by D_2O), 2.69 (8 H, m), 2.95 (3 H, s); mass spectrum, *m/e* 366 (M^+). Anal. Calcd for $C_{25}H_{34}O_2$: C, 81.92; H, 9.35. Found: C, 82.02; H, 9.32.

Oxidation of 6a with $Tl(OCOCF_3)_3$. To a standard solution of 100 mL of trifluoroacetic acid (TFA) containing 69.3 mmol of $Tl(TFA)_3$ was added 5.28 g (15 mmol) of **6a**, and the resulting deep red mixture stirred at room temperature for 4.5 h. The bulk of the TFA was then removed by evaporation under reduced pressure and the residue poured into ice water. The quinone that separated at this stage was extracted with chloroform, and the chloroform extracts were washed with water and dried over Na_2SO_4. Concentration of the solution gave the crude quinone, that after recrystallization from acetone gave 2.66 g (66%) of **7a**: pale yellow prisms (acetone); mp 285–290 °C dec; IR (KBr) 3050, 2950, 1660, 1610, 1290, 1200, 935, 890, 800 cm^{-1}; UV ($CHCl_3$) λ_{max} 263 nm (ϵ 31 560); NMR ($CDCl_3$) δ 2.78 (8 H, A_2B_2 pattern, J = 8 Hz), 6.44 (4 H, s); mass spectrum, *m/e* 268 (M^+). Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.63; H, 4.51. Found: C, 71.44; H, 4.67.

Oxidation of 6b with $Tl(OCOCF_3)_3$. To a solution of 136 mg (0.371 mmol) of **6b** in 1 mL of TFA was added 0.93 mL (0.817 mmol) of freshly prepared TTFA solution. After the reaction mixture was stirred at room temperature for 2 h, it was poured into ice water and treated as described above. Chloroform extracts were evaporated in vacuo to leave a residue that after recrystallization from hexane gave 84 mg (70%) of **7b**: yellow needles (hexane); mp 208–209 °C; IR (KBr) 3040, 2960, 1650, 1600, 1480, 1270, 1210, 1010, 880, 790 cm^{-1}; UV (CH_3CN)λ_{max} 257 nm (ϵ 18 000); NMR ($CDCl_3$) δ 1.35 (9 H, s), 2.35–3.14 (8 H, m), 3.53 (3 H, s), 6.31 (2 H, s), 7.01 (2 H, s); mass spectrum, *m/e* 324 (M^+). Anal. Calcd for $C_{21}H_{24}O_3$: C, 77.75; H, 7.46. Found: C, 77.51; H, 7.46.

Trans-*tert*-butylation of 6a. To a solution of 1.57 g (4.46 mmol) of **6a** in 60 mL of benzene was added a solution of 4.5 g (33.75 mmol) of anhydrous aluminum chloride in 6 mL of nitromethane. After the reaction mixture was stirred for 24 h at room temperature, the reaction was quenched by the addition of 10% hydrochloric acid, and the solution was washed with water, dried over sodium sulfate, and concentrated in vacuo to leave a residue that gave upon recrystallization from hexane:benzene (1:1) 0.752 g (70%) of **9b**: pale yellow prisms (hexane); mp 223–228 °C; IR (KBr) 3570, 1590, 1460, 1255, 1195, 1170, 900, 815, 770, 735 cm^{-1};

NMR ($CDCl_3$) δ 2.57 (2 H, s), 2.76 (8 H, m), 7.02 (6 H, m); mass spectrum, *m/e* 240 (M^+). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.69; H, 6.73.

Nitrosoation of 9b. To a solution of 240 mg (1 mmol) of **9b** and 2.5 mL of concentrated hydrochloric acid in 15 mL of dioxane was added a solution of 0.21 g (3 mmol) of sodium nitrite in 10 mL of water at room temperature. The yellow precipitate that formed was collected and washed with water, ethanol, and hexane to give **12** quantitatively: pale yellow prisms; mp 280–300 °C dec; IR (KBr) 3000–3400, 1625, 1420, 1305, 1100, 900, 800 cm^{-1}; NMR (Me_2SO-d_6) δ 2.70 (8 H, m), 6.88 (2 H, d, J = 2.8 Hz), 7.29 (2 H, d, J = 2.8 Hz), 12.84 (1 H, s); mass spectrum, *m/e* 298 (M^+). Anal. Calcd for $C_{16}H_{14}O_4N_2 \cdot 0.25H_2O$: C, 63.46; H, 4.83; N, 9.25. Found: C, 63.35; H, 5.00; N, 9.17.

Reaction of 7a with Hydroxylamine. To a solution of 268 mg (1 mmol) of **7a** in 50 mL of tetrahydrofuran was added a solution of 500 mg (7.1 mmol) of $NH_2OH \cdot HCl$ and 200 mg (5 mmol) of sodium hydroxide in 10 mL of water. After the reaction mixture was refluxed for 5 h on a water bath, the solvent was evaporated in vacuo to leave a residue was left that was washed with water, ethanol, and hexane and gave 190 mg (64%) of **12**.

Preparation of [2.2]Metacyclophanequinone (7a) from 12. To a solution of 60 mg (0.2 mmol) of **12** in 20 mL of acetic acid was added 5 g of zinc powder. After the reaction mixture was refluxed for 20 min on a water bath, it was filtered and the filtrate was directly added to a solution of 2 mL of fuming nitric acid in 100 mL of water at room temperature. When the reddish brown solution was heated for 10 min on a water bath, it turned pale yellow and, after standing overnight at room temperature, formed a pale yellow precipitate. It was filtered and washed with water, ethanol, hexane, and acetone to give 37 mg (68.5%) of **7a**.

Acetylation of Diamino Derivatives 13. To a solution of 33 mg (0.1 mmol) of **12** in 8 mL of ethanol and 10 mL of acetic anhydride was added 4.8 g of freshly prepared W-2 Raney nickel, and the reaction mixture was heated under reflux for 30 min. After the solution was filtered and concentrated, the residue was washed with water and hexane to give 10 mg of **14**: colorless prisms; mp >300 °C; IR (KBr) 3360 (ν_{NH}), 3530 (ν_{OH}), 1630 ($\nu_{C=O}$), 1545, 1470 cm^{-1}; NMR (Me_2SO-d_6) δ 2.16 (6 H, s), 2.60 (8 H, m), 6.60 (4 H, s), 6.60 (2 H, s); mass spectrum, *m/e* 354 (M^+). Anal. Calcd for $C_{20}H_{22}O_4N_2 \cdot 0.5H_2O$: C, 66.10; H, 6.38; N, 7.52. Found: C, 66.40; H, 6.24; N, 7.05.

Reduction of 7a with Raney Ni (W-2). Freshly prepared W-2 Raney Ni (4.8 g) was added to a solution of 134 mg (0.5 mmol) of **7a** in 8 mL of ethanol and the mixture was heated under reflux for a few minutes. After the solution was filtered and concentrated, the residue was washed with water and hexane to give 122 mg (90%) of **15**: pale purple prisms; mp 270–280 °C dec; IR (KBr) 3450, 3225 (λ_{OH}) 1595, 1460, 1440, 1340, 1280, 1120, 1190, 980, 890, 850, 770, 730 cm^{-1}; UV λ_{max}^{EtOH} 304 (ϵ 4290), 209 (ϵ 18 800) nm; NMR (Me_2SO-d_6) δ 2.5 (8 H, m), 5.0 (2 H, s, exchanged by D_2O); mass spectrum, *m/e* (relative intensity) 272 (M^+, 100), 255 ($M^+ - OH$, 53), 238 ($M^+ - 2OH$, 63). Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.58; H, 5.92. Found: C, 70.70; H, 5.95.

Reduction of 7a with Zinc Powder in Acetic Acid. To a solution of 500 mg (1.87 mmol) of **7a** in 50 mL of acetic acid was added 8 g of zinc powder, and the solution was heated under reflux for 10 min. After the pale yellow reaction mixture became colorless, it was filtered, concentrated to leave a residue that after washing with water and hexane gave 453 mg (89%) of **15**.

Reduction of 7a with Zinc Powder in the Presence of HCl. To a solution of 50 mg (0.187 mmol) of **7a** in 10 mL of acetic acid was added 800 mg of zinc powder, 10 mL of acetic anhydride, and 0.2 mL of concentrated hydrochloric acid. After the pale yellow reaction mixture became colorless, it was filtered and concentrated to leave after washing the residue with water, ethanol, and hexane, 65.3 mg (80%) of **17**: colorless prisms; mp > 300 °C; IR (KBr) 1750, 1445, 1430, 1365, 1220, 1210, 1170, 1120, 1010, 930, 900, 805, 730, 710 cm^{-1}; NMR ($CDCl_3$) δ 1.84 (6 H, s), 2.25 (6 H, s), 2.08–2.85 (8 H, m), 6.96 (4 H, s); mass spectrum, *m/e* 440 (M^+). Anal. Calcd for $C_{24}H_{24}O_8 \cdot 0.25H_2O$: C, 64.79; H, 5.55. Found: C, 64.76, H, 5.51.

Oxidation of 15 with 10% NaOH Solution. To 50 mg (0.184 mmol) of **15** was added 5 mL of 10% NaOH solution. The reaction mixture immediately turned pale yellow and a pale yellow precipitate formed. This solid was collected and washed with water, ethanol, and hexane to give **7a** in quantitative yield.

Reduction of 7a with Zinc Powder in Acetic Acid–Anhydrous Acetic Acid. To a solution of 67 mg (0.25 mmol) of **7a** in 10 mL of acetic acid and 10 mL of acetic anhydride was added 3 g of zinc powder. After the pale yellow reaction mixture became colorless, it was filtered and concentrated to leave the residue, which was washed with water, ethanol, and hexane to give 64.2 mg (72%) of **16**: colorless prisms; mp 250–280 °C dec; IR (KBr) 3530, 2940, 1735, 1590, 1470, 1465, 1430, 1365, 1250, 1210, 1120, 1010, 970, 880, 850, 770, 740, 700 cm^{-1}; NMR (Me_2SO-d_6) δ 2.16 (6 H, s), 2.60 (8 H, m), 6.60 (4 H, s), 6.60 (2 H, s); mass spectrum, *m/e* 356 (M^+). Anal. Calcd for $C_{20}H_{20}O_6$: C, 67.41; H, 5.66. Found: C, 67.56; H, 5.60.

Acetylation of 16 To Give 17. To a solution of 50 mg (0.140 mmol) of **16** in 20 mL of acetic anhydride was added 0.5 mL of concentrated hydrochloric acid. After the reaction mixture was refluxed for a few minutes, it was concentrated to leave the residue, which was washed with water, ethanol, and hexane, to give **17** in quantitative yield.

Oxidation of 15 in Ethanol. A solution of 50 mg (0.184 mmol) of **15** in 30 mL of ethanol was refluxed for a few minutes. After the reaction mixture was cooled, a small amount of colorless prisms precipitated. These were collected and washed with ethanol and hexane to give **18**: colorless prisms; mp >300 °C; IR (KBr) 3400, 1670, 1610 cm^{-1}; UV λ_{max}^{EtOH} 206 (log ϵ 4.14), 261 (log ϵ 4.22), 457 (log ϵ 2.42); NMR (Me_2SO-d_6) δ 2.5 (8 H, m), 6.24 (2 H, s), 6.32 (2 H, s), 7.80 (1 H, s), 8.80 (1 H, s); mass spectrum, *m/e* 270 (M^+). Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 71.10; H, 5.17.

Oxidation of 15 with *p*-Benzoquinone. To a solution of 50 mg (0.184 mmol) of **15** in 30 mL of ethanol was added 39.8 mg (0.368 mmol) of *p*-benzoquinone (**19**). After the reaction mixture was refluxed for a few minutes, it was cooled to give **18** in almost quantitative yield.

Reaction of 15 and 7a To Give 18. To a solution of 50 mg (0.184 mmol) of **15** in 30 mL of tetrahydrofuran was added 50 mg (0.187 mmol) of **7a**. After the reaction mixture was refluxed for 1 h, it was cooled and gave **18** in almost quantitative yield.

Reduction of 18 with Zinc Powder in Acetic Acid. To a solution of 50 mg (0.185 mmol) of **18** in 10 mL of acetic acid was added 800 mg of zinc powder, and the solution was heated under reflux for 10 min. After the pale yellow reaction mixture became colorless, it was filtered and concentrated and after the residue was washed with water and hexane, gave **15** in quantitative yield.

Oxidation of 18 with 10% NaOH Solution. To 50 mg (0.185 mmol) of **18** was added 5 mL of 10% NaOH solution. The colorless reaction mixture immediately turned pale yellow and a pale yellow precipitate formed. This solid was collected and washed with water, ethanol, and hexane to give **7a** in quantitative yield.

Acetylation of 18 with Acetic Anhydride. To a suspension of 160 mg (0.59 mmol) of **18** in 30 mL of acetic anhydride was added 1 mL of concentrate hydrochloric acid. After the reaction mixture was refluxed for a few minutes, it was concentrated and upon recrystallization from hexane–benzene (1:1) gave **21** in quantitative yield: yellow prisms (hexane–benzene 1:1); mp 230–250 °C dec; IR (KBr) 2920, 1760, 1645, 1460, 1365, 1210, 1170, 1025, 900, 785 cm^{-1}; UV $\lambda_{max}^{CHCl_3}$ 257 (log λ 4.28), 320 (log ϵ 3.01) nm; NMR ($CDCl_3$) δ 2.10 (3 H, s), 2.28 (3 H, s), 2.42–3.10 (8 H, m), 6.37 (2 H, s), 6.86 (2 H, s); mass spectrum, *m/e* 354 (M^+). Anal. Calcd for $C_{20}H_{18}O_6$: C, 67.79; H, 5.12. Found: C, 67.89; H, 5.15.

Reduction of 21 with Zinc Powder in Acetic Acid. To a solution of 210 mg (0.593 mmol) of **21** in 15 mL of acetic acid was added 3 g of zinc powder, and the solution was heated under reflux for 10 min. After the pale yellow reaction mixture became colorless, it was filtered and concentrated to leave the residue, which was washed with water, ethanol, and hexane gave 150 mg (71%) of **22**: colorless crystals; mp 192–207 °C dec; IR (KBr) 3460, 3350, 2930, 1750, 1730, 1590, 1455, 1365, 1220, 1180, 1010, 975, 910 cm^{-1}; NMR (Me_2SO-d_6) δ 1.80 (3 H, s), 2.20 (3 H, s), 2.5–2.7 (8 H, m), 6.14 (1 H, s, exchanged by D_2O), 6.38 (2 H, s), 6.83 (2 H, s), 8.36 (1 H, s, exchanged by D_2O); mass spectrum, *m/e* 356 (M^+). Anal. Calcd for $C_{20}H_{20}O_6 \cdot 0.5H_2O$: C, 65.75; H, 5.79. Found: C, 65.75; H, 5.53.

Acetylation of 22 with Acetic Anhydride. To a suspension of 35 mg (0.01 mmol) of **22** in 8 mL of acetic anhydride was added 0.5 mL of concentrated hydrochloric acid. After the reaction mixture was stirred for 2 days at room temperature, the resulting precipitate was filtered and washed with hexane to give 20 mg (46%) of **17**.

Registry No. 5, 72523-20-7; **6a**, 71777-27-0; **6b**, 72523-21-8; **7a**, 71777-29-2; **7b**, 81688-20-2; **9b**, 81688-21-3; **12**, 81688-22-4; **14**, 81704-70-3; **15**, 81688-23-5; **16**, 81688-24-6; **17**, 81688-25-7; **18**, 81688-26-8; **21**, 106-51-4; **22**, 81688-28-0.