Nonbonded Interactions between Proximate Phenyl and Polyfluorophenyl Rings. Reactivity in Polyfluoro[2.2]cyclophanes

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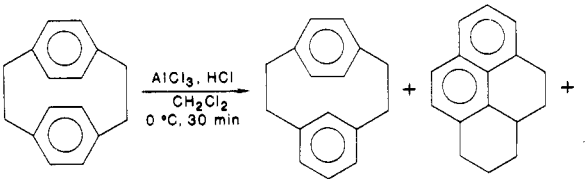
The replacement of a phenyl ring by tetrafluorophenyl in [2.2]paracyclophane causes a remarkable deactivation of the other phenyl ring toward electrophilic substitution (acetylation, bromination) and acid-catalyzed rearrangement to the [2.2]metaparacyclophane. This behavior reflects the decreased basicity of the phenyl ring, caused by transannular drain of π-electrons from C_6H_4 to C_6F_4 and is consistent with the diminution in stability of the TCNE complex relative to that of [2.2]paracyclophane. NMR studies show that there is no transannular "through-space" coupling between aryl hydrogen and fluorine.

Introduction

In previous papers,[2-5] we reported the syntheses of polyfluoroaryl [2.2]- and [4.2]cyclophanes. In continuation of studies on the effect of polyfluoroaryl groups on the reactivity of organic compounds,[6] we prepared these phanes in order to examine nonbonded intramolecular interactions between closely disposed phenyl and polyfluorophenyl rings in sterically constrained molecules.

Results and Discussion

Electrophilic Reactivity. Cram et al.[7] demonstrated that [2.2]paracyclophane (1) undergoes facile acid-catalyzed ($AlCl_3$) rearrangement, via a protonated σ-complex, to the metaparacyclophane **2** and other products. A measure of the influence of the polyfluoroaryl ring on the electrophilic reactivity of the phenyl ring in tetrafluoro[2.2]paracyclophane **3** would be the rate of a comparable rearrangement. When the same procedure was used with **3**, an orange solution was observed, but 96% of starting material was recovered, with no evidence of rearrangement, even under more stringent conditions.



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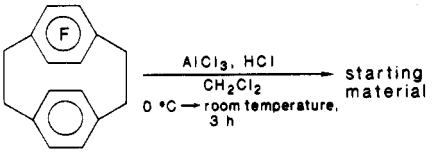
$(C_6H_5CH_2)_2$

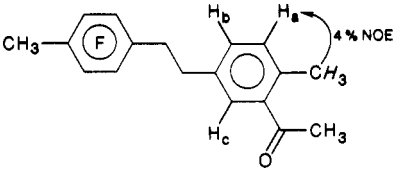


3

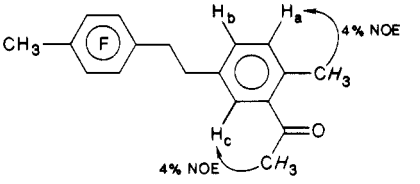
In order to ascertain whether the colored solution was due to the formation of the conjugate acid, **3** was treated with deuterium chloride and $AlCl_3$ and the resulting solution examined by ^1H NMR. The relative integration of the δ 6.84 (aromatic H) to 3.03 (bridge CH_2) absorptions changed from 1:2 to 1:3.9. Mass spectral analysis of the isolated product confirmed the presence of starting material, mono-, di-, tri-, and tetradeuteriated tetrafluoro[2.2]paracyclophane (eq 1).

Chart I. Nuclear Overhauser Enhancement Experiments

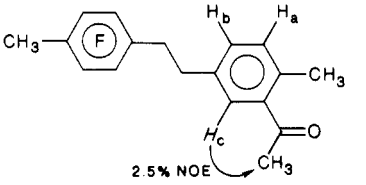
1. Irradiation at 4'-CH_3:

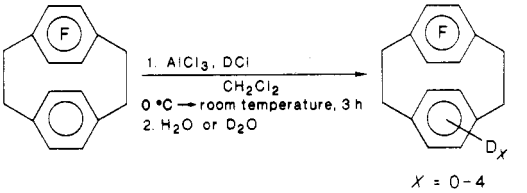


2. Irradiation at 4'-CH_3 minus CH_3CO:



3. Irradiation at H_c:





(1)

$X = 0-4$

Although the phenyl ring in **3** undergoes protonation, the subsequent skeletal rearrangement, which in **1** is facilitated by relief of strain energy associated with π-π repulsions and the lower energy of the conjugate acid, failed to occur.

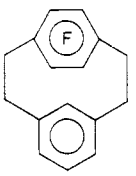
We surmise that these rate-enhancing factors are insufficient to offset the electronic attractions of the π-base C_6H_4 and π-acid C_6F_4 rings in close proximity. Such energetically favorable interactions would be lost in tetrafluoro[2.2]metaparacyclophane **4**, in which the rings are orthogonal. This conclusion, implying a marked diminu-

(1) Abstracted, in part, from the dissertations of G.L.C. (1985) and E.W.C. (1969), in partial fulfillment of the requirements for the Ph.D. in the Department of Chemistry, Illinois Institute of Technology, Chicago, IL.

(2) Filler, R.; Cantrell, G. L.; Wolanin, D.; Naqvi, S. M. *J. Fluorine Chem.* **1986**, *30*, 399.
(3) Filler, R.; Choe, E. W. *J. Am. Chem. Soc.* **1969**, *91*, 1862.
(4) Filler, R.; Choe, E. W. *Can. J. Chem.* **1975**, *53*, 1491.
(5) Filler, R.; Miller, F. N. *Chem. Ind. (London)* **1965**, 767.
(6) Filler, R. *Fluorine Chemistry Reviews*; Tarrant, P., Ed.; Marcel Dekker: New York, 1977; Vol 8, pp 1-37.
(7) Cram, D. J.; Helgeson, R. C.; Lock, D.; Singer, L. A. *J. Am. Chem. Soc.* **1966**, *88*, 1324.

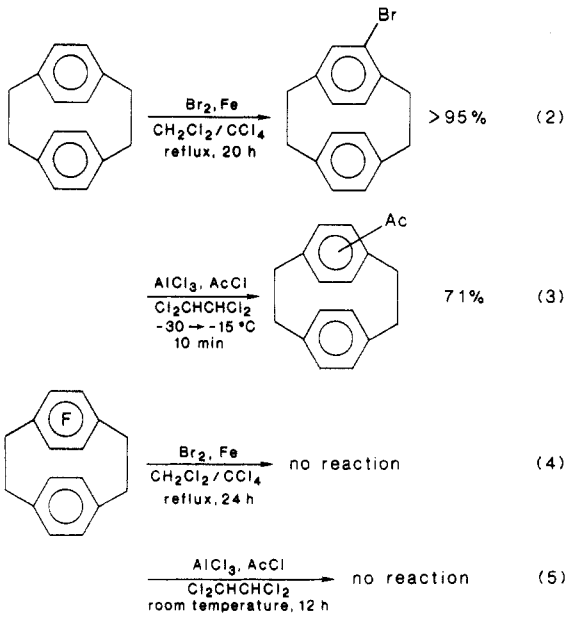
0022-3263/87/1952-0511$01.50/0

tion of $\pi-\pi$ repulsions and insinuating a donor–acceptor transannular interaction between the rings, is strongly supported by spectral comparisons of **1** and **3** and by the observations in reaction chemistry which follow. Compound **4** was subsequently prepared by another route.[2]



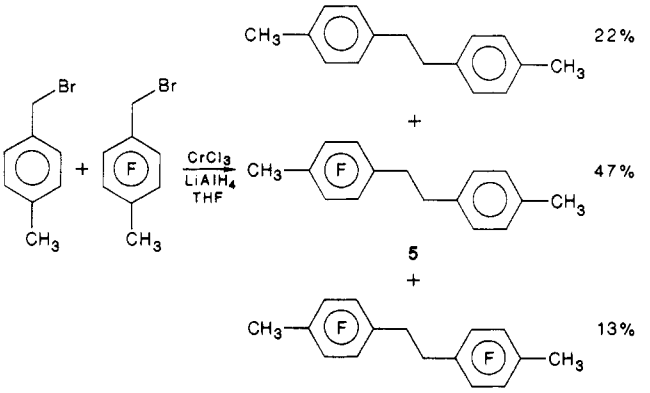
4

The successful protonation of **3** led to the study of its reactivity toward other electrophiles. Nuclear bromination of **1** gives the monobromo product in high yield.[8] By use of a similar procedure with **3**, 94% of starting material was recovered, with no evidence of bromination. Friedel–Crafts acylation was then attempted. Whereas, **1** undergoes rapid acetylation in 71% yield at −15 °C,[9] **3** failed to react at room temperature after 12 h, with 95% of reactant recovered (eq 2–5).

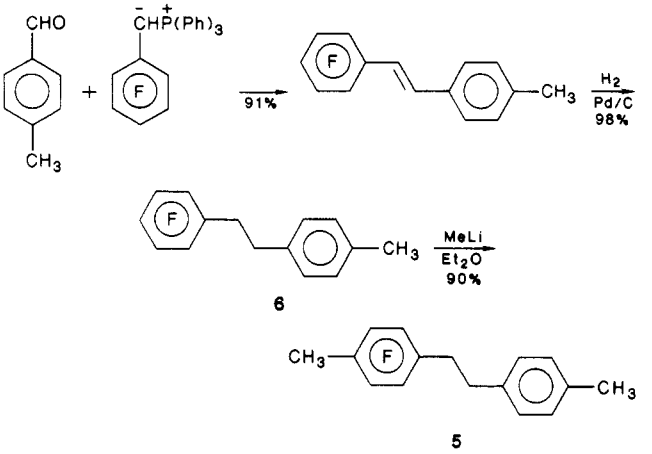


In order to clearly establish whether this remarkable lack of electrophilic reactivity was due to a transannular interaction between the disparate rings in **3**, it was essential to assess the reactivity of the open-chain analogue, 4,4′-dimethyl-2,3,5,6-tetrafluorobibenzyl (**5**), in which electronic effects must be transmitted through σ-bonds.[10] A less than satisfactory preparation of **5** involved the coupling of α-bromo-*p*-xylene with α-bromo-2,3,5,6-tetrafluoro-*p*-xylene in the presence of chromium(II),[11] to yield a statistical distribution of symmetric and cross-products.

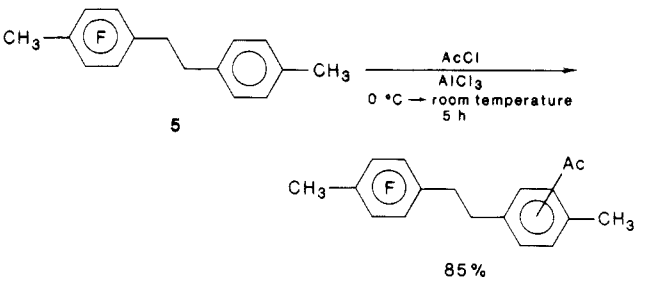
A multistep procedure proved to be a better approach to **5**. 2,3,4,5,6-Pentafluoro-4′-methyl-*trans*-stilbene was obtained in 91% yield by reaction of *p*-tolualdehyde with a Wittig reagent, prepared from (pentafluorobenzyl)triphenylphosphonium bromide. Hydrogenation in methanol



gave 98% of the pentafluoro-4′-methylbibenzyl **6**. Nucleophilic methylation of **6** afforded a 90% yield of **5**. An overall yield of 80% was achieved by the sequence.



In sharp contrast to the behavior of **3**, acetylation of **5** proceeded rapidly at 0–5 °C during 1 h to give an excellent yield of monoacylated product, as determined by NMR and IR. To elucidate the position of acylation (2′ or 3′),



a series of nuclear Overhauser enhancement (NOE) experiments was carried out as shown in Chart I. Irradiation of the 4′-methyl group gave an approximate resonance enhancement of 4% on proton H_a. No enhancement of proton H_c was noted, implying its remoteness from the site of irradiation.

A difference spectrum between the 4′-methyl and acetyl spectra indicated that the 4% NOE of H_a and 4% NOE of H_c were mutually exclusive effects, due solely to the respective groups adjacent to each. A reduction in the observed NOE of H_c would have been expected, if it were at the 3′-position. Irradiation at the resonance of H_c afforded a 2.5% enhancement of the methyl protons on the acetyl group. The result is consistent with having H_c at the 2′-position, remote from the 4′-methyl. We conclude, therefore, that the structure of the monoacetylated product is 3′-acetyl-4,4′-dimethyl-2,3,5,6-tetrafluorobibenzyl.

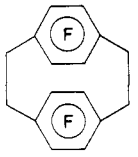
The lack of reactivity of the phenyl ring in **3** toward electrophiles compared with the facile substitution in **5**

(8) Cram, D. J.; Day, A. C. *J. Org. Chem.* **1966**, *31*, 1227; Cram, D. J.; Kierstead, R. W. *J. Am. Chem. Soc.* **1955**, *77*, 1186; Cram, D. J.; Wechter, W. J.; Kierstead, R. W. *J. Am. Chem. Soc.* **1958**, *80*, 3126.
(9) Cram, D. J., Allinger, N. L. *J. Am. Chem. Soc.* **1955**, *77*, 6289.
(10) A more rigorous test of reactivity would utilize another open-chain analogue, *p*-$(C_6F_5CH_2CH_2)_2C_6H_4$. We plan to prepare and examine the reactivity of this compound.
(11) Okude, Y.; Hiyama, T.; Nozaki, H. *Tetrahedron Lett.* **1977**, 3829.

reinforces the argument for a through-space intramolecular donor–acceptor interaction. The fluorinated ring behaves as an electron sink and drains sufficient π-electron density from the proximate phenyl to inhibit electrophilic reaction. Previous studies by Cram[8,9] provide ample precedence for such deactivation when a phenyl ring possesses an electron-withdrawing group, as in [2.2]paracyclophanequinone, acetyl[2.2]paracyclophane, and even the acetyl [4.4] analogue.

In contrast to **1**, the transition state for the acetylation or bromination of **3** is not stabilized as effectively, because the developing partial positive charge cannot be as readily distributed over both the phenyl and the tetrafluorophenyl rings, since fluorine would destabilize the charge on the neighboring ring carbon.

Nucleophilic Reactivity. If, indeed, the tetrafluorophenyl ring in **3** draws π-electron density from the phenyl, we would anticipate that the electron-enriched fluorinated ring would be somewhat less susceptible to nucleophilic attack than a fluorinated ring in the symmetrical octafluoro[2.2]paracyclophane **7**,[2] in which net electron flow should be at a standoff. In a preliminary experiment, we



7

observed that, although both **3** and **7** reacted with methoxide ion to form monomethoxy products, the rate of the reaction with **7** appeared to be somewhat faster than with **3**.

Spectroscopic Studies. Ultraviolet Spectra. We reported previously[3] and have now reconfirmed the presence in **3** of an absorption band at 297 nm, absent in the symmetrical **1** and **7**, which we attribute to attractive transannular interactions (TAIs) between the π-electrons of the C_6H_4 and C_6F_4 rings in excited states. The absence in **3** of absorption near 243 nm, found in both **1** and **7**, suggests that this maximum is associated with transannular repulsions between like aryl rings. Dilution studies demonstrated that these interactions are intramolecular, since the extinction coefficient is independent of concentration and polarity of solvent.

As expected, the spectrum of tetrafluoro[2.2]metaparacyclophane (**4**) was similar to that of its nonfluorinated analogue,[7] with no evidence of a donor–acceptor band.

Spectra of TCNE Complexes. A more definitive measure of the influence of TAIs on the basicity of an aryl ring is the stability of intermolecular donor–acceptor π-complexes between alkylbenzenes as donors and tetracyanoethylene (TCNE) as acceptor. The long wavelength absorption band of the complex in the visible region correlates well with the electron-releasing ability of the π-base.[12] Cram and Bauer[13] conducted detailed spectral studies on such complexes of cyclophanes.

In our study, the spectral properties of TCNE complexes of **1**,[13] **3** and **7** and open-chain analogues in dichloromethane solution were examined. While a detailed discussion is beyond the scope of this paper, it will suffice to report that the absorptions for the complexes of **3** and **7** show substantial hypsochromic and hypochromic shifts from that of the 1:1 complex of **1**, yet the maxima are

(12) Merrifield, R. E.; Phillips, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 2778.
(13) Cram, D. J.; Bauer, R. H. *J. Am. Chem. Soc.* **1959**, *81*, 5971.

Table I. TCNE Complexes of [2.2]Paracyclophanes 1, 3, and 7 and Open-Chain Models

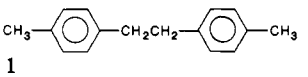
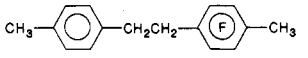
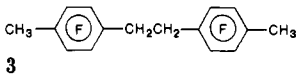
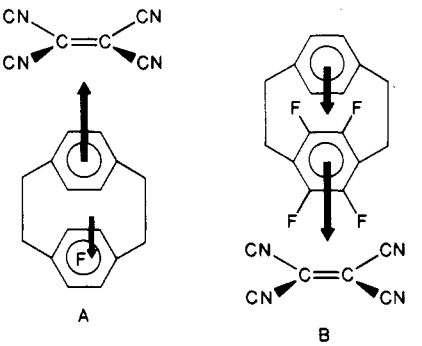
π-base	λ_{max}, nm
p-xylene	460
	420, 460
1	521
2,3,5,6-tetrafluoroxylene	360
	415, 450
	358
3	425, 465
7	390, 420

Chart II. TCNE π-Complexes of Tetrafluoro[2.2]paracyclophane 3



bathochromically shifted from those of their open-chain analogues (Table I).

The TCNE–**3** complex shows two maxima at 425 and 465 nm, whereas TCNE–**1** exhibits only one absorption at 521 nm. In **3**, the more basic phenyl ring is the favored site for complexing (λ_{max} 465 nm). The blue-shift relative to TCNE–**1** reflects the substantial decrease in basicity of the phenyl ring in **3**, brought about by transannular π-electron flow (Chart IIA). TCNE also forms a somewhat weaker complex (λ_{max} 425 nm) with the less basic tetrafluorophenyl ring (which serves as *donor*) of **3** (Chart IIB). Even open-chain models of **3** form weak complexes (Table I).

These observations provide strong evidence that transannular π-electron flow, in the excited state of **3**, lowers the basicity of the phenyl ring, while increasing the basicity of the otherwise "π-acid" tetrafluorophenyl ring.

NMR. We suggested in an earlier paper,[3] that the presence of a quintet at δ 6.84 (aromatic, 4 H, J = 0.8 Hz) in the ^{1}H NMR spectrum of **3** might be explained by a weak transannular "through-space" H–F coupling. More detailed examination of ^{1}H and ^{19}F NMR has now clearly established that there is no such transannular interaction.

A high-resolution 300-MHz spectrum resolved the previously reported δ 3.03 multiplet into two complex multiplets, one centered at δ 3.07 (4 H) and the other at δ 2.98 (4 H). The deshielded and less complex multiplet was assigned to the methylene protons adjacent to the nonfluorinated ring. Irradiation of this δ 3.07 complex caused the δ 6.84 resonance to collapse to a singlet. Conversely, irradiation of the δ 6.84 resonance simplified the δ 3.07 complex. The coupling observed, therefore, was not due to a transannular effect. Confirmation for this conclusion was found in the ^{19}F spectrum of **3**. A single resonance at 138.4 ppm was observed. Through-space coupling would have produced a quintet.

The nature of the interaction between the aryl and neighboring methylene protons in **3** is still unclear. We

hope that X-ray crystallographic analysis will help to resolve this issue.

Experimental Section

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 in KBr. Ultraviolet spectra were measured on a Cary Model 15 spectrophotometer. The visible spectra of TCNE complexes were recorded at 25 °C on a Beckman DK-2 spectrophotometer, in a 1.00-cm cell, with dichloromethane as solvent. The routine ^1H NMR spectra were determined at 60 MHz on a Varian T-60 spectrometer, while high-resolution ^1H NMR was performed on a Nicolet spectrometer at 300 MHz. ^{13}C NMR spectra were obtained on a Varian CFT-20 spectrometer, while ^{19}F NMR spectra were recorded on a JEOL FX-90Q spectrometer with chemical shifts reported in ppm relative to $CFCl_3$. Mass spectra were measured with a Finnigan MAT 44s Quadrupole MS at an ionizing energy of 70 eV. Microanalytical determinations were conducted by Micro-Tech Laboratories of Skokie, IL.

Attempted Acid-Catalyzed Rearrangement of 4,5,7,8-Tetrafluoro[2.2]paracyclophane (3). The procedure has been described previously.[2]

Deuterium Chloride Reaction with 4,5,7,8-Tetrafluoro-[2.2]paracyclophane (3). Anhydrous deuterium chloride, generated from benzoyl chloride and D_2O, was used to saturate a mixture of dichloromethane (300 mL) and aluminum chloride (372 mg, 2.79 mmol). Compound **3** (744 mg, 2.66 mmol) was introduced to the stirred solution at room temperature. After 3 h, one-half of the reaction mixture was quenched in D_2O and the other half in water. The two halves were worked up separately. Both solutions afforded white solids, which gave the same relative ^1H NMR integration of approximately 1:4 (δ 6.84 to 3.03). The two samples were combined and weighed to give 723 mg. Mass spectroscopy affirmed that incorporation of deuterium had occurred as a mixture of starting material and mono-, di-, tri-, and tetradeuterio derivatives: MS, m/e (M^+) calcd 280, obsd 280, (M^+ + D) 281, (M^+ + 2D) 282, (M^+ + 3D) 283, (M^+ + 4D) 284, $(C_8H_4F_4)^+$ 176, $(C_8H_8)^+$ 104, $(C_8H_7D)^+$ 105, $(C_8H_6D_2)^+$ 106, $(C_8H_5D_3)^+$ 107, $(C_8H_4D_4)^+$ 108.

The procedure was repeated on the mixture obtained above. The reaction was stirred for 9 h. After quenching in D_2O and workup, the same relative ^1H NMR integration (1:3.9) was recorded.

Attempted Bromination of 4,5,7,8-Tetrafluoro[2.2]paracyclophane (3). A procedure outlined by Cram[8] was employed. Into a 100 mL flask were placed dichloromethane (5 mL), iron powder (10 mg), and 1 mL of a solution of bromine (481 mg, 3.01 mmol) in carbon tetrachloride (12 mL), and the mixture was stirred at room temperature for 2 h. After more dichloromethane (50 mL) had been added, 4,5,7,8-tetrafluoro[2.2]paracyclophane (**3**) (784 mg, 2.80 mmol) was introduced. The solution was heated to reflux. The remaining bromine solution (11 mL) was added dropwise over a 30-min period and the mixture allowed to reflux for 24 h. The solution was washed with a thiosulfate solution (5%, 10 mL × 3), with water (10 mL × 2), and with a saturated sodium chloride solution (10 mL). The organic layer was dried over anhydrous sodium sulfate (1 g). A yellowish white solid remained on removal of the solvents. Flash chromatography on silica gel (60–200 mesh) using hexanes as the eluent afforded a white crystalline solid on evaporation of the solvent. The compound was identified as starting material by spectral comparison (^1H NMR, IR) and melting point (mp 188–190 °C), 736 mg, 2.63 mmol, 94% recovery.

Attempted Acylation of 4,5,7,8-Tetrafluoro[2.2]paracyclophane (3). The conditions described by Cram[9] were utilized. Anhydrous aluminum chloride (650 mg, 4.87 mmol) was added to a solution of acetyl chloride (371 mg, 4.73 mmol) in 1,1,2,2-tetrachloroethane (10 mL) under dry nitrogen. The solution was cooled to ice-bath temperature with stirring. Compound **3** (679 mg, 2.43 mmol) was introduced into the 15-mL flask. The reaction was monitored by TLC (hexanes/dichloromethane, 90:10). After 1 h, no apparent reaction had taken place. The mixture was allowed to warm to room temperature. On stirring for 9 h, no new products were detected on TLC. The reaction mixture was hydrolyzed with dilute hydrochloric acid (2 mL) and washed with water (10 mL × 2) and sodium bicarbonate solution (5 mL × 2, 5%). The organic phase was dried over anhydrous magnesium sulfate. An off-white solid remained on removal of the solvent. Flash chromatography on silica gel using hexanes as eluent gave a crystalline solid on evaporation of the solvent. The ^1H NMR and IR spectra confirmed that the starting material (645 mg, 2.30 mmol, 95%) had been recovered: mp 189–190 °C.

4,4′-Dimethyl-2,3,5,6-tetrafluorobibenzyl. The $CrCl_3$–$LiAlH_4$ reagent described by Hiyama[11] was utilized to couple α-bromo-*p*-xylene with α-bromo-2,3,5,6-tetrafluoroxylene by a modified procedure.[14] A suspension of chromium(II) chloride was prepared by reducing anhydrous chromium(III) chloride (5.23 g, 33.0 mmol) in anhydrous tetrahydrofuran with $LiAlH_4$ (626 mg, 16.5 mmol) at 0 °C under a flow of nitrogen. The solution immediately turned black with evolution of hydrogen. The α-bromo-*p*-xylene (2.03 g, 11.0 mmol) was added to the suspension. After the mixture was stirred for 30 min, α-bromo-2,3,5,6-tetrafluoroxylene[2] (2.78 g, 10.8 mmol) in dry THF (20 mL) was added by syringe. The solution was stirred at room temperature for 8 h. At the end of this period, the reaction mixture was carefully poured over ice and the organic material dissolved in hexanes (200 mL). The hexane layer was extracted with water (50 mL), filtered, and dried over anhydrous magnesium sulfate and the solvent partially evaporated. The concentrate was chromatographed on a column of silica gel (Brinkman, Type 60) with hexanes as eluent. Three coupling products eluted in the following order: 1,2-bis(4-methyl-2,3,5,6-tetrafluorophenyl)ethane (497 mg, 1.41 mmol, 13%), 1,2-bis(4-methylphenyl)ethane (498 mg, 2.38 mmol, 22%), and 4,4′-dimethyl-2,3,5,6-tetrafluorobibenzyl (1.43 g, 5.07 mmol, 47%). The products were identified by ^1H NMR, ^{13}C NMR, and IR spectral comparison with those of authentic samples.[15] Mixtures with authentic samples gave no melting point depression.

(2,3,4,5,6-Pentafluorobenzyl)triphenylphosphonium Bromide. A mixture of 26.2 g. (0.1 mol) of triphenylphosphine and 26.1 g (0.1 mol) of pentafluorobenzyl bromide[16] in 180 mL of *p*-xylene was heated under reflux for 20 h. A white solid, which began to separate within 0.5 h, was collected and washed with 100 mL of *p*-xylene. Recrystallization from a 95:5 mixture of ether and methanol gave 51 g (97.5%) of phosphonium salt, mp 240–241 °C. Anal. Calcd for $C_{25}H_{17}F_5BrP$: C, 57.38; H, 3.27. Found: C, 57.27; H, 3.11.

2,3,4,5,6-Pentafluoro-4′-methyl-*trans*-stilbene. A three-necked 250-mL flask was equipped with a mechanical stirrer, addition funnel, reflux condenser on a Claisen adaptor, and a 25 mL Erlenmeyer flask connected by Gooch tubing. A flow of prepurified nitrogen was maintained through the apparatus to a bubbler. (Pentafluorobenzyl)triphenylphosphonium bromide (5.13 g, 9.81 mmol) was placed in the 25-mL Erlenmeyer for addition. The ice-cooled flask was charged with anhydrous ethyl ether (40 mL). Methyllithium (7.2 mL, 1.39 M in ether) was transferred by syringe into the addition funnel, which was open to the flask. The phosphonium bromide was carefully added over a 15-min period. The resulting dark red solution was stirred at room temperature for 3 h. To the phosphorane was added *p*-tolualdehyde (1.18 g, 9.82 mmol) in anhydrous ether (25 mL). The brown filter cake was washed with 25 mL of ether and 30 mL of benzene. The solvents were removed under reduced pressure and the remaining brown solid was sublimed (100 °C, 0.1 mmHg) to give 2,3,4,5,6-pentafluoro-4′-methyl-*trans*-stilbene (2.5 g, 8.93 mmol, 91%): mp 143 °C (lit.[15] mp 142.5–143.5 °C); IR (KBr) 3045, 2935, 2860, 1647, 1600, 1511, 1490, 1418, 1335, 1255, 1140, 1120, 1004, 962, 803, 658, 505 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.57–6.92 (m, 6 H), 2.33 (s, 3 H).

2,3,4,5,6-Pentafluoro-4′-methylbibenzyl (6). 2,3,4,5,6-Pentafluoro-4′-methyl-*trans*-stilbene (2.0 g, 7.04 mmol) was dissolved in methanol (75 mL) contained in a Parr bottle. To the solution was added Pd/C (0.2 g, 5%). The hydrogenation was carried out over 11 h at 40 psi (initial). The catalyst was filtered and the methanol evaporated to give a white solid. Sublimation (100 °C, 0.1 mmHg) gave the product as white needles

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(1.97 g, 6.90 mmol, 98%): mp 92 °C (lit.[15] mp 91-92 °C); IR (KBr) 3030, 2975, 2955, 2940, 2865, 1658, 1520-1490, 1460, 1422, 1375, 1302, 1166, 1130, 1117, 1025, 1003, 960, 941, 852, 821, 813, 728, 650, 615, 523 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.03 (s, 4 H), 2.88 (br s, 4 H), 2.30 (s, 3 H).

4,4'-Dimethyl-2,3,5,6-tetrafluorobibenzyl (5). To a solution of 2,3,4,5,6-pentafluoro-4'-methylbibenzyl (1.49 g, 5.21 mmol) in 25 mL of anhydrous ether under nitrogen was added methyllithium (3.8 mL, 1.39 M in ether) dropwise by syringe, and the mixture was refluxed for 3 h. Any remaining lithiate was carefully quenched with ammonium chloride solution (5 mL, 5%) at room temperature. The organic phase was separated and dried over anhydrous magnesium sulfate. Evaporation under reduced pressure afforded a yellow solid. Sublimation gave 4,4'-dimethyl-2,3,5,6-tetrafluorobibenzyl (1.33 g, 4.68 mmol, 90%) as white needles: mp 99 °C (lit.[15] mp 99 °C); IR (KBr) 3029, 2992, 2985, 2934, 2851, 1495, 1478, 1460, 1370, 1275, 1250, 1158, 1110, 1050, 1005, 932, 920, 877, 808, 632, 590, 510 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.06 (s, 4 H), 2.88 (br s, 4 H), 2.30 (s, 3 H), 2.21 (t, 3 h, J = 2.4 Hz); ^{13}C NMR ($CDCl_3$) δ 152.12-149.28 (m) and 139.82-137.01 (m) [J_{CF} = 245.6 Hz], 137.59 (s), 135.86 (s), 129.73-127.21 (m), and 118.06-115.21 (m) [J_{CF} = 236.6 Hz], 129.18 (s), 128.24 (s), 115.22-111.74 (m), 35.17 (s), 20.92 (s). Anal. Calcd for $C_{16}H_{10}F_4$: C, 68.08; H, 4.99; Found: C, 68.42; H, 5.36.

3'-Acetyl-4,4'-dimethyl-2,3,5,6-tetrafluorobibenzyl. Anhydrous aluminum chloride (948 mg, 7.10 mmol) was added to a solution of acetyl chloride (550 mg, 7.0 mmol) in 1,1,2,2-tetrachloroethane (15 mL) at ice-bath temperature, and 4,4'-dimethyl-2,3,5,6-tetrafluorobibenzyl (5) (1.01 g, 3.58 mmol) was added in one portion. After the mixture was stirred under nitrogen for 1 h, TLC (silica gel; hexanes/dichloromethane, 90:10) indicated a large amount of starting material remained along with product (R_f 0.38). The ice bath was removed. The reaction was quenched after 4 h, short of completion. The reaction mixture was hydrolyzed with dilute hydrochloric acid (2 ml) and washed with water (10 mL × 2) and sodium bicarbonate solution (5 mL × 2, 5%). The organic phase was dried over anhydrous magnesium sulfate and evaporated to dryness. The amorphous white solid was chromatographed on silica gel by gradient elution (hexanes/dichloromethane) and the remaining starting material (61 mg, 0.22 mmol, 6.1%) was eluted in hexanes. The acylated product was removed from the column by hexanes/dichloromethane (90:10). After evaporation of the solvents, the sample was sublimed [110 °C (0.1 mmHg)] as white needles (949 mg, 7.04 mmol, 85%): mp 75 °C (ethanol); IR (KBr) 3048, 2970, 2955, 2875, 1676, 1564, 1485, 1357, 1300, 1282, 1262, 1175, 1060, 938, 904, 885, 830, 596, 530 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.43 (br s, 1 H), 7.15 (m, 2 H), 2.93 (br s, 4 H), 2.53 (s, 3 H), 2.46 (s, 3 H), 2.22 (t, 3 H, J = 1.8 Hz); ^{19}F NMR ($CDCl_3$) 144.94-145.34 (m, 2 F), 146.73-147.14 (m, 2 F) ppm; ^{13}C NMR ($CDCl_3$) δ 201.74 (s), 138.14 (s), 137.96 (s), 136.26 (s), 132.23 (s), 131.42 (s), 129.06 (s), 34.83 (s), 29.55 (s), 24.57 (s), 21.03 (br s). (Note: fluoroaryl carbons not resolved.) Anal. Calcd for $C_{18}H_{16}F_4O$: C, 66.67; H, 4.97; F, 23.43. Found: C, 66.60; H, 5.06; F, 23.52.

The Protonated Cyclopropane Route to Bicyclic Cations

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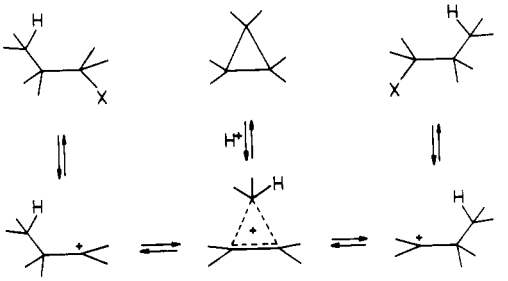
The protolytic cleavage of tricyclo[2.2.0.0^{2,6}]hexane (**3**), tricyclo[3.2.0.0^{2,7}]heptane (**10**), methyltricyclo[3.2.0.0^{2,7}]heptanes (**26**), tricyclo[3.3.0.0^{2,8}]octane (**53**), and tricyclo[3.2.1.0^{2,7}]octane (**58**) in acetic acid and in aqueous dioxane has been investigated. Protonation occurred at a specific site (**3**, **36b,d**, **58**) or competitively at two sites (**10**, **26c**, **53**), depending on the stability of the incipient carbocations. Product distributions and label redistributions, where applicable, were in good to excellent agreement with previous solvolytic studies. We conclude that the protonated cyclopropane and σ routes are equivalent in generating bridged carbocations. Edge-protonated cyclopropanes play a minor role, if any, in product formation. Stereoselectivity appears to be an intrinsic property of the cationic intermediates, largely independent of the specific orientation of their counterions.

Reactions in which carbocations undergo 1,2 alkyl shifts are common and have long been studied.[1] In considering possible intermediates and transition states for the Wagner-Meerwein rearrangement, one is virtually required to invoke structures containing three-membered rings with seven substituent atoms or groups (alkyl-bridged ions). Such cations might arise from the addition of a proton to a cyclopropane ring (Scheme I). Protonated cyclopropanes are well-established species, both experimentally and theoretically.[2,3] The stereochemistry and kinetics of the acid-induced ring opening of cyclopropanes have been

Scheme I



examined extensively.[3,4] The data indicate that proton transfer is rate determining and that the reaction proceeds toward the more stable carbocation. The products are formed in major extent by capture of the protonated

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