Friedel–Crafts Alkylation of Aromatics with *exo*-2-Chloro- and 7-Chloronorbornane[1]

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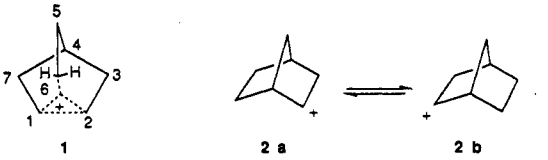
exo-2-Chloro- and 7-chloronorbornane in the presence of tin(IV) chloride or aluminum chloride react with benzene and substituted benzenes to give the corresponding norbornylated products. Mechanistic aspects of the reactions proceeding through carbocationic intermediates are discussed.

Introduction

There is substantial interest in the structure and reactivity of 2-norbornyl (bicyclo[2.2.1]heptyl) cation. In 1949, Winstein and Trifan[2] found that the rates of solvolysis of *exo*-2-norbornyl derivatives showed great enhancement relative to the corresponding *endo* isomers. They proposed the "σ-bridged nonclassical norbornyl cation" **1** as the intermediate for the solvolysis of the *exo*-2-norbornyl derivatives. Brown[3] argued against the σ-bridged structure **1** and proposed that the steric hindrance of the C6 *endo* C–H bond in *endo*-2-norbornyl derivatives is causing retardation of the *endo* rate leading to high *exo*/*endo* rate ratios. He also argued that the carbocations **2a,b** were stablized by inductive and hyperconjugative effects, involving an insignificant change in the molecular structure. Extensive studies of the norbornyl cation using long-lived stable ion conditions, including NMR (both solution and solid state), IR, ESCA, and theoritical calculations established the nonclassical, σ-delocalized nature of the long-lived ion.[4]

There is similar interest in the structure and reactivity of the 7-norbornyl cation **3**. Winstein, Woodward, and co-workers[5] reported that the rate of acetolysis of 7-norbornyl *p*-toluenesulfonate (tosylate) is 10^7 times slower



1 **2a** **2b**

than that of cyclohexyl tosylate. Roberts and co-workers[6] have previously prepared a number of chloro derivatives of norbornane including 7-norbornyl chloride. They remarked that 7-norbornyl chloride is exceptionally unreactive compared to cyclopentyl chloride in 80% ethanol. Later, Roberts[7] suggested that at least three factors could be attributed to the sluggish reactivity of 7-norbornyl chloride. First, solvation of the 7-norbornyl cation would be difficult due to repulsive interactions (steric origin). Second, during carbocation formation the change in

3a **3b**

hybridization at C7 will be associated with increased steric strain. Finally, the most important factor is the lack of C–H hyperconjugative stabilization[6-9] of the cationic center due to inefficient overlap. The vacant p orbital of the 7-norbornyl cation cannot effectively overlap with the bridgehead C–H or C–C bonds (the corresponding resonance forms would violate Bredts rule). Extensive studies of 7-norbornyl derivatives by Roberts,[8] Winstein,[9] Foote,[10] Schleyer,[11] Gassman,[12] Sunko,[13] and Olah[14] concluded that the 7-norbornyl cation is either nonclassical or nonplanar. Attempts to generate the 7-norbornyl cation in antimony pentafluoride–sulfur dioxide solution[14] gave the 2-norbornyl cation by rapid rearrangement.

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Table 1. Tin(IV) Chloride Catalyzed Alkylation of Substituted Benzenes with *exo*-2-Norbornyl Chloride

arene substrate	*exo*-2-norbornylarene product[a] % *ortho*	% *meta*	% *para*	reactn time (day)	isolated yield (%)
benzene				4, 82 °C	29
toluene	34.4	16.5	49.1	2, 83 °C	30
m-xylene	6.3[c]		93.6[d]	4 h, 94 °C	24
chlorobenzene	33.2	4.4	62.4	11, 81 °C	29
fluorobenzene	35.3		64.7[b]	5, 75 °C	32

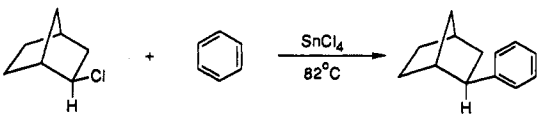
[a] Isomer ratios are determined by GC. [b] ^{19}F NMR shows *o*:*p* = 36.1:63.9. [c] *exo*-2-(2,6-Dimethylphenyl)norbornane. [d] *exo*-2-(2,4-Dimethylphenyl)norbornane.

The structure of 7-norbornyl cation has also been probed by theory.[15–18] Hoffmann[15] in his early Hückel MO calculations indicated that the equilibrium geometry of the 7-norbornyl cation should have a symmetrical structure (C_{2v}). In contrast, semiempirical MINDO/3 calculations[16c,17] favored an unsymmetrical structure with regard to the C1–C7–C4 plane. *Ab initio* calculations at the 6-31G* level,[16b] however, have shown that the cation prefers a planar (or symmetrical) structure, in accordance with Hoffmann's earlier suggestion.[15] Recently, Kirmse et al.[18a] have reported that 2-oxo- and 1-cyano-7-norbornyl cations were generated from various derivatives of bicyclo-[3.2.0]heptane. More recently, Schleyer and Sunko et al. report infrared studies and claimed to have observed the 7-norbornyl cation under low temperature matrix isolation conditions.[18b] They have also calculated the structural and energetic aspects of 7-norbornyl cation at MP4 (sdq, fc)/6.31G*//MP2(full)/6-31G* + ZPE (MP2(full)/6.31G*) level. At this high level of theory the unsymmetrical C–C σ-bridged nonclassical 7-norbornyl cation was found to be 2.9 kcal/mol more stable than the C_s classical structure. The symmetrical C_{2v} classical structure was found be to be much higher in energy by 5.2 kcal/mol.

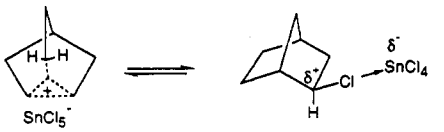
Despite extensive studies of norbornyl systems, Friedel–Crafts alkylation with halonorbornanes remained relatively unexplored. Schmerling[18c] in 1949 investigated the reaction of norbornene with benzene under H_2SO_4 catalysis and obtained 2-mono- and 2-dinorbornylated benzenes. In continuation of our studies on electrophlic aromatic substitution and carbocation reactivity, we report here on the Friedel–Crafts reaction of *exo*-2-chloro- and 7-chloronorbornanes with aromatics giving the corresponding norbornylated derivatives and discuss the mechanistic consequences of our investigations.

Results and Discussion

Alkylation of benzene, toluene, *m*-xylene, and halobenzenes with *exo*-2-norbornyl chloride in the presence of tin(IV) chloride at 75–94 °C gave the results shown in Table 1. Under the reaction conditions, the 2-norbornylation gave the kinetically prefered *para* isomers as the major products. Small amounts of di(2-norbornyl) aromatics were also formed (≤1% as determined by GC-MS). Strongly acidic aluminum chloride catalyst, in contrast, caused rapid isomerization of the products even at 0 °C. Reaction of toluene with *exo*-2-norbornyl chloride in the presence of aluminum chloride for 1 h even at 0 °C gave the thermodynamically prefered *meta* isomer as the major product (*ortho*:*meta*:*para* = 3.2:75.9:20.9). Significant amounts of di(2-norbornyl) aromatics were also formed (≈5–8%), indicative of the intermolecular nature of the isomerization. When *exo*-2-phenylnorbornane itself was allowed to react with excess toluene in the presence of aluminum chloride at 0 °C, *exo*-2-(methylphenyl)norbornane isomers were generated. This result is in contrast to the reaction of toluene with 1-phenylnorbornane.[1] These results confirm the intermolecular nature of the present reaction.[19] When *exo*-2-norbornyl chloride was reacted with excess benzene in the presence of aluminum chloride for 10 min at ambient temperature, *exo*-2-phenylnorbornane and 2-phenyl-2-norbornene were obtained. Competitive norbornylation of benzene and toluene with *exo*-2-norbornyl chloride in the presence of tin(IV) chloride was also carried out (k_T/k_B (by GC) is 7.2±0.2 and showed no significant variation for 1 h at 65 °C).



Due to the high stability of the 2-norbornyl cation, the reaction is considered to proceed through the free carbocation rather than through a polarized donor–acceptor complex (or a tight ion pair). In fact, secondary 2-norbornyl cation is as stable as a tertiary alkyl carbocation. Further, S_N2-like substitution reaction is also not feasible as backside approach by the aromatics is not possible. Frontside S_N2-like displacement, on the other hand, is not known.[20] The results of Friedel–Crafts alkylation of aromatics with *exo*-2-chloronorbornane are not unlike those observed with *tert*-butyl chloride.



7-Chloronorbornane also reacts with benzene, toluene, *m*-xylene, and halobenzenes. In this case, anhydrous aluminum chloride was used as catalyst at 0 °C. With tin(IV) chloride catalyst, the alkylation is too slow to be conveniently studied. When the reaction was carried out at room temperature, olefinic byproducts were also obtained. The results are summarized in Table 2. Small amounts of di(7-norbornyl) aromatics were also formed in the reactions (≤1%). The 7-norbornylation of toluene under similar reaction conditions gives the thermodynamically prefered *meta* product (*meta* to *para* in 3:1 ratio). Reaction of *m*-xylene gives three positional isomers in 1:5:5 ratio (see Table 2). In the case of chloro- and fluorobenzene, the reaction gives *ortho*:*meta*:*para* products

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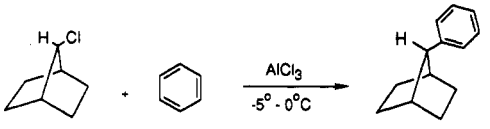
Table 2. Aluminum Chloride Catalyzed Alkylation of Substituted Benzenes with 7-Chloronorbornane

arene substrate	7-norbornylarene product[a] % ortho	% meta	% para	reactn condtn	isolated yield (%)
benzene				−5 to 0 °C, 30 min	51
toluene		76.7	23.3	−2 to 0 °C, 20 min	55
m-xylene	8.8[c]	47.5[d]	43.7[e]	0 °C, 20 min	32
chlorobenzene	61.2	18.7	20.1	0 °C, 30 min	37
fluorobenzene	45.9	15.7	38.4[b]	0 °C, 30 min	42

[a] Isomer ratios are determined by GC. [b] ^{19}F NMR shows *o*:*m*:*p* = 44.2:18.8:37. [c] 7-(2,6-Dimethylphenyl)norbornane. [d] 7-(3,5-Dimethylphenyl)norbornane. [e] 7-(2,4-Dimethylphenyl)norbornane.

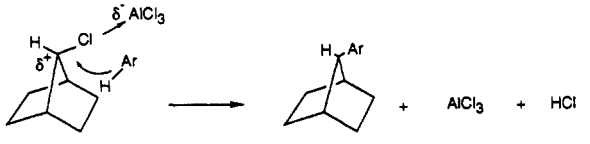
in 3:1:1 and 3:1:2 ratios, respectively. Because of apparent rapid isomerization, no reliable toluene/benzene rate ratio (k_T/k_B) could be determined. When 7-phenylnorbornane itself was allowed to react with excess toluene in the presence of aluminum chloride at 0 °C, 7-(methylphenyl)-norbornane isomers were formed, indicative of the intermolecular nature of the isomerization.[19]



The question arises why otherwise less reactive 7-chloronorbornane reacts readily with aromatics under Friedel–Crafts catalysis even at 0 °C?

As shown earlier, angle deformation at C7 in the ground state of 7-norbornyl tosylate results in an $sp^{2.46}$ hybridization of the C7 carbon[21] as contrasted by an sp^3 hybridization in 2-adamantyl derivatives. Recent high level *ab initio* calculations[18b] have shown that the nonclassical 7-norbornyl cation is the energy minimum and is stabilized over the classical structures. Therefore, it is highly probable that a free nonclassical norbornyl cation is involved as a *de facto* intermediate.

An alternative pathway involving S_N2-like displacement of a polarized donor–acceptor complex (or a tight ion-pair) would be highly restricted due to steric hindrance. There would be also steric repulsion between the aromatic substrate and the leaving group if an unprecedented frontside displacement took place. As indicated earlier



no such frontside S_N2 substitution was so far demonstrated.[20] Thus, it is considered most likely that a free 7-norbornyl cation is involved in the Friedel–Crafts alkylation process.

Recently, we have also succeeded in carrying out Friedel–Crafts alkylation of aromatics with 1-chloronorbornane, fluorocubane, and 3-chloro- and 3-bromonoradamantanes, demonstrating the reactivity of highly strained bridgehead halides.[1]

Conclusions

exo-2-Chloro- and 7-chloronorbornane, in the presence of tin(IV) chloride or aluminum chloride, respectively alkylate benzene and substituted benzenes. Friedel–Crafts 2-norbornylation is considered to involve the intermediacy of the highly stabilized 2-norbornyl cation. 7-Norbornylation may, however, also involve the 7-norbornyl cation as a *de facto* reactive intermediate.

(21) Hybridization at C7 has been calculated for norbornane. Eckert-Maksic, M.; Maksic, Z. *J. Mol. Struct.* **1974**, *22*, 445.

Experimental Section

Benzene, toluene, *m*-xylene, chlorobenzene, fluorobenzene, tetrahydrofuran, ether, and dichloromethane were distilled before use. *exo*-2-Norbornyl chloride, tin(IV) chloride, and trifluoroacetic acid were obtained from Aldrich. Aluminum chloride was from EM Science, trimethylsilane from Hüls, and magnesium turnings from Mallinckrodt. GC analysis of the reaction mixtures were conducted on a Varian 3740 gas chromatograph with a J&W Scientific DB-WAX fused silica capillary column (30 m, 0.25 mm). GC/MS analyses were performed on a Finnigan-Mat/Incos-50 mass spectrometer equipped with a Varian 3400 or on a Hewlett Packard 5971 mass spectrometer equipped with Hewlett Packard 5890 gas chromatograph. NMR spectra were recorded on Varian Associates Model VXR 200 or Unity 300 NMR spectrometers. The ^1H and ^{13}C NMR chemical shifts were referenced to the tetramethylsilane signal. The ^{19}F NMR signals were referenced from the $CFCl_3$ signal. Multiplicities shown in the ^{13}C NMR data refer to C–H coupling.

***exo*-2-Phenylnorbornane.** *exo*-2-Norbornyl chloride (0.63 mL, 5 mmol) was reacted with excess benzene (4.47 mL, 0.05 mol) in the presence of tin(IV) chloride (0.59 mL, 5 mmol) at ambient temperature and heated to 82 °C. The reaction was continued for 4 days. After quenching with ice–water, it was extracted with pentane, dried over magnesium sulfate, and filtered, and the solvent was rotary evaporated. The residue was distilled in vacuum to give *exo*-2-phenylnorbornane (0.25 g, 29%): bp 82–86 °C under 2 mmHg, lit.[18c,19] bp 76 °C under 0.8 mmHg. MS (*m*/*z*): 81 (27), 91 (33), 92 (44), 104 (100), 172 (38). ^1H NMR (in $CDCl_3$): δ 1.2, 1.58 (8H), 2.35 (2H), 2.72 (1H), 7.22, 7.27 (5H). ^{13}C NMR (in $CDCl_3$): δ 43.0 (C1), 47.4 (C2), 36.2 (C3), 37.0 (C4), 29.0 (C5), 30.7 (C6), 39.2 (C7), 147.5 (C1), 126.9 (C2,6), 128.1 (C3,5), 125.2 (C4). $C_{13}H_{16}$ requires: 172.1252. Found: 172.1254 amu.

Reactions of *exo*-2-norbornyl chloride with other aromatics were carried out similarly and the isomer distributions were determined by GC-MS analyses. All the isomeric mixtures gave satisfactory ^1H, ^{13}C, and ^{19}F (where applicable) NMR spectra and exact mass analyses.

***exo*-2-Tolylnorbornanes (o:m:p 34.4:16.5:49.1).** MS (*m*/*z*): 81 (22), 91 (31), 94 (24), 105 (53), 106 (99), 115 (27), 117 (39), 118 (100), 119 (31), 128 (20), 129 (22), 186 (58). ^1H NMR ($CDCl_3$): 7.23–6.9 (m, 4H), 2.78, 2.68 (m, 1H), 2.38, 2.3 (b, 3H), 2.24 (s, 5H), 1.82–1.05 (m, 8H). ^{13}C NMR ($CDCl_3$): 147.5 (s), 145.5 (s), 144.6 (s), 137.6 (s), 136.1 (s), 134.7 (s), 130.2 (d), 128.8 (d), 128.1 (d), 127.9 (d), 126.9 (d), 126.1 (d), 125.6 (d), 125.2 (d), 124.7 (d), 124.0 (d), 47.2 (d), 46.9 (d), 43.9 (d), 43.1 (d), 42.9 (d), 41.4 (d), 39.1 (t), 38.7 (t), 36.9 (d), 36.8 (d), 36.3 (t), 36.1 (t), 36.0 (t), 30.6 (t), 29.1 (t), 28.9 (t), 21.5 (q), 20.9 (q), and 20.1 (q). Exact mass: $C_{14}H_{18}$ requires 186.1408. Found: 186.1400 amu.

***exo*-2-(Chlorophenyl)norbornanes (o:m:p 33.2:4.4:62.4).** MS (*m*/*z*): 67 (35), 81 (29), 94 (24), 125 (24), 138 (100), 140 (34), 206 (31). ^1H NMR ($CDCl_3$): 7.0–7.4 (m, 4H), 3.05, 2.7 (m, 1H), 2.3 (m, 2H), and 1.15–1.95 (m, 8H). ^{13}C NMR ($CDCl_3$): 146.0 (s), 144.5 (s), 134.4 (s), 130.9 (s), 129.5 (d), 128.3 (d), 128.2 (d), 126.6 (d), 126.4 (d), 126.3 (d), 46.7 (d), 44.2 (d), 42.8 (d), 41.4 (d), 39.1 (t), 38.4 (t), 36.9 (d), 36.8 (d), 36.3 (t), 36.0 (t), 30.5 (t), 30.2 (t), 28.9 (t), and 28.8 (t). $C_{13}H_{15}Cl$ requires, 206.0862. Found: 206.0862 amu.

***exo*-2-(Fluorophenyl)norbornanes (o:p 35.3:64.7).** MS (*m*/*z*): 67 (22), 109 (35), 122 (100), 190 (27). ^1H NMR ($CDCl_3$): 7.22–6.84 (m, 4H), 2.92, 2.62 (m, 1H), 2.3 (m, 2H), and 1.05–1.8 (m, 8H). ^{13}C NMR ($CDCl_3$): 160.9 (s, J_{C-F} = 243.5 Hz), 160.7 (s, J_{C-F} = 241.3 Hz), 143.2 (s), 134.3 (s), 128.2 (d, J_{C-C-F} = 7.7 Hz), 126.7 (d, J_{C-C-F} = 10.1 Hz), 123.5 (d), 115.0 (d), 114.7 (d, J_{C-C-F} = 21 Hz), 46.2 (d), 42.9 (d), 41.3 (d), 39.6 (d), 39.2 (t), 38.1 (t), 36.7 (d), 36.1 (t), 35.9 (d), 30.4 (d), 30.2 (d), 28.8 (d), 28.7 (d). ^{19}F

NMR ($CDCl_3$): δ −117.6 (b), −119.2 (m). $C_{13}H_{15}F$ requires 190.1157. Found: 190.1167 amu.

2-Xylylnorbornanes. MS (*m/z*): 39 (31), 41 (34), 67 (28), 77 (25), 79 (39), 91 (43), 94 (69), 105 (47), 115 (52), 117 (56), 119 (85), 120 (100), 128 (46), 129 (35), 131 (23), 132 (68), 133 (47), 141 (20), 143 (28), 200 (72). ^1H NMR ($CDCl_3$): 7.15 (d, 1H), 6.95 (b, 2H), 2.8 (m, 1H), 2.28–2.4 (m and s, 8H), 1.2–1.88 (m, 9H). ^{13}C NMR ($CDCl_3$): 142.5 (s), 136.0 (s), 134.5 (s), 131.1 (d), 126.2 (d), 124.7 (d), 43.5 (d), 41.6 (d), 38.7 (t), 36.9 (d), 36.3 (t), 30.5 (t), 29.1 (t), 20.7 (q), and 20.0 (q). $C_{15}H_{20}$ requires 200.1565. Found: 200.1573 amu.

7-Chloronorbornane and **7-norbornanone** were prepared by known procedures.[22,23]

7-Phenylnorbornane. 7-Chloronorbornane (0.65 g, 5 mmol) was reacted with excess benzene (4.45 mL,0.05 mol) in the presence of aluminum chloride (0.67 g, 5 mmol) between −5 and 0 °C. The reaction was continued for 0.5 h. After quenching with ice–water, it was extracted with pentane, dried over magnesium sulfate, and filtered, and the solvent was rotary evaporated. The residue was distilled in vacuum to give 7-phenylnorbornane (0.86 g, 51%). Bp 90–92 °C under 2 mmHg lit.[24] bp_{bath} 105 °C under 6 mmHg. MS (*m/z*): 80 (49), 81 (66), 91 (68), 92 (30), 104 (100), 115 (57), 117 (53), 128 (31), 129 (59), 130 (61), 172 (69). ^1H NMR (in $CDCl_3$): δ 1.17, 1.34 (4H, methylenes, J = 8 Hz), 1.50, 1.74 (4H, methylenes, J = 6 Hz), 2.9 (b, 2 H), 7.25, 7.27 (5H). ^{13}C NMR (in $CDCl_3$): δ 39.3 (C1), 27.3, 30.2 (C2 or C6), 53.4 (C7), 141.5 (C1), 127.8 (C2,6), 128.0 (C3,5), 125.5 (C4). $C_{13}H_6$ requires 172.1252. Found: 172.1248.

Similar reactions with 7-chloronorbornane were carried out with other aromatics and the obtained isomeric mixtures were analyzed by GC-MS, ^1H, ^{13}C, and ^{19}F (where applicable) NMR spectroscopy, and exact mass analyses.

Isomeric 7-Tolylnorbornanes (m:p 76.7:23.3). MS (*m/z*): 80 (61), 81 (49), 91 (46), 106 (66), 106 (76), 115 (46), 118 (95), 128 (37), 129 (59), 131 (41), 143 (40), 186 (100). ^1H NMR ($CDCl_3$): δ 7.18–6.9 (m, 4H), 2.83 (s, 1H), 2.7 (s, 2H), 2.3 (s, 3H), 1.6 (AX pattern, 4H), 1.3 (AX pattern, 4H). ^{13}C NMR ($CDCl_3$): 141.5 (s), 138.5 (s), 137.5 (s), 133.0 (s), 128.8 (d), 128.7 (d), 128.0 (d), 127.7 (d), 126.3 (d), 124.9 (d), 53.4 (t), 53.1 (t), 40.8 (t), 38.4 (t), 30.3 (d), 28.4 (d), 27.4 (d), 21.6 (q), 21.1 (q). $C_{14}H_{18}$ requires 186.1408. Found: 186.1407 amu.

Isomeric 7-(chlorophenyl)norbornanes (o:m:p 61.2:18.7:20.1). MS (*m/z*): 81 (100), 115 (43), 129 (62), 138 (60), 171 (40), 206 (51). ^1H NMR ($CDCl_3$): δ 7.7–7.08 (m, 4H), 2.92, 2.82 (s, 1H), 2.64, 2.50 (s, 2H), 1.85–1.15 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 148.0 (s), 143.7 (s), 140.0 (s), 139.0 (s), 134.7 (s), 131.1 (s), 129.6 (d), 129.3 (d), 129.2 (d), 128.5 (d), 128.1 (d), 128.0 (d), 127.1 (d), 126.2 (d), 126.0 (d), 125.7 (d), 53.2 (d), 52.8 (d), 39.4 (d), 39.3 (d), 39.2 (d), 30.4 (t), 30.2 (t), 30.1 (t), 28.0 (t), 27.5 (t), 27.1 (t). $C_{13}H_{15}Cl$ requires 206.0862. Found: 205.0859 amu.

Isomeric 7-xylylnorbornanes. MS (*m/z*): 80 (32), 119 (68), 120 (100), 128 (31), 132 (61), 143 (42), 145 (37), 157 (33), 200 (78). ^1H NMR ($CDCl_3$): δ 7.18–6.67 (m, 3H), 2.79 (s, 1H), 2.5, 2.44 (s, 2H), 2.3 (b, 6H), 4.78–1.1 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 141.4 (s), 137.3 (s), 136.7 (s), 136.4 (s), 135.1 (s), 131.2 (s), 127.1 (d), 127.0 (d), 126.8 (d), 125.9 (d), 125.6 (d), 124.9 (d), 53.2 (d), 52.2 (d), 39.3 (d), 30.4 (t), 30.2 (t), 28.1 (t), 27.4 (t), 21.4 (q), 20.8 (q), 20.3 (q). $C_{15}H_{20}$ requires 200.1565. Found: 200.1574 amu.

Isomeric 7-(Fluorophenyl)norbornanes (o:m:p 45.9:15.7:38.4). MS (*m/z*): 81 (82), 109 (51), 122 (100), 133 (30), 135 (34), 147 (33), 148 (50), 190 (59). ^1H NMR ($CDCl_3$): 7.19–6.7 (m, 4H), 2.75, 2.7 (s, 1H), 2.5, 2.38 (s, 2H), 1.68–0.98 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 161.7 (s, J_{C-F} = 244.05 Hz), 160.9 (s, J_{C-F} = 241.7 Hz), 137.1 (s), 129.3 (d, J_{C-C-F} = 17.3 Hz), 129.2 (d, J_{C-C-F} = 19.6 Hz), 128.0 (s), 127.4 (d), 127.3 (d), 115.2 (d, J_{C-C-F} = 22.3 Hz), 114.7 (d, J_{C-C-F} = 21.0 Hz), 53.2 (d), 52.7 (d), 48.8 (d), 39.5 (d), 39.1 (d), 30.2 (t), 30.1 (t). ^{19}F NMR ($CDCl_3$): δ −130.2 (b), 126.1 (m). $C_{13}H_{15}F$ requires 190.1157. Found: 190.1158 amu.

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