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SYNTHESIS OF POLYFLUOROARYL [2.2] CYCLOPHANES

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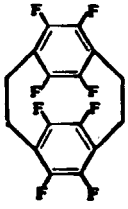
SUMMARY

New and improved syntheses of 4,5,7,8-tetrafluoro- and 4,5,7,8,12,13,15,16-octafluoro[2.2]paracyclophanes are described. The preparation of the new compound, 4,5,7,8-tetrafluoro[2.2]metaparacyclophane, is outlined.

INTRODUCTION

As part of our studies of intramolecular interactions between closely disposed phenyl and polyfluorophenyl rings in sterically constrained molecules, we reported previously the preparation of the octafluoro[2.2]paracyclophane 1[2], the tetrafluoro[2.2]paracyclophane 2[3], and the corresponding[4.2]paracyclophanes [4]. As a prelude to an expanded discussion of the effects of such interactions on reactivity in these systems, we now report, in detail, new methods and refinements for the synthesis of 1 and 2 and the first preparation of the tetrafluoro[2.2]metaparacyclophane 3.



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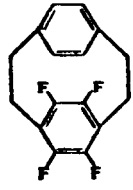

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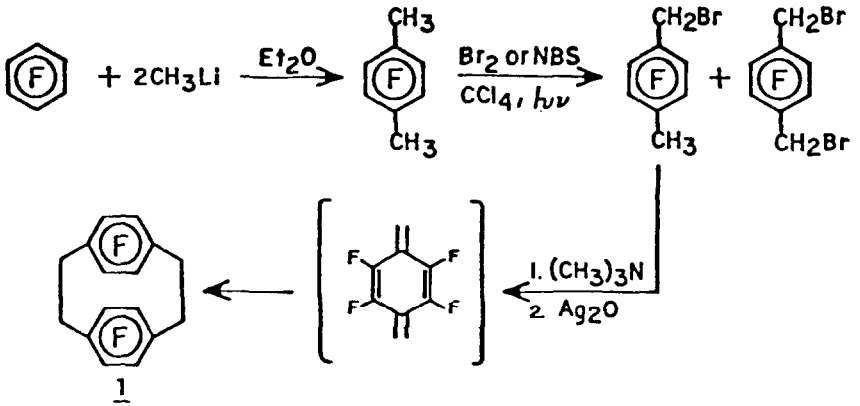
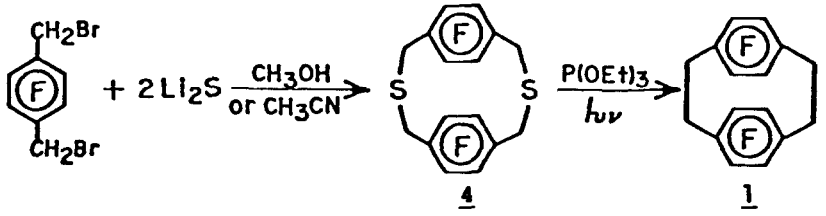
RESULTS AND DISCUSSION

Compound 1 is most efficiently prepared by 1,6 Hofmann elimination from the quaternary ammonium hydroxide derived from 4-methyltetrafluorobenzyl bromide, via the unstable tetrafluoro-p-xylylene (Scheme I). With vigorous mixing in dilute solutions, a 42% yield of 1 was obtained in the final step.



Scheme I

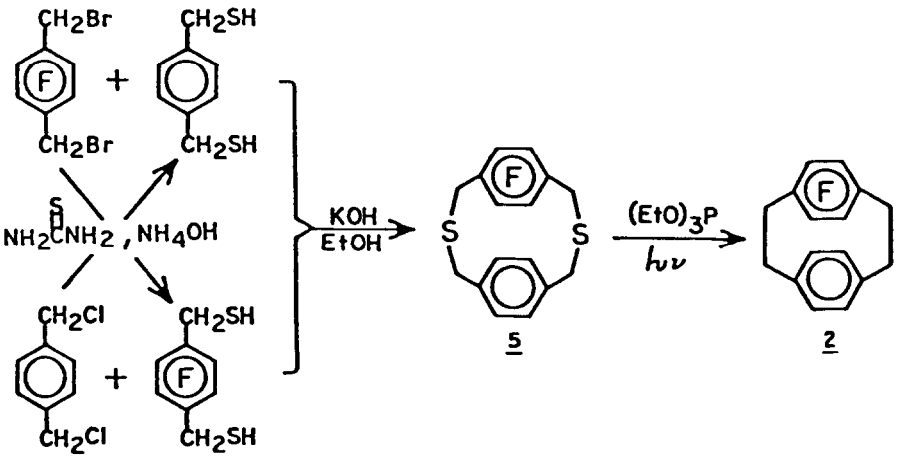
An alternate and reasonably satisfactory route to 1 is the photoextrusion of sulfur from 2,11-dithia-octafluoro [3.3] paracyclophane 4, in the presence of triethyl phosphite as scavenger [5] (Scheme II). Although 1 was obtained in only 26% yield, 4 was readily prepared in one step in 54% yield by reaction of 1,4-bis (bromomethyl)-2,3,5,6-tetrafluorobenzene with lithium sulfide under conditions of high dilution in methanol or acetonitrile.



Scheme II

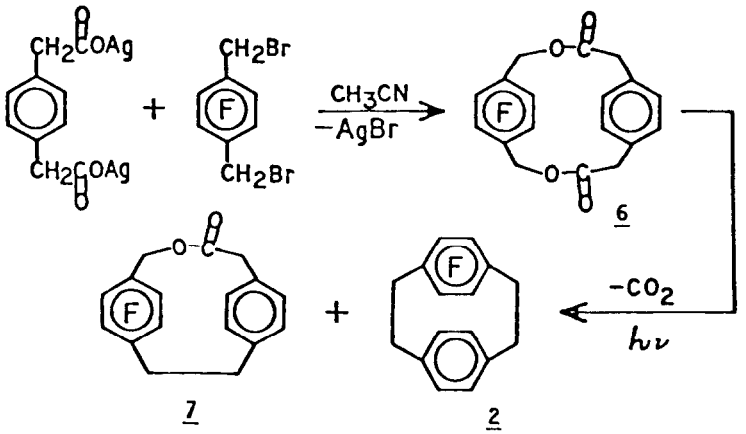
For the synthesis of 2 we previously attempted the ' cross-breeding ' of p-xylylene and tetrafluoro-p-xylylene. The only substances isolated were the symmetrical products 1 and [2.2] paracyclophane, along with polymeric material. The failure to isolate unsymmetrical compound 2 can probably be ascribed to substantially different rates of elimination of the quaternary ammonium bases to form the p-xylylenes, owing to the enhanced acidity of the methyl hydrogens adjacent to the fluorinated ring. We subsequently succeeded in preparing 2 in less than 1% overall yield by a long, tedious 12-step process [3].

In the present study, we obtained 2 by two vastly improved approaches, both involving photoextrusion. As shown in Scheme III, 5,6,8,9-tetrafluoro-2,11-dithia [3.3] paracyclophane (5) was obtained in high yields by condensation of either of two pairs of molecules. Extrusion of the two sulfur atoms in 5 afforded 2 in 24% yield.

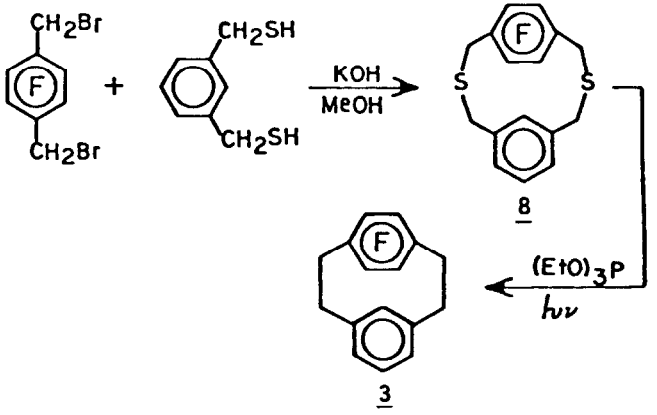


Scheme III

A better route to 2 is the photoextrusion of two molecules of CO_2 from the dilactone 6 [6,7] (Scheme IV). Although the yield of 6 was only 31%, decarboxylation in methanol proceeded smoothly to give 84% of 2 and 10% of the monolactone 7.



Scheme IV



Scheme V

In the metaparacyclophanes, one aryl ring lies orthogonal to the other, leading to differences in reactivity relative to isomeric paracyclophanes. We attempted, without success, to prepare the tetrafluoro [2.2] metaparacyclophane 3 by acid-catalyzed rearrangement of 2. The reaction did not proceed beyond the initial protonation. By this method, the all-hydrogen analog of 3 was obtained in 44% yield, in addition to other products [8]. As shown in Scheme V, 3 was prepared in two steps, a condensation reaction to yield 8 (86%), followed by the photoextrusion of sulfur to give 3 (24%).

EXPERIMENTAL

Melting points (uncorrected) were determined on a Melt-Temp capillary apparatus. A Pye-Unicam 3-300 spectrophotometer was used to record infrared spectra of samples on NaCl cells (liquid) or in KBr (solid). The routine ^{1}H NMR spectra were determined at 60 MHz on a Varian T-60 spectrometer. High resolution ^{1}H NMR was performed on a Nicolet spectrometer at 300 MHz. The ^{13}C NMR spectra were run on a Varian CFT-20 spectrometer at 20 MHz in $CDCl_3$. The chemical shifts were recorded in parts per million relative to tetramethylsilane. The ^{19}F NMR spectra were measured on a JEOL FX-90Q spectrometer with chemical shifts reported in parts per million relative to $CFCl_3$. Microanalytical determinations were conducted by Micro-Tech Laboratories of Skokie, Illinois. Fluorinated aromatic starting materials were purchased from SCM/PCR of Gainesville, Florida, and Aldrich Chemical Company.

1,4-Dimethyl-2,3,5,6-tetrafluorobenzene

(2,3,5,6-Tetrafluoroxylene)

To a stirred solution of hexafluorobenzene (83.7g, 450mmol) and anhydrous ether (500g) under nitrogen was added methyllithium (1L, 1.7M in ether). The methyllithium was added dropwise at a rate such that a gentle reflux was

maintained in the condenser. Once the addition was complete, the cloudy brown mixture was stirred an additional 3h. The ether was removed under reduced pressure. The remaining liquor was filtered to remove the insoluble lithium fluoride and the filtrate was distilled. The major fraction boiled at 140-142°C (143-144° [9]). The distillate was condensed in an air-cooled condenser to avoid crystallization. The product, 2,3,5,6-tetrafluoroxylene, (62.0g, 348mmol, 77%) solidified in the receiver as a clear crystalline solid: IR (NaCl, neat), 2940, 2860, 1640, 1480, 1375, 1276, 1205, 1110, 1080, 930, 920, 870cm^{-1}; ^{1}H NMR ($CDCl_3$), δ 2.15 ppm (quintet, J_{HF} = 0.9 Hz).

1-Bromomethyl-4-methyl-2,3,5,6-tetrafluorobenzene

(α,α'-Dibromo-2,3,5,6-tetrafluoroxylene

A solution of bromine (49.7g, 310mmol) in carbon tetrachloride (53mL) was added dropwise to 2,3,5,6-tetrafluoroxylene (55.0g, 310mmol) in carbon tetrachloride (256ml) and the mixture was irradiated with a 150 watt tungsten sunlamp. The rate of addition was regulated so as to maintain only a light orange color in the flask and a mild reflux in the condenser. After the addition of the bromine was completed, the solution was heated to reflux for an additional 0.5h until the HBr evolution ceased. The solvent was evaporated in vacuo at room temperature. Distillation of the brown liquid afforded the monobrominated product (39.7g, 155mmol, 50%) as a colorless oil; bp 49°C (0.4mm); ^{1}H NMR (CCl_4) δ 84.48 (t, ^{J}HF 135 Hz), δ 229 ppm (t, ^{J}HF = 2.13 Hz), ^{19}F NMR (C_6F_6) δ 19.3 ppm. From the solid residue, α,α'-dibromo-2,3,5,6-tetrafluoroxylene[9] (20.2g, 6mmol, 20%) was sublimed at room temperature (0.1mm Hg) and recrystallized from ethanol· mp 68-70°C; (lit. [9] 68-70°); IR ($CHCl_3$), 3050, 2990, 1490, 1205, 1158, 990, 950 cm^{-1}; ^{1}H NMR (CCl_4) δ 4.48 (quintet, ^{J}HF = 0.9 Hz).

Warning Both products are powerful irritants and lachrymators.

1,4-Bis (bromomethyl)-2,3,5,6-tetrafluorobenzene

(α-Bromo-2,3,5,6-tetrafluoroxylene)

A solution of bromine (120g, 750mmol) in carbon tetrachloride (500mL) was added dropwise to 2,3,5,6-tetrafluoroxylene (62g, 348mmol) in carbon tetrachloride (600mL) and the mixture was irradiated with a 150 watt tungsten sunlamp. The rate of addition was controlled such that the solution maintained a light orange color in the flask, a mild reflux in the condenser, and a slow evolution of hydrogen bromide gas. After the addition was complete (4h), the reaction was allowed to reflux (2h). The volatile components were removed under reduced pressure. The light orange-brown liquid which remained was distilled. The α-bromo-2,3,5,6-tetrafluoroxylene (14.3g, 55.6mmol, 16%) distilled (36°C, 0.1mm) as a colorless oil. The residue was placed in a sublimation apparatus. The product, α,α'-dibromo-2,3,5,6-tetrafluoroxylene (84.2g, 250mmol, 72%) sublimed at room temperature (0.5mm Hg) and recrystallized from ethanol; mp 68-70°C (lit. [9], 68-70°C).

4-Methyl-2,3,5,6-tetrafluorobenzyltrimethylammonium Bromide

Anhydrous trimethylamine (20 mL) was evaporated from an ice-cooled flask and passed into a stirred solution of α-bromo-2,3,5,6-tetrafluoroxylene (37.6g, 146mmol) in dry ether (100mL) for 3h. The resulting white suspension was filtered and washed several times with ether. The 4-methyl-2,3,5,6-tetrafluorobenzyltrimethylammonium bromide (44.0g, 140mmol, 96%) was air-dried and collected as a white solid.

4-Methyl-2,3,5,6-tetrafluorobenzyltrimethylammonium Hydroxide

To a solution of 4-methyl-2,3,5,6-tetrafluorobenzyltrimethylammonium bromide (15.1g, 47.9mmol) in water (62.5mL) was added freshly prepared silver (I) oxide (16.5g, 70mmol). The resulting thick suspension was stirred at room temperature for 1.5h. The silver bromide precipitate was collected by

filtration and washed with water to give 100 mL of an aqueous solution of 4-methyl-2,3,5,6-tetrafluorobenzyltrimethylammonium hydroxide. The solution was used without further purification for the preparation of 4,5,7,8,12,13,15,16-octafluoro(2.2)paracyclophane (1).

4,5,7,8,12,13,15,16-Octafluoro(2.2)paracyclophane(1)

A solution of 4-methyl-2,3,5,6-tetrafluorobenzyltrimethylammonium hydroxide (100mL, 0.479M) was placed in a 500 mL flask along with phenothiazine (0.625g) and toluene (250mL). The flask was fitted with a mechanical stirrer and a Dean-Stark apparatus. The vigorously stirred solution was heated to reflux. The water was removed continuously from the dark red solution. After 8h, no further trimethylamine evolution occurred and no additional water was collected. The mixture was allowed to cool to room temperature. The insoluble polymeric material was separated by filtration. The toluene filtrate was used in a 4h continuous extraction (Soxhlet) of the residue. The toluene was removed under reduced pressure to give a red solid. Sublimation (100°C, 0.2mm Hg) afforded a yellow solid. Recrystallization from methylcyclohexane gave pure 4,5,7,8,12,13,15,16-octafluoro(2.2)paracyclophane 1 (3.53g, 10.0mmol, 42%) as a white solid; sublimed above 205°C; IR (KBr) 2950, 1475, 1270, 1177, 950, 720, 580 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.29 ppm; ^{19}F NMR ϕ 141.3 (s) ppm; ^{13}C NMR ($CDCl_3$) δ 153.6-141.0 (dm, ^{J}CF = 252 Hz), 117.7(m), 21.2(s)ppm. Anal Calcd for $C_{16}H_8F_8$: C, 54.56; H, 2.29; F, 43.15. Found: C, 54.80; H, 2.32; F, 43.00.

5,6,8,9,14,15,17,18-Octafluoro-2,11-dithia(3.3)-paracyclophane(4)

The α,α'-dibromo-2,3,5,6-tetrafluoroxylene (13.4g, 40.1mmol) in benzene (100 mL) was added simultaneously with a solution of lithium sulfide (1.90g, 41.3mmol) in methanol (150mL) to a flask containing methanol (1500mL) under nitrogen. The two solutions were added over a 4h period and allowed to stir overnight. A white solid remained after the removal of the solvents under

reduced pressure. To the concentrate, 50mL of benzene was added and the insoluble salts were filtered off. The filtrate, on evaporation, yielded a yellowish solid. Chromatography on neutral alumina, using hexanes/dichloromethane as co-eluents, afforded the pure bis thioether as a crystalline solid (4.50g, 11.1mmol, 54%), mp 205°C, IR(KBr) 3005, 2955, 1480, 1420, 1390, 1300, 1284, 1243, 1195, 1000, 935, 857, 758, 740, 676, 605 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.83 (br s) ppm; ^{19}F NMR ($CDCl_3$) ϕ 141.9 (s) ppm.

4,5,7,8,12,13,15,16-Octafluoro(2.2)paracyclophane(1)

A photoapparatus containing 5,6,8,9,14,15,17,18-octafluoro-2,11-dithia (3.3)paracyclophane(4) (3.09g, 7.32mmol) in triethyl phosphite (200mL) was irradiated for 11h under a flow of nitrogen using a high-pressure Hanovia lamp (450 W) with a Vycor filter placed in a quartz immersion tube. The solution was cooled by a continuous flow of water through the jacketed immersion tube. The unreacted triethyl phosphite was recovered by distillation under reduced pressure. Water (75mL) was added to the oily brown residue and the solution was extracted with n-hexanes/benzene (90:10). The organic layers (50mL x 3) were combined and extracted with water (75 mL x 3). After drying over anhydrous magnesium sulfate, the solvents were partially evaporated. The yellow oil was flash-chromatographed on a short column of neutral alumina using n-hexane/benzene (90:10) as eluents. The fractions containing the product were combined and the solvents removed. After sublimation at 110°C (0.1mm Hg), the 4,5,7,8,12,13,15,16-octafluoro(2.2)paracyclophane (0.67g, 1.9mmol, 26%) was identified by comparison of ^{1}H, ^{13}C NMR, and IR spectra with those of an authentic sample.

1,3-Bis (mercaptomethyl)benzene (m-Xylylene Dimercaptan)

m-Xylylene dichloride (24.3g, 139mmol) in ethanol (150mL) was slowly introduced to a warm solution of thiourea (26.6g, 350mmol) in ethanol (250mL).

The well-stirred solution became milky-white on addition of the dichloride. Once the addition was complete, the mixture was heated at reflux for 2h. On cooling, the diisothiuronium salt precipitated as a white solid. The salt was hydrolyzed with aqueous ammonia (24mL, 58%) at reflux for 1h. After the solution had cooled to room temperature, it was acidified with 10M sulfuric acid. The product was extracted with ether (100mL x 3) and the combined ether extracts washed with water (75mL x 2). The ether layer was dried over magnesium sulfate and the ether removed under reduced pressure. The resulting oil was distilled under vacuum to give 1,3-bis(mercaptomethyl)-benzene (21.4g, 126mmol, 90%) as a colorless oil (75-77°C, 0.1mm Hg).

1,4-Bis(mercaptomethyl)-2,3,5,6-tetrafluorobenzene

α,α'-Dibromotetrafluoro-p-xylene (42.0g, 125mmol) was added to a 500mL flask containing 100mL of isopropyl alcohol. A suspension of thiourea (24.0g, 313mmol) in 100mL of water was added to the well-stirred solution. After the initial exothermic reaction had subsided, the mixture was heated under reflux for 1h. Upon cooling to room temperature, the white diisothiuronium salt precipitated. The salt was hydrolyzed with aqueous ammonia (20mL, 58%) and heated to reflux for 0.5h. An oil phase was noted on the bottom of the flask. The solution was acidified with 10M sulfuric acid while still warm. On cooling to ice-bath temperature, the oily later solidified. The solid material was filtered and sublimed (rt, 0.2mm Hg). The white sublimate, 1,4-bis-(mercaptomethyl)-2,3,5,6-tetrafluorobenzene (nc) (27.0g, 112mmol, 89%) was crystallized from 95% ethanol, mp 59-60°C; IR (KBr) 3000, 2948, 2354, 1480, 1420, 1295, 1280, 1243, 1182, 1020, 928, 904, 770, 716, 657, 568 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.87-3.72 (d, 2H, J_{CH_2-SH} = 9.1 Hz), δ 2.07 (t, 1H, J_{HS-CH_2} = 9.1 Hz) ppm; ^{19}F NMR ($CDCl_3$) ϕ 145.14 (s) ppm; Anal Calcd for $C_8H_6F_4S_2$: C, 39.59; H, 2.49; F 31.32; S, 26.43. Found: C, 39.51; H, 2.42; F, 31.27; S, 27.68.

5,6,8,9-Tetrafluoro-2,11-dithia(3.3)paracyclophane(5) (Method A)

A solution of 1,4-bis(mercaptomethyl)-2,3,5,6-tetrafluorobenzene (4.84g, 20.0mmol) and 1,4-bis-(chloromethyl) benzene (3.84g, 19.9mmol) in benzene (100mL) was added simultaneously with a solution of KOH (2.7g, 48.2mmol) in 150mL of ethanol to a flask containing 1500mL of ethanol, under nitrogen. The exothermic reaction was maintained at a temperature below 50°C during the addition (2h). The cloudy solution was allowed to stir overnight. A white solid remained after the solvents were removed. The white residue was dissolved in 50mL of benzene and the solution filtered. The filtrate was evaporated to dryness and the yellowish-white solid was sublimed (180°C, 1mm Hg). The sublimate, 5,6,8,9,-tetrafluoro-2,11-dithia(3.3)paracyclophane (nc), (5.20g, 15.1mmol, 76%) was collected as colorless crystals: mp 199-200°C, IR (KBr) 2990, 2975, 2930, 2890, 1480, 1415, 1389, 1280, 1250, 1223, 1142, 1100, 978, 885, 818, 782, 734, 691, 598, 543 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.22 (s, 4H), δ 3.87 (s, 4H), δ 3.78 (s,4H) ppm; ^{19}F NMR ($CDCl_3$) ϕ 143.4 (s) ppm. Anal Calcd for $C_{16}H_{12}F_4S_2$: C, 55.80; H, 3.51; F, 22.07; S, 18.62. Found C, 55.71; H, 3.50; F, 22.27; S, 19.84.

5,6,8,9-Tetrafluoro-2,11-dithia (3.3)paracyclophane(5) (Method B)

A solution of 1,4-bis(bromomethyl)-2,3,5,6-tetrafluorobenzene (4.53g, 13.5mmol) in 100mL of benzene was added dropwise simultaneously with a solution of 1,4-bis(mercaptomethyl) benzene (1.86g, 13.5mmol) and sodium hydroxide (1.10g, 27.0mmol) in 150mL of methanol into a 2L flask containing 1.5L of methanol, under nitrogen. After addition was complete (2.5h), the white mixture was stirred under reflux for 7h. A white solid remained after the evaporation of the solvents. The crude product was dissolved in 75mL of benzene and the inorganic salts were separated by filtration. The benzene was removed under reduced pressure. The 5,6,8,9-tetrafluoro-2,11-dithia(3.3)paracyclophane (4.02g,

11.7mmol, 87%) sublimed (180°C, 0.5mm Hg) as a crystalline solid. The ^{1}H and ^{19}F NMR, as well as the IR spectrum, were identical to an authentic sample obtained by Method A. A mixture of samples from Methods A and B exhibited no depression in melting point; mp 200°C.

4,5,7,8-Tetrafluoro(2.2)paracyclophane(2) (Method I)

A solution of freshly distilled triethyl phosphite (175mL) containing 5,6,8,9-tetrafluoro-2,11-dithia(3.3)paracyclophane (4.87g, 14.2mmol) was photolyzed for 14h using Hanovia lamp (450 W) with a Vycor filter. The phosphite was removed by simple distillation under a partial vacuum. The residual brown oil was partially dissolved in hexanes/benzene (90:10, 125mL) and filtered through activated charcoal on Celite. The filtrate was extracted with water (50mL x 3) and dried over anhydrous sodium sulfate. The liquor was concentrated by evaporation of the solvents and the yellow oil flash-chromatographed on a column of neutral alumina using hexanes as eluent. The product eluted in the first few fractions. A white solid remained after removal of the hexanes. Sublimation afforded 4,5,7,8-tetrafluoro(2.2)paracyclophane (743mg, 2.65mmol, 19%): mp 188-190°C [3]; IR (KBr) 2970, 2950, 2857, 1590, 1500-1440, 1317, 1280, 1260, 1163, 1000, 930, 890, 870, 795, 719, 597, 547 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.84 (quintet, 4H, J = 0.8 Hz), δ 3.05 (m, 8H); ^{19}F NMR ($CDCl_3$) ϕ 138.44 (s) ppm. ^{13}C NMR ($CDCl_3$) δ 152.20 (m), δ 140.29 (m), δ 139.03 (s), δ 129.61 (s), δ 128.18 (m), δ 118.85 (m), δ 32.95 (s), δ 22.03 (s) ppm. Anal Calcd for $C_{16}H_{12}F_4$: C, 68.57; H, 4.32; F, 27.12. Found: C, 68.98; H, 4.47; F, 27.14.

2,3,5,6-Tetrafluoro-p-xylylene-1,4-benzenediacetate (6)

The diargentous salt of 1,4-phenylenediacetic acid (3.79g, 9.24mmol) in 1500mL of acetonitrile reacted heterogeneously with α,α'-dibromo-4,5,7,8-tetrafluoro-p-xylene (3.10g, 9.23mmol). The dibromide in 100mL of acetonitrile

was added dropwise to the refluxing solution over 4h. Once the addition was complete, the cloudy tan mixture was allowed to reflux for 6h. The silver bromide which precipitated was separated by filtration and the acetonitrile recovered by simple distillation. The crude dilactone remained as a light brown solid. Sublimation (180°C, 0.1mm Hg) afforded a crystalline solid (1.00g , 2.86mmol, 31%), (nc), mp 247-9°C (ethanol), IR(KBr) 3055, 3010, 2970, 2948, 1770-1 1490, 1450, 1373, 1320-1240, 1185, 1140-1090, 1080, 990, 950, 894, 820, 778, 760, 690, 640, 576 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.05 (s, 4H), δ 5.27 (quintet, 4H, J = 0.9 Hz), δ 3.45 (s, 4H) ppm; ^{19}F NMR ($CDCl_3$) ϕ 142.2 (s) ppm. Anal Calcd for $C_{18}H_{12}F_4O_4$: C, 58.71; H, 3.28; F, 20.63, Found: C, 58.68; H, 3.31; F, 20.69.

4,5,7,8-Tetrafluoro(2.2)paracyclophane (Method II)

The dilactone (926mg, 2.65mmol) was dissolved in 200mL of anhydrous methanol and purged with dry nitrogen. The solution was irradiated under nitrogen using a high-pressure Hanovia lamp (450 W) unfiltered through quartz. The solution was cooled by means of a jacketed immersion tube containing the mercury lamp. The progress of the reaction was followed by ^1H NMR of aliquots taken at 1h intervals. After 10h, no starting material could be detected and irradiation was stopped. The solvent was removed and the products chromatographed on silica gel. The 4,5,7,8-tetrafluoro(2.2)paracyclophane (623mg, 2.23mmol, 84%) was eluted with hexanes. The ^1H NMR and IR spectra were identical to those obtained by the previous method. No depression of melting point was noted in a mixed sample. The intermediate monolactone (7) (nc) (86mg, 0.29mmol, 10%) was eluted with hexanes/dichloromethane (90:10): mp 228-230°C, IR ($CDCl_3$) 1745, 1495, 1368, 1295, 1240-1210, 1117, 993, 895 cm^{-1}; ^1H NMR ($CDCl_3$)δ 6.77 (s, 4H), δ 5.08 (t, 2H, J = 1.6 Hz) δ 3.35 (s, 2H), δ 3.10 (t, 4H, J = 1.5 Hz) ppm.

14,15,17,18-Tetrafluoro-2,11-dithia(3.3)metaparacyclophane(8)

A solution of 1,3-bis(chloromethyl) benzene (3.23g, 18.5mmol) in 100mL of benzene was added dropwise simultaneously along with a solution of 1,4-bis(mercaptomethyl)-2,3,5,6-tetrafluorobenzene (3.17g, 18.6mmol) and KOH (1.04 g, 18.6mmol) in 150mL of methanol into a 2L flask containing 1.5L of boiling methanol. The solution was stirred vigorously under nitrogen during the addition (3h) as well as the reflux period (8h) that followed. A white solid remained after removal of the solvents. Direct sublimation (160°C, 0.1mm Hg) gave the bis thioether (5.48g, 15.9mmol, 86%) as a crystalline solid; mp 159-160°C (from ethanol)(nc); IR (KBr) 2996, 2975, 2934, 2880, 1488-1477, 1440-1397, 1284, 1206, 1148, 1084, 983, 781, 704, 667, 605 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.13 (m, 3H), δ 6.10 (br s, 1H), δ 3.88 (s, 4H), δ 3.56 (s, 4H) ppm; ^{19}F NMR ($CDCl_3$) ϕ 144.07-144.56 (m) ppm; ^{13}C NMR ($CDCl_3$) δ 151.84, δ 149.95 (m) and δ 139.54-137.65 (m) [d, ^{J}CF = 246.10 Hz], δ 138.87 (s), δ 128.65 (s), δ 127.50 (s), δ 125.54 (s), δ 117.46, δ 115.25 (m) δ 35.45 (s), δ 22.87 (m, ^{J}CF = 2.2 Hz) ppm. Anal Calcd for $C_{16}H_{12}F_4S_2$: C, 55.80; H, 3.51; F, 22.07. Found: C, 55.74; H, 3.48; F, 22.19.

12,13,14,15-Tetrafluoro(2.2)metaparacyclophane(3)

A solution of triethyl phosphite (175mL) containing 14,15,17,18-tetrafluoro-2,11-dithia(3.3)metaparacyclophane (5.03g, 14.06mmol) was irradiated (12h) under a flow of nitrogen using a high-pressure Hanovia lamp (450 W) with a Vycor filter contained in a water-cooled quartz immersion tube. After irradiation, the unreacted triethyl phosphite was recovered by distillation under reduced pressure. To the oily brown residue, n-hexane/benzene (90:10), 125mL) was added. The cloudy solution was filtered through activated charcoal (0.5g) on Celite. The filtrate was extracted with water (50mL x 3) and dried over anhydrous magnesium sulfate. The liquid was concentrated by partial

evaporation of the solvents. The remaining light brown oil was flash-chromatographed on neutral alumina using hexanes/benzene (90:10) as the solvent system. The early fractions, which contained UV active material, as determined by TLC (Eastman), were combined and the solvents removed. The product, 12,13,14,15-tetrafluoro(2.2)metaparacyclophane(nc) (0.96g, 3.43mmol, 24%), sublimed at 110°C (0.2mm Hg) as a white solid: mp 127-128°C; IR (CCl_4) 3018, 2990, 2960, 2945, 2868, 1477, 1440, 1322, 1260, 1162, 1018, 947, 898 cm^{-1}; ^1H NMR ($CDCl_3$) 7.29-6.77 (m, 3H); 5.89 (br s, 1H), δ 3.25-2.19 (m, 8H) ppm; ^{19}F NMR ($CDCl_3$) ϕ 144.67 (d, J = 9.5 Hz), 146.38 (d, J = 9.8 Hz) ppm; ^{13}C NMR ($CDCl_3$) 155.95-151.85 (m), δ 143.64-139.38 (m), δ 138.83 (s), 131.65 (s) δ 128.51 (s), δ 126.73 (s), δ 120.00-117.10 (m), δ 33.62 (s) δ 25.30 (s) ppm. Anal. Calcd for $C_{16}H_{12}F_4$: C, 68.57; H, 4.32; F, 27.12. Found: C, 68,58; H, 4.50; F, 27.39.

Attempted Acid-Catalyzed Rearrangement of 4,5,7,8-Tetrafluoro (2.2)paracyclophane (2)

A procedure similar to that used in the preparation of (2.2)metapara-cyclophane was utilized[8]. Thus, 4.5,7,8-tetrafluoro(2.2)paracyclophane (8.49mg, 3.03mmol) was added by means of Gooch tubing into a 500mL three-necked flask containing dry dichloromethane (300mL) saturated with anhydrous hydrogen chloride and aluminum chloride (450mg, 3.38mmol) under nitrogen at 0°C. Although the solution attained a light orange color after stirring for 1 hour, no new products were noted on TLC (hexanes/dichloromethane 95:5) with a UV indicator (Eastman). The ice-bath was removed and the flask was allowed to warm to room temperature. The color intensified to bright orange on warming. Again, no new products were indicated by TLC. After 2h, the reaction mixture was poured into 100mL of water. The color was immediately extinguished. The clear dichloro-methane layer was neutralized with 5% sodium bicarbonate solution and dried over anhydrous magnesium sulfate. A white solid remained on removal of the solvent.

The ^1H NMR and IR spectra, as well as the melting point (188-190°C), were that of 4,5,7,8-tetrafluoro(2.2)-paracyclophane (822mg, 2.90mol), 96% recovered.

On repeating the above procedure using deuterium oxide to quench the reaction, no incorporation of deuterium occurred, as evident from ^1H NMR integration of the resonance at δ 6.84 (4H) to that at δ 3.05 (8H).

REFERENCES

1 Abstracted, in part, from the dissertation of G. L. C., in partial fulfillment of the requirements for the Ph.D. degree in the Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois.

2 R. Filler and F. N. Miller, Chemistry and Industry, (1965) 767.

3 R. Filler and E. W. Choe, J. Am. Chem. Soc., 91, (1969) 1862.

4 R. Filler and E. W. Choe, Canadian J. Chem., 53, (1975) 1491.

5 M. Brink, Synthesis, (1975) 807.

6 M. L. Kaplan and E. A. Truesdale, Tetrahedron Lett., (1976) 3665.

7 M. Hibert and G. Solladie, J. Org. Chem., 45, (1980) 4496.

8 D. J. Cram, R. C. Helgeson, D. Lock, and L. A. Singer, J. Am. Chem. Soc., 88. (1966) 1324.

9 A. K. Barbour, M. W. Buxton, P. L. Coe, R. Stephens, and J. C. Tatlow, J. Chem. Soc., (1961), 808.