Table I. Boiling Points and ^1H and ^{13}C NMR Chemical Shift Data of the Prepared Acylals, $PhCH(OCH_3)OCOR$

		^1H NMR chemical shifts (δ/ppm) in DMSO					
R	bp/°C (p/mmHg)	OCOR	Ph	CH	OMe	OCOMe	$OCOCH_2CH_3$
H	108–110 (15)	8.46	7.40	6.71	3.47		
Me	93–94 (5)		7.40	6.61	3.46	2.12	
Et	127–128 (17)		7.40	6.62	3.45		2.44, 1.07

	^{13}C NMR chemical shifts (δ/ppm) in $CDCl_3$					
R	OCOR	Ph	CH	OMe	OCOMe	$OCOCH_2CH_3$
H	160.6	136.7, 129.5 128.6, 126.4	98.6	56.7		
Me	170.7	137.3, 129.2 128.5, 126.3	98.5	56.45	21.2	
Et	174.1	137.5, 129.1 128.5, 126.3	98.3	56.4		27.8, 9.0

Table II. Rate Constants for the Formation of Benzaldehyde in the Hydrolytic Decomposition of Acylals, $PhCH(OCH_3)OCOR$, in Succinic Acid Buffer Solution at 15 °C. UV Spectroscopic Method

	k(obs)/10^{-3} s^{-1} at X(DMSO) =			
R	0	0.1	0.2	0.3
H	11.06	5.77	3.75	[a]
	10.43	5.74	3.56	
Me	11.41	5.81	[a]	0.342
	10.86	5.69		0.333
Et	10.32	5.59	[a]	0.153
	10.49	5.42		0.157

[a] ln ($A_\infty - A_t$) vs t curved.

Table III. Rate Constants for the Hydrolytic Decomposition of Acylals, $PhCH(OCH_3)OCOR$, in Deuteriated Succinic Acid Buffer Solution, X(DMSO) = 0.2, 15 °C. ^1H NMR Method

R	$k_1/10^{-3}$ s^{-1}	$k_2/10^{-3}$ s^{-1}
H		1.04[a]
Me	7.89	1.24
Et	3.07	0.945

[a] Measured by the UV spectroscopic method

reaction A + B → C, where both steps are first order and irreversible.[13] The rate constants k_1 and k_2 can be solved from eq 2 and 3 and are presented in Table III.

$$[B]_t = [A]_0 \frac{k_1}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) \quad (2)$$

$$[C]_t = [A]_0 - [A]_t - [B]_t = [A]_0\left[1 - e^{-k_1 t} - \frac{k_1}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t})\right] \quad (3)$$

So, two consecutive reactions, formation of hemiacetal and its decomposition, were found by NMR spectroscopic methods to be operative. The rate constant for the formation of benzaldehyde measured by the UV spectroscopic method is in agreement with the other k_2 values, which are averages of several parallel determinations. The decompositions of α-methoxybenzyl acetate and formate occur faster than that of the propionate because of the better leaving groups since the order of decomposition rates depends on the acidity of the carboxylic acid formed. Two minutes after dissolution no formate and only small acetate signals can be seen in the ^1H NMR spectra while carboxylic acid signals had reached their maxima already.

Therefore, it is understandable, that the formation of benzaldehyde obeys first-order kinetics (Tables II and III) in the hydrolytic decomposition of α-methoxybenzyl formate and that the value of k_1 cannot be solved. In this case the k_2 values are determined from the semilogaritmic plots of ($I_\infty - I_t$) or ($A_\infty - A_t$) against time.

Further increases of DMSO (mole fraction > 0.2) led to the observation of individual first-order kinetics for acetate and propionate derivatives. This indicates that the formation of the common intermediate with rates differing from each other had become the rate-limiting step.

Dimethyl sulfoxide as a solvent has a decisive effect on the relative velocities of the two-step acylal hydrolysis reaction in the succinate buffer conditions. It slows down the specific oxonium ion catalyzed formation more than the general acid catalyzed decomposition of the benzaldehyde methyl hemiacetal as could be expected in light of the effect of DMSO on the buffer equilibria.

A solvent-induced change in the rate-limiting step has also been postulated by Young[14] in the hydrolysis of benzaldehyde dimethyl acetal in pure water and water–dioxane solvent mixtures. It was shown that as the concentration of dioxane is increased, the rate of the acetal hydrolysis decreases faster than that of the hemiacetal hydrolysis, causing the change in the rate-limiting step.

Registry No. α-Methoxybenzyl formate, 119012-14-5; α-methoxybenzyl acetate, 51835-45-1; α-methoxybenzyl propionate, 119012-15-6; benzaldehyde methyl hemiacetal, 55685-73-9.

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Metacyclophanes and Related Compounds. 23. Preparation of Fluorinated [2.2]Metacyclophanes[1]

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Although [2.2]metacyclophanes ([2.2]MCPs) having functional groups such as alkyl,[2] halomethyl,[3] alkoxy,[4] hydroxy,[5] formyl,[6] and fluorine[7] have been reported, there

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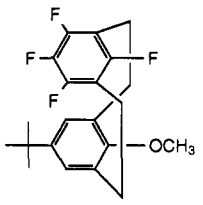
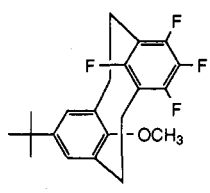


syn-8c



anti-8c

Figure 1.

are no reports concerning the preparation of [2.2]MCPs having many fluorine atoms.

It is well known that perfluorobenzene is reactive toward various nucleophilic reagents. This suggests that polyfluoro[2.2]MCPs might react with various nucleophilic reagents to afford substituted [2.2]MCPs, which cannot be prepared directly.

We describe here the preparation of [2.2]MCPs having four and eight aromatic fluorines and their reaction with $NaOCH_3$. The conformations of these [2.2]MCPs and their precursor, dithia[3.3]MCPs are also discussed.

Results and Discussion

Preparation. 2,6-Bis(chloromethyl)-1,3,4,5-tetrafluorobenzene (4) was prepared via diethyl 2,4,5,6-tetrafluoroisophthalate (2) and 2,6-bis(hydroxymethyl)-1,3,4,5-tetrafluorobenzene (3) from tetrafluoroisophthalic acid (1). The cyclization of 4 with bis(mercaptomethyl)benzenes 5 under highly dilute conditions in 10% CsOH–EtOH or KOH–EtOH in the presence of $NaBH_4$ gave the corresponding dithia[3.3]MCPs, 6. The yield of **6b** was difficult to reproduce because **6b** is too unstable to be purified. Alternatively, the reaction of 4 with Na_2S afforded **6b** in 22% yield, together with a trace amount of ethoxy derivative **6f**. Oxidation of 6 with 30% aqueous H_2O_2 afforded the corresponding disulfones 7 in good yield. Pyrolysis of 7 at 470 °C under reduced pressure (0.5 Torr) afforded the desired cyclophanes 8. It should be noted that both of the two isomers, *anti*-**8c** and *syn*-**8c** (Figure 1), were isolated in the pyrolysis of *syn*-**7c** (Scheme I).

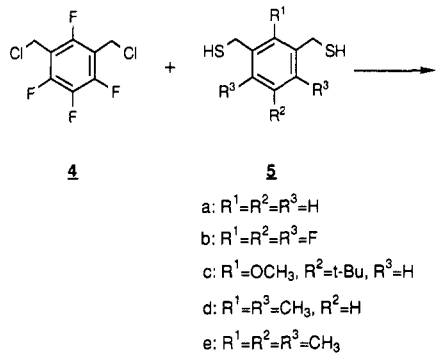
Reactions of **8b** and **8d** with $NaOCH_3$ were carried out in a mixed solvent of CH_3OH and DMF. The results are summarized in Scheme II.

The reaction of **8b** with $NaOCH_3$ at 60–70 °C afforded tetramethoxy[2.2]MCP, **9**, while the reaction of **8d** gave monomethoxy[2.2]MCP, **10** in a good yield. The structures of the products, **9** and **10** were determined by their spectral data and elemental analysis.

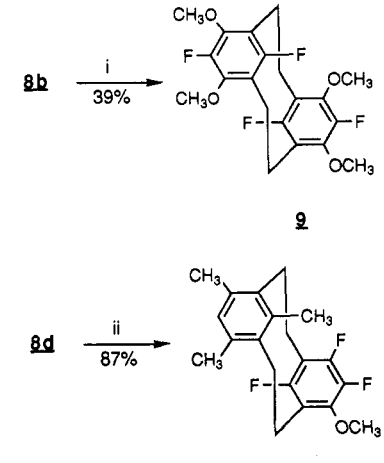
No reaction occurred when **8a** was treated with NaCN, CuCN, and BuMgBr. The reaction of **8a** with CH_3Li and BuLi afforded only a complex mixture.

Conformation. Dithia[3.3]MCPs and [2.2]MCPs may exist in two possible conformations, syn and anti. The ^1H NMR signals of the internal aromatic and alkyl protons of the anti conformer should show an up-field shift due to shielding from the ring current of the opposing aromatic ring. Compound **6a** exists as an anti conformer and **6c** as a syn conformer. Compounds **6d** and **6e** are an inseparable mixture of anti and syn conformers. The anti/syn ratios are 1/1.4 in **6d** and 1/1 in **6e**. These observations are in accordance with the reported substituent effect,[8] which claims that electron-withdrawing groups increase the yield of syn isomers, while bulky groups decrease the yield.

Scheme I



Scheme II[a]



[a] (i) $NaOCH_3$ (20 equiv), MeOH/DMF, 60–70 °C, 24 h; (ii) $NaOCH_3$ (10 equiv), MeOH/DMF, 60–70 °C, 24 h.

The [2.2]MCPs, **8a** and **8d**, assume anti conformations. As previously mentioned, anti-**8c** and *syn*-**8c** were isolated in the pyrolysis of disulfone *syn*-**7c** in 39 and 6% yields, respectively. Their conformations were elucidated on the basis of their ^1H NMR spectra; methoxy group signals were

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observed at 3.56 ppm in the spectrum of *syn*-**8c** and at 3.10 ppm in that of *anti*-**8c**. Contrary to dithia[3.3]MCPs **6**, chemical shifts (39.8–44.7 ppm) of the fluorine atoms on the 8- and 16-positions of *anti*-[2.2]MCPs **8a**, **8c**, and **8d** are fairly different from that (61.0 ppm) in *syn*-**8c**. Thus, the conformation of **8b** is tentatively deduced as anti.

There are a few reports concerning *syn*-[2.2]MCPs.[9] The 8,16-unsubstituted *syn*-[2.2]MCPs are labile and were easily converted to the corresponding anti conformers by standing at room temperature. On the other hand, *syn*-[2.2]MCPs bearing substituents on both 8- and 16-positions are thermally stable due to the steric interaction of these substituents in the ring-flipping process. Although van der Waals radii of a fluorine and a hydrogen atom are 1.35 and 1.10 Å, respectively, a fluorine atom is often considered as small as a hydrogen atom. Thus, *syn*-8-methoxy-16-fluoro[2.2]MCP (*syn*-**8c**) was expected to show an intermediate thermal stability between unsubstituted [2.2]MCP and 8,16-disubstituted [2.2]MCP. *Syn*-**8c** is thermally stable and did not change its conformation to *anti*-**8c** even at its melting point. This seems to suggest that introduction of one substituent on a internal position (8- or 16-position) makes *syn*-[2.2]MCP thermally stable, though the CT interaction between the electron-deficient tetrafluorobenzene ring and the electron-rich *tert*-butylmethoxy-substituted ring in *syn*-**8c** might contribute to the thermal stability of *syn*-**8c**.

Experimental Section

All melting points are uncorrected. ^{1}H NMR spectra were recorded at 100 MHz with a Nippon Denshi JEOL FT-100 NMR or at 270 MHz with a Nippon Denshi JEOL FT-270 NMR spectrometer with Me_4Si as an internal reference. ^{19}F NMR spectra were recorded at 100 MHz with a Nippon Denshi JEOL FT-100 NMR spectrometer with C_6F_6 as an internal reference. Spectra were taken in $CDCl_3$ unless otherwise stated. IR spectra were measured with a Nippon Bunko IR-A-102 spectrometer. Mass spectra were obtained on a Nippon Denshi JMS-01SG-2 spectrometer at 75 eV using a direct inlet system.

Diethyl 2,4,5,6-Tetrafluoroisophthalate (2). A mixture of 29 g (120 mmol) of tetrafluoroisophthalic acid (**1**), 7.2 mL of concentrated H_2SO_4, 35 mL of ethanol, and 150 mL of benzene was refluxed with a Dean–Stark condensor for 48 h. It was washed with water, dried over $MgSO_4$, and evaporated in vacuo. The residue was distilled under reduced pressure to give 27 g (77%) of **2** as a colorless oil: bp 126–129 °C (4 Torr); IR (NaCl) 3000, 1740, 1640, 1490, 1370, 1330, 1240, 1020, 960 cm^{-1}; ^{1}H NMR δ 1.38 (6 H, t, J = 7 Hz), 4.22 (4 H, q, J = 7 Hz); ^{19}F NMR δ −0.3 (1 F, dt, J = 12, 22 Hz), 34.8 (2 F, d, J = 22 Hz), 48.3 (1 F, d, J = 12 Hz); MS m/z 294 (M$^+$). Anal. Calcd for $C_{12}H_{10}O_4F_4$: C, 48.99; H, 3.43. Found: C, 48.77; H, 3.42.

2,6-Bis(hydroxymethyl)-1,3,4,5-tetrafluorobenzene (3). To a suspension of 7.57 g (200 mmol) of $NaBH_4$ and 13.6 g (100 mmol) of $ZnCl_2$ in 50 mL of dioxane was added a solution of 14.7 g (50 mmol) of **2** in 12.1 g (100 mmol) of *N,N*-dimethylaniline under nitrogen. After the reaction mixture was stirred at reflux for 2 h, it was cooled to room temperature and poured into dilute hydrochloric acid. The organic layer was extracted with ether. The ether extract was dried over $MgSO_4$ and evaporated in vacuo to leave a residue, which was recrystallized from benzene to afforded 6.83 g (65%) of **3** as colorless prisms: mp 138–140 °C; IR (KBr) 3320, 2970, 1650, 1500, 1100, 1050, 1020, 1000, 920, 880, 770 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 4.48 (4 H, d, J = 6 Hz), 5.40 (2 H, t, J = 6 Hz, exchangeable with D_2O); ^{19}F NMR (DMSO-d_6) δ −3.9 (1 F, dt, J = 11, 22 Hz), 23.4 (2 F, d, J = 22 Hz), 37.9 (1 F, d, J = 11 Hz); MS m/z 210 (M$^+$). Anal. Calcd for $C_8H_6O_2F_4$: C, 45.73; H, 2.88. Found: C, 45.62; H, 2.67.

2,6-Bis(chloromethyl)-1,3,4,5-tetrafluorobenzene (4). To a stirred mixture of 4.20 g of **3** (20 mmol) and 2 mL of pyridine in 100 mL of benzene was added dropwise 28.55 g (240 mmol) of thionyl chloride. After the reaction mixture was refluxed for 24 h, it was evaporated in vacuo. The residue was dissolved in CH_2Cl_2, washed with water, dried over $MgSO_4$, and evaporated in vacuo, leaving a liquid, which, on distillation, afforded 4.42 g (90%) of **4** as a pale yellow liquid: bp 105 °C (6 Torr); IR (NaCl) 3000, 1650, 1500, 1440, 1390, 1310, 1270, 1200, 1180, 1100, 1000, 970, 920, 850, 770, 700 cm^{-1}; ^{1}H NMR δ 4.62 (4 H, s); ^{19}F NMR δ −1.2 (1 F, dt, J = 12, 20 Hz), 27.7 (2 F, d, J = 20 Hz), 39.4 (1 F, d, J = 12 Hz); MS m/z 250, 248, 246 (M$^+$).

2,6-Bis(mercaptomethyl)-1,3,4,5-tetrafluorobenzene (5b). After a solution of 8.13 g (33 mmol) of **4** and 6.01 g of thiourea (79 mmol) in 60 mL of DMSO was stirred at room temperature under nitrogen for 24 h, it was poured into 150 mL of 10% aqueous NaOH. The mixture was stirred at room temperature for 1 h, neutralized with dilute hydrochloric acid, and extracted with CH_2Cl_2. The extract was washed with water, dried over $MgSO_4$, and evaporated in vacuo to give 5.96 g (75%) of **5b** as a pale yellow liquid: IR (NaCl) 2950, 2550, 1640, 1500, 1480, 1430, 1300, 1250, 1200, 1100, 940, 920, 740, 700 cm^{-1}; ^{1}H NMR δ 2.04 (2 H, t, J = 8 Hz), 3.74 (4 H, d, J = 8 Hz); ^{19}F NMR δ −2.4 (1 F, dt, J = 12, 22 Hz), 22.8 (2 F, d, J = 22 Hz), 36.5 (1 F, d, J = 12 Hz); MS m/z 242 (M$^+$). As **5b** is too unstable to be purified, crude **5b** was used in the reaction with **4**.

Tetrafluoro-2,11-dithia[3.3]metacyclophanes 6. Typical Procedure. A solution of 4.65 g (19 mmol) of **4** and 3.45 g (20 mmol) of **5a** in a mixture of 80 mL of benzene and 200 mL of ethanol was added dropwise for 24 h from a Hershberg funnel with stirring to a refluxing solution of 7.57 g (51 mmol) of CsOH and 1.53 g (40 mmol) of $NaBH_4$ in 3 L of ethanol. When the addition was completed, the mixture was concentrated, and to the residue was added water (1 L). The mixture was extracted with CH_2Cl_2 (500 mL). The extract was washed with dilute hydrochloric acid and water, dried over $MgSO_4$, and evaporated in vacuo, leaving a residue which was chromatographed on silica gel, with a 1:1 mixture of hexane and benzene as an eluant, to give colorless solids. Recrystallization from hexane afforded 2.30 g (36%) of *syn*-**6a** as colorless prisms: mp 172–174 °C; IR (KBr) 1640, 1500, 1290, 1220, 1150, 1100, 980, 960, 920, 800, 760, 720, 700 cm^{-1}; ^{1}H NMR δ 3.50–4.10 (8 H, m), 7.00–7.30 (4 H, m); ^{19}F NMR δ −3.8 (1 F, dt, J = 11, 22 Hz), 25.2 (2 F, d, J = 22 Hz), 41.1 (1 F, d, J = 11 Hz); MS m/z 343 (M$^+$). Anal. Calcd for $C_{16}H_{12}F_4S_2$: C, 55.80; H, 3.51. Found: C, 55.84; H, 3.59.

Compounds **6b–e** were synthesized similarly, with KOH as a base instead of CsOH.

5,6,7,9,14,15,16,18-Octafluoro-2,11-dithia[3.3]metacyclophane (6b): yield 24%; colorless prisms (hexane); mp 196–198 °C; IR (KBr) 3000, 2940, 1640, 1490, 1410, 1310, 1230, 1210, 1190, 1110, 990, 960, 760, 660 cm^{-1}; ^{1}H NMR δ 3.62 (4 H, d, J = 14 Hz), 4.16 (4 H, d, J = 16 Hz); ^{19}F NMR δ −2.2 (2 F, tt, J = 6, 20 Hz), 27.9 (4 F, d, J = 20 Hz), 38.8 (2 F, t, J = 5 Hz); MS m/z 416 (M$^+$). Anal. Calcd for $C_{16}H_8F_8S_2$: C, 46.19; H, 1.94. Found: C, 45.97; H, 2.18.

***syn*-15-*tert*-Butyl-18-methoxy-2,11-dithia-5,6,7,9-tetrafluoro[3.3]metacyclophane (*syn*-6c)**: yield 33%; colorless prisms (c-hexane); mp 171–174 °C; IR (KBr) 2960, 1640, 1490, 1200, 1100, 1000, 980 cm^{-1}; ^{1}H NMR δ 1.24 (9 H, s), 3.20–3.56 (4 H, m), 3.62 (3 H, s), 3.80–4.50 (4 H, m), 7.22 (2 H, s); ^{19}F NMR δ −3.4 (1 F, dt, J = 10, 20 Hz), 25.4 (2 F, d, J = 20 Hz), 40.3 (F, d, J = 10 Hz); MS m/z 430 (M$^+$). Anal. Calcd for $C_{21}H_{22}F_4OS_2$: C, 58.59; H, 5.15. Found: C, 58.79; H, 5.47.

***anti*- and *syn*-5,6,7,9-tetrafluoro-14,16,18-trimethyl-2,11-dithia[3.3]metacyclophane (6d)**: yield 47%; colorless prisms (c-hexane); mp 196–198 °C; IR (KBr) 2920, 1490, 1390, 1100, 980 cm^{-1}; ^{1}H NMR δ 1.79 and 2.47 (total 3 H, each s), 2.29 and 2.44 (total 6 H, each s), 3.38–4.31 (8 H, m), 6.60 and 7.02 (total 1 H, each s); ^{19}F NMR δ −4.0 and −4.6 (total 1 F, each dt, J = 11, 20 Hz, and J = 11, 21 Hz, respectively), 25.1 and 25.6 (total 2 F, each d, J = 21 Hz and J = 20 Hz, respectively), 42.1 and 45.0 (total 1 F, each d, J = 12 Hz and J = 10 Hz, respectively); MS m/z 386 (M$^+$). Anal. Calcd for $C_{19}H_{18}F_4S_2$: C, 59.05; H, 4.69. Found: C, 59.02; H, 4.78.

***anti*- and *syn*-5,6,7,9-tetrafluoro-14,15,16,18-tetramethyl-2,11-dithia[3.3]metacyclophane (6e)**: yield 19%; colorless

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prisms (c-hexane); mp 179–191 °C; IR (KBr) 3000, 2900, 1640, 1490, 1100, 970 cm^{-1}; ^1H NMR δ 1.76 and 2.46 (total 3 H, s and d with J = 3 Hz), 2.06 and 2.28 (total 3 H, each s), 2.22 and 2.42 (total 6 H, each s), 3.26–4.42 (8 H, m); ^{19}F NMR δ −5.3 and −4.3 (total 1 F, each dt, J = 12, 22 Hz and J = 11, 21 Hz, respectively), 25.4 and 25.7 (total 2 F, each d, each J = 22 Hz), 42.2 and 44.1 (total 1 F, each d, J = 10 Hz and J = 12 Hz, respectively); MS m/z 399 ($M^+ - 1$). Anal. Calcd for $C_{20}H_{20}F_4S_2$: C, 59.98; H, 5.03. Found: C, 60.12; H, 5.10.

Preparation of 6b by the Reaction of 4 with Na_2S. A mixture of 5.00 g (20 mmol) of 4 in 200 mL of ethanol and a mixture of 11.65 g (49 mmol) of Na_2S $9H_2O$ in 100 mL of ethanol and 100 mL of H_2O were added at the same rate from separate addition funnels to 3 L of refluxing ethanol over 24 h. After the addition was completed, the solvent was evaporated. To the residue was added 1 L of H_2O, and the mixture was extracted with 500 mL of CH_2Cl_2. The extracte was dried over $MgSO_4$ and evaporated in vacuo to leave a residue, which was chromatographed on silica gel elutions with a 50:1 mixture of hexane and ethyl acetate, giving 0.93 g (22%) of **6b** and 0.05 g (0.5%) of **5-ethoxy-6,7,9,14,15,16,18-heptafluoro-2,11-dithia[3.3]metacyclophane (6f)**: mp 152–155 °C; IR (KBr) 3000, 1640, 1490, 1480, 1100 cm^{-1}; ^1H NMR δ 1.40 (3 H, dt, J = 1, 6 Hz), 3.20–4.52 (10 H, m); ^{19}F NMR δ −3.3 (1 F, dt, J = 11, 21 Hz), 4.0 (1 F, dd, J = 11, 19 Hz), 25.4 (1 F, d, J = 20 Hz), 27.2 (1 F, dd, J = 6, 21 Hz), 37.5 (1 F, dd, J = 11, 71 Hz), 39.2 (1 F, dd, J = 11, 71 Hz); MS m/z 442 (M^+). Anal. Calcd for $C_{18}H_{13}F_7OS_2$: C, 48.87; H, 2.96. Found: C, 49.16; H, 3.00.

Preparation of 5,6,7,9-Tetrafluoro-2,11-dithia[3.3]metacyclophane 2,2,11,11-Tetraoxide (7a). Typical Procedure. A mixture of 1.00 g (2.90 mmol) of **6a** in 20 mL of acetic acid and 8.7 mL of 35% aqueous H_2O_2 was refluxed for 20 h. After the reaction mixture was cooled, it was poured into 30 mL of 20% aqueous KOH. The solid precipitates were collected by filtration and washed with water to afford 1.11 g (93%) of **7a**: colorless prisms; mp >300 °C; IR (KBr) 2950, 1500, 1390, 1330, 1300, 1200, 1160, 1150, 1130, 1120, 990, 910, 840, 810, 740, 700 cm^{-1}; MS m/z 408 (M^+). Anal. Calcd for $C_{16}H_{12}F_4O_4S_2$: C, 47.06; H, 2.96. Found: C, 47.27; H, 3.11.

Compounds **7b–d** were synthesized in a similar manner.

5,6,7,9,14,15,16,18-Octafluoro-2,11-dithia[3.3]metacyclophane 2,2,11,11-tetraoxide (7b): yield 91%; colorless prisms; mp >300 °C; IR (KBr) 2940, 1500, 1340, 1310, 1140, 1000, 980 cm^{-1}; MS m/z 352 ($M^+ - 2SO_2$).

***syn*-15-*tert*-Butyl-18-methoxy-5,6,7,9-tetrafluoro-2,11-dithia[3.3]metacyclophane 2,2,11,11-tetraoxide (*syn*-7c)**: yield 86%; colorless prisms; mp >300 °C; IR (KBr) 2960, 1500, 1320, 1300, 1120, 990 cm^{-1}; ^1H NMR δ 1.22 (9 H, s), 3.60 (3 H, s), 3.90–5.12 (8 H, m), 7.70 (2 H, s); ^{19}F NMR δ −0.4 (1 F, dt, J = 10, 21 Hz), 34.5 (2 F, d, J = 21 Hz), 49.3 (1 F, d, J = 10 Hz); MS m/z 494 (M^+). Anal. Calcd for $C_{21}H_{22}F_4O_5S_2$: C, 51.01; H, 4.48. Found: C, 51.05; H, 4.59.

5,6,7,9-Tetrafluoro-14,16,18-trimethyl-2,11-dithia[3.3]metacyclophane 2,2,11,11-tetraoxide (7d): yield 89%; colorless prisms; mp >300 °C; IR (KBr) 3000, 1500, 1300, 1130, 1110, 990 cm^{-1}; MS m/z 450 (M^+). Anal. Calcd for $C_{19}H_{18}F_4O_4S_2$: C, 50.66; H, 4.03. Found: C, 50.84; H, 3.74.

Pyrolysis of disulfones 7 was carried out in an apparatus of consisting of a horizontal tube (15 mm in diameter) passing through a tube furnace (20-cm long). Disulfone **7a** (1.00 g) was pyrolyzed at 470 °C under reduced pressure (0.5 Torr), and the pyrolysate was dissolved in CH_2Cl_2 and chromatographed on silica gel elutions with hexane to yield the desired [2.2]metacyclophane **8a**. Recrystallization from hexane afforded 0.30 g (44%) of ***anti*-5,6,7,9-tetrafluoro[2.2]metacyclophane (*anti*-8a)**: colorless prisms (hexane); mp 139–142 °C; IR (KBr) 2960, 1490, 1340, 1290, 1270, 1190, 1150, 1090, 1010, 940, 920, 870, 860, 790, 740, 720 cm^{-1}; ^1H NMR δ 2.00–2.60 (4 H, m), 2.80–3.40 (4 H, m), 4.56 (1 H, br s), 7.00–7.36 (3 H, m); ^{19}F NMR δ −3.9 (1 F, dt, J = 12, 22 Hz), 19.8 (2 F, d, J = 22 Hz), 44.7 (1 F, d, J = 12 Hz); MS m/z 280 (M^+). Anal. Calcd for $C_{16}H_{12}F_4$: C, 68.57; H, 4.36. Found: C, 68.70; H, 4.54.

Compounds **8b–d** were synthesized in the same manner as described above.

***anti*-4,5,6,8,12,13,14,16-Octafluoro[2.2]metacyclophane (*anti*-8b)**: yield 88%; colorless prisms; mp 140–142 °C; IR (KBr) 2970, 1620, 1480, 1450, 1400, 1260, 1180, 1110, 940, 860, 850, 750 cm^{-1}; ^1H NMR δ 2.49 (4 H, A_2B_2 pattern, J = 10 Hz), 3.22 (4 H, A_2B_2 pattern, J = 10 Hz); ^{19}F NMR δ −3.0 (2 F, dt, J = 12, 21 Hz), 21.5 (4 F, d, J = 22 Hz), 37.6 (2 F, d, J = 10 Hz); MS m/z 352 (M^+). Anal. Calcd for $C_{16}H_8F_8$: C, 54.56; H, 2.29. Found: C, 54.52; H, 2.31.

***syn*-13-*tert*-Butyl-16-methoxy-4,5,6,8-tetrafluoro[2.2]metacyclophane (*syn*-8c)**: yield 6%; colorless prisms (methanol); mp 58–59 °C; IR (KBr) 2950, 1480, 1260, 1240, 1200, 1090, 1010 cm^{-1}; ^1H NMR δ 1.16 (9 H, s), 2.48–3.54 (8 H, m), 3.56 (3 H, s), 6.52 (2 H, s); ^{19}F NMR δ −4.5 (1 F, dt, J = 12, 22 Hz), 19.2 (2 F, d, J = 22 Hz), 61.0 (1 F, d, J = 14 Hz); MS m/z 366 (M^+). Anal. Calcd for $C_{21}H_{22}F_4O$: C, 68.84; H, 6.05. Found: C, 69.15; H, 6.53.

***anti*-13-*tert*-Butyl-16-methoxy-4,5,6,8-tetrafluoro[2.2]metacyclophane (*anti*-8c)**: yield 39%; colorless prisms (methanol); mp 112–113 °C; IR (KBr) 2950, 1480, 1190, 1160, 1140, 1080, 1020, 1000, 920 cm^{-1}; ^1H NMR δ 1.32 (9 H, s), 1.98–3.32 (8 H, m), 3.10 (3 H, s), 7.08 (2 H, s); ^{19}F NMR δ −7.5 (1 F, dt, J = 10, 21 Hz), 18.6 (2 F, d, J = 22 Hz), 39.8 (1 F, d, J = 10 Hz); MS m/z 366 (M^+). Anal. Calcd for $C_{21}H_{22}F_4O$: C, 68.84; H, 6.05. Found: C, 68.89; H, 6.15.

***anti*-4,5,6,8-Tetrafluoro-12,14,16-trimethyl[2.2]metacyclophane (8d)**: yield 44%; colorless prisms (hexane); mp 184–186 °C; IR (KBr) 2960, 1480, 1090, 950 cm^{-1}; ^1H NMR δ 0.89 (3 H, d, J = 2 Hz), 2.28 (6 H, s), 2.20–3.32 (8 H, m), 6.76 (1 H, br s); ^{19}F NMR δ −5.3 (1 F, dt, J = 11, 21 Hz), 19.0 (2 F, d, J = 22 Hz), 44.3 (1 F, d, J = 12 Hz); MS m/z 322 (M^+). Anal. Calcd for $C_{19}H_{18}F_4$: C, 70.80; H, 5.63. Found: C, 71.03; H, 5.61.

Reaction of 5b and 5d with CH_3ONa. Typical Procedure. To a solution of CH_3ONa (2.84 mmol) in methanol (prepared from 70 mg of sodium and 2 mL of anhydrous methanol) was added 50 mg (0.14 mmol) of **8b** and 10 mL of DMF. After the mixture was stirred at 60–70 °C under nitrogen for 24 h and cooled to room temperature, it was poured into water and extracted with ether. The extract was washed with water, dried over $MgSO_4$, and evaporated in vacuo to leave a residue, which, on chromatography on silica gel elutions with chloroform, afforded 22 mg (39%) of ***anti*-5,8,13,16-tetrafluoro-4,6,12,14-tetramethoxy[2.2]metacyclophane (*anti*-9)**: colorless prisms (hexane); mp 137–140 °C; IR (KBr) 2960, 1610, 1470, 1430, 1420, 1350, 1200, 1170, 1110, 1000, 990, 920, 900, 840 cm^{-1}; ^1H NMR δ 2.30 (4 H, d, J = 8 Hz), 3.15 (4 H, d, J = 8 Hz), 3.94 (12 H, d, J = 2 Hz); ^{19}F NMR δ 8.8 (2 F, d, J = 13 Hz), 37.3 (2 F, d, J = 13 Hz); MS m/z 400 (M^+). Anal. Calcd for $C_{20}H_{20}F_4O_4$: C, 60.00; H, 5.04. Found: C, 60.20; H, 5.15.

***anti*-4,5,8-Trifluoro-6-methoxy-12,14,16-trimethyl[2.2]metacyclophane (*anti*-10)** was obtained in a similar manner as described above as colorless prisms (hexane): yield 87%; mp 142–143 °C; ^1H NMR δ 0.80 (3 H, s), 2.24 (6 H, s), 1.94–3.24 (8 H, m), 3.92 (3 H, d, J = 2 Hz), 6.68 (1 H, br s); ^{19}F NMR δ 0.7 (1 F, dd, J = 12, 21 Hz), 17.4 (1 F, d, J = 20 Hz), 43.4 (1 F, d, J = 10 Hz); MS m/e 334 (M^+). Anal. Calcd for $C_{20}H_{21}F_3O$: C, 71.84; H, 6.33. Found: C, 71.81; H, 6.56.

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Alkylsilyl Isoselenocyanate: A New Silicon Pseudohalide. Synthesis, Characterization, and Reaction with Carbonyl Compounds

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Silicon pseudohalides,[1] typically trimethylsilyl cyanide (Me_3SiCN),[2] trimethylsilyl azide,[3] and trimethylsilyl iso-

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