methine, C-2 methylene), 1.4–1.7 (m, 2 H, C-4 methylene); ^{13}C NMR (neat) δ 171.79, 171.30 (carbonyl), 52.84, 52.43 (carboxylate methyl), 51.29 (C-5 methylene), 50.12 (methoxyl), 39.70 (C-3 methine), 34.59 (C-2 methylene), 25.69 (C-4 methylene); mass spectrum *m/e* 204 (M$^+$, 4), 173 (92), 158 (74), 145 (100). Anal. Calcd for $C_9H_{16}O_5$: C, 52.93; H, 7.90. Found: C, 53.12; H, 7.82.

The third product was identified as the diester **27** (30%): ^{1}H NMR (CDCl$_3$) δ 3.9 (s, 6 H, carboxylate methyl), 3.45 (d, J = 7 Hz, C-5 methylene), 3.3 (s, 3 H, methoxyl), 2.4–2.75 (m, 5 H, C-2 methylene, C-4 methine), 1.4–1.7 (m, 2 H, C-3 methylene); ^{13}C NMR (neat) δ 175.10, 172.38 (carbonyl), 52.91, 52.64 (carboxylate methyl), 51.28 (C-5 methylene), 50.59 (methoxyl), 34.92 (C-4 methine), 30.96 (C-2 methylene), 23.33 (C-3 methylene); mass spectrum (relative intensity) *m/e* 204 (M$^+$, 11), 173 (67), 159 (100), 158 (88), 131 (28). Anal. Calcd for $C_9H_{16}O_5$: C, 52.93; H, 7.90. Found: C, 53.28; H, 7.64.

About 10% of unreacted 3-butenol could be recovered by GC.

Carboxylation of But-3-en-1-yl Acetate. Formation of 25 and Methyl 3-(Carbomethoxy)-5-hydroxypentanoate (29). A solution of 2.85 g (25.0 mmol) of 3-buten-1-yl acetate in 75 mL of methanol was subjected to carboxylation under the standard conditions. The product workup was effected after 60 h when no further carbon monoxide uptake was observed. VPC analysis indicated the presence of two products. The minor component (19%) was identified as **25** by VPC and ^{1}H NMR analysis.

The second product (81%) was identified as the diester **29**: IR (neat) 3400–3500 (br, hydroxyl), 1735 (carbonyl) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.2 (br, 1 H, disappears after D$_2$O exchange), 3.85 (s, 6 H, carboxylate methyl), 3.4–3.5 (br, 2 H, C-5 methylene), 2.4–2.8 (m, 3 H, C-3 methine, C-2 methylene), 1.9 (m, 2 H, C-4 methylene); ^{13}C NMR (neat) δ 174.10, 172.31 (carbonyl), 52.40, 52.11 (carboxylate methyl), 50.92 (C-5 methylene), 34.92 (C-3 methine), 30.93 (C-2 methylene), 24.48 (C-4 methylene); mass spectrum (relative intensity) *m/e* 189 (M$^+$ – H, 100), 172 (66), 159 (91), 146 (34), 145. Anal. Calcd for $C_8H_{14}O_5$: C, 50.52; H, 7.42. Found: C, 50.24; H, 7.82.

Acknowledgment. This research was supported by the National Science Foundation (Grant CHE 77-08349).

Registry No. 1, 40745-20-8; **2**, 71195-17-0; **4**, 35262-43-2; **5**, 71195-18-1; **6**, 71195-19-2; **7**, 71195-20-5; **8**, 71195-21-6; **9**, 71195-22-7; **11**, 71195-23-8; **12**, 71195-24-9; **13**, 1069-40-5; **14**, 71195-25-0; **15**, 71195-26-1; (*E*)-**16**, 13168-99-5; (*Z*)-**16**, 25665-54-7; **17a**, 70354-00-6; **17b**, 25126-93-6; **19**, 71195-27-2; **20**, 71195-28-3; **21**, 10420-33-4; **22**, 591-12-8; **23**, 69285-43-4; **24**, 18797-18-7; **25**, 50782-87-1; **26**, 71195-29-4; **27**, 16096-26-7; **28**, 50782-89-3; **29**, 71195-30-7; PdCl$_2$, 7647-10-1; ethylene, 74-85-1; dimethyl succinate, 106-65-0; succinic acid, 110-15-6; propylene, 115-07-1; dimethyl 2-methylsuccinate, 1604-11-1; 2-methylsuccinic acid, 498-21-5; vinylcyclohexane, 695-12-5; α-cyclohexylsuccinic acid, 1489-63-0; *trans*-3-(2-carboxycyclohexyl)propanoic acid, 71195-31-8; 3-phenyl-1-propene, 300-57-2; α-benzylsuccinic acid, 884-33-3; 1,5-hexadiene, 592-42-7; 3,6-dicarboxyoctane-1,8-dioic acid, 4388-94-7; 1-hexene, 592-41-6; 4-vinylcyclohexene, 100-40-3; 1,4-pentadiene, 591-93-5; 1,4-cyclohexadiene, 628-41-1; *cis*-cyclohex-4-ene-1,3-dicarboxylic acid, 71195-32-9; dimethyl *cis*-cyclohexane-1,3-dicarboxylate, 6998-82-9; *cis*-cyclohexane-1,3-dicarboxylic acid, 2305-31-9; *trans*-cyclohex-4-ene-1,3-dicarboxylic acid, 71195-33-0; dimethyl *trans*-cyclohexane-1,3-dicarboxylate, 10021-92-8; *trans*-cyclohexane-1,3-dicarboxylic acid, 2305-30-8; *trans*-hex-3-ene-1,6-dioic acid, 29311-53-3; dimethyl adipate, 627-93-0; adipic acid, 124-04-9; *cis*-hex-3-ene-1,6-dioic acid, 26472-26-4; dibenzyl *trans*-hex-3-ene-1,6-dioate, 71195-34-1; 1,3-butadiene, 106-99-0; 1,3-cyclohexadiene, 592-57-4; *cis*-cyclohex-2-ene-1,4-dicarboxylic acid, 3919-11-7; dimethyl *cis*-cyclohexane-1,4-dicarboxylate, 3399-21-1; *cis*-cyclohexane-1,4-dicarboxylic acid, 619-81-8; *trans*-cyclohex-2-ene-1,4-dicarboxylic acid, 3919-12-8; dimethyl *trans*-cyclohexane-1,4-dicarboxylate, 3399-22-2; *trans*-cyclohexane-1,4-dicarboxylic acid, 619-82-9; but-3-en-2-one, 78-94-4; β-acetylpropionic acid, 123-76-2; cyclopent-2-en-1-one, 930-30-3; methyl β-chloropropionate, 6001-87-2; 3-oxocyclopentanecarboxylic acid, 98-78-2; 3-oxocyclopentanecarboxylic acid DNP, 71195-35-2; *trans*-3-oxocyclopentane-1,2-dicarboxylic acid, 71195-36-3; prop-2-en-1-ol, 107-18-6; allyl methyl ether, 627-40-7; prop-2-en-1-yl acetate, 591-87-7; but-3-en-1-ol, 627-27-0; but-3-en-1-yl acetate, 1576-84-7.

Metalation of Polymethylnaphthalenes

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The reaction of several polymethylnaphthalenes with excess *n*-BuLi–TMEDA in THF–hexane resulted mainly in monometalation of a methyl substituent. In contrast with what might be expected from simple molecular orbital calculations, metalation of a C$_2$ methyl group was preferred over that of a C$_1$ methyl group.

Polyamine-chelated alkali-metal compounds such as *n*-butyllithium–*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (BuLi–TMEDA)[1,2] are useful metalating agents for aromatic hydrocarbons.[3] Mono- or polymetalation is possible, depending on the particular substrate and reaction conditions, and metalation may occur on the ring or in benzylic positions. For example, toluene can be polylithiated to give mainly the α,α,p, α,p, and α,o derivatives,[4] and mesitylene can be converted mainly to 1,3,5-tris(lithiomethylene)benzene.[5a] The metalation of other tri- and tetramethylbenzenes has been described.[5b] Metalated hydrocarbons prepared in this way can be useful synthetic intermediates through reaction with carbon dioxide, alkyl halides, and a variety of other electrophiles.

The metalation of methylnaphthalenes has been examined briefly. 1,8-Dimethylnaphthalene gave only the α-lithio derivative, even when it was treated for prolonged periods with a large excess of BuLi,[6] whereas with *n*-amylsodium–TMEDA the α,α'-disodio derivative was produced quantitatively.[7] Other isomers, such as 1,2-, 1,3- and 1,6-dimethylnaphthalene (and *o*- and *m*-xylene), also formed α,α'-disodio derivatives, but 1,4-dimethylnaphthalene (and *p*-xylene) was only monometalated. A reasonable explanation for the relative reactivities of the

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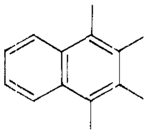
0022-3263/79/1944-3482$01.00/0

isomeric xylenes and dimethylnaphthalenes has been offered,[7] based primarily on the assumption that the second proton is the more difficult one to remove, and that the relative ease of removal of a particular second proton will depend on the charge density at various positions in the monoanion. For example, since the negative charge in the benzylanion is delocalized into the ring positions in the order para > ortho > meta,[8] the observed reverse order for dimetalation of the xylenes (meta > ortho > para) is easily rationalized. In the naphthalene series, the high reactivity of 1,3-dimethylnaphthalene and the low reactivity of the 1,4 isomer toward dimetalation can be similarly rationalized, since self-consistent field (SCF) calculations for the 1-naphthyl anion show that C_4 carries 10× more negative charge than C_3.[9] There are indications, however, that factors other than charge density in the monoanion may be important (for example, charge density calculations[9] lead one to predict that 1,8-dimethylnaphthalene would be more easily dimetalated than the 1,3 isomer, whereas experimentally the reverse is true,[7] possible because of peri interactions in the 1,8 isomer).

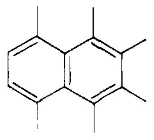
In this paper, we describe the metalation of several polymethylnaphthalenes; the results are somewhat surprising, in that metalation of a C_2 methyl group is preferred over a C_1 methyl, although charge density calculations[9] would have led to the opposite prediction.

Results and Discussion

Treatment of 1 mmol of polymethylnaphthalenes **1**–**3**



1



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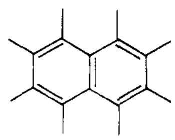
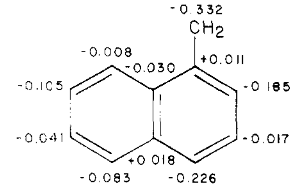


3

with excess (5 mmol) BuLi-TMEDA in THF-hexane at room temperature for 7 h was followed by quenching with either trimethylsilyl chloride or methyl iodide. The products were purified by gas-liquid chromatography (GLC) and identified by NMR and high-resolution mass spectrometry. The results are summarized in Table I.

Despite the substantial excess of metalating agent, the exclusive or predominant reaction was monometalation of the aromatic hydrocarbon. Perhaps the resistance to polymetalation can be attributed to electron release by the methyl substituents (although other highly substituted arenes have been polymetalated).[5] More surprising was the metalation of the C_2 methyl group. Calculations on the 1- and 2-naphthyl carbanions[9] and simple resonance theory predict that the negative charge is more dispersed in the former, thus leading one to expect that metalation at the C_1 methyl might be preferred.



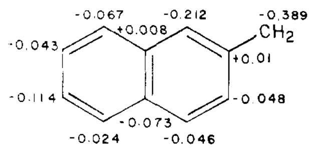
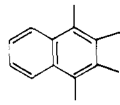
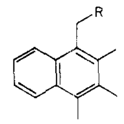
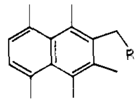
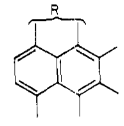
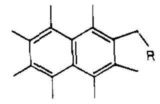
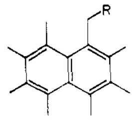


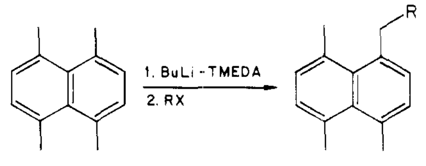
Table I. Products from the Metalation of Polymethylnaphthalenes[a]

starting mat.	R	products (%)		% recov starting mat.
1				
	$SiMe_3$	**4** (80)	**5** (11)	9
	CH_3	**6** (83)	**7** (9)	8
2				
	$SiMe_3$	**8** (57)	**9** (12)[b]	31
	CH_3	**10** (57)		43
3				
	$SiMe_3$	**11** (51, 66[c])	**12** (12, 9[c])	37, 25[c]
	CH_3	**13** (57)		43

[a] See Experimental Section for details of the procedure. [b] The ratio of the two isomers was about 1:1. [c] The mole ratio of BuLi-TMEDA to **3** was 10:1 instead of the usual 5:1.

The coplanarity of the methyl substituents and the aromatic ring, however, may be an important factor. The C_2 methyls are closer to coplanarity with the naphthalene ring than are the C_1 methyls (particularly in **2** and **3**[10]). The calculations shown above for the 1- and 2-naphthyl carbanions assumed a planar geometry. In the polymethylnaphthalenes which we have studied, the possibility for charge dispersion in the C_1 carbanion will be diminished relative to that of the C_2 carbanion as a consequence of this molecular distortion, and, depending on the severity of these distortions, the balance may even swing in favor of the C_2 carbanion. Also, according to the above calculations, the amount of negative charge at the methyl-substituted carbons will be less for the C_2 carbanion than for the C_1 carbanion. Finally, BuLi-TMEDA, which is a rather large base, may attack the C_2 methyl to avoid the large steric interactions at the peri positions.

The relatively slow rate of reaction at the C_1 methyl group was also evident when we metalated 1,4,5,8-tetramethylnaphthalene (**14**). Reaction with BuLi-TMEDA



14

15, R = $SiMe_3$
16, R = CH_3

for 18 h (compared with 7 h for **1**–**3**) still gave 56–57% of recovered starting material and only 38% of **15** or **16**, and even after 48 h much starting material was recovered.

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(10) In **3**, for example, the angle between the C_2 and C_3 methyls and the mean molecular plane is 20 and 10°, respectively. Hart, H.; Ward, D. unpublished results. See also Donaldson, D. M.; Robertson, J. M. *J. Chem. Soc.* **1953**, 17.

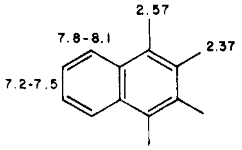
Table II. NMR Spectra of Metalation Products[a]

	ring positions						
compd no.	1	2	3	4	5,8	6,7	Me_3Si
4	2.58	2.48[b]	2.39	2.63	7.92-8.07	7.35-7.47	0.05
5	2.66[b]	2.38	2.43	2.63	7.86-8.06	7.34-7.46	0.02
6	2.61	2.89, 1.18[c]	2.46	2.64	7.96-8.07	7.35-7.47	
7[d]	3.13, 1.24[c]						
8	2.57	2.40[b]	2.31	2.60	2.72, 2.73	7.01	0.07
9[e]							- 0.18, −0.23
10	2.57[f]	2.85, 1.22[g]	2.37	2.62[f]	2.69, 2.70	7.00	
11	2.45	2.28[b]	2.34	2.49	2.49, 2.51	2.34	0.04
12[h]							−0.20
13[i]	2.47	2.81, 1.14[j]	2.33	2.49	2.49, 2.52	2.32	
15	*k*	*l*	*l*	*k*	*k*	*l*	−0.13
16	3.20, 1.22[m]	*o*	*o*	*n*	*n*	*o*	

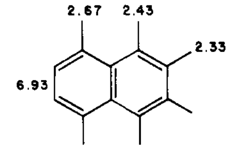
[a] Chemical shifts from Me_4Si are given in δ units. Spectra were determined in $CDCl_3$ at 180 MHz on a WH-180 spectrometer. Peaks at positions 1-4 integrate for 3 H each unless otherwise specified, and peaks at positions 5-8 integrate for either methyl or aromatic protons as appropriate. [b] Integrates for 2 H. [c] A quartet and triplet for 2 H and 3 H, respectively, J = 7.43 Hz. [d] Peaks not indicated were obscured by those of 6. [e] Multiplets appeared at δ 2.33-2.41 (8 H), 2.57-2.66 (6 H), 2.69-2.76 (6 H), and 6.87-7.06 (2 H); integration of the singlets for the trimethylsilyl protons indicated a 1.1:1 mixture of the isomers with peaks at −0.23/−0.18. [f] These assignments may be interchanged. [g] A quartet and triplet for 2 H and 3 H, respectively, J = 7.6 Hz. [h] Peaks not indicated were obscured by those of 3. [i] mp 89-90 °C. [j] A quartet and triplet for 2 H and 3 H, respectively, J = 7.5 Hz. [k] Singlets at δ 2.81 and 2.85. [l] Multiplet at δ 6.96-7.12. [m] A quartet and triplet for 2 H and 3 H, respectively, J = 7.8 Hz. [n] Singlets at δ 2.81 and 2.84 for 3 H and 6 H, respectively. [o] Multiplet at δ 7.04-7.18.

Some polymetalation (about 5%) occurred, mainly of ring protons.

Product Identification. The location of the R groups in the metalation products was established by ^1H NMR spectroscopy and in particular by the chemical shifts of the various methyl and methylene groups. Hydrocarbons



1



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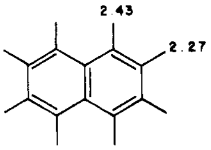

3

1-3 labeled with deuterium in specific positions were synthesized (Experimental Section) to permit unequivocal NMR assignments, as shown. In all cases, methyls at the 1, 4, 5, and 8 positions appear at lower field than those at the 2, 3, 6, and 7 positions.

The NMR assignments of the metalation products are summarized in Table II.

Experimental Section

General Lithiation Procedure. Into a septum-sealed, 100-mL, three-necked flask under nitrogen and cooled to 0 °C was injected 2 mL of 2.5 M *n*-butyllithium in hexane (5 mmol) followed by 0.8 mL (5 mmol) of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), and the mixture was stirred magnetically for 15 min. To this mixture was added 1 mmol of polymethylnaphthalene in 7-8 mL of tetrahydrofuran (THF, freshly distilled from benzophenone–sodium). After 15 min, the ice bath was removed and the mixture was stirred for 7 h. A deep red color developed after a short time. Excess trapping agent (trimethylchlorosilane or methyl iodide) was injected at 0 °C and left for at least 30 min (in the case of trimethylchlorosilane, the mixture was usually left overnight). The reaction mixture was poured onto excess ice and dilute hydrochloric acid, extracted several times with dichloromethane, washed with aqueous sodium bicarbonate, and dried ($MgSO_4$). The crude product mixture (90–100% yield) was separated into its components by GLC on a 6 ft. × 0.625 in. column containing 10% SE-30 on Chromosorb W at 210–260 °C and 60 psi He. The products were identified by their NMR spectra (at 60 and 180 MHz) and by high-resolution mass spectrometry.

The results of the high-resolution mass spectrometry were as follows. Calcd for **4**, **5**, and **15**: 256.16473. Found: **4**, 256.16495; **5**, 256.16443; **15**, 256.16342. Calcd for **6**, **7**, and **16**: 198.14084. Found: **6** and **7** (mixture) 198.14105; **16**, 198.14076. Calcd for **8** and **9**: 284.1959. Found: **8**, 284.1969; **9**, 284.1966. Calcd for **10**: 226.17204. Found: 226.17180. Calcd for **11** and **12**: 312.22717. Found: **11**, 312.22704; **12**, 312.22668. Calcd for **13**: 254.20344. Found: 254.20321.

The low-resolution mass spectra of the metalation products showed the following significant peaks, *m/e* (relative intensity): **4**, 256 (69, M^+), 183 (26, $M^+ - SiMe_3$), 73 (100, $SiMe_3$); **5**, 256 (84, M^+), 183 (39, $M^+ - SiMe_3$), 73 (100, $SiMe_3$); **6**, 198 (100, M^+), 183 (100, $M^+ - Me$); **8**, 284 (100, M^+), 211 (28, $M^+ - SiMe_3$), 73 (67, $SiMe_3$); **10**, 226 (100, M^+), 211 (46, $M^+ - Me$); **11**, 312 (100, M^+), 241 (100, $M^+ - SiMe_3$), 73 (98, $SiMe_3$); **12**, 312 (100, M^+); **13**, 254 (100, M^+), 239 (45, $M^+ - Me$); **15**, 256 (56, M^+), 183 (26, $M^+ - SiMe_3$), 73 (100, $SiMe_3$); **16**, 198 (80, M^+), 183 (100, $M^+ - Me$).

In one experiment with **3**, the metalation reaction mixture was quenched with D_2O; mass spectrometry showed only monodeuteration.

Preparation of Deuterium-Labeled 1, 2, and 3. Details for the preparation of **1** labeled with a CD_3 group at C_2 are being published elsewhere.[11] Its ^1H NMR spectrum was identical with that of 1,2,3,4-tetramethylnaphthalene (see structure) except that the peak at δ 2.37 was reduced in area to 3 H.

In an analogous manner except for the use of 3,6-dimethylbenzyne in place of benzyne, and with the final step being carried out for 70 h in refluxing mesitylene, a sample of 2-trideuteriomethyl-1,3,4,5,8-pentamethylnaphthalene was prepared;[12] its ^1H NMR spectrum was identical with that of 1,2,3,4,5,8-hexamethylnaphthalene except that the peak at δ 2.30 was reduced in area to 3 H.

Reduction of 0.9 g of 6,7-bis(bromomethyl)-1,2,3,4,5,8-hexamethylnaphthalene[12] with 0.5 g of lithium aluminum deuteride in 50 mL of ether gave a 67% yield of 6,7-bis(deuteriomethyl)-1,2,3,4,5,8-hexamethylnaphthalene whose ^1H NMR spectrum was identical with that of octamethylnaphthalene[12] except that the peak at δ 2.30 was reduced in area to 10 H.

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Registry No. **1**, 3031-15-0; **2**, 36230-30-5; **3**, 18623-61-5; **4**, 71185-22-3; **5**, 71185-23-4; **6**, 71185-24-5; **7**, 71185-25-6; **8**, 71185-26-7; **9** isomer 1, 71185-27-8; **9** isomer 2, 71185-28-9; **10**, 71185-29-0; **11**, 71185-30-3; **12**, 71185-31-4; **13**, 71185-32-5; **14**, 2717-39-7; **15**, 71185-33-6; **16**, 71185-34-7; methyl iodide, 74-88-4; trimethylchlorosilane, 75-77-4; 6,7-bis(bromomethyl)-1,2,3,4,5,8-hexamethylnaphthalene, 62571-66-8; 6,7-bis(deuteriomethyl)-1,2,3,4,5,8-hexamethylnaphthalene, 71185-35-8.

Xenon Difluoride Fluorination. 3. Mechanism and Selectivity of Boron Trifluoride Etherate Catalysis in the Norbornene Model

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The boron trifluoride etherate initiated fluorination of norbornene with xenon difluoride in dichloromethane solvent selectively produces the novel compound 2-*exo*,5-*exo*-difluoronorbornane and its analogues 2-*endo*,5-*exo*-difluoronorbornane isomer. Initially the two 2,5-difluoronorbornanes represent about half of the directly fluorinated reaction products, and the well-known *anti*- and *syn*-2,7-difluoronorbornane isomers comprise the remainder. Subsequently the boron trifluoride etherate catalyzes selective isomerization of both 2,7-difluoronorbornanes and produces a nearly exclusive yield of the 2-*exo*,5-*exo*- and 2-*endo*,5-*exo*-difluoronorbornane isomers. A change to diethyl ether solvent yields the normal *anti*- and *syn*-2,7-difluoronorbornane isomers as the major difluoride products and quenches the boron trifluoride etherate isomerization. Substitution of lithium tetrafluoroborate for the boron trifluoride etherate in diethyl ether again provides the unique 2,5-difluoronorbornanes as the major difluoride products. The 2,5-difluoronorbornane isomers were unambiguously identified by the direct fluorination of deuterated norbornene. The deuterated norbornene also permitted the initial fluorination mechanism and the selective isomerization pathway in dichloromethane solvent to be studied.

A previously reported open-system, bench-top procedure proved xenon difluoride to be a safe direct fluorinating reagent for aliphatic alkenes.[2] This convenient procedure employed boron trifluoride etherate to catalytically initiate direct alkene fluorination in a dichloromethane suspension. It was conducted in standard chemical glassware and required only such general items as a drybox for storing and weighing the xenon difluoride plus a bench-top fume hood. When norbornene was fluorinated by this procedure, an unprecedented high yield of 2-*exo*,5-*exo*-difluoronorbornane (**1**) and its analogous 2-*endo*,5-*exo* isomer (**2**) resulted.[3] This provided a distinct contrast to previously reported halogen and interhalogen additions to norbornene that selectively produce the *anti*- and *syn*-2,7-dihalonorbornane isomers through an ionic mechanism or the 2-*exo*,3-*exo*- and 2-*endo*,3-*exo*-dihalonorbornanes from a radical pathway.[4-10] Two past norbornene fluorinations produced three major products common to each reaction. Fluorination with lead tetraacetate/hydrogen fluoride in a Freon 112/dichloromethane solvent[9] and a more recent fluorination using difluoroiodobenzenes with a dichloromethane/hydrogen fluoride solvent[10] both afforded the ionically rearranged 2-*exo*,7-*anti*-difluoronorbornane **3** and 2-*exo*,7-*syn*-difluoronorbornane **4**, plus nortricyclyl fluoride **11** as the major products. In both cases the *syn*-2,7-difluoronorbornane **4** proved to be the predominant species. A more recent hydrogen fluoride initiated reaction between norbornene and xenon difluoride in dichloromethane solvent provided the nortricyclyl fluoride **11** as its major product. The 2,7-, 2,5-, and 2,3-difluoronorbornane isomer sets comprised the six additional isolated products.[11]

Table I. Difluoronorbornane Isomer Product Distribution from Boron Trifluoride Etherate Catalysis in CH_2Cl_2 Solvent

run	conditions[a]	1	2[g]	3	4	5	6	7	11
1	A	98.5		1.5	0	0	0	D	0
3	A	45	17	38	0	0	0	D	0
4	A	66.5	30	3	0	0	0	D	0
5	A	64	29	7	0	0	0	D	0
6	A (dark)	65	31	4	0	0	0	D	0
7	B[b]	58	26	3	0	0	0	13	0
	C[c]	24.5	26	43	7	0	0	0	0
8	B[d]	62	26	3	0	0	0	9	0
	C[e]	40	17	31	12	0	0	0	0
9	C[f]	22	26	42	9	0	0	0	0
10	A (no catalyst)	19	28	37	5	0	4	0	8
	(HF catalyst)[11]	11	20	19.5	6	2	3.5	0	38

[a] A, −78 °C to room temperature, 20–22 h; B, −46 °C to room temperature, 20–22 h; C, −46 to −39 °C, 1 h; D, not determined. [b] Product percentages change to 66% for **1**, 30% for **2**, and 4% for **3** when unknown **7** is not considered. [c] −43 to −39 °C during XeF_2 consumption. [d] Product percentages change to 68% for **1**, 28% for **2** and 4% for **3** when unknown **7** is not considered. [e] −46 °C during XeF_2 consumption. [f] −41 °C during XeF_2 consumption. [g] Combined.

The boron trifluoride etherate catalyzed fluorination of norbornene with xenon difluoride represents the first

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