6.0 Hz, 1 H), 7.23–7.60 (m, 4 H), 8.15–8.30 (m, 2 H). This molecule is quite sensitive to handling, but an analytical sample could be obtained. Anal. Calcd for $C_{20}H_{22}O_6BBr$: C, 53.49; H, 4.94. Found: C, 53.17; H, 5.10.

22b. To a mixture of 0.118 g (0.256 mmol) of **21** and 0.039 g (1.03 mmol, 4 equiv) of sodium borohydride at 0 °C was added 2 mL of methanol. After 3 h the reaction was quenched by the addition of 2 mL of acetone and 1 mL of a 5% sodium hydroxide solution. The reaction mixture was concentrated in vacuo at ca. 50 °C. An extractive workup (dichloromethane) gave **22b** (99%) as white crystals: mp 86–87 °C; IR (KBr) 3430 (m), 3350 (m), 2960 (m), 2860 (m), 1470 (s), 1235 (m), 1065 (m), 1020 (vs), 995 (s), 935 (m), 835 (s), 820 (m), 790 (m); ^{1}H NMR −0.10 (s, 3 H), 0.10 (s, 3 H), 0.80 (s, 9 H), 1.00 (t, J = 7.5 Hz, 3 H), 1.50–1.70 (br s disappeared with D_2O, 1 H), 1.70–2.05 (highly structured m, 3 H), 2.15 (dd, J = 2.3, 15.3 Hz, 1 H), 3.72 (s, 3 H), 3.78 (s, 3 H), 4.48 (center of AB, J = 12 Hz, $\Delta\nu_{AB}$ = 27 Hz, 2 H which collapsed to a s at 4.58 upon addition of D_2O), 5.30 (dd, J = 2.3, 5.5 Hz, 1 H), 6.98 (s, 1 H); ^{13}C NMR −5.1, −5.0, 7.0, 17.8, 25.3, 33.2, 44.3, 55.6, 61.9, 62.5, 69.0, 74.8, 115.0, 117.3, 127.0, 136.0, 149.7, 152.5 ppm. Anal. Calcd for $C_{20}H_{33}O_5SiBr$: C, 52.06; H, 7.21. Found: C, 52.30; H, 7.26.

20. To 0.050 g (0.14 mmol) of the *trans*-diol α-tetralone **18** were added 1.5 mL of dichloromethane, 60 μL (0.43 mmol, 3 equiv) of triethylamine, and 23 μL (0.29 mmol, 2 equiv) of methanesulfonyl chloride. The reaction mixture was stirred under nitrogen at room temperature for 0.5 h and then quenched by addition of 5% sodium bicarbonate solution. An extractive workup with methylene chloride gave a quantitative yield of crude mesylate which was used in the next step without purification. To the mesylate was added ca. 5 mg of *p*-toluenesulfonic acid and 1.5 mL of dimethylformamide, and the reaction was stirred at 60 °C under nitrogen for 18 h. The dimethylformamide was then removed at reduced pressure, and the residue was dissolved in dichloromethane. The workup yielded 0.055 g of a yellow oil which was purified by flash chromatography (5.5 in. × 0.5 in.). Elution proceeded as follows: 50 mL of 12% E/H, nil; 75 mL of 12% E/H, 0.026 g (57%) of **20** as a yellow oil [IR (neat) 2940 (w), 1695 (m), 1570 (w), 1465 (m), 1430 (w), 1395 (w), 1290 (m), 1260 (br, m), 1150 (m), 1050 (m), 1025 (w); ^{1}H NMR 0.88 (t, J = 7.5 Hz, 3 H), 1.40–2.10 (strong m, 2 H), 3.73 (s, 1 H, disappeared with D_2O), 3.80 (s, 3 H), 3.88 (s, 3 H), 6.48 (AB, J = 9.8 Hz, $\Delta\nu$ = 35.3 Hz, 2 H), 7.20 (s, 1 H); ^{13}C NMR 8.0, 33.7, 56.4, 62.3, 79.7, 118.1, 118.4, 121.1, 127.3, 136.5, 139.2, 150.2, 151.3, 203.6 ppm; exact mass calcd for $C_{11}H_{15}O_4Br$ m/e 326.0154, obsd m/e 326.0161.

When the cis isomer **9** was reacted as above, **20** was obtained in 43% yield.

7-Bromo-5,8-dimethoxy-2-ethyl-1-naphthol from 20. A mixture of 33 mg (0.10 mmol) of **20**, 13 mg (0.20 mmol, 2 equiv) of zinc–copper couple, 1.5 mL of tetrahydrofuran, 0.5 mL of acetic acid, and 0.1 mL of water was stirred at room temperature for 10 h. The reaction mixture was neutralized with a saturated sodium bicarbonate solution. Extractive workup with methylene chloride yielded a yellow oil which was purified by flash chromatography (5.5 in. × 0.5 in. silica gel column). Elution proceeded as follows: 25 mL of 1% E/H, nil; 50 mL of 1% E/H, 22 mg of the naphthol as a clear oil which crystallized with E/H to afford white crystals which showed spectroscopic properties identical with those reported earlier, mp 45.8–46.8 °C.

22a. A mixture of 0.10 g (0.29 mmol) of **18** and 0.023 g (1.58 mmol) of sodium borohydride in 2 mL of methanol was stirred at 0 °C for 1 h. The reaction was quenched by the addition of 1 mL of acetone and 1 mL of a 5% sodium hydroxide solution. The reaction mixture was partially concentrated at 50 °C, and the product was extracted with dichloromethane. The workup gave 0.093 g (92%) of the triol **22a** as a white foam. The product can be crystallized from chloroform to yield white needles, mp 145.8–146.8 °C. The crystals sometimes melt above 120 °C and then resolidify and melt at 145–147 °C: IR (KBr) 3510 (m), 3420 (s), 3360 (m), 2960 (m), 1470 (s), 1430 (m), 1375 (m), 1290 (m), 1235 (s), 1060 (m), 1030 (s), 990 (s); ^{1}H NMR (see text); ^{13}C NMR 6.5, 31.4, 35.8, 56.1, 62.2, 63.8, 68.1, 74.0, 115.1, 116.2, 127.9, 133.4, 150.2, 154.2 ppm; exact mass calcd for $C_{14}H_{19}O_5Br$ m/e 346.0416, obsd m/e 346.0424.

Acknowledgment. We gratefully acknowledge primary support from the National Institutes of Health and partial support from the National Science Foundation.

Registry No. 1, 93-02-7; **2**, 83436-65-1; *cis*-**3**, 84944-53-6; *trans*-**3**, 84944-64-9; **4**, 84944-54-7; **5**, 84944-55-8; **6**, 84959-61-5; **7**, 83923-01-7; **8**, 83923-03-9; **9**, 83923-02-8; **10**, 83923-04-0; **11**, 83923-05-1; **12**, 84944-56-9; **13**, 83923-09-5; **14**, 83923-08-4; **15**, 83923-07-3; **16**, 83923-06-2; **17**, 83923-10-8; **18**, 84944-57-0; **19**, 84944-58-1; **20**, 84944-59-2; **21**, 84944-60-5; **22a**, 84944-61-6; **22b**, 84944-62-7; $H_2C{=}C(OCH_3)CH_3$, 116-11-0; $PhB(OH)_2$, 98-80-6; butyric acid, 107-92-6; 7-bromo-5,8-dimethoxy-2-ethyl-1-naphthol, 84944-63-8.

Metacyclophanes and Related Compounds. 8. Preparation and Reaction of 8,16-Diformyl[2.2]metacyclophanes[1]

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Received August 17, 1982

As key synthetic compounds, 8,16-diformyl[2.2]metacyclophanes **4a,b** were prepared from the corresponding 8,16-bis(bromomethyl)metacyclophanes **1a,b** by Kröhnke's procedure. From compounds **4**, [2.2]metacyclophanes having CN, COOH, CH(OH)R, or CH=CHR groups at the internal positions were easily prepared. Effects of ring current of the opposite aromatic rings on chemical shifts of protons of the internal groups of the metacyclophanes prepared in this work are also discussed.

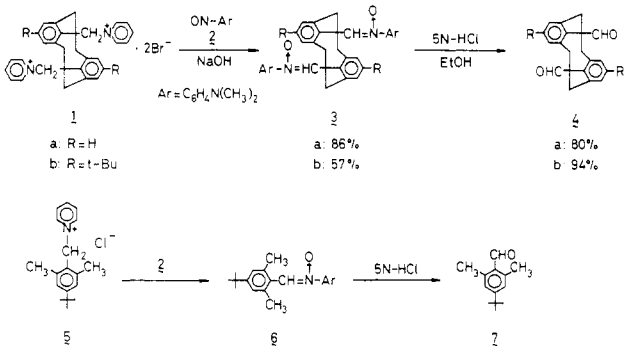
Although some [2.2]metacyclophanes (MCP) having functions such as alkyl-,[2-5] halomethyl-,[5] alkoxy-,[6] and hydroxy groups[7] at their 8,16-positions have been reported, there are few reports concerning the preparation of [2.2]MCP having other functions at these internal positions.

We report the preparation of the title compounds **4**, which seem to be an important synthetic key compounds

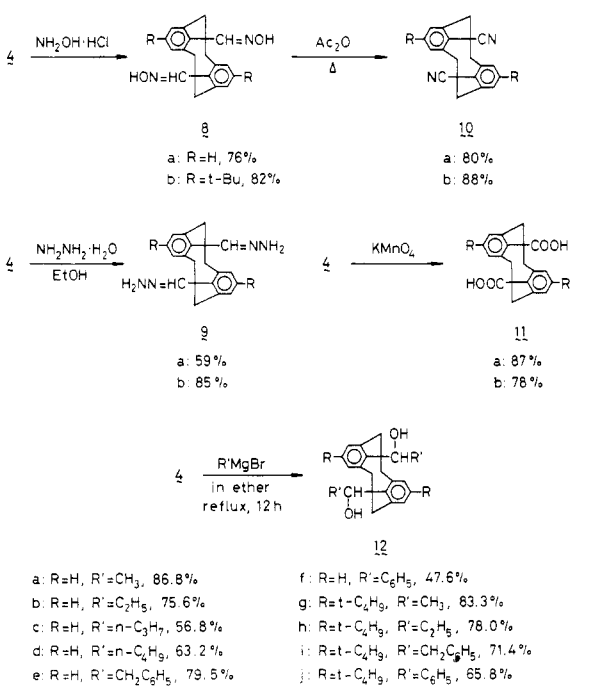
(1) Part 7: Tashiro, M.; Koya, K.; Yamato, T. *J. Am. Chem. Soc.* **1982**, *104*, 3707.
(2) Boekelheide, V.; Phillips, J. B. *J. Am. Chem. Soc.* **1967**, *89*, 1695.
(3) Boekelheide, V.; Miyasaka, T. *J. Am. Chem. Soc.* **1970**, *92*, 1709.
(4) Boekelheide, V.; Hylton, T. A. *J. Am. Chem. Soc.* **1970**, *92*, 3669.
(5) Tashiro, M.; Yamato, T. *J. Org. Chem.* **1981**, *46*, 1543.
(6) Tashiro, M.; Yamato, T. *J. Org. Chem.* **1981**, *46*, 4556.
(7) Tashiro, M.; Yamato, T. *Chem. Lett.* **1980**, 1127.

0022-3263/83/1948-1461$01.50/0

Scheme I



Scheme II



for the preparation of [2.2]MCP having various functions at 8,16-positions.

Results and Discussion

Preparation and Reaction of 4. The reaction of 8,16-bis(pyridiniomethyl)-2,7-di-*tert*-butyl- (**1a**),[6] or 2,7-di-*tert*-butyl[2.2]metacyclophane dibromide (**1b**)[6] with *p*-nitrosodimethylaniline (**2**) was carried out at room temperature according to the Kröhnke's procedure to give the corresponding dinitrone **3a** or **3b** in good yield (Scheme I). In contrast to the reaction of **2** with the model compound **5**,[6] which required 90 min for completion,[8] reaction with **1a** or **1b** was complete in 5 min.

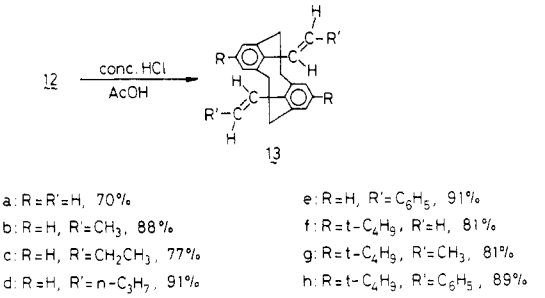
When **3a,b** were treated with 5 N HCl solution at room temperature for a few minutes, the desired 8,16-diformyl[2.2]MCP **4a,b** were obtained in good yields. Similarly, compound **7** was obtained in good yield.

Compounds **4a,b** reacted with carbonyl reagents such as hydroxyamine and hydrazine hydrate and with $KMnO_4$ to afford the corresponding dioximes **8a,b**, dihydrazones **9a,b**, and dicarboxylic acids **11a,b**, respectively, in good yields.

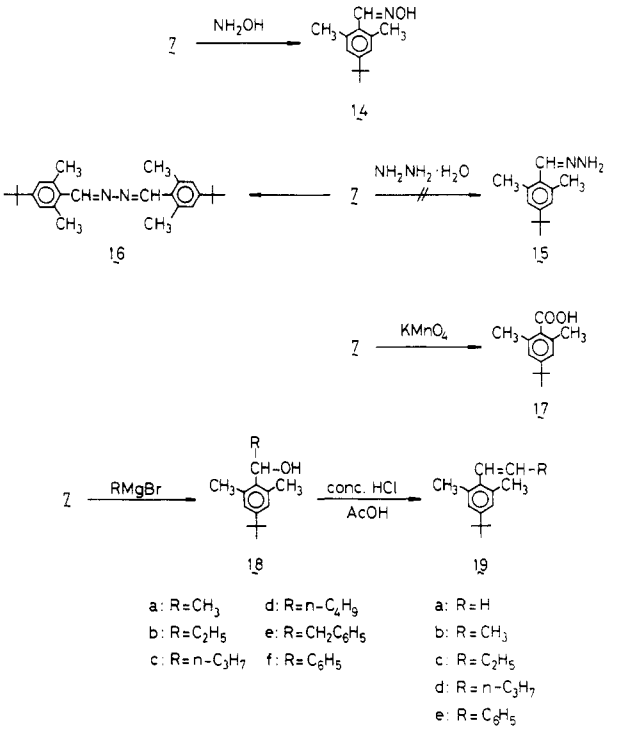
When **8a,b** were treated with boiling acetic anhydride, the corresponding dinitriles **10a,b** were obtained in good yields.

(8) Kröhnke, F. *Angew. Chem.* **1953**, *65*, 605.

Scheme III



Scheme IV



Reaction of **4** with some Grignard reagents afforded the corresponding dialcohols **12** in good yields, respectively (Scheme II). The existence of these compounds (**12a–j**) as mixture of isomers, although they were purified several times by recrystallization, was indicated by their broad melting points and NMR spectra (vide infra).

Treatment of **12a–j** with concentrated HCl in acetic acid gave the expected **13a–h**, respectively, in good yields (Scheme III). Their structures were determined by analysis of NMR spectral data.

2-Substituted 5-*tert*-butyl-*m*-xylenes (BMX) corresponding to the MCPs described were prepared from **7** as a standard reference materials (Scheme IV). However, reaction of **7** with hydrazine hydrate did not give the expected hydrazone, but the corresponding azine **16** was formed.

^{1}H NMR Spectra. The chemical shifts of only the internal protons of the substituents in positions 8 and 16 of MCP are summarized in Tables I–III. The corresponding proton signals of the corresponding substituents in position 2 of BMX and the differences ($\Delta\delta$) of the chemical shifts of MCP from those of BMX are also shown in these tables.

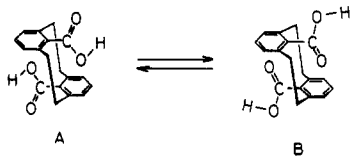
The effect of the ring current of the opposite aromatic ring on the internal protons may be judged by the values of the shift differences ($\Delta\delta$) since there is no ring current of the opposite aromatic ring in the BMX system. The data of the Table I show that the protons of the internal

Table I. Chemical Shifts of the Protons of the Internal Groups of 4a,b, 8a,b, 9a,b, and 11a,b

compd	group	chemical shifts, ppm	$\Delta\delta$ [a]
4a	CHO	8.84	1.68
4b	CHO	8.90	1.62
7	CHO	10.52	
8a	CH=NOH	6.26	2.01
	CH=NOH	10.54	0.54
8b	CH=NOH	6.31	1.96
	CH=NOH	10.46	0.62
14	CH=NOH	8.27	
	CH=NOH	11.08	
9a	$CH=NNH_2$	6.04	
	$CH=NNH_2$	4.92	
9b	$CH=NNH_2$	6.00	
	$CH=NNH_2$	4.87	
11a	COOH	11.50	−1.46
11b	COOH	11.16	−1.12
17	COOH	10.04	

[a] $\Delta\delta = \delta_{BMX} - \delta_{MCP}$.

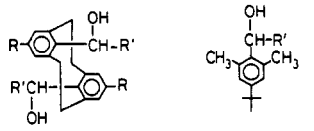
positions of most of the MCP systems are clearly shifted upfield by the ring current of the opposite aromatic ring. However, the proton signals of carboxylic acids of MCP were observed at ca. 11.0–11.5 ppm, and the calculated values of $\Delta\delta$(COOH) were −1.1 to −1.5 ppm. These results suggest that the protons of the carboxylic acids of MCP were in a shielding region of the ring current of the opposite aromatic rings; that is, it is concluded that **9a,b** have the conformers A and B and that **11a** and **11b** might exist in conformer B.



A B

As are shown in the Tables II and III, the internal proton signals of **12a–j** and **13a–h** were also affected by the ring current of the opposite aromatic rings. The data of the

Table II. Chemical Shifts of the Internal Protons of 12



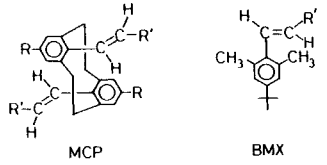
MCP BMX

		OH			CH			ω-CH_3		
R	R'	δ^{OH}_{MCP}	δ^{OH}_{BMX}	$\Delta\delta$(OH)	δ^{CH}_{MCP}	δ^{CH}_{BMX}	$\Delta\delta$(CH)	$\delta^{CH_3}_{MCP}$	$\delta^{CH_3}_{BMX}$	$\Delta\delta(CH_3)$
H	CH_3	0.87	1.83	0.96	3.68-4.04 (3.86)[a]	5.28	1.42	0.70 (d)[b] 0.73 (d)	1.48 (d)	0.78 0.75
H	C_2H_5	1.04	2.05	1.01	3.60-4.00 (3.80)	4.94	1.14	0.48 (br t)	0.92 (t)	0.44
H	n-C_3H_7	0.83	1.80	0.97	3.64-4.03 (3.84)	5.09	1.25	0.67 (br t)	0.94 (t)	0.27
H	n-C_4H_9	0.84	1.81	0.97	3.68-4.03 (3.86)	5.08	1.22	0.73 (br t)	0.91 (t)	0.18
t-Bu	CH_3	0.87	1.83	0.96	3.80-4.02 (3.91)	5.28	1.37	0.72 (d) 0.74 (d)	1.48 (d)	0.76 0.74
t-Bu	C_2H_5	0.88	2.05	1.17	3.60-4.03 (3.82)	4.94	1.12	0.48 (br t)	0.92 (t)	0.44
H	C_6H_5	1.17 1.19	2.17	1.00 0.98	4.50 4.58	6.28	1.78 1.70			
t-Bu	C_6H_5	1.16 1.19	2.17	1.01 0.98	4.48 4.60	6.28	1.80 1.68			
H	$CH_2C_6H_5$	0.86	1.78	0.92	3.70-4.20 (3.95)	5.24	1.29			
t-Bu	$CH_2C_6H_5$	0.85	1.78	0.93	3.68-4.10 (3.89)	5.24	1.35			

		CH_2			aromatic protons: ortho			aromatic protons: meta + para		
R	R'	$\delta^{CH_2}_{MCP}$	$\delta^{CH_2}_{BMX}$	$\Delta\delta(CH_2)$	$\delta^{H_o}_{MCP}$	$\delta^{H_o}_{BMX}$	$\Delta\delta(H_o)$	$\delta^{H_{pm}}_{MCP}$	$\delta^{H_{pm}}_{BMX}$	$\Delta\delta(H_{pm})$
H	CH_3									
H	C_2H_5		[c]							
H	n-C_3H_7		[c]							
H	n-C_4H_9		[c]							
t-Bu	CH_3									
t-Bu	C_2H_5		[c]							
H	C_6H_5				6.54-6.76 (6.65)	7.16-7.32 (7.24)	0.59	6.92-7.28 (7.10)	7.16-7.32 (7.24)	0.14
t-Bu	C_6H_5				6.52-6.68 (6.60)	7.16-7.32 (7.24)	0.64	6.92-7.16 (7.04)	7.16-7.32 (7.24)	0.20
H	$CH_2C_6H_5$	2.00-2.40 (2.2)	3.18 2.92	0.98 0.92	6.64-6.82 (6.73)	7.16-7.28 (7.22)	0.49	6.84-7.20 (7.02)	7.16-7.28 (7.22)	0.20
t-Bu	$CH_2C_6H_5$	2.10-2.32 (2.21)	3.18 2.92	0.97 0.71	6.56-6.76 (6.66)	7.16-7.28 (7.22)	0.56	6.80-7.15 (6.98)	7.16-7.15 (7.22)	0.24

[a] Midpoint values of multiplets in parentheses. [b] d = doublet, br t = broad triplet, t = triplet. [c] Although signals of methylene protons were observed, their values were not shown here (see Experimental Section) since they include both signals of internal and bridged methylene protons.

Table III. Chemical Shifts of the Internal Protons of 8,16-Alkenyl MCP



		α-CH=			β-CH=			ω-CH_3			CH_2			aromatic		
R	R′	δ_{MCP}	δ_{BMX}	Δδ-(α-CH=)	δ_{MCP}	δ_{BMX}	Δδ-(β-CH=)	δ_{MCP}	δ_{BMX}	Δδ-(ω-CH_3)	δ_{MCP}	δ_{BMX}	Δδ-(CH_2)	δ^{ArH}_{MCP}	δ^{ArH}_{BMX}	Δδ-(ArH)
H	H	4.82	6.64	1.82	4.45	5.22	0.77									
					4.65	5.47	0.82									
H	CH_3	4.42	6.28	1.86	4.81	5.64	0.83	1.42	1.88	0.46						
H	C_2H_5	4.41	6.26	1.85	4.93	5.66	0.73	0.84	1.08	0.24	1.63–1.92 (1.78)[a]	2.06–2.40 (2.23)	0.45			
H	n-C_3H_7	4.40	6.30	1.90	4.88	5.61	0.73	0.84	0.96	0.12	1.07–1.42 (1.25)	1.38–1.60 (1.49)	0.24			
											1.62–1.82 (1.72)	2.08–2.40 (2.24)	0.52			
H	C_6H_5	5.20	7.09	1.87	5.82	6.57	0.75							7.00–7.35 (7.18)	7.12–7.52 (7.32)	0.14
t-C_4H_9	H	4.91	6.64	1.73	4.48	5.22	0.74									
					4.62	5.47	0.85									
t-C_4H_9	CH_3	4.52	6.28	1.76	4.86	5.64	0.75	1.42	1.88	0.46						
t-C_4H_9	C_6H_5	5.39	7.09	1.70	5.83	6.57	0.74							7.00–7.20 (7.10)	7.12–7.52 (7.32)	0.22

[a] Midpoint values of multiplets in parentheses.

Table II show that most of the calculated values of $\Delta\delta$(OH) are in narrow range of 0.9–1.0 ppm though R and R′ groups are widely changed. Similar results for $\Delta\delta$(CH) were observed in the range of 1.2–1.8 ppm. The values of $\Delta\delta(\omega\text{-}CH_3)$ are affected by the length of the chain of the R′ groups but not by the kind of R′ groups; that is, the values of $\Delta\delta(\omega\text{-}CH_3)$ with one, two, three, and four atoms removed are ca. 0.8, ca. 0.4, ca. 0.3, and ca. 0.2, respectively. Similar results were observed for the values of $\Delta\delta(\omega\text{-}CH_3)$ in the alkenyl MCP (**13**) as shown in Table III. That is, the values for three, four, and five atoms removed are ca. 0.45, ca. 0.2, and ca. 0.1 ppm, respectively.

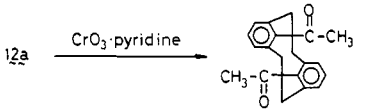
The values described above agreed with those of $\Delta\delta(CH_3)$ in alkyl- and alkoxymethyl MCP; the values for one, two, three, four, and five atoms removed were 0.75, ca. 0.5, ca. 0.3, ca. 0.2, and ca. 0.13, respectively.[6]

The data of Table II show that most of the calculated values of $\Delta\delta(\alpha\text{-}CH{=})$ and $\Delta\delta(\beta\text{-}CH{=})$ are in a narrow range of 1.7–1.9 ppm, and 0.7–0.8 ppm, respectively. The values of $\Delta\delta$(CH=) are also affected by the distance from the attached aromatic ring.

There are two kinds of internal aromatic proton signals of **12a–j** at the 6.5–6.8-ppm and 6.8–7.2-ppm range in ratio of 2:3 (Table II). The latter signals might belong to the protons of the ortho positions of the internal aromatic rings. The calculated values of $\Delta\delta(ArH_o)$ and $\Delta\delta(ArH_{pm})$ are ca. 0.5–0.6 ppm and ca. 0.1–0.2 ppm, respectively. While the values of $\Delta\delta$(ArH) for **13** are ca. 0.1–0.2 ppm (Table III).

The results described above show that the effect of the ring current of the opposite aromatic ring on the internal protons on the substituents decreases gradually with increasing distance from the attached aromatic ring.

It should be noted that two kinds of ω-methyl, OH, and methine protons are observed in some cases as shown in Table II. These results, together with the broad melting points and satisfactory elemental and mass spectral analyses, indicate compounds **12a–j** to be mixtures of isomers. Confirmation of this is provided by the sharp melting point and ^{1}H NMR spectrum of **20**,[9] obtained by the oxidation of **12a**, which showed the internal methyl group signal as a singlet at 1.84 ppm.



20

From the above results, it is concluded that compounds **12a–j** might be a mixture of meso and racemic forms but not the following mixture of conformeric isomers; that is, the single bond between the aromatic carbon and α-carbon of the internal group could freely rotate.

Experimental Section

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

Reaction of 8,16-Bis(pyridiniomethyl)[2.2]metacyclophane Dibromide (1a) with *p*-Nitrosodimethylaniline (2). To a solution of 4.7 g (8 mmol) of **1a**, 2.4 g (16 mmol) of *p*-nitrosodimethylaniline (**2**) in 12 mL of water, and 80 mL of ethanol was added 20 mL of a 1 N sodium hydroxide solution while stirring with a magnetic stirrer at room temperature. After 5 min, the green solution turned to pale yellow and a pale yellow solid precipitated. The pale yellow solid was filtered and washed with water, methyl alcohol, and hexane to give 3.66 g (86.0%) of **3a**, pale yellow prisms: mp 273–276 °C dec; IR (KBr) 3080, 3040, 2920, 2800, 1600, 1570, 1510, 1440, 1360, 1230, 1160, 1105, 880, 815, 790, 740 cm^{-1}; MS, *m/e* 532 (M^+). Anal. Calcd for $C_{34}H_{36}O_2N_4{\cdot}H_2O$: C, 74.15; H, 6.96; N, 10.17. Found: C, 74.36; H, 6.65; N, 9.84. Similarly, **3b** was synthesized in the same manner as described above. **3b**, pale yellow prisms: mp >300 °C; IR (KBr) 3060, 2940, 1600, 1505, 1360, 1230, 1155, 1100, 865, 810 cm^{-1}; MS, *m/e* 644 (M^+). Anal. Calcd for $C_{42}H_{52}O_2N_4$: C, 78.22; H, 8.13; N, 8.69. Found: C, 77.90; H, 8.10; N, 8.50.

Preparation of 8,16-Diformyl[2.2]metacyclophane (4a). To a solution of 3.66 g (6.88 mmol) of **3a** in 80 mL of ethanol was added 20 mL of a 5 N HCl solution while stirring with a magnetic stirrer at room temperature. After a few minutes, the pale yellow suspension turned to reddish brown and a pale yellow solid precipitated. The pale yellow solid was filtered and recrystallized from ethanol to give 1.46 g (80.4%) of **4a**, pale yellow prisms (EtOH): mp 275–278 °C dec; IR (KBr) 3040, 2920, 2890, 2760, 1660, 1573, 1460, 1215, 1180, 1160, 850, 810, 780, 740, 700 cm^{-1}; NMR ($CDCl_3$) δ 2.90–3.80 (8 H, m), 7.13 (6 H, s), 8.84 (2 H, s); MS, *m/e* 207 ($M^+ - C_2HO_2$). Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.46; H, 6.21.

Preparation of 5,13-Di-*tert*-butyl-8,16-diformyl[2.2]metacyclophane (4b). To a suspension of 4.5 g (6.99 mmol) of **3b** in 80 mL of ethanol was added 20 mL of a 5 N HCl solution while stirring with a magnetic stirrer at room temperature. After a few minutes, the reaction mixture was treated as described above to give 2.46 g (93.5%) of **4b**, pale yellow prisms (EtOH): mp 284–287 °C dec; IR (KBr) 3050, 2940, 2870, 2760, 1665, 1585, 1440, 1360, 1215, 1080, 890, 760 cm^{-1}; NMR ($CDCl_3$) δ 1.29 (18 H, s), 2.82–3.80 (8 H, m), 7.12 (4 H, s), 8.90 (2 H, s); MS, *m/e* 377 (M^+). Anal. Calcd for $C_{26}H_{32}O_2$: C, 82.93; H, 8.57. Found: C, 82.71; H, 8.77.

Preparation of 2,6-Dimethyl-4-*tert*-butylbenzaldehyde (7). To a solution of 5.5 g (18.7 mmol) of **5** and 2.81 g (18.7 mmol) of *p*-nitrosodimethylaniline (**2**) in 40 mL of ethanol was added 20 mL of a 1 N NaOH solution while stirring with a magnetic stirrer at room temperature. After 90 min, 10 mL of a 5 N HCl solution was added to the reaction mixture while stirring at room temperature. After 30 min, the reaction mixture was extracted with dichloromethane and the dichloromethane extract was washed with water, dried over sodium sulfate, and evaporated in vacuo to give the residue, which was recrystallized from hexane to afford 2.5 g (70.4%) of **7**, colorless prisms (hexane): mp 61–62 °C; IR (KBr) 3050, 2960, 2790, 1680, 1600, 1410, 1375, 1230, 1115, 870, 760 cm^{-1}; NMR ($CDCl_3$) δ 1.31 (9 H, s), 2.60 (6 H, s), 7.05 (2 H, s), 10.52 (1 H, s); MS, *m/e* 190 (M^+). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 81.75; H, 9.54.

Reaction of 4a with Hydroxylamine. A mixture of 200 mg (0.76 mmol) of **4a**, 140 mg (2 mmol) of hydroxylamine hydrochloride, 80 mg (2 mmol) of sodium hydroxyde, and 20 mL of ethanol was refluxed for 2 h. After the reaction mixture was cooled, the solvent was removed in vacuo to leave the residue, which was washed with water and recrystallized from ethanol to give 170 mg (76.1%) of **8a**, colorless prisms (EtOH): mp 275–285 °C dec; IR (KBr) 3220, 3040, 2930, 1570, 1460, 1440, 1305, 1300, 1180, 970, 920, 860, 780, 740, 715 cm^{-1}; NMR (Me_2SO-d_6) δ 2.81–3.01 (8 H, m), 6.26 (2 H, s), 6.90–7.20 (6 H, m), 10.54 (2 H, s); MS, *m/e* 294 (M^+). Anal. Calcd for $C_{18}H_{18}O_2N_2$: C, 73.41; H, 6.16; N, 9.56. Found: C, 73.42; H, 6.22; N, 9.11.

Reaction of 4b with Hydroxylamine. A mixture of 200 mg (0.532 mmol) of **4b**, 111.2 mg (1.60 mmol) of hydroxylamine hydrochloride, 64 mg (1.60 mmol) of sodium hydroxide, and 20 mL of ethanol was refluxed for 2 h.

The reaction mixture was treated as described above to give 180 mg (83.3%) of **8b** colorless prisms (EtOH): mp 271–274 °C

(9) Pale brown prisms (hexane), mp 218–220 °C. The oxidation of **12** will be reported in detail in the near future.

dec; IR (KBr) 3440, 3260, 3040, 2950, 2860, 1580, 1480, 1445, 1300, 1220, 945, 920, 885, 860, 835, 735 cm^{-1}; NMR (Me_2SO-d_6) δ 1.30 (18 H, s), 2.70–3.05 (8 H, m), 6.31 (2 H, s), 7.11 (4 H, s), 10.46 (2 H, br s); MS, m/e 406 (M^+). Anal. Calcd for $C_{26}H_{34}N_2O_2$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.69; H, 8.44; N, 6.78.

Reaction of 4a with Hydrazine Hydrate. A mixture of 140.4 mg (0.532 mmol) of **4a**, 213 mg (4.26 mmol) of hydrazine hydrate ($NH_2NH_2 \cdot H_2O$), and 20 mL of ethanol was refluxed for 12 h. After the reaction mixture was cooled, the solvent was removed in vacuo to leave the residue, which was washed with water and hexane to give 92 mg (59.4%) of **9a**, colorless prisms: mp >300 °C; IR (KBr) 3390, 3250, 3050, 2930, 1580, 1510, 1440, 1180, 1100, 1080, 920, 780, 740 cm^{-1}; NMR ($CDCl_3$) δ 2.40–3.40 (8 H, m), 4.92 (4 H, br s), 6.04 (2 H, s), 6.55–7.42 (6 H, m); MS, m/e 292 (M^+). Anal. Calcd for $C_{18}H_{20}N_4$: C, 73.94; H, 6.90; N, 19.16. Found: C, 73.65; H, 6.89; N, 19.20.

Reaction of 4b with Hydrazine Hydrate. A mixture of 200 mg (0.532 mmol) of **4b**, 213 mg (4.26 mmol) of hydrazine hydrate ($NH_2NH_2 \cdot H_2O$), and 20 mL of ethanol was refluxed for 12 h. The reaction mixture was treated as described above to give 182 mg (84.7%) of **9b** colorless prisms: mp 253–256 °C dec; IR (KBr) 3400, 3270, 3040, 2950, 2850, 1585, 1470, 1450, 1440, 1380, 1355, 1195, 920, 885, 720 cm^{-1}; NMR ($CDCl_3$) δ 1.30 (18 H, s), 2.73–3.18 (8 H, m), 4.87 (4 H, br s), 6.00 (2 H, s), 7.09 (4 H, s); MS, m/e 404 (M^+). Anal. Calcd for $C_{26}H_{36}N_4$: C, 77.18; H, 8.97; N, 13.85. Found: C, 76.53; H, 8.98; N, 13.92.

Preparation of 8,16-Dicyano[2.2]metacyclophane (10a). A suspension of 100 mg (0.34 mmol) of **8a** in 10 mL of acetic anhydride was refluxed for 3 h. On cooling, a crystalline material was separated to give **10a**, colorless prisms (Ac_2O): mp >300 °C; IR (KBr) 3050, 2940, 2860, 2200, 1580, 1455, 1440, 1180, 1160, 1000, 895, 795, 770, 740 cm^{-1}; NMR ($CDCl_3$) δ 2.80–3.48 (8 H, m), 7.36–7.48 (6 H, m); MS, m/e 258 (M^+). Anal. Calcd for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.85. Found: C, 83.17; H, 5.47; N, 11.40.

Preparation of 5,13-Di-*tert*-butyl-8,16-dicyano[2.2]metacyclophane (10b). A suspension of 100 mg (0.245 mmol) of **8b** in 10 mL of acetic anhydride was refluxed for 3 h. The reaction mixture was treated as described above to give 80 mg (88.2%) of **10b** colorless prisms (Ac_2O): mp >300 °C; IR (KBr) 3040, 2940, 2850, 2200, 1590, 1430, 1355, 1220, 1185, 890, 865, 745, 685 cm^{-1}; NMR ($CDCl_3$) δ 1.33 (18 H, s), 2.84–3.35 (8 H, m), 7.38 (4 H, s); MS, m/e 370 (M^+). Anal. Calcd for $C_{26}H_{30}N_2$: C, 84.05; H, 8.14; N, 7.54. Found: C, 84.19; H, 8.17; N, 7.42.

Preparation of [2.2]Metacyclophane-8,16-dicarboxylic Acid (11a). To a solution of 100 mg (0.379 mmol) of **4a** in 20 mL of acetone was added 8 mL of 3.2% patassium permanganate solution with stirring during the course of 1 h under reflux conditions. After filtration, the filtrate was made acidic and 98 mg (87.3%) of a crystalline material was collected. **11a**, colorless prisms: mp >300 °C; IR (KBr) 3040, 2930, 2860, 2770, 2600, 1780, 1750, 1575, 1450, 1280, 1250, 1115, 940, 880, 780, 720, 710 cm^{-1}; NMR (Me_2SO-d_6) δ 2.71–3.86 (8 H, m), 6.88–7.24 (6 H, m), 11.50 (2 H, br s); MS, m/e 296 (M^+). Anal. Calcd for $C_{18}H_{16}O_4 \cdot 0.25H_2O$: C, 71.87; H, 5.52. Found: C, 71.73; H, 5.59.

Preparation of 5,13-Di-*tert*-butyl[2.2]metacyclophane-8,16-dicarboxylic Acid (11b). To a solution of 142.5 mg (0.379 mmol) of **4b** in 20 mL of acetone was added 8 mL of 3.2% of potassium permanganate solution with stirring during the course of 1 h under reflux conditions. After filtration, the filtrate was treated as described above to give 120 mg (77.6%) of **11b**, colorless prisms: mp >300 °C; IR (KBr) 3050, 2960, 2870, 2530, 1660, 1580, 1440, 1280, 1240, 1210, 1130, 890, 860, 765, 710 cm^{-1}; NMR (Me_2SO-d_6) δ 1.27 (9 H, s), 2.76–3.85 (8 H, m), 7.04 (4 H, s), 11.16 (2 H, br s); MS, m/e 408 (M^+). Anal. Calcd for $C_{26}H_{32}O_4$: C, 76.44; H, 7.90. Found: C, 76.93; H, 7.95.

Reaction of 4a with Methylmagnesium Bromide. To a solution of MeMgBr [prepared from 1.14 g (12 mmol) of methyl bromide and 243 mg (10 mmol) of magnesium] in 20 mL of ether was added a solution of 264 mg (1 mmol) of **4a** in 10 mL of ether dropwise under the conditions of gentle refluxing. After the reaction mixture was refluxed for an additional 12 h, it was quenched with 10% ammonium chloride and extracted with dichloromethane. The dichloromethane extract was dried over sodium sulfate and evaporated in vacuo to leave the residue, which was recrystallized from hexane to give 257 mg (86.8%) of **12a**, pale yellow prisms (hexane): mp 190–195 °C; IR (KBr) 3540, 3480, 3440, 3040, 2950, 2910, 1560, 1435, 1315, 1250, 1170, 1090, 1030, 990, 880, 795, 760, 740 cm^{-1}; NMR ($CDCl_3$) δ 0.70, 0.73 (6 H, d, J = 7 Hz), 0.87 (2 H, br s), 2.68–3.10 (6 H, m), 3.68–4.04 (4 H, m), 6.88–7.22 (6 H, m); MS, m/e 252 ($M^+ - C_2H_4O$), 207 ($M^+ - C_4H_9O_2$). Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.71; H, 8.04.

Reaction of 4a with Ethylmagnesium Bromide. To a solution of EtMgBr [prepared from 1.31 g (12 mmol) of ethyl bromide and 243 mg (10 mmol) of magnesium] in 20 mL of ether was added a solution of 264 mg (1 mmol) of **4a** in 10 mL of ether dropwise under the conditions of gentle refluxing. After the reaction mixture was refluxed for an additional 12 h, it was treated as described above to give 245 mg (75.6%) of **12b**, pale yellow prisms (hexane): mp 185–190 °C; IR (KBr) 3500, 3450, 3040, 2970, 2930, 2880, 1570, 1440, 1330, 1220, 1170, 1150, 1100, 1045, 980, 850, 885, 970, 840, 790 cm^{-1}; NMR ($CDCl_3$) δ 0.48 (6 H, t, J = 7 Hz), 1.04 (2 H, s), 0.76–1.20 (4 H, m), 2.70–3.06 (6 H, m), 3.60–4.00 (4 H, m), 6.90–7.18 (6 H, m); MS, m/e 266 ($M^+ - C_3H_6O$), 207 ($C_6H_{13}O_2$). Anal. Calcd for $C_{22}H_{28}O_2$: C, 81.43; H, 8.70. Found: C, 81.97; H, 8.63.

Reaction of 4a with *n*-Propylmagnesium Bromide. To a solution of *n*-PrMgBr [prepared from 1.31 g (12 mmol) of *n*-propyl bromide and 243 mg (10 mmol) magnesium] in 20 mL of ether was added a solution of 264 mg (1 mmol) of **4a** in 10 mL of ether dropwise under the conditions of gentle refluxing. After the reaction mixture was refluxed for an additional 12 h, it was treated as described above to give 200 mg (56.8%) of **12c**, colorless prisms (hexane): mp 137–140 °C; IR (KBr) 3550, 3040, 2960, 1570, 1440, 1320, 1280, 1165, 1050, 1020, 995, 770, 730 cm^{-1}; NMR ($CDCl_3$) δ 0.67 (6 H, t, J = 7 Hz), 0.83 (2 H, s), 0.80–1.06 (8 H, m), 2.72–3.05 (6 H, m), 3.64–4.03 (4 H, m), 6.84–7.20 (6 H, m); MS, m/e 280 ($M^+ - C_4H_8O$), 207 ($M^+ - C_8H_{17}O_2$). Anal. Calcd for $C_{24}H_{32}O_2$: C, 81.77; H, 9.15. Found: C, 81.59; H, 9.26.

Reaction of 4a with *n*-Butylmagnesium Bromide. To a solution of *n*-BuMgBr [prepared from 1.64 g (12 mmol) of *n*-butyl bromide and 243 mg (10 mmol) of magnesium] in 20 mL of ether was added a solution of 264 mg (1 mmol) of **4a** in 10 mL of ether dropwise under the conditions of gentle refluxing. After the reaction mixture was refluxed for an additional 12 h, it was treated as described above to give 240 mg (63.2%) of **12d**, colorless prisms (hexane): mp 125–130 °C; IR (KBr) 3540, 3450, 3050, 2950, 2880, 1580, 1455, 1180, 1040, 1005, 785, 740 cm^{-1}; NMR ($CDCl_3$) δ 0.73 (6 H, t, J = 7 Hz), 0.84 (2 H, br s), 0.80–1.20 (12 H, m), 2.76–3.05 (6 H, m), 3.68–4.03 (4 H, m), 6.88–7.24 (6 H, m); MS, m/e 294 ($M^+ - C_5H_{10}O$), 208 ($M^+ - C_{10}H_{20}O_2$), 207 ($M^+ - C_{10}H_{21}O_2$). Anal. Calcd for $C_{26}H_{36}O_2$: C, 82.06; H, 9.54. Found: C, 82.34; H, 9.82.

Reaction of 4a with Benzylmagnesium Bromide. To a solution of $PhCH_2MgBr$ [prepared from 2.05 g (12 mmol) of benzyl bromide and 243 mg (10 mmol) of magnesium] in 20 mL of ether was added a solution of 264 mg (1 mmol) of **4a** in 10 mL of ether dropwise under the conditions of gentle refluxing. After the reaction mixture was refluxed for an additional 12 h, it was treated as described above to give 310 mg (79.5%) of **12e**, pale yellow prisms (hexane): mp 168–173 °C; IR (KBr) 3540, 3040, 2910, 1595, 1490, 1445, 1320, 1280, 1180, 1140, 1070, 1040, 795, 770, 740, 700 cm^{-1}; NMR ($CDCl_3$) δ 0.86 (2 H, br s), 2.00–2.40 (4 H, m), 2.70–3.12 (6 H, m), 3.70–4.20 (4 H, m), 6.64–6.82 (4 H, m), 6.84–7.20 (12 H, m); MS, m/e 328 ($M^+ - C_8H_8O$), 207 ($M^+ - C_{16}H_{17}O_2$). Anal. Calcd for $C_{32}H_{32}O_2$: C, 85.68; H, 7.19. Found: C, 85.68; H, 7.19.

Reaction of 4a with Phenylmagnesium Bromide. To a solution of PhMgBr [prepared from 1.88 g (12 mmol) of bromobenzene and 243 mg (10 mmol) of magnesium] in 20 mL of ether was added a solution of 264 mg (1 mmol) of **4a** in 10 mL of ether dropwise under the conditions of gentle refluxing. After the reaction mixture was refluxed for an additional 12 h, it was treated as described above to give 200 mg (47.6%) of **12f**, colorless prisms (hexane:benzene, 1:1): mp 246–250 °C; IR (KBr) 3350, 3450, 3040, 2940, 1565, 1490, 1445, 1160, 1040, 780, 760, 740, 700, 670 cm^{-1}; NMR ($CDCl_3$) δ 1.17, 1.19 (2 H, d, J = 5 Hz), 2.51–2.76 (4 H, m), 2.80–3.10 (2 H, m), 3.80–4.10 (2 H, m), 4.50, 4.58 (2 H, d, J = 5 Hz), 6.54–6.76 (4 H, m), 6.92–7.28 (6 H, m), 7.30–7.36 (2 H, m); MS, m/e 402 ($M^+ - H_2O$), 384 ($M^+ - 2H_2O$). Anal. Calcd for $C_{30}H_{28}O_2$: C, 85.68; H, 6.72. Found: C, 86.02; H, 6.88.

Reaction of 4b with Methylmagnesium Bromide. To a solution of MeMgBr [prepared from 1.14 g (12 mmol) of methyl bromide and 243 mg (10 mmol) of magnesium] in 20 mL of ether

was added a solution of 376 mg (1 mmol) of **4b** in 10 mL of ether dropwise under the conditions of gentle refluxing. After the reaction mixture was refluxed for an additional 12 h, it was treated as described above to give 340 mg (83.3%) of **12g**, pale yellow prisms (hexane): mp 236–239 °C; IR (KBr) 3510, 3040, 2950, 2850, 1580, 1450, 1355, 1320, 1260, 1205, 1100, 1040, 1005, 895, 860, 755 cm^{-1}; NMR ($CDCl_3$) δ 0.72, 0.74 (6 H, d, J = 7 Hz), 0.87 (2 H, br s), 1.32 (18 H, s), 2.72–2.96 (6 H, m), 3.80–4.02 (4 N, m), 6.90–6.97 (2 H, m), 7.08–7.15 (2 H, m); MS, m/e 391 (M^+ – OH), 364 (M^+ – C_2H_4O), 347 (M^+ – $C_2H_5O_2$). Anal. Calcd for $C_{28}H_{40}O_2$: C, 82.30; H, 9.87. Found: C, 82.45; H, 9.93.

Reaction of 4b with Ethylmagnesium Bromide. To a solution of EtMgBr [prepared from 1.31 g (12 mmol) of ethyl bromide and 245 mg (10 mmol) of magnesium] in 20 mL of ether was added a solution of 376 mg (1 mmol) of **4b** in 10 mL of ether dropwise under the conditions of gentle refluxing. After the reaction mixture was refluxed for an additional 12 h, it was treated as described above to give 340 mg (78.0%) of **12h**, pale yellow prisms (hexane): mp 188–191 °C; IR (KBr) 3570, 3040, 2980, 1590, 1460, 1280, 1040, 980, 890, 860, 810, cm^{-1}; NMR ($CDCl_3$) δ 0.48 (6 H, t, J = 7 Hz), 0.88 (2 H, s), 0.80–1.00 (4 H, m), 1.32 (18 H, s), 2.72–2.95 (6 H, m), 3.60–4.03 (4 H, m), 6.84–6.96 (2 H, m), 7.04–7.16 (2 H, m); MS, m/e 378 (M^+ – C_3H_6O), 361 (M^+ – C_3H_6O, OH). Anal. Calcd for $C_{30}H_{44}O_2$: C, 82.51; H, 10.16. Found: C, 82.64; H, 10.15.

Reaction of 4b with Benzylmagnesium Bromide. To a solution of $PhCH_2MgBr$ [prepared from 2.05 g (12 mmol) of benzyl bromide and 243 mg (10 mmol) of magnesium] in 20 mL of ether was added a solution of 376 mg (1 mmol) of **4b** in 10 mL of ether dropwise under the conditions of gentle refluxing. After the reaction mixture was refluxed for an additional 12 hr, it was treated as described above to give 400 mg (71.4%) of **12i**, colorless prisms (hexane): mp 169–171 °C; IR (KBr) 3560, 3040, 2970, 1585, 1495, 1450, 1270, 1050, 860, 750, 725, 700 cm^{-1}; NMR ($CDCl_3$) δ 0.85 (2 H, br s), 1.22 (18 H, s), 2.10–2.32 (4 H, m), 2.64–3.00 (6 H, m), 3.68–4.10 (4 H, m), 6.56–6.76 (4 H, m), 6.80–7.15 (10 H, m); MS, m/e 524 (M^+ – $2H_2O$), 440 (M^+ – C_8H_8O). Anal. Calcd for $C_{40}H_{48}O_2$: C, 85.62; H, 8.63. Found: C, 85.92; H, 8.65.

Reaction of 4b with Phenylmagnesium Bromide. To a solution of PhMgBr [prepared from 1.88 g (12 mmol) of bromobenzene and 243 mg (10 mmol) of magnesium] in 20 mL of ether was added a solution of 376 mg (1 mmol) of **4b** in 10 mL of ether dropwise under the conditions of gentle refluxing. After the reaction mixture was refluxed for an additional 12 h, it was treated as described above to give 350 mg (65.8%) of **12j**, pale yellow prisms (hexane): mp 245–251 °C; IR (KBr) 3550, 3030, 2960, 1580, 1490, 1475, 1450, 1275, 1210, 1180, 1150, 1040, 1000, 820, 760, 720, 695 cm^{-1}; NMR ($CDCl_3$) δ 1.16, 1.19 (2 H, d, J = 5.0 Hz), 1.40 (18 H, s), 2.52–2.74 (4 H, m), 2.80–3.06 (2 H, m), 3.84–4.16 (2 H, m), 4.48–4.60 (2 H, d, J = 5.0 Hz), 6.52–6.68 (4 H, m), 6.92–7.16 (6 H, m), 7.29–7.33 (2 H, m); MS, m/e 515 (M^+ – HO), 409 (M^+ – C_7H_6O, HO). Anal. Calcd for $C_{38}H_{44}O_2$: C, 85.67; H, 8.33. Found: C, 85.80; H, 8.21.

Dehydration of 12 To Give 13. Dehydration of 12a To Give 13a. A suspension of 130 mg (0.439 mmol) of **12a** in a mixture of 8 mL of acetic acid and 2 mL of concentrated hydrogen chloride was heated on a water bath for 30 min. On cooling, a crystalline material was separated and recrystallized from methanol to give 80 mg (70.1%) of **13a**, colorless prisms (MeOH): mp 196–198 °C; IR (KBr) 3040, 2930, 1575, 1435, 1180, 985, 905, 760, 740 cm^{-1}; NMR ($CDCl_3$) δ 2.74–3.00 (8 H, m), 4.45 (2 H, dd, J_{ba} = 15 Hz, J_{bc} = 6 Hz), 4.65 (2 H, dd, J_{ca} = 11 Hz, J_{cb} = 6 Hz), 4.82 (2 H, dd, J_{ab} = 15 Hz, J_{ac} = 11 Hz), 6.82–7.16 (6 H, m); MS, m/e 260 (M^+). Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.38; H, 7.73.

Similarly, **13b–h** were synthesized in the same manner as described above.

13b, colorless prisms (MeOH): mp 190–192 °C; IR (KBr) 3050, 1580, 1430, 1180, 965, 935, 880, 770, 730, 695 cm^{-1}; NMR ($CDCl_3$) δ 1.42 (6 H, dd, J_{cb} = 6.5 Hz, J_{ca} = 1.5 Hz), 2.70–2.96 (8 H, m), 4.42 (2 H, dd, J_{ab} = 16 Hz, J_{ac} = 1.5 Hz), 4.81 (2 H, dq, J_{bc} = 6.5 Hz, J_{ba} = 16 Hz), 6.80–7.12 (6 H, m); MS, m/e 288 (M^+). Anal. Calcd for $C_{22}H_{24}$: C, 91.62; H, 8.39. Found: C, 91.66; H, 8.51.

13c, colorless plates (MeOH): mp 115–116 °C; IR (KBr) 3050, 2960, 2930, 1575, 1450, 1180, 965, 765, 730 cm^{-1}; NMR ($CDCl_3$) δ 0.84 (6 H, t, J = 6.5 Hz), 1.63–1.92 (4 H, m), 2.60–3.04 (8 H, m), 4.41 (2 H, d, J_{ab} = 16 Hz), 4.93 (2 H, dt, J_{bc} = 6.5 Hz, J_{ba} = 16 Hz), 6.79–7.12 (6 H, m); MS, m/e 316 (M^+). Anal. Calcd for $C_{24}H_{28}$: C, 91.08; H, 8.92. Found: C, 91.05; H, 9.08.

13d, colorless prisms (MeOH): mp 69–70 °C; IR (KBr) 3070, 2950, 1580, 1455, 1435, 1180, 975, 800, 780, 735 cm^{-1}; NMR ($CDCl_3$) δ 0.84 (6 H, t, J = 7 Hz), 1.07–1.42 (4 H, m), 1.62–1.82 (4 H, m), 4.40 (2 H, dd, J_{ab} = 16 Hz, J_{ac} = 1.5 Hz), 4.88 (2 H, dt, J_{bc} = 6.5 Hz, J_{ba} = 16 Hz), 6.80–7.12 (6 H, m); MS, m/e 344 (M^+). Anal. Calcd for $C_{26}H_{32}$: C, 90.64; H, 9.36. Found: C, 90.97; H, 9.41.

13e, colorless prisms (hexane:benzene, 2:1): mp 232–234 °C; IR (KBr) 3050, 2990, 2940, 2860, 1595, 1580, 1490, 1450, 1175, 1150, 965, 780, 750, 735, 690 cm^{-1}; NMR ($CDCl_3$) δ 2.78–3.05 (8 H, m), 5.20 (2 H, d, J = 16.5 Hz), 5.82 (2 H, d, J = 16.5 Hz), 7.00–7.35 (16 H, m); MS, m/e 412 (M^+). Anal. Calcd for $C_{32}H_{28}$: C, 93.16; H, 6.84. Found: C, 92.65; H, 6.86.

13f, colorless prisms (MeOH): mp 239–240 °C; IR (KBr) 3080, 2960, 1590, 1450, 1390, 1360, 1275, 1180, 995, 900, 860, 760 cm^{-1}; NMR ($CDCl_3$) δ 1.30 (18 H, s), 2.72–3.02 (8 H, m), 4.48 (2 H, dd, J_{ba} = 16.5 Hz, J_{bc} = 4 Hz), 4.62 (2 H, dd, J_{ca} = 11 Hz, J_{cb} = 4 Hz), 4.91 (2 H, dd, J_{ab} = 16.5 Hz, J_{ac} = 11 Hz), 7.08 (4 H, s); MS, m/e 372 (M^+). Anal. Calcd for $C_{28}H_{36}$: C, 90.26; H, 9.74. Found: C, 89.54; H, 9.78.

13g, colorless plates (MeOH): mp 246–248 °C; IR (KBr) 3050, 2980, 1590, 1445, 1360, 1280, 970, 885, 860, 720 cm^{-1}; NMR ($CDCl_3$) δ 1.31 (18 H, s, t-Bu), 1.42 (6 H, dd, J_{cb} = 6.5 Hz, J_{ca} = 1.5 Hz), 2.64–2.95 (8 H, m), 4.52 (2 H, dd, J_{ab} = 16 Hz, J_{ac} = 1.5 Hz), 4.86 (2 H, dq, J_{bc} = 6.5 Hz, J_{ba} = 16 Hz), 7.04 (4 H, s); MS, m/e 400 (M^+). Anal. Calcd for $C_{30}H_{40}$: C, 89.94; H, 10.06. Found: C, 89.70; H, 10.03.

13h, colorless prisms (hexane:benzene, 2:1): mp 302–304 °C; IR (KBr) 3050, 2950, 1580, 1445, 1180, 960, 865, 740, 690 cm^{-1}; NMR ($CDCl_3$) δ 1.24 (18 H, s), 2.80–3.12 (8 H, m), 5.39 (2 H, d, J = 17 Hz), 5.83 (2 H, d, J = 17 Hz), 7.00–7.20 (14 H, m); MS, m/e 524 (M^+). Anal. Calcd for $C_{40}H_{44}$: C, 91.55; H, 8.45. Found: C, 91.61; H, 8.47.

Reaction of 7 with Hydroxylamine. A mixture of 500 mg (2.63 mmol) of **7**, 240 mg (3.42 mmol) of hydroxylamine hydrochloride, 160 mg (4 mmol) of sodium hydroxide, and 20 mL of ethanol was refluxed for 2 h. After the reaction mixture was cooled, the solvent was removed in vacuo to leave the residue, which was washed with water and recrystallized from hexane to give 460 mg (85.3%) of **14**, colorless prisms (hexane): mp 102–104 °C; IR (KBr) 3250, 3020, 2950, 1595, 1550, 1475, 1445, 1415, 1375, 1335, 1235, 965, 940, 920, 865, 840, 780, 730, 710 cm^{-1}; NMR (Me_2SO-d_6) δ 1.25 (9 H, s), 2.33 (6 H, s), 7.04 (2 H, s), 8.27 (1 H, s), 11.08 (1 H, s); MS, m/e 205 (M^+). Anal. Calcd for $C_{13}H_{19}NO$: C, 76.05; H, 9.33; N, 6.82. Found: C, 76.40; H, 9.52; N, 7.13.

Reaction of 7 with Hydrazine Hydrate. A mixture of 1.01 g (5.32 mmol) of **7**, 2.13 mg (42.6 mmol) of hydrazine hydrate (NH_2NH_2·H_2O), and 40 mL of ethanol was refluxed for 12 h. After the reaction mixture was cooled, the solvent was removed in vacuo to leave the residue, which was washed with water and hexane to give 690 mg (69%) of **16**, pale yellow prisms: mp 244–245 °C; IR (KBr) 3040, 2960, 1610, 1445, 1360, 1335, 1235, 955, 870, 780, 730 cm^{-1}; NMR ($CDCl_3$) δ 1.31 (18 H, s), 2.53 (12 H, s), 7.08 (4 H, s), 8.94 (2 H, s); MS, m/e 376 (M^+). Anal. Calcd for $C_{26}H_{36}N_2$: C, 82.92; H, 9.64; N, 7.44. Found: C, 82.50; H, 9.39; N, 7.43.

Preparation of 2,6-Dimethyl-4-*tert*-butylbenzenecarboxylic Acid (17). To a solution of 1.9 g (10 mmol) of **7** in 10 mL of acetone was added 20 mL of 3.2% potassium permanganate solution with stirring during the course of 1 h under reflux conditions. After filtration, the filtrate was made acidic and colorless crystalline material was collected, which was recrystallized from hexane to give 804 mg (61.8%) of **17**, colorless prisms (hexane): mp 163–165 °C; IR (KBr) 3040, 2960, 2850, 2640, 2540, 1680, 1600, 1425, 1290, 1150, 1080, 920, 870, 760, 720 cm^{-1}; NMR (Me_2SO-d_6) δ 1.26 (9 H, s), 2.28 (6 H, s), 7.04 (2 H, s), 10.04 (1 H, s); MS, m/e 206 (M^+). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 76.27; H, 8.99.

Reaction of 7 with Methylmagnesium Bromide. To a solution of MeMgBr [prepared from 7.85 g (72 mmol) of methyl bromide and 1.46 g (60 mmol) of magnesium] in 30 mL of ether was added a solution of 5.7 g (30 mmol) of **7** in 20 mL of ether dropwise under the conditions of gentle refluxing. After the reaction mixture was refluxed for an additional 3 h, it was quenched with 10% ammonium chloride and extracted with

dichloromethane. The dichloromethane extract was dried over sodium sulfate and evaporated in vacuo to give 5.4 g (87.4%) of **18a**, colorless prisms (MeOH): mp 114–115 °C (lit.[10] 113–113.5 °C); IR (KBr) 3300, 3040, 2950, 2850, 1600, 1475, 1400, 1355, 1290, 1225, 1165, 1000, 925, 880, 860, 740 cm^{-1}; NMR ($CDCl_3$) δ 1.27 (9 H, s), 1.48 (3 H, d, J = 8 Hz), 1.83 (1 H, s), 2.40 (6 H, s), 5.28 (1 H, q, J = 8Hz), 6.92 (2 H, s).

Reaction of 7 with Ethylmagnesium Bromide. To a solution of EtMgBr [prepared from 7.85 g (72 mmol) of ethyl bromide and 1.46 g (60 mmol) of magnesium] in 30 mL of ether was added a solution of 5.7 g (30 mmol) of **7** in 20 mL of ether dropwise under the conditions of gentle refluxing. After the reaction mixture was refluxed for an additional 3 h, it was treated as described above to give 5.61 g (85%) of **18b**, colorless prisms (MeOH): mp 41–42 °C; bp 121–123 °C (2 mmHg); IR (KBr) 3250, 3040, 2950, 2850, 1600, 1475, 1450, 1350, 1225, 1120, 1070, 1040, 1000, 960, 860, 820, 740 cm^{-1}; NMR ($CDCl_3$) δ 0.92 (3 H, t, J = 8 Hz), 1.25 (9 H, s), 1.62–1.94 (2 H, m), 2.05 (1 H, s), 2.36 (6 H, s), 4.94 (1 H, dd, J_{ab} = 5 Hz, J_{ac} = 9 Hz), 6.91 (2 H, s); MS, m/e 220 (M^+). Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.78; H, 10.95.

Reaction of 7 with *n*-Propylmagnesium Bromide. To a solution of *n*-propylmagnesium bromide [prepared from 8.9 g (72 mmol) of *n*-propyl bromide and 1.46 g (60 mmol) of magnesium] in 30 mL of ether was added a solution of 5.7 g (30 mmol) of **7** in 20 mL of ether dropwise under the conditions of gentle refluxing. After the reaction mixture was refluxed for an additional 3 h, it was treated as described above to give 5.6 g (79.8%) of **18c**, colorless prisms (MeOH): mp 60–62 °C; bp 124–126 °C (2 mmHg); IR (KBr) 3250, 3050, 2960, 1600, 1480, 1460, 1360, 1230, 1130, 1040, 990, 865, 750 cm^{-1}; NMR ($CDCl_3$) δ 0.94 (6 H, t, J = 8 Hz), 1.27 (9 H, s), 1.16–2.02 (4 H, m), 1.80 (1 H, br s), 5.09 (1 H, dd, J_{ab} = 5 Hz, J_{ac} = 9 Hz), 6.94 (2 H, s); MS, m/e 234 (M^+). Anal. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 82.08; H, 11.34.

Reaction of 7 with *n*-Butylmagnesium Bromide. To a solution of *n*-BuMgBr [prepared from 9.86 g (72 mmol) of *n*-butyl bromide and 1.46 g (60 mmol) of magnesium in 30 mL of ether was added a solution of 5.7 g (30 mmol) of I in 20 mL of ether dropwise under the conditions of gentle refluxing. After the reaction mixture was refluxed for an additional 3 h, it was treated as described above to give 5.68 g (76.3%) of **18d**, colorless liquid: bp 145–146 °C (2 mmHg); IR (NaCl) 3360, 3050, 2960, 1600, 1480, 1460, 1360, 1230, 1040, 1000, 860, 740 cm^{-1}; NMR ($CDCl_3$) δ 0.91 (3 H, t, J = 7 Hz), 1.20–1.48 (4 H, m), 1.28 (9 H, s), 1.81 (1 H, s), 1.72–1.96 (2 H, m), 5.08 (1 H, dd, J_{ab} = 5 Hz, J_{ac} = 9 Hz), 6.94 (2 H, s); MS, m/e 248 (M^+). Anal. Calcd for $C_{17}H_{28}O$: C, 82.20; H, 11.36. Found: C, 82.04; H, 11.23.

Reaction of 7 with Benzylmagnesium Bromide. To a solution of $PhCH_2MgBr$ [prepared from 12.31 g (72 mmol) of benzyl bromide and 1.46 g (60 mmol) of magnesium] in 30 mL of ether was added a solution of 5.7 g (30 mmol) of **7** in 20 mL of ether dropwise under the conditions of gentle refluxing. After the reaction mixture was refluxed for an additional 12 h, it was treated as described above to give 7.59 g (89.7%) of **18e**, colorless prisms (hexane): mp 80–82 °C; IR (KBr) 3580, 3425, 3050, 2980, 1605, 1500, 1485, 1455, 1360, 1230, 1080, 1050, 1030, 870, 745, 700 cm^{-1}; NMR ($CDCl_3$) δ 1.28 (9 H, s), 1.78 (1 H, br s), 2.43 (6 H, s), 2.92 (1 H, dd, J_{ba} = 5 Hz, J_{bc} = 14 Hz), 3.18 (1 H, dd, J_{cb} = 14 Hz, J_{ca} = 9 Hz), 5.24 (1 H, dd, J_{ac} = 9 Hz, J_{ab} = 5 Hz), 6.98 (2 H, s), 7.23 (5 H, br s); MS, m/e 282 (M^+). Anal. Calcd for $C_{20}H_{26}O$: C, 85.05; H, 9.28. Found: C, 85.04; H, 9.30.

Reaction of 7 with Phenylmagnesium Bromide. To a solution of PhMgBr [prepared from 11.30 (72 mmol) of bromobenzene and 1.46 g (60 mmol) of magnesium] in 30 mL of ether was added a solution of 5.7 g (30 mmol) of **7** in 20 mL of ether dropwise under the conditions of gentle refluxing. After the reaction mixture was refluxed for an additional 12 h, it was treated as described above to give 7.25 g (90.2%) of **18f**, colorless prisms (hexane): mp 116–118 °C; IR (KBr) 3580, 3040, 2960, 1600, 1480, 1450, 1270, 1080, 1050, 875, 740, 730, 700 cm^{-1}; NMR ($CDCl_3$) δ 1.28 (9 H, s), 2.17 (1 H, br s), 2.24 (6 H, s), 6.28 (1 H, br s), 6.98 (2 H, s), 7.16–7.32 (5 H, m); MS, m/e 268 (M^+). Anal. Calcd for $C_{19}H_{24}O$: C, 85.02; H, 9.01. Found: C, 84.54; H, 9.04.

Dehydration of 18 To Give 19. Dehydration of 18a To Give 19a. A suspension of 3.09 g (15 mmol) of **18a** in a mixture of 24 mL of acetic acid and 6 mL of concentrated hydrogen chloride was heated on a water bath for 30 min. On cooling, the reaction mixture was extracted with dichloromethane and washed with 10% sodium bicarbonate solution and water. The dichloromethane extract was dried over sodium sulfate and evaporated in vacuo to leave the residue, which was distilled under the reduced pressure to give 1.4 g (49.6%) of **19a**, colorless liquid: bp 94–95 °C (2 mmHg) (lit. 170.2 °C (100 mmHg)).

Similarly, **19b–e** were synthesized in the same manner as described above.

19b, colorless liquid: bp 98–100 °C (2 mmHg); IR (NaCl) 3040, 2960, 1600, 1480, 1450, 1360, 1230, 1200, 965, 860, 715 cm^{-1}; NMR ($CDCl_3$) δ 1.28 (9 H, s), 1.88 (6 H, dd, J_{cb} = 6.5 Hz, J_{ca} = 1.5 Hz), 2.28 (6 H, s), 5.64 (1 H, dq, J_{bc} = 6.5 Hz, J_{ba} = 16.5 Hz), 6.28 (1 H, dd, J_{ab} = 16.5 Hz, J_{ac} = 1.5 Hz), 7.00 (2 H, s); MS, m/e 202 (M^+). Anal. Calcd for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 89.00; H, 10.95.

19c, colorless liquid: bp 105–107 °C (2 mmHg); IR (NaCl) 3050, 2970, 1600, 1480, 1455, 1370, 1360, 1230, 1200, 970, 860, 710 cm^{-1}; NMR ($CDCl_3$) δ 1.08 (3 H, t, J = 7 Hz), 1.28 (9 H, s), 2.06–2.04 (2 H, m), 2.28 (6 H, s), 5.66 (1 H, dt, J_{bc} = 6.5 Hz, J_{ba} = 16.5 Hz), 6.26 (1 H, d, J_{ab} = 16.5 Hz), 7.00 (2 H, s); MS, m/e 216 (M^+). Anal. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 88.90; H, 11.16.

19d, colorless liquid: bp 125–127 °C (2 mmHg); IR (NaCl) 3040, 2960, 1600, 1480, 1455, 1370, 1360, 1230, 1200, 970 cm^{-1}; NMR ($CDCl_3$) δ 0.96 (3 H, t, J = 7 Hz), 1.29 (9 H, s), 1.38–1.60 (2 H, m), 2.08–2.40 (2 H, m), 2.28 (6 H, s), 5.61 (1 H, dt, J_{bc} = 6.5 Hz, J_{ba} = 16.5 Hz), 6.30 (1 H, d, J_{ab} = 16.5 Hz), 7.00 (2 H, s); MS, m/e 230 (M^+). Anal. Calcd for $C_{17}H_{26}$: C, 88.62; H, 11.38. Found: C, 88.47; H, 11.14.

19e, colorless prisms (MeOH): mp 57–58 °C; IR (KBr) 3040, 2960, 1595, 1480, 1450, 1360, 1225, 970, 870, 745, 690 cm^{-1}; NMR ($CDCl_3$) δ 1.31 (9 H, s), 2.37 (6 H, s), 6.57 (1 H, d, J = 16.5 Hz), 7.09 (1 H, d, J = 16.5 Hz), 7.07 (2 H, s), 7.12–7.52 (5 H, m); MS, m/e 264 (M^+). Anal. Calcd for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.94; H, 9.19.

Registry No. **1a**, 78919-80-9; **1b**, 85201-29-2; **2**, 138-89-6; **3a**, 85151-90-2; **3b**, 85151-91-3; **4a**, 85151-92-4; **4b**, 85151-93-5; **5**, 78919-93-4; **6**, 85151-94-6; **7**, 85151-95-7; **8a**, 85151-96-8; **8b**, 85151-97-9; **9a**, 85152-00-7; **9b**, 85152-01-8; **10a**, 85151-98-0; **10b**, 85151-99-1; **11a**, 85152-02-9; **11b**, 85152-03-0; *meso*-**12a**, 85152-04-1; (±)-**12a**, 85152-05-2; *meso*-**12b**, 85152-06-3; (±)-**12b**, 85152-07-4; *meso*-**12c**, 85152-08-5; (±)-**12c**, 85152-09-6; *meso*-**12d**, 85152-10-9; (±)-**12d**, 85152-11-0; *meso*-**12e**, 85152-12-1; (±)-**12e**, 85152-13-2; *meso*-**12f**, 85152-14-3; (±)-**12f**, 85152-15-4; *meso*-**12g**, 85152-16-5; (±)-**12g**, 85152-17-6; *meso*-**12h**, 85152-18-7; (±)-**12h**, 85152-19-8; *meso*-**12i**, 85152-20-1; (±)-**12i**, 85152-21-2; *meso*-**12j**, 85152-22-3; (±)-**12j**, 85152-23-4; **13a**, 85152-24-5; **13b**, 85152-25-6; **13c**, 85152-26-7; **13d**, 85152-27-8; **13e**, 85152-28-9; **13f**, 85152-29-0; **13g**, 85152-30-3; **13h**, 85152-31-4; **14**, 85152-32-5; **16**, 85152-33-6; **17**, 58537-98-7; **18a**, 56222-53-8; **18b**, 85152-34-7; **18c**, 1703-87-3; **18d**, 85152-35-8; **18e**, 85152-36-9; **18f**, 85152-37-0; **19a**, 85152-38-1; **19b**, 85152-39-2; **19c**, 1703-88-4; **19d**, 85152-40-5; **19e**, 85152-41-6.

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