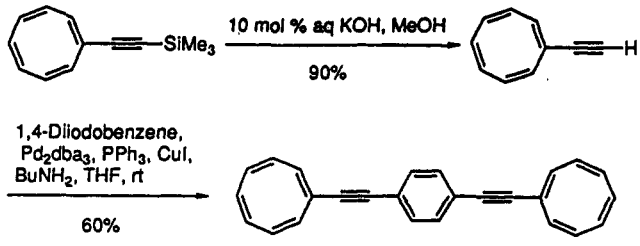
Table II. Palladium-Catalyzed Coupling of Bromocyclooctatetraene with Terminal Alkynes or Alkynylstannanes

alkyne	conditions	product	yield (%)
ethynyltrimethylsilane	Pd_2dba_3, PPh_3, CuI, $BuNH_2$, THF, rt	[(trimethylsilyl)ethynyl]cyclooctatetraene	95
tributyl[(trimethylsilyl)ethynyl]stannane	Pd_2dba_3, $Pfur_3$, THF, rt		63
ethynylbenzene	Pd_2dba_3, PPh_3, CuI, $BuNH_2$, THF, rt	(phenylethynyl)cyclooctatetraene	90
tributyl(phenylethynyl)stannane	Pd_2dba_3, $Pfur_3$, THF, rt		64
acetylene	Pd_2dba_3, PPh_3, CuI, $BuNH_2$, THF, rt	dicyclooctatetraenylethyne (**3a**)	80
1,2-bis(tributylstannyl)ethyne (**2a**)	Pd_2dba_3, $Pfur_3$, THF, rt		55

Scheme I



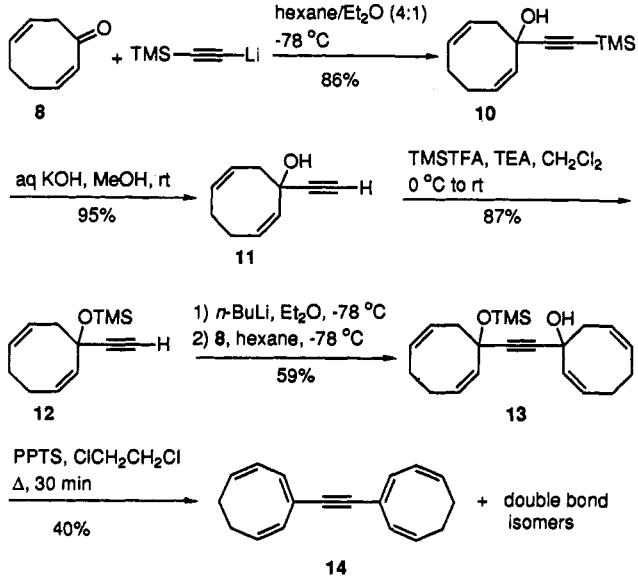
tatetraenes that we investigated involves the initial addition of an organolithium or Grignard reagent to 2,6-cyclooctadien-1-one. Dehydration of the alcohol obtained from the addition of an organometallic reagent to 2,6-cyclooctadien-1-one was expected to afford a substituted cyclooctatriene that could be doubly deprotonated to the cyclooctatetraene dianion, which could then be oxidized to the substituted cyclooctatetraene.[23,24] 2,4,6-Cyclooctatrien-1-one cannot be used for this strategy because previous work by Kröner has shown that this compound readily undergoes electrocyclic ring opening upon 1,2-addition of Grignard reagents.[25]

2,6-Cyclooctadien-1-one (**8**) was prepared[26] as the major component of an approximately 10:1 mixture with 2,5-cyclooctadien-1-one (**9**).[27] Since the synthetic sequence called for the conversion of the cyclooctadienone to a cyclooctatriene and ultimately to a cyclooctatetraene, it was not expected that the presence of **9** would present a problem.

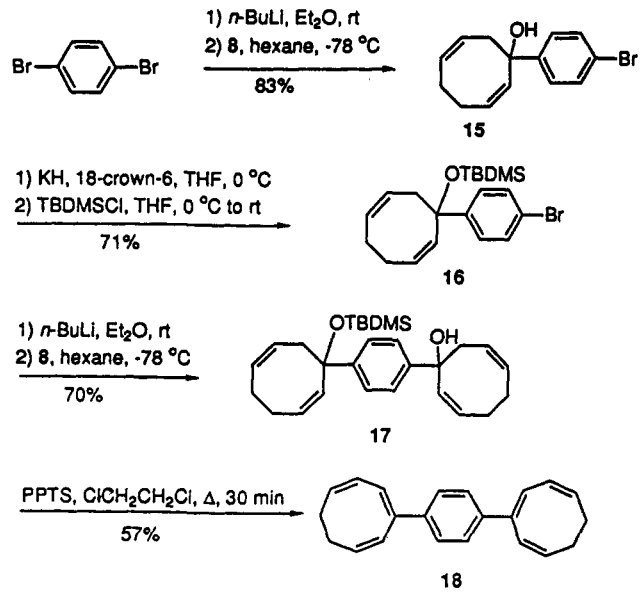
The preparation of alkyne-bridged dicyclooctatriene **14** is given in Scheme II. The reaction of lithium (trimethylsilyl)acetylide with the mixture of **8** and **9** (for convenience referred to as **8/9**) afforded acetylenic alcohol **10** in 87% yield, but only when the solvent was predominantly hexane (4:1 hexane/ether). Only enough ether was used to ensure the solubility of the lithium acetylide. If any THF was used, no **10** was obtained and only **8/9** was recovered. When the reaction mixture in THF at −78 °C was quenched with chlorotrimethylsilane, the silyl enol ether of **8** was isolated,[28] indicating that enolization of the ketone rather than nucleophilic addition occurs in the more polar solvent.

The conversion of **13** to **14** was effected in a one-pot procedure with *p*-pyridinium tosylate (PPTS) according to the procedure of Heathcock and co-workers.[29] This afforded the unstable **14** in relatively low yield (40%) after SG chromatography.[30] The ^1H NMR spectrum indicated

Scheme II



Scheme III



that the major isomer in the product mixture was a di-1,3,5-cyclooctatrienyl isomer based on a multiplet at δ 2.4–2.5. The presence of 1,3,6-cyclooctatrienyl isomers is indicated by diallylic signals at δ 2.8 and 2.9. The ratio of the integrated area of the δ 2.4–2.5 multiplet to that of the diallylic signals was 10:1.

Aryl-bridged dicyclooctatrienes were prepared by a similar synthetic sequence (Scheme III). For the preparation of **17**, the alcohol **15** was protected as its TBDMS

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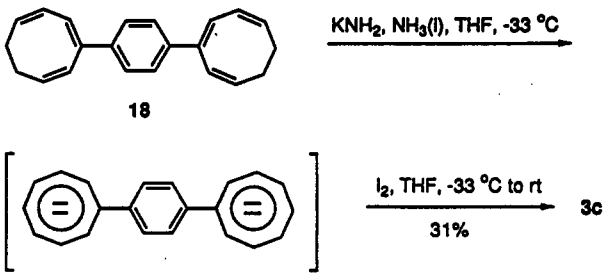
(30) The Burgess reagent, BF_3·OEt_2, $SOCl_2$/pyridine, and 2,4-dinitrobenzenesulfenyl chloride, were also investigated for the dehydration of the bridged diol. All these methods either failed or gave a very low yield of bridged dicyclooctatriene.

ether according to the procedure of Braish and Fuchs.[31] The deprotective–dehydration step was then effected with PPTS to afford aryl-bridged dicyclooctatrienes 18 in moderate yield (57%). The ^{1}H NMR spectrum displayed two equal-area multiplets at δ 2.4 and 2.55 indicating that only di-1,3,5-cyclooctatriene isomers were isolated.

Oxidation of Bridged Dicyclooctatrienes to Dicyclooctatetraenes. Previous conversions of substituted cyclooctatrienes to cyclooctatetraenes[23,24,32] used KNH_2 as the base for deprotonation to the cyclooctatetraene dianion and I_2 as the subsequent oxidant. We anticipated that 18 and 3c would be more stable to the reaction conditions than 14 and 3a, so the former conversion was examined first.

A solution of 18 in THF was added to a suspension of KNH_2 in liquid ammonia to produce a deep-purple reaction mixture. A solution of I_2 in THF was then added, and 3c was obtained in 31% yield after workup and SG chromatography. Changing the base to $NaNH_2$ gave a similar yield. Use of O_2 as the oxidant[33] led to a mixture of 3c and 18.



Addition of a solution of 14 in THF to KNH_2 in liquid ammonia followed by I_2 oxidation afforded a 20% yield of 3a. Because of our success with preparing 3a through the coupling of 1 with 2a or acetylene, we did not examine any modifications of the conditions for this conversion. The overall yield of 3a from 8/9 in six steps was 3.3% whereas the overall yield of 3c from 8/9 in five steps was 7.2%.

Summary. Bridged dicyclooctatetraenes have been prepared by three synthetic routes: (1) the palladium-catalyzed coupling of distannanes with bromocyclooctatetraene, (2) the palladium/copper-catalyzed coupling of terminal alkynes with bromocyclooctatetraene or with 1,4-diiodobenzene, and (3) the synthesis of bridged dicyclooctatrienes followed by the oxidative conversion to dicyclooctatetraenes. The latter route is a linear synthesis that suffers from low yields in the final steps, which makes it difficult to prepare bridged dicyclooctatetraenes in gram quantities. The Stille coupling route is highly convergent and works reasonably well for the coupling of distannanes 2a–c with 1. Finally, the coupling of 1 with terminal alkynes using palladium/copper catalyst affords high yields and is superior to the Stille coupling for the synthesis of alkynylcyclooctatetraenes and alkynyl-bridged dicyclooctatetraenes.

Experimental Section

General. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium metal/benzophenone ketyl. Hexane and triethylamine (TEA) were distilled from calcium hydride. Dichloromethane and 1,2-dichloroethane were passed through a column of activity I basic alumna immediately before use. All other reagents were commercially available and were used as received. Air- and/or moisture-sensitive reactions were carried out under a nitrogen atmosphere. All organic extracts were dried over $MgSO_4$ and concentrated with a rotary evaporator. Brine refers to saturated aqueous NaCl. Preparative column chromatography was performed on 40-μm silica gel (SG) according to the procedure of Still and co-workers.[34] NMR spectra were obtained for $CDCl_3$ solutions at 300 MHz for ^{1}H and 75 MHz for ^{13}C unless indicated otherwise. Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN). Mass spectra were recorded by the University of Pittsburgh Mass Spectrometry Facility.

General Procedure for the Pd-Catalyzed Coupling of Distannanes with Bromocyclooctatetraene (1). 1,2-Dicyclooctatetraenylethyne (3a). To a solution of 1 (190 mg, 1 mmol), tris(dibenzylideneacetone)dipalladium(0) (23 mg, 0.025 mmol, 0.05 mmol Pd), and tri(2-furyl)phosphine (24 mg, 0.1 mmol) in 1 mL of THF was added a solution of 1,2-bis(tributylstannyl)-ethyne (370 mg, 0.6 mmol) in 1 mL of THF. After 2 h the reaction mixture was diluted with 15 mL of EtOAc and 20 mL of 50% sautrated aqueous KF was added. The mixture was stirred for 15 min, filtered, and the organic layer was washed with 1 × 20 mL of 50% saturated aqueous KF, 2 × 20 mL of H_2O, and 1 × 20 mL of 50% brine. The combined aqueous layers were extracted with 10 mL of EtOAc and the combined organic layers were dried. The residue was dissolved in 20 mL of hexane and 2 g of SG was added. The mixture was then evaporated and chromatographed on 20 g of SG with 10% CH_2Cl_2/hexane to afford 65 mg (55%) of a yellow-orange film: ^{1}H NMR (THF-d_8, −50 °C) δ 6.1 (m, 2 H), 5.8–5.9 (m, 10 H), 5.7 (d, J = 11.4 Hz, 2 H); ^{13}C NMR (THF-d_8, −50 °C) δ 138.6, 133.5, 133.1, 132.7, 132.5, 132.0, 131.6, 126.1, 88.2; IR 3000, 2930, 2850, 1640 cm^{-1}; HRMS calcd for $C_{18}H_{14}$ (M^+) 230.1096, found 230.1087; TLC R_f = 0.27 (10% CH_2Cl_2/hexane).

(*E*)-1,2-Dicyclooctatetraenylethylene (3b). (*E*)-1,2-Bis(tributylstannyl)ethylene (370 mg, 0.6 mmol) was coupled with 1 (190 mg, 1 mmol) using tri(2-furyl)phosphine (24 mg, 0.1 mmol) as ligand in THF over 5 h. After workup, the residue was dissolved in 20 mL of hexane and 2 g of SG was added. The mixture was evaporated and chromatographed on 20 g of SG with 10% CH_2Cl_2/hexane to afford 75 mg (65%) of a yellow-orange oil: ^{1}H NMR (THF-d_8, −5 °C) δ 6.2 (s, 2 H), 5.7–6.0 (m, 14 H); ^{13}C NMR (THF-d_8, −5 °C): δ 141.1, 133.3, 132.8, 132.5, 132.1, 131.6, 131.3; TLC R_f = 0.27 (10% CH_2Cl_2/hexane). The ^{1}H and ^{13}C chemical shifts at room temperature agreed with previously reported values.[5]

1,4-Dicyclooctatetraenylbenzene (3c). 1,4-Bis(tributylstannyl)benzene (400 mg, 0.6 mmol) was coupled with 1 (190 mg, 1 mmol) using triphenylarsine (31 mg, 0.1 mmol) as ligand in THF over 24 h. After workup, the residue was dissolved in 20 mL of hexane, and 2 g of SG was added. The mixture was evaporated and chromatographed on 20 g of SG with 10% CH_2Cl_2/hexane to afford 43 mg (30%) of a light-yellow solid: mp 127–128 °C; ^{1}H NMR (THF-d_8, −5 °C) δ 7.31 (s, 4 H), 6.25 (d, J = 3.9 Hz, 2 H), 5.8–6.1 (m, 12 H); ^{13}C NMR (THF-d_8, −5 °C) δ 142.2, 140.2, 133.6, 133.3, 133.1, 132.9, 132.5, 132.3, 128.7, 126.7; IR 3050, 2990, 1265 cm^{-1}; HRMS calcd for $C_{22}H_{18}$ (M^+) 282.1409, found 282.1369; TLC R_f = 0.2 (10% CH_2Cl_2/hexane). Anal. Calcd for $C_{22}H_{18}$: C, 93.56; H, 6.44. Found: C, 93.16; H, 6.52.

General Procedure for the Pd/Cu-Catalyzed Coupling of Terminal Alkynes with 1: [(Trimethylsilyl)ethynyl]cyclooctatetraene. Pd_2dba_3 (37 mg, 0.04 mmol), PPh_3 (42 mg, 0.16 mmol), CuI (61 mg, 0.32 mmol), and *n*-butylamine (0.28 mL, 2.8 mmol) were added to a solution of 1 (370 mg, 2 mmol) in 2 mL of THF. Ethynyltrimethylsilane (0.34 mL, 2.4 mmol) in 2 mL of THF was then added. After 2 h the reaction mixture was poured into 20 mL of Et_2O and washed with 1 × 15 mL of saturated NH_4Cl, 2 × 15 mL of H_2O, and 1 × 15 mL of brine. The organic layer was dried and evaporated, and the residue was chromatographed on 20 g of silica gel with hexane to yield 400 mg (95%) of a yellow oil: ^{1}H NMR (acetone-d_6, −50 °C) δ 6.15 (m, 1 H), 5.8

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(34) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(m, 5 H), 5.65 (m, 1 H), 0.2 (s, 9 H); ^{13}C NMR (acetone-d_6, −50 °C) δ 139.5, 133.4, 133.2, 132.5, 132.2, 131.6, 131.1, 125.7, 105.7, 91.5, −0.42; IR 3010, 2140, 1250, 1150 cm^{-1}; HRMS calcd for $C_{18}H_{16}Si$ (M^+) 200.1021, found 200.1013; TLC R_f = 0.24 (hexane).

(Phenylethynyl)cyclooctatetraene. Ethynylbenzene (120 mg, 1.2 mmol) was coupled with **1** (190 mg, 1 mmol) according to the general procedure. After 1 h the reaction mixture was worked up, evaporated, and chromatographed on 20 g of silica gel with 10% CH_2Cl_2/hexane to yield 187 mg (90%) of a yellow oil: ^1H NMR (acetone-d_6, −50 °C) δ 7.45 (m, 2 H), 7.4 (m, 3 H), 6.28 (m, 1 H), 5.9 (m, 6 H); ^{13}C NMR (acetone-d_6, −50 °C) δ 138.7, 133.4, 133.3, 132.6, 132.2, 131.9, 131.7, 131.3, 129.3, 129.2, 125.6, 123.2, 90.2, 87.2; IR 3008, 2200 (w) cm^{-1}; HRMS calcd for $C_{16}H_{10}$ (M^+ − 2) 202.0783, found 202.0758; TLC R_f = 0.3 (10% CH_2Cl_2/hexane).

Ethynylcyclooctatetraene. Aqueous 0.5 M KOH (150 μl, 0.075 mmol) was added to a solution of [(trimethylsilyl)ethynyl]-cyclooctatetraene (560 mg, 2.8 mmol) in 10 mL of MeOH. After 1 h the reaction mixture was poured into 10 mL of H_2O and extracted with 4 × 10 mL of Et_2O. The combined organic layers were washed with 15 mL of brine and dried over $MgSO_4$ to yield 369 mg (90%) of an unstable yellow-orange oil that was used immediately in the next step without purification: ^1H NMR (acetone-d_6, −50 °C) δ 6.2 (m, 1 H), 5.8 (m, 6 H), 3.6 (s, 1 H); ^{13}C NMR (acetone-d_6, −50 °C) δ 139.5, 133.4, 132.5, 132.1, 131.5, 131.0, 124.9, 84.3, 77.2; IR 3295, 3000, 2960, 2145 cm^{-1}.

1,4-Bis(cyclooctatetraenylethynyl)benzene (4). Ethynylcyclooctatetraene (290 mg, 2.27 mmol) was coupled with 1,4-diiodobenzene (360 mg, 1.1 mmol) according to the general procedure. After 1 h the reaction mixture was worked up, evaporated with 4 g of SG, and chromatographed on 40 g of SG with 10% CH_2Cl_2/hexane to yield 238 mg (65%) of a yellow solid: recrystallized from CH_2Cl_2 (−20 °C); mp 129–131 °C dec; ^1H NMR (THF-d_8, −50 °C) δ 7.4 (s, 4 H), 6.25 (m, 2 H), 5.85 (m, 12 H); ^{13}C NMR (THF-d_8, −50 °C) δ 139.2, 133.8, 133.5, 132.8, 132.5, 132.3, 131.9, 131.6, 126.0, 123.7, 92.5, 87.2; IR: 3050, 3010, 2200 (w), 1500, 1265 cm^{-1}; HRMS calcd for $C_{26}H_{18}$ (M^+) 330.1409, found 330.1408; TLC R_f = 0.3 (20% CH_2Cl_2/hexane). Anal. Calcd for $C_{26}H_{18}$: C, 94.50; H, 5.50. Found: C, 94.11; H, 5.40.

1,3-Bis(cyclooctatetraenylethynyl)benzene (5). 1,3-Diethynylbenzene[21] (126 mg, 1 mmol) was coupled with **1** (300 mg, 1.67 mmol) using tri(2-furyl)phosphine (31 mg, 0.134 mmol) as the ligand according to the general procedure. After 1 h the reaction mixture was worked up, evaporated with 3 g of SG, and chromatographed on 30 g of SG with 10% CH_2Cl_2/hexane to yield 176 mg (60%) of a yellow-orange residue. The residue was dissolved in petroleum ether and allowed to crystallize at −20 °C: mp 64–6 °C dec; ^1H NMR (THF-d_8, −50 °C) δ 7.5 (m, 1 H), 7.4 (m, 3 H), 6.25 (m, 2 H), 5.85 (m, 12 H); ^{13}C NMR (THF-d_8, −50 °C) δ 139.2, 135.1, 133.7, 133.5, 132.8, 132.5, 132.0, 131.9, 131.6, 129.7, 126.0, 124.3, 91.2, 86.5; IR 3050, 3010, 2200 (w), 1475 cm^{-1}; HRMS calcd for $C_{26}H_{18}$ (M^+) 330.1409, found 330.1441; TLC R_f = 0.3 (20% CH_2Cl_2/hexane).

Preparation of a Mixture of 2,6-Cyclooctadien-1-ol (6) and 2,5-Cyclooctadien-1-ol (7). An approximately 1:1 mixture of 3-bromo-1,5-cyclooctadiene and 6-bromo-1,4-cyclooctadiene[35] was converted to a mixture of **6** and **7** in 86% yield according to the procedure of Echter and Meier:[26] IR 3353, 3015, 2938, 2882, 2825, 1651, 1426, 1040 cm^{-1}; ^1H NMR δ 5.6 (m, 4 H), 4.9 (m, 1 H), 2.75 (m, 1 H), 2.1–2.5 (m, 5 H), 1.85 (bs, 1 H).

The ^{13}C NMR chemical shifts for **6** and **7** were determined from the mixture. Major Isomer: δ 133.4, 129.7, 127.6, 125.5, 69.9, 36.8, 28.5, 27.5. Minor Isomer: δ 133.9, 129.3, 128.9, 127.4, 69.3, 31.8, 29.3, 23.4.

2,6-Cyclooctadien-1-one (8) and 2,5-Cyclooctadien-1-one (9). An approximately 10:1 mixture of **8** and **9** was prepared in 51% yield from the mixture of **6** and **7** according to the procedure of Cantrell and Solomon:[36] Bp 43–45 °C/0.25 mm (lit. bp 42–44 °C/0.2 mm); IR 3020, 2960, 2890, 2830, 1670, 1650, 1480, 1280, 1220 cm^{-1}; TLC R_f = 0.35 (20% EtOAc/hexane). Anal. Calcd for $C_8H_{10}O$: C, 78.70; H, 8.19. Found: C, 78.89; H, 7.85.

The NMR data for **8** and **9** were obtained from the mixture. **8**: ^1H NMR δ 6.4 (d of t, J = 8.4, 12 Hz, 1 H), 6.0 (d, J = 12.3 Hz, 1 H), 5.6 (m, 2 H), 3.37 (d, J = 6.6 Hz, 2 H), 2.74 (m, 2 H), 2.36 (m, 2 H); ^{13}C NMR δ 201.3, 142.3, 131.5, 130.9, 121, 43.8, 27.1, 26.9. **9**: ^1H NMR δ 6.56 (d of t, J = 7, 12.6 Hz, 1 H), 6.0 (d, J = 12.3 Hz, 1 H), 5.75 (m, 2 H), 3.12 (m, 2 H), 2.9 (m, 2 H), 2.5 (m, 2 H); ^{13}C NMR δ 205.0, 142.8, 132.1, 131.5, 125.8, 41.4, 36.9, 24.7.

1-[(Trimethylsilyl)ethynyl]-2,6-cyclooctadien-1-ol (10). To a solution of ethynyltrimethylsilane (3.6 mL, 25.2 mmol) in 9 mL of Et_2O at −78 °C was added 17.5 mL (25.2 mmol) of 1.44 M *n*-BuLi in hexanes. After 30 min this solution was added to **8/9** (2.05 g, 16.8 mmol) in 18 mL of hexane at −78 °C. After an additional 1 h the reaction mixture was poured into 50 mL of saturated aqueous NH_4Cl. The aqueous layer was extracted with 2 × 20 mL of Et_2O, and the combined organic layers were washed twice with 30 mL of H_2O and once with 30 mL of brine and dried. The residue was chromatographed on 190 g of SG with 10% EtOAc/hexane to yield 3.2 g (86%) of a colorless oil: IR 3370, 3030, 2959, 2890, 2830, 2164, 1658, 1243, 860 cm^{-1}; ^1H NMR δ 5.6 (m, 4 H), 3.1 (m, 1 H), 2.7 (m, 1 H), 2.6 (m, 1 H), 2.1–2.4 (m, 4 H), 0.16 (s, $SiCH_3$, 9 H); ^{13}C NMR δ 133.5, 131.8, 127.7, 123.2, 108.4, 88.2, 71.6, 39.6, 29.2, 25.3, 0.0; TLC R_f = 0.3 (10% EtOAc/hexane). Anal. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.08. Found: C, 70.83; H, 9.36.

The following NMR signals were detected for the 2,5-isomer: ^1H NMR δ 0.18 (integration 1:15 with respect to the 2,6-isomer); ^{13}C NMR δ 135.0, 131.0, 130.5, 130.0, 23.0.

1-Ethynyl-2,6-cyclooctadien-1-ol (11). To a solution of **10** (2.1 g, 9.6 mmol) in 15 mL of MeOH was added 2.1 mL of 0.5 M KOH. The reaction mixture was stirred for 1 h at rt, poured into 15 mL of H_2O, and extracted with 3 × 15 mL of Et_2O. The combined Et_2O layers were washed once with 20 mL of brine and dried to afford 1.4 g (95%) of a colorless oil that was used directly in the next step: IR 3395, 3300, 3030, 2945, 2890, 2832, 2110, 1650, 1020 cm^{-1}; ^1H NMR δ 5.6–5.7 (m, 4 H), 3.1 (m, 1 H), 2.8 (m, 1 H), 2.65 (m, 1 H), 2.55 (s, 1 H), 2.0–2.4 (m, 4 H); ^{13}C NMR δ 133.2, 131.8, 127.9, 122.9, 86.9, 72.1, 71.0, 39.3, 29.1, 25.2; TLC R_f = 0.3 (20% EtOAc/hexane).

The following NMR signals were detected for the 2,5-isomer: ^{13}C NMR δ 134.3, 130.7, 130.0, 129.7, 85.8, 72.6, 36.5, 25.9, 23.4.

TMS Ether of 11 (12). Trimethylsilyl trifluoroacetate (2.5 mL, 14.4 mmol) was added to a solution of **11** (1.4 g, 9.6 mmol) and triethylamine (4 mL, 28.8 mmol) in 35 mL of CH_2Cl_2 at 0 °C. The reaction mixture was warmed to rt, stirred for 2 h, and poured into 40 mL of saturated aqueous $NaHCO_3$. The aqueous layer was extracted with 2 × 15 mL of CH_2Cl_2 and the combined organic layers were dried. The residue was chromatographed on 65 g of SG with 10% CH_2Cl_2/hexane to afford 1.8 g (87%) of a colorless oil: IR 3300, 3029, 2959, 2900, 2830, 2100, 1650, 1250, 1060 cm^{-1}; ^1H NMR δ 5.6 (m, 4 H), 2.9 (m, 2 H), 2.6 (s, 1 H), 2.5 (m, 2 H), 2.3 (m, 2 H), 0.22 (s, 9 H); ^{13}C NMR δ 134.8, 131.0, 126.8, 124.1, 87.9, 73.3, 72.5, 40.9, 28.9, 25.5, 2.0; TLC R_f = 0.3 (10% CH_2Cl_2/hexane).

The following NMR signals were detected for the 2,5-isomer: ^1H NMR δ 0.21 (integration 1:15 with respect to the 2,6-isomer); ^{13}C NMR δ 136.6, 130.9, 129.5, 128.9, 73.5, 71.8, 40.6, 25.7, 23.4, 1.9.

Alkynyl-Bridged Dicyclooctadienes 13. To a solution of **12** (970 mg, 4.4 mmol) in 2 mL of Et_2O at −60 °C was added 3.1 mL (4.4 mmol) of 1.44 M *n*-BuLi in hexanes. After 1 h this solution was added dropwise to **8/9** (530 mg, 4.35 mmol) in 5 mL of hexane at −78 °C. After an additional 1 h, the reaction mixture was poured into 40 mL of saturated aqueous $NaHCO_3$, the aqueous layer was extracted with 2 × 15 mL of Et_2O, and the combined organic layers were dried. The residue was chromatographed on 150 g of SG with 10% EtOAc/hexane to afford 889 mg (59%) of a pale-yellow viscous oil: IR 3430, 3022, 2952, 2900, 2830, 1650, 1250, 1060 cm^{-1}; ^1H NMR δ 5.6 (m, 8 H), 3.1 (m, 1 H), 2.8 (m, 1 H), 2.5–2.7 (m, 4 H), 2.2–2.4 (m, 6 H), 2.1 (s, 1 H), 0.2 (s, 9 H); ^{13}C NMR δ 135.0, 133.4, 131.8, 130.9, 127.3, 126.1, 124.2, 123.5, 87.6, 72.5, 71.3, 41.1, 39.5, 29.3, 28.9, 25.5, 25.2, 2.0; TLC R_f = 0.3 (10% EtOAc/hexane).

The following NMR signal was detected for the 2,5-isomer: ^1H NMR δ 0.19 (integration 1:15 with respect to the 2,6-isomer).

(35) Cope, A. C.; Stevens, C. L.; Hochstein, F. A. *J. Am. Chem. Soc.* **1950**, *72*, 2510.
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1-(4-Bromophenyl)-2,6-cyclooctadien-1-ol (15). To a solution of 1,4-dibromobenzene (3.96 g, 16.8 mmol) in 24 mL of Et_2O at rt was added 10.5 mL (16.8 mmol) of 1.6 M *n*-BuLi in hexanes. After 1 h this solution was added to **8/9** (1.46 g, 12 mmol) in 18 mL of hexane at −78 °C. After an additional 1 h the reaction mixture was poured into 50 mL of saturated aqueous NH_4Cl and the aqueous layer was extracted with 3 × 20 mL of Et_2O. The combined organic layers were washed once each with 40 mL of H_2O and 40 mL of brine and dried. The residue was chromatographed on 170 g of SG with 20% EtOAc/hexane to afford 2.79 g (83%) of a colorless oil: IR 3440, 3020, 2960, 2920, 2880, 1650, 1500, 1020 cm^{-1}; ^1H NMR δ 7.45 (d, J = 8.7 Hz, 2 H), 7.36 (d, J = 8.7 Hz, 2 H), 5.5–5.9 (m, 4 H), 3.1 (d of d of d, J = 14.4, 8.4, 0.6 Hz, 1 H), 2.9 (m, 1 H), 2.2–2.6 (m, 5 H); ^{13}C NMR δ 145.5, 135.7, 132.1, 131.1, 127.3, 126.9, 123.6, 120.7, 79.5, 41.3, 29.9, 25.2; chemical ionization MS: m/z 261 $[M + H - H_2O]^+$; TLC R_f = 0.35 (20% EtOAc/hexane).

The following NMR signals were detected for the 2,5-isomer: ^{13}C NMR δ 146.7, 135.2, 128.1, 126.1, 77.9, 39.8, 25.9, 24.8.

TBDMS Ether of 15 (16). A solution of **15** (2.4 g, 8.6 mmol) in 20 mL of THF was added to a slurry of KH (35% in oil, 1.12 g, 9.73 mmol, washed three times with petroleum ether) and 18-crown-6 (30 mg, 0.086 mmol) in 10 mL of THF at 0 °C. After gas evolution ceased, a solution of *tert*-butyldimethylsilyl chloride (1.43 g, 9.46 mmol) in 20 mL of THF was added. The reaction mixture was warmed to rt, and after 1 h was cooled to 0 °C and quenched with 0.5 mL of H_2O. After evaporation of most of the THF, the residue was dissolved in 40 mL of Et_2O, washed once each with 40 mL of H_2O and 40 mL of brine, and dried. The residue was chromatographed on 140 g of SG with hexane to afford 2.4 g (71%) of a white solid: mp 38–41 °C; IR 3015, 2960, 2930, 2860, 1460, 1250, 1060 cm^{-1}; ^1H NMR δ 7.41 (d, J = 8.7 Hz, 2 H), 7.33 (d, J = 8.7 Hz, 2 H), 5.85 (d of t, J = 12, 8.7 Hz, 1 H), 5.65 (d, J = 12 Hz, 1 H), 5.53 (d of t, J = 11.4, 4.2 Hz, 1 H), 5.3 (m, 1 H), 2.8 (d of d, J = 14.1, 8.7 Hz, 1 H), 2.6 (m, 3 H), 2.35 (m, 2 H), 0.9 (s, 9 H), 0.1 (s, 3 H), 0.02 (s, 3 H); ^{13}C NMR δ 147.6, 135.3, 130.6, 130.3, 128.3, 127.6, 125.2, 120.4, 81.8, 42.6, 29.5, 26.0, 25.5, 18.6, −2.2; TLC R_f = 0.4 (hexane). Anal. Calcd for $C_{20}H_{29}BrOSi$: C, 61.05; H, 7.37. Found: C, 61.23; H, 7.26.

The following NMR signals were detected for the 2,5-isomer: ^{13}C NMR δ 146.7, 134.6, 131.6, 131.4, 127.7, 127.3, 124.9, 120.6, 81.1, 41.0, 25.1, −2.4.

Aryl-Bridged Dicyclooctadienes 17. To a solution of **16** (1.2 g, 3.05 mmol) in 4.4 mL of Et_2O at rt was added 1.9 mL (3.05 mmol) of 1.6 M *n*-BuLi in hexane. After 1 h this solution was added dropwise to **8/9** (310 mg, 2.54 mmol) in 4 mL of hexane at −78 °C. The reaction mixture was stirred for an additional 1 h and then poured into 40 mL of saturated aqueous $NaHCO_3$. The aqueous layer was extracted with 2 × 15 mL of Et_2O, and the combined organic layers were dried. The residue was chromatographed on 110 g of SG with 10% EtOAc/hexane to afford 785 mg (70%) of a colorless viscous oil: IR 3444, 3022, 2959, 2931, 2900, 2850, 1650, 1460, 1250, 1070 cm^{-1}; ^1H NMR δ 7.44 (s, 4 H), 5.5–5.9 (m, 8 H), 2.2–3.2 (m, 13 H), 0.9 (s, 9 H), 0.1 (s, 3 H), 0.02 (s, 3 H); TLC R_f = 0.3 (10% EtOAc/hexane).

General Procedure for the Preparation of Bridged Dicyclooctatrienes (18). A solution of **17** (1.04 g, 2.4 mmol) and *p*-pyridinium tosylate (120 mg, 0.48 mmol) in 65 mL of 1,2-dichloroethane was heated to reflux. After 30 min the reaction mixture was cooled to rt, diluted with 40 mL of CH_2Cl_2, and washed with 60 mL of 50% brine. The organic layer was dried, 7 g of SG was added, and the mixture was evaporated and chromatographed on 70 g of SG with 10% CH_2Cl_2/hexane to afford 412 mg (57%) of **18** as a white oily solid: ^1H NMR δ 7.38 (s, 4 H), 6.2 (m, 6 H), 5.9 (m, 4 H), 2.55 (m, 4 H), 2.4 (m, 4 H); ^{13}C NMR δ 140.3, 137.3, 136.1, 133.4, 128.9, 126.6, 126.2, 123.9, 28.8, 26.4; HRMS calcd for $C_{22}H_{22}$ (M^+) 286.1722, found 286.1675; TLC R_f = 0.25 (5% CH_2Cl_2/hexane).

Alkynyl-Bridged Dicyclooctatrienes 14. **13** (680 mg, 2 mmol) was converted to **14** according to the general procedure. The residue after workup was chromatographed on 50 g of SG with 10% CH_2Cl_2/hexane to afford 200 mg (40%) of an unstable viscous oil that was not purified further: IR 2186, 1640 cm^{-1}; ^1H NMR: δ 6.15 (m, 2 H), 5.8–6.1 (m, 8 H), 2.45 (m, 8 H); ^{13}C NMR δ 136.1, 135.5, 132.6, 127.9, 125.4, 119.9, 89.3, 28.5, 26.6; TLC R_f = 0.3 (10% CH_2Cl_2/hexane).

General Procedure for the Oxidative Conversion of Bridged Dicyclooctatrienes to Dicyclooctatetraenes 3c and 3a. To a round-bottomed flask equipped with a dry ice condenser and containing $FeCl_3$ (obtained by heating 40 mg of $FeCl_3 \cdot 6H_2O$) was condensed 50 mL of liquid ammonia. The flask was cooled to −78 °C and potassium (380 mg, 9.6 mmol) was added. The resulting blue solution was allowed to warm to −33 °C until it became a gray suspension. To this was added 20 mL of THF followed by a solution of **18** (343 mg, 1.2 mmol) in 20 mL of THF. The reaction mixture turned a deep purple color. After 1 h I_2 (1 g, 4 mmol) in 10 mL of THF was added and the flask was warmed to rt. After evaporation of the NH_3, the reaction mixture was poured into 100 mL of saturated aqueous $Na_2S_2O_3$ and filtered, and the filtrate was extracted with 2 × 40 mL of CH_2Cl_2. The combined organic layers were washed with 20 mL of 50% brine and dried, and 3 g of SG was added. The mixture was evaporated and chromatographed on 30 g of SG with 10% CH_2Cl_2/hexane to yield 105 mg (31%). The ^1H NMR spectrum was identical to that listed above for **3c**. The same procedure was used to prepare **3a** from **14** in 15% yield. The ^1H NMR spectrum of the product was identical to that listed above for **3a**.

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Supplementary Material Available: Copies of NMR spectra of **3a**, **3b**, **5**, **11–14**, **17**, **18**, [(trimethylsilyl)ethynyl]-cyclooctatetraene, ethynylcyclooctatetraene, and (phenylethynyl)cyclooctatetraene (18 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Toward an Understanding of the Cubyl and Related Caged Carbocations

Ernest W. Della,*[1] Nicholas J. Head,[1] Wit K. Janowski,[1] and Carl H. Schiesser*[2]

School of Physical Sciences, Flinders University, GPO Box 2100, Adelaide, South Australia, 5001, and School of Chemistry, University of Melbourne, Parkville, Victoria, 3052, Australia

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The product ratios observed upon fluorodeiodination of a series of caged cyclobutane-containing iodides are explained on the basis of the relative energies of the intermediate cations involved. The relative energies of these cations have been evaluated by *ab initio* calculations with the inclusion of electron correlation (MP2/6-31G*//RHF/3-21G; MP2/6-31G**), the results of which lend support to the view that hyperconjugative involvement of the cationic center with the α,β and β,γ C–C bonds in each cyclobutyl moiety is the critical factor responsible for the stability of the cation in each case. The degree of stabilization of the cations is a reflection of the number and relative importance of several resonance contributors (corresponding to the involvement of the carbon σ-framework) to their overall structure and is strongly dependent on the geometry of the rigid carbon framework in each case.

Introduction

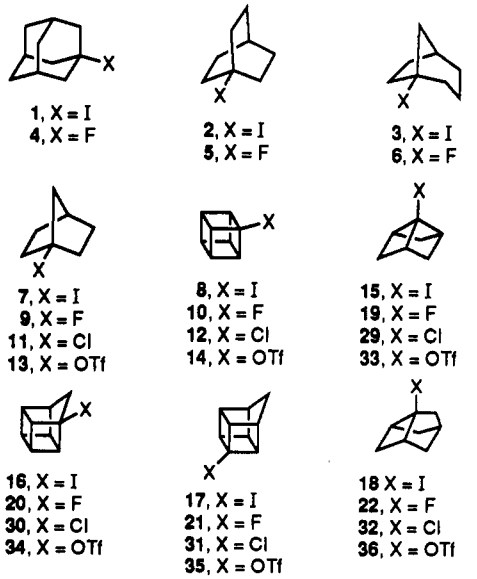
We reported recently that fluorodeiodination of a series of bridgehead iodides by xenon difluoride in methylene chloride represents an excellent procedure for the synthesis of bridgehead fluorides.[3] While in most cases the conversion proceeded satisfactorily and gave the fluoride cleanly, it was observed that in two of the systems under investigation the product was contaminated with variable amounts of the corresponding chloride. Thus, whereas 1-iodoadamantane (**1**), 1-iodobicyclo[2.2.2]octane (**2**), and 1-iodobicyclo[3.2.1]octane (**3**) yielded the respective fluorides **4–6** without any detectable quantities of the related chloride, 1-iodobicyclo[2.2.1]heptane (**7**) and iodocubane (**8**) gave bridgehead fluoride/chloride mixtures of 75:25 (**9**, **11**) and 94:6 (**10**, **12**), respectively.

Evidence was presented to support the intermediacy of bridgehead carbocations in these fluorodeiodination processes (Scheme I), and the production of chlorine-containing products was ascribed to interception of the intermediate cations by solvent. It is noteworthy that the chloride contaminants are produced particularly from those systems in which the bridgehead cations are of relatively high energy; both cubyl triflate (**14**)[4] and 1-bicyclo[2.2.1]heptyl triflate (**13**)[5] for example have been shown to possess very slow rates of solvolysis. If one accepts the reasonable correlation that these high-energy cations are also extremely reactive, then the production of chlorides is simply a manifestation of the indiscriminate nature of the more energetic cations. Accordingly, abstraction of chloride from the solvent by the cubyl and 1-bicyclo[2.2.1]heptyl cations is seen to be competitive with their capture by fluoride ion. Furthermore, the different ratios observed in the case of the cubyl and 1-bicyclo[2.2.1]heptyl systems is a reflection of the relative stabilities of the corresponding cations, a measure of which

Scheme I

$$RI + XeF_2 \longrightarrow RIF_2 + Xe$$
$$RIF_2 \longrightarrow R^+ + IF_2^-$$
$$IF_2^- \longrightarrow IF + F^-$$
$$R^+ + F^- \longrightarrow RF$$

is provided by the knowledge that cubyl triflate (**14**) solvolyzes much more readily than 1-bicyclo[2.2.1]heptyl triflate (**13**). It is highly significant that the solvolytic behavior of **13** and **14** is reinforced by the results of *ab initio* calculations at the MP2/6-31G*//RHF/3-21G level. In the latter context, Hrovat and Borden[6] have determined that the cubyl cation requires considerably less energy for its formation than does the 1-norbornyl cation.



In the interim we have been attempting to extend the fluorodeiodination procedure to the synthesis of other caged bridgehead fluorides, viz., 6-fluorotricyclo[3.1.1.$0^{3,6}$]-heptane (**19**), 1- and 4-fluorohomocubane (**20**) and (**21**),

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(1) Flinders University.

(2) University of Melbourne.

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(4) (a) Eaton, P. E.; Yang, C.-X.; Xiong, Y. *J. Am. Chem. Soc.* **1990**, *112*, 3225. (b) Moriarty, R. M.; Tuladhar, S. M.; Penmasta, R.; Awasthi, A. K. *J. Am. Chem. Soc.* **1990**, *112*, 3228.

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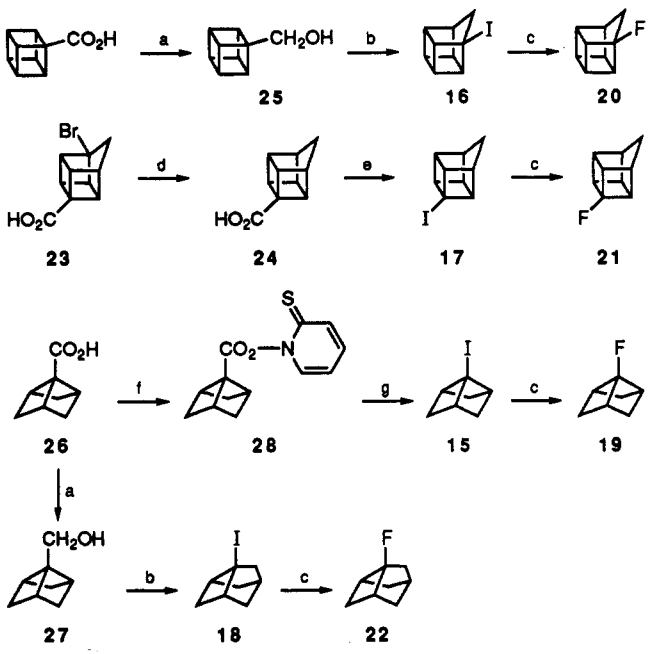
Scheme II[a]



[a](a) $LiAlH_4$; (b) (1) Ph_3PI_2, (2) silica gel; (c) XeF_2; (d) Bu_3SnH, AIBN, hν; (e) $Pb(OAc)_4$, I_2, hν; (f) $HONC_5H_4S$, DCC; (g) CF_3CH_2I, CH_2Cl_2, hν.

and 6-fluorotricyclo[3.2.1.$0^{3,6}$]octane (**22**) from their iodides **15–18**. We now wish to report the results of this investigation, and, in view of several interesting observations made during the course of these experiments, we also present details of some *ab initio* calculations we have undertaken on the corresponding caged cations.

Results and Discussion

The precursor iodides new to this study were obtained via the reactions depicted in Scheme II. The acid **24** was converted into the corresponding iodide **17** in high yield (90%) with lead tetraacetate and iodine.[3] However, owing to its volatile nature, iodide **15** was synthesized more conveniently via Barton ester methodology.[3] 1-Iodohomocubane (**16**) and 6-iodotricyclo[3.2.1.$0^{3,6}$]octane (**18**) were prepared by taking advantage of the propensity of the hydroxymethyl derivatives **25** and **27** to undergo Wagner–Meerwein rearrangement. Thus, the carbinols **25** and **27** were readily transformed into the ring-expanded iodides **16** and **18**, respectively, with triphenylphosphine diiodide and silica gel.

Conversion of the iodides **7** and **8** into their corresponding fluorides has been described previously,[3] and, under the relatively mild conditions employed, 4-iodohomocubane (**17**) was found to give the fluoride **21** rapidly in high yield without contamination. The reactive nature of **17** toward fluorination is not surprising in view of the comparable rates of solvolysis of 4-homocubyl triflate (**35**)[7] and cubyl triflate (**14**).[4] The triflate **35** actually solvolyzes 1 order of magnitude faster that **14** suggesting that production of the corresponding carbocation **41** from iodide **17** should be even more facile than that of the cubyl cation **38** from **14**. The related iodides **15**, **16**, and **18**, however, proved to be highly resistant to fluorination under these conditions. It was found that only under more drastic conditions, viz., by exposure to xenon difluoride at rather higher temperatures and for extended periods of time, could these iodides be induced to react. Even then, 6-iodotricyclo[3.2.1.$0^{3,6}$]octane (**18**) proved to be practically inert. The product in these cases was shown to consist of mixtures of the desired fluoride and the corresponding chloride. Identification of the components was performed by GC-MS and, for the chlorides, by comparison with authentic samples.

Table I. Products of Fluorodeiodination of the Caged Iodides 7, 8, 15–18

substrate	products (RF/RCl)[a]	normalized solvolysis rates[b]
7	9, 11 (75:25)	1.4×10^{-4}
8	10, 12 (94:6)	1.5×10^{-1}
15	19, 29 (72:28)	na[c]
16	20, 30 (62:38)	na[c]
17	21, 31 (95:5)	1
18	22, 32 (60:40)	na[c]

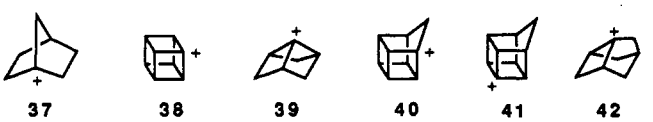
[a] Given as percentage ratios to facilitate comparisons. These are not yields. [b] For details see Müller, P.; Milin, D. *Helv. Chem. Acta* **1991**, *74*, 1808. [c] Not available.

Clearly, the viability of fluorodeiodination as a synthetic procedure to the systems under study here has validity only in the case of iodides **7**, **8**, and **17**. For the other iodides, the major product was a dark intractable oil, and the fluoride/chloride mixture was isolated as a minor product.

As the data in Table I illustrate, the proportion of the chlorides **29**, **30**, and **32** accompanying the fluorides **19**, **20**, and **22** can be quite significant, particularly in the case of the 1-homocubyl and 6-tricyclo[3.2.1.$0^{3,6}$]octyl systems. Interestingly, the ratio of halides **21** and **31** produced in the reaction of 4-iodohomocubane with xenon difluoride is comparable with that obtained from iodocubane. This observation is predictable in light of the similar rates of solvolysis of 4-homocubyl triflate (**35**)[7] and cubyl triflate (**14**)[4] as discussed above.

Unfortunately, it was not possible to test the existence of a correlation between the fluoride/chloride ratios from fluorodeiodination of the iodides **15**, **16**, and **18** and the rates of solvolysis of the triflates **33**, **34**, and **36** because the latter information is unavailable. While we acknowledge the danger of drawing conclusions from the composition of a minor identifiable product of a reaction and that the ratio of chloride to fluoride in these reactions must therefore be regarded as tenuous, nevertheless the high proportion of chloride obtained in these cases, leads us to suggest that the corresponding cations must be of high energy. Support for this premise is provided by the associated observation that the precursor bridgehead iodides in question are so much less reactive toward the reagent. Accordingly, we predict that the triflates **33**, **34**, and **36** will be most reluctant to undergo the S_N1 process.

In the absence of solvolytic data for these systems, and as an alternative guide to the relative energies of the cations **37–42**, we sought recourse to the Hrovat–Borden approach[6] for the determination of MP2/6-31G*//RHF/3-21G energies of the cations in an attempt to provide a theoretical basis for the observed fluorodeiodination product compositions.



Geometries of the cations (**39–42**) and corresponding hydrocarbons were optimized at the RHF/3-21G *ab initio*

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