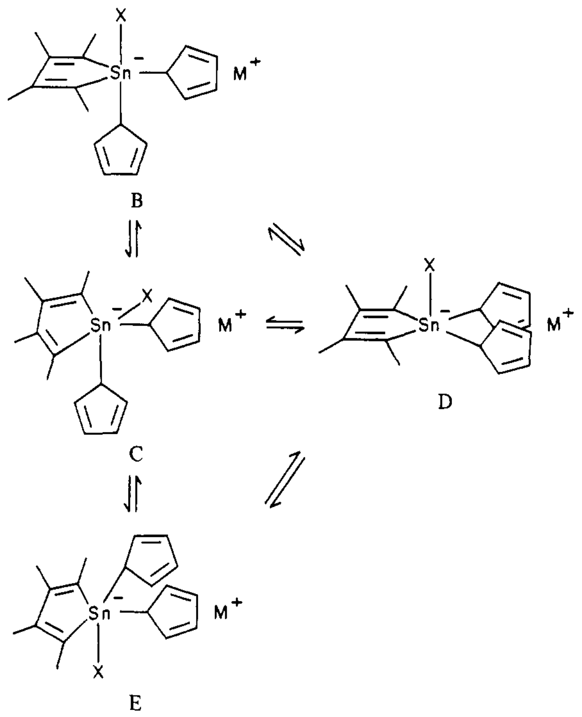
J. Am. Chem. Soc. 1981, 103, 4131-4135



heterocycles. While no structural data are available for any of the fourth group metalloles,[37] the heterocyclic ring in the related pentaphenylaluminole diethyl ether complex is completely planar.[39] Structure B in which the stannole ring spans two equatorial positions would require an unreasonable expansion of the carbon–tin–carbon bond angles. Conversion of structure B to the square pyramidal form E would thus be expected to be accompanied by considerable release of strain. Square-pyramidal intermediates have been proposed to rationalize the temperature-dependent proton NMR of 2-biphenyl-bis(4,4-bitolyl)antimony whose singlet tolyl methyl resonance becomes a quartet at −60 °C ($\Delta E^\ddagger = 11.6$ kcal/mol).[40,41] Solid pentaphenylantimony has a square-pyramidal structure.[42,43]

An alternative proposal based upon lithium ion association with the stannole ring in 1,1-bis(η^1-cyclopentadienyl)stannole and a bromide gegenion would rationalize the temperature-dependent spectra in terms of a dissociation of the metal–heterocycle complex, but this is ruled out by the lack of chemical shift dependence on temperature and by the presence of an easily assignable tin bromide stretching frequency in the infrared. The chemical shifts of the bromo derivative are sensitive to the change in metal ion from lithium to thallium, however, the lack of appreciable conductivity in nitrobenzene and easy solubility in hydrocarbons suggests significant ion pairing.

The synthesis of the $[X(\eta^1\text{-}C_5H_5)_2SnC_4(C_6H_5)_4]^-M^+$ species can proceed through either a 1-(η^1-C_5H_5)-1-halostannole, followed by adduct formation with $C_5H_5^-$ anion or via $(\eta^1\text{-}C_5H_5)_2SnC_4(C_6H_5)_4$ with subsequent metal halide uptake. The appearance of both cyclopentadienyltin resonances from the onset of reaction rules out the former, and the addition of 1,4-dilithio-1,2,3,4-tetraphenylbuta-1,3-diene to bis(η^1-cyclopentadienyl)tin dichloride[25] from the redistribution reaction between tetrakis(η^1-cyclopentadienyl)tin(IV)[24] and tin(IV) chloride did not, in our hands, yield a pure tin-containing material. The oily product gave a Mössbauer spectrum arising from more than one tin site.

Tetraorganotin compounds show no Lewis acid activity, but the as yet unisolated 1,1-bis(η^1-cyclopentadienyl)-2,3,4,5-tetraphenylstannole apparently takes up halide ion during its formation from lithium or thallium cyclopentadiene in THF–hexane to form the $[X(\eta^1\text{-}C_5H_5)_2SnC_4(C_6H_5)_4]^-$ anion rather than precipitating the metal halide. The addition of pyridine has no effect on these products.

Acknowledgment. Our work is supported by the Office of Naval Research and the National Science Foundation through Grant CHE-78-26548. We thank M&T Chemicals for the donation of organotin starting materials.

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Synthesis and Carbon-13 Nuclear Magnetic Resonance Studies of Some Bridgehead Fluorides: Carbon–Fluorine Coupling Constants

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Received November 19, 1980

Abstract: The synthesis of 1-fluorobicyclo[2.2.1]heptane, 1-fluorobicyclo[3.1.1]heptane, 1-fluorobicyclo[2.1.1]hexane, and 1-fluorobicyclo[1.1.1]pentane is described. The ^{13}C NMR spectra of these fluorides together with that of 1-fluorotricyclo[3.3.0.0^{2,6}]octane were examined in order to gauge, in particular, the importance of Fermi contact contributions to the one-bond ^{13}C–F spin–spin coupling constants. It is found that the magnitude of $^1J(^{13}C\text{–}F)$ increases with enhanced s character of the carbon bonding orbital. At the same time it is noted that vicinal ^{13}C–F coupling involving bridgehead carbons increases dramatically as the number of three-bond paths also increases, although through-space interactions appear to play a significant role in determining the magnitude of this parameter. It is suggested that these nonbonded interactions also account for the shielding effect exerted by the antiperiplanar fluorine atoms on the bridgehead γ-carbon atoms. Such shielding increases markedly as the system becomes more constrained.

There is, currently, widespread interest in spin–spin coupling between various nuclei and the factors which influence this phenomenon. Some time ago Ramsey[1] discussed the theory appropriate to such coupling in terms of the following electron-

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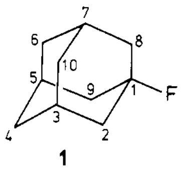
coupled mechanisms: (a) interaction between the nuclear moments and the electronic spins in s orbitals, the (Fermi) contact term, J_{FC}; (b) interaction between the spin magnetic moments of the electrons and the nucleus, the dipolar term, J_D; and (c) interaction between the nuclear moments and the electronic currents produced by the orbiting electrons, the orbital term, J_O:

$$J_{Tot} = J_{FC} + J_O + J_D \qquad (1)$$

While these three contributions may vary in sign as well as in magnitude, calculations indicate that coupling between the majority of first-row elements is dominated by Fermi contact[2-7] and, as a result, would be expected to correlate with the product of the s electron densities at the coupled nuclei. These predictions are supported by experimental observations.[5-7]

In the particular case involving coupling between carbon and fluorine, however, theoretical approaches generally suggest that the contributions from the noncontact terms, b and c above, are not insignificant and must be included with that of the Fermi contact interaction.[2,3,8-10] At the same time there has been considerable effort in attempting to provide experimental values of ^nJ(CF),[5-7,10-13] and in the particular case of one-bond coupling, evidence exists for an increase in ^1J(CF) values with increasing s content of the carbon orbital.[13] It occurred to us that the group of substrates **1**–**7** would provide additional carbon–fluorine coupling data and prove to be of some assistance toward a better understanding of the coupling phenomenon. The bridgehead carbon atom bonded to fluorine assumes progressively more s character along the series,[14] and it seemed of interest to determine if the one-bond carbon–fluorine couplings showed some correlation with this trend. In addition, we felt that by virtue of their rigid geometry the caged compounds **1**–**7** would provide valuable information about vicinal carbon–fluorine coupling, inasmuch as it has been suggested[13] that the magnitude of ^3J(CF) is a function of the dihedral angle, θ, between the nuclei according to the expression

$$^3J(\mathrm{CF}) = 11.0 \cos^2 \theta \qquad (2)$$



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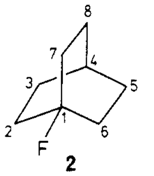

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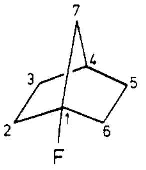

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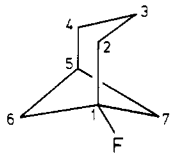

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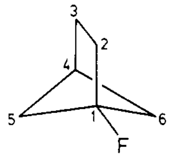

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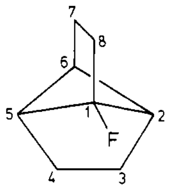

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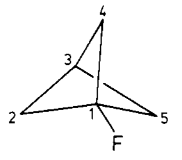

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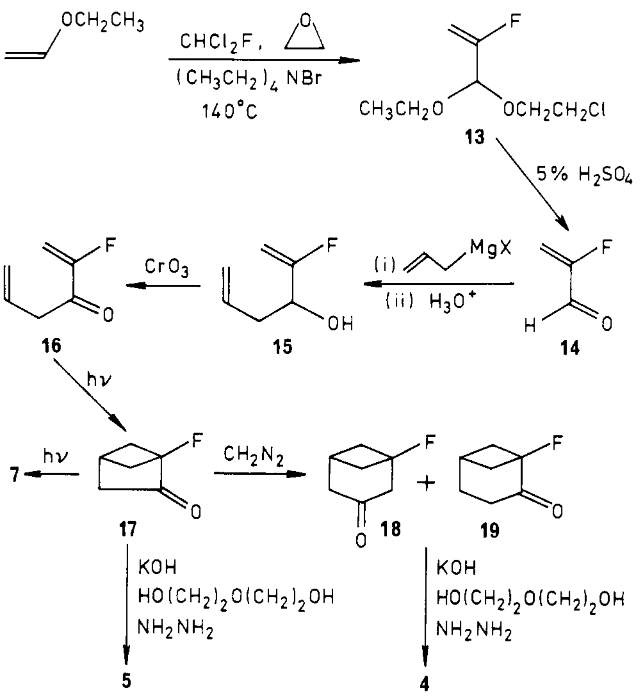
Scheme I

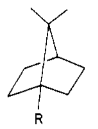


The required ^{13}C NMR spectral data of 1-fluoroadamantane (**1**)[15] and 1-fluorobicyclo[2.2.2]octane (**2**)[16] have been thoroughly documented. Accordingly we directed our attention to the remaining substrates **3**–**7**.

Results and Discussion

Syntheses. The fluorides **3**–**7** have not yet been reported in the literature. We synthesised 1-fluorobicyclo[2.2.1]heptane (**3**) from the corresponding alcohol **8** employing the procedure described by Beak and co-workers[17] for the preparation of 1-fluoroapocamphane (**9**) from 1-apocamphanol (**10**), which involves conversion of the alcohol to the chloroformate **11** followed by treatment of the latter with silver tetrafluoroborate. A more recent method[18] in which the alcohol **8** is treated with sulfur tetrafluoride

8



9, R = F
10, R = OH
11, R = OCOCl

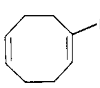


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Table I. Carbon-13 Chemical Shifts[a] of the Fluorides **1-7**

	carbon atom									
compd	1	2	3	4	5	6	7	8	9	10
1[b]	90.79	43.37	31.82	36.55	31.82	36.55	31.82	43.37	43.37	36.55
	(28.75)	(38.24)	(28.75)	(38.24)	(28.75)	(38.24)	(28.75)	(38.24)	(38.24)	(38.24)
2[c]	92.48	31.19	27.27	24.27	27.27	31.19	31.19	27.27		
	(24.00)	(26.00)	(26.00)	(24.00)	(26.00)	(26.00)	(26.00)	(26.00)		
3	103.84	32.19	29.75	33.18	29.75	32.19	41.14			
	(36.60)	(30.00)	(30.00)	(36.60)	(30.00)	(30.00)	(38.60)			
4	93.75	33.35	17.63	26.68	25.02	39.72	39.72			
	(34.20)	(29.40)	(16.00)	(29.40)	(34.20)	(33.30)	(33.30)			
5	95.21	26.98	27.95	27.09	43.10	43.10				
	(39.50)	(26.28)	(26.28)	(39.50)	(39.00)	(39.00)				
6	96.90	51.45	22.30	22.30	51.45	39.05	21.89	25.13		
	(50.60)	(50.60)	(25.40)	(25.40)	(50.60)	(50.60)	(25.40)	(25.40)		
7	74.93	53.18	14.79	53.18	53.18					
	(33.49)	(50.75)	(33.49)	(50.75)	(50.75)					

[a] ±0.02 ppm. Numbers in parentheses are the shifts of the relevant carbon atoms in the corresponding unsubstituted hydrocarbon (data of Della and associates, ref 14). [b] Data of Maciel, Dorn, Greene, Kleschick, Peterson, and Wahl (ref 15a). [c] Data of Maciel and Dorn (ref 16).

under relatively mild conditions gives **3** directly, and in superior yield. We recently described[19] the synthesis of 1-fluorotricyclo[3.3.0.0^{2,6}]octane (**6**) by photoinduced cyclization of 1-fluorocycloocta-1,5-diene (**12**). The fluorides **4**, **5**, and **7** were obtained from a common precursor, 1-fluorobicyclo[2.1.1.]hexan-2-one (**17**), as illustrated in Scheme I. The projected route to the fluoroketone **17** was based on that described[20,21] for the synthesis of a number of substituted bicyclo[2.1.1]hexan-2-ones from the corresponding acyclic 1,5-dienones. 2-Fluoropropenal (**14**) was synthesized from ethyl vinyl ether as depicted, following a procedure developed[22] for the analogous conversion of *n*-butyl vinyl ether into **14**. In view of its relative instability, the aldehyde **14** was not normally isolated but converted directly into the alcohol **15** by treatment with allylmagnesium chloride. Oxidation of dienols related to **15** to the corresponding dienones has generally been found to proceed, at best, in only moderate yield.[20,21] We encountered similar difficulties in the conversion of **15** into **16**. It was our experience that while the use of mild oxidants such as PCC[23] and PDC[24] offers more favorable conditions in which to generate the ketone **16**, aqueous chromic acid in a modified Brown procedure proved not only to be simple, convenient, and rapid in action, but was also found to be more efficient despite some loss of dienone under the more drastic conditions. Isolation of the dienone **16** was not usually performed and its solution in ether was irradiated immediately with Pyrex-filtered light from a Hanovia 450-W lamp. The overall yield of the fluoride **17** from the alcohol **15** was 27%. Although conversion of **17** to 1-fluorobicyclo[2.1.1]hexane (**5**) could be carried out by reduction of the derived tosylhydrazone with sodium cyanoborohydride[25] as reported for the analogous preparation of bicyclo[2.1.1]hexane,[14a] it was found more convenient to reduce **17** directly to **5** under standard Wolff-Kischner conditions. 1-Fluorobicyclo[3.1.1]heptane (**4**) was obtained by a diazomethane-induced ring expansion of **17** which gave predominantly a 5:95 mixture of the fluoroketones **18** and **19** together with small quantities of higher homologues. The ketones **18** and **19** were readily distinguished on the basis of their ^{13}C NMR spectra. The major product, **19**, was converted into the required fluoride **4** via Wolff-Kischner reduction.

Finally, mercury-sensitized decarbonylation of **17** to produce 1-fluorobicyclo[1.1.1]pentane was effected, in rather low yield (ca. 10%), by gas-phase ultraviolet irradiation through quartz. Contrary to observations on the parent hydrocarbon,[26] it was found that irradiation through Vycor proved to be ineffective. The fluoride **7** was contaminated with small quantities of unsaturated isomers (NMR analysis) which were removed by passing the product through neutral aqueous potassium permanganate. In addition, **7** proved to be more labile than the parent hydrocarbon and it was found adventitious to rinse all glassware with base before use, and to store deuterochloroform for NMR use over anhydrous potassium carbonate. When these precautions were observed the product **7** could be handled without decomposition.

Nuclear Magnetic Resonance Data. ^{13}C Chemical Shifts. The carbon-13 chemical shifts of the fluorides **3-7** are collected in Table I which also contains the reported data for **1**[15a] and **2**,[16] together with the corresponding ^{13}C resonances of the parent hydrocarbons. The assignment of shifts in the fluorides was facilitated by a comparison with those of the hydrocarbons and by the relative intensities of signals in the proton broad-band decoupled spectra. As expected, the α carbons of compounds **1-7** experience enormous paramagnetic shifts, ranging from 46 to 68 ppm. The influence of the fluorine on the β carbons was generally not very pronounced; these carbon atoms are almost all deshielded to some extent, the magnitude of the substituent shift ranging from 0.7 to 5.2 ppm. Of particular interest, however, are the γ substituent chemical shifts. Eliel and co-workers[27] have demonstrated that nitrogen, oxygen, and fluorine normally exert a shielding effect on γ-carbon atoms when oriented in an anti-periplanar position to those carbons. A notable exception was found to occur when the heteroatom is located at the bridgehead position, as illustrated by the paramagnetic substituent shift of C3 in both 1-fluoroadamantane (**1**) and 1-fluorobicyclooctane (**2**).[27] We find that, in accordance with these observations, the γ-carbon atoms C3 in both **4** and **5** are deshielded in comparison with the corresponding nuclei in the parent hydrocarbons. However, as can be seen in Table I, C3 and C7 in the fluoride **6** and C3 in fluoride **3** together with the bridgehead carbons C4 (in **3**), C5 (in **4**), C4 (in **5**), C6 (in **6**), and C3 (in **7**) display prodigious upfield shifts consistent with the effects above noted by Eliel and his associates.[27] It is noteworthy that these bridgehead γ carbons which are strongly shielded by the anti-periplanar fluorine are also strongly coupled to it (see below), and indeed these effects are essentially linearly related. Accordingly, it appears that the increased shielding is governed to a large extent by the same kind of through-space interaction that has an important bearing on the extent of coupling between the nuclei.

Carbon-Fluorine Coupling Constants. Table II contains the various ^nJ(CF) values of compounds **1-7**. The two parameters

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Table II. Carbon-Fluorine Coupling Constants[a] in the Fluorides **1**-**7**

compd	$^1J^b$	^2J	^3J	^4J
1[c]	185.9 (133.4)	17.7 (C2, C8, C9)	10.4 (C3, C5, C7)	1.25 (C4, C6, C10)
2[d]	185.3 (134.3)	18.4 (C2, C6, C7)	9.4 (C3, C5, C8)	3.3 (C4)
3	208.1 (140.1)	20.3 (C2, C6) 18.5 (C7)	8.2 (C3, C5) 7.9 (C4)	
4	233.4 (144.9)	18.6 (C2) 18.6 (C6, C7)	8.3 (C3) 17.1 (C5)	1.0 (C4)
5	257.6 (150.5)	19.0 (C2) 18.4 (C5, C6)	5.9 (C3) 23.6 (C4)	
6	260.3 (147.9)	20.0 (C8) 18.1 (C2, C5)	7.4 (C7) 22.5 (C6) <1.0 (C3, C4)	
7	332.5 (167.8)	20.5 (C2, C4, C5)	42.5 (C3)	

[a] In Hz, ±0.05 Hz. [b] Numbers in parentheses refer to the values of $^1J(^{13}C-H)$ of the bridgehead carbon in the parent hydrocarbons corresponding to **1**-**7** (data of Della and associates, ref 14). [c] Data of Maciel, Dorn, Greene, Kleschick, Peterson, and Wahl (ref 15a). [d] Data of Maciel and Dorn (ref 16).

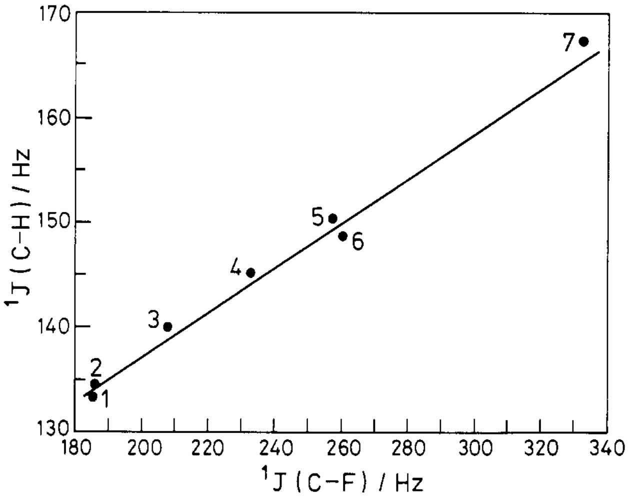

Figure 1. Plot of $^1J(^{13}C-H)$ of the bridgehead carbon in the parent hydrocarbons vs. $^1J(^{13}C-F)$ in the fluorides **1**-**7**.

of special interest are the one-bond and the vicinal coupling constants. The data of Table II illustrate quite clearly that the magnitude of $^1J(^{13}C-F)$ in the fluorides **1**-**7** increases dramatically with increasing s character of the carbon bonding orbital. In fact, $^1J(^{13}C-F)$ displays a linear correlation with $^1J(^{13}C-H)$ in the parent hydrocarbons, as demonstrated in Figure 1. On the one hand this may be interpreted as strong evidence that the contributions of the dipolar (J_D) and orbital (J_O) mechanisms to ^1J(CF) are either negligible or otherwise fortuitously cancel each other. The much more likely explanation, however, is that ^1J(CF) is determined by Fermi contact but only because the noncontact terms, while significant, are relatively constant in the series of fluorides **1**-**7** under investigation.

The geminal couplings do not vary greatly from system to system. Such constancy has been noted previously.[13] As can be seen (Table II) the variation in the magnitude of the vicinal couplings is very pronounced, the values of $^3J(^{13}C-F)$ ranging from <1.0 Hz for C3(C4) in **6** (CCCF dihedral angle, ca. 70°) to 42.5 Hz for C3 in **7** (CCCF dihedral angle, 180°). The Karplus-type relationship between $^3J(^{13}C-F)$ and the relevant dihedral angle (eq 2), which appears to hold for many of the fluorides examined by Schneider and his co-workers,[13] has some relevance when applied to nonbridgehead carbons, e.g., C3 in **2**-**6** and C7 in **6**. However the vicinal couplings involving bridgehead carbon atoms show a dramatic increase in magnitude along the series **2**-**7**. Thus the ^3J(CF) values of the bridgehead carbons in **2**, **3**, **4**, **5**, and **7** are respectively 3.3, 7.9, 17.1, 23.6, and 42.5 Hz. It is apparent that these couplings are strongly influenced by the number of three-bond pathways between the coupled nuclei.[28] For instance, the three-bond coupling constant between fluorine and the bridgehead carbon in **4** (two three-bonds paths) is 2.3 times that in **3** (one three-bond path). However, it is equally true that through-space interactions arising as a result of the proximity of the bridgehead carbons must also play an important role in determining the magnitude of the coupling. For example, ^3J(C-bridgehead-F) in **5** is 1.4 times that in **4**, and yet there are two three-bond paths in each case. In a recent study involving derivatives of the hydrocarbons corresponding to **2**, **3**, and **5**, viz., those substituted with deuterium, ^{13}COOH, or $^{13}CH_2OH$ at the bridghead, Barfield, Marshall, and their associates[28] reported a similar increase in vicinal coupling between the substituent and the bridgehead carbon compared with other γ-carbon atoms. In accordance with predictions based on theoretical calculations, these workers found that, despite the greater number of three-bond paths along the series, there is a decreased enhancement in the magnitude of the coupling, and they ascribed this fact to the fact that the nonbonded interactions oppose through-bond effects. It can be seen that the through-space interactions in the fluorides **2**-**7** augment rather than oppose the contributions along the three-bond paths, as illustrated by the extraordinary value of the vicinal coupling constant in the fluoride **7** (three three-bond paths) which has ^3J(C-bridgehead-F) 5.7 times that in **3** and 1.8 times that in **5**.

Experimental Section

General. Infrared spectra were obtained using a Perkin-Elmer 237 grating spectrophotometer. ^{1}H NMR spectra were recorded on Varian A60-D and Jeolco FX90Q instruments, and most ^{13}C NMR spectra were recorded on the Jeolco FX90Q (22.50 MHz) with several taken on a Bruker WH270 spectrometer (67.89 MHz); chemical shifts are reported in parts per million downfield from internal Me_4Si. Mass spectra were obtained from an AEI MS30 spectrometer. Analytical GC was performed on a Varian 1740 instrument, using 10 ft × 0.25 in. stainless steel columns packed with 5% SE-30 on Chromosorb W or 5% Carbowax 20M on Chromosorb G. Preparative GC was carried out on a Varian Aerograph 920 instrument, using helium gas. Microanalyses were performed by the Australian Microanalytical Service, Melbourne.

Bicyclo[2.2.1]heptan-1-ol (8). Bicyclo[2.2.1]heptane-1-carboxylic acid[29] (12.5 g, 0.09 mol) was dissolved in concentrated sulfuric aid (100 mL) and cooled to −10 °C. Aqueous hydrogen peroxide (100 mL, 30% w/v) was added dropwise at such a rate that the temperature did not rise above 0 °C. The mixture was stirred at room temperature for 8 h and then poured onto ice (200 g). The aqueous phase was extracted with ether (2 × 100 mL) and the combined ether layers were washed with 10% aqueous sodium hydrogen carbonate (2 × 80 mL) and water (2 × 90 mL) and then dried ($MgSO_4$). Solvent was removed by distillation through a 15-in. column packed with glass helices leaving a solid which was recrystallized from hexane to give bicyclo[2.2.1]heptan-1-ol (**8**) as colorless plates (7.1 g; 72%), mp 150–151 °C (lit.[30] mp 152–154 °C).

1-Fluorobicyclo[2.2.1]heptane (3). A stirred solution of the alcohol **8** (5.5 g, 0.05 mol) in ether (6 mL) maintained at 10–15 °C under a nitrogen atmosphere was treated dropwise with a 1.6 M solution of methyllithium in ether (31 mL). The white precipitate was redissolved by addition of THF (8 mL), and the resulting solution transferred

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dropwise via cannula into a stirred solution of phosgene (18 g) in benzene (125 mL) held at 15 °C. The purple mixture was stirred at ambient temperature for a further 2 h and then flushed with nitrogen in order to remove excess phosgene. The solvent was removed in vacuo, the residue extracted with hexane, and the hexane extracts chromatographed on a Florex column. The chloroformate **9** (2.1 g), which was obtained as a light brown oil upon elution with hexane, was immediately dissolved in chlorobenzene (10 mL) and added slowly with stirring to a mixture of silver tetrafluoroborate (1.7g) and tetramethyllurea (1.9 g) in chlorobenzene (10 mL). Stirring was continued for 4 h at 25 °C. The precipitated silver salts were filtered off and the filtrate washed successively with 5% hydrochloric acid (3 × 10 mL) and water (3 × 10 mL) and then dried ($MgSO_4$). Preparative GC of the product allowed the separation of 1-fluorobicyclo[2.2.1]heptane (0.7 g; 12%); ^{1}H NMR ($CDCl_3$) δ 1.15–2.20 (m); mass spectrum, *m/e* (relative intensity) 114 (M^+, 6), 99 (18), 85 (100), 72 (44).

2-Fluoropropenal Ethyl 2-Chloroethyl Acetal (13). Ethyl vinyl ether (32 g, 0.4 mol), dichlorofluoromethane (45 g, 0.44 mol), ethylene oxide (90 mL, 1.8 mol), and tetraethylammonium bromide (3 g) were heated in an autoclave for 5 h at 135 °C.[22] The product was distilled to give ethylene chlorohydrin (18 g), bp 45 °C (26 mm Hg), followed by **13** (51.6 g, 57%): bp 84 °C (26 mmHg); IR(neat) 1687 (C=C), 1150 and 1130 (acetal) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.9–5.3 (m, 2 H, *cis*-HC=CF– and 3-H), 4.6 (dd, 1 H, J= 16, 3 Hz, *trans*-HC=CF–), 3.4–4.0 (m, 6 H, OCH_2 and $ClCH_2$), 1.09–1.35 (t, 3 H, J = 7.2 Hz, CH_3); mass spectrum *m/e* (relative intensity), 155 and 153 (1.5 and 4), 139 and 137 (5 and 18), 119 (8), 103 (48), 91 (12), 75 (100). Anal. Calcd for $C_7H_{12}ClFO_2$: C, 46.01; H, 6.68. Found: C, 46.03; H, 6.58.

2-Fluorohexa-1,5-dien-3-ol (15). The acetal **13** (21 g, 0.115 mol) was added dropwise with stirring to 5% sulfuric acid (20 mL) held at 80 °C,[22] and the volatile products were swept out of the reaction flask in a slow stream of nitrogen into a cooled receiver (−50 °C). When all the acetal had been added the temperature of the hydrolyzate was raised to 100 °C and stirring continued for a further 30 min. NMR analysis of the product showed it to consist of a 1:1:1 mixture of 2-fluoropropenal (**14**) (mass spectrum *m/e* 74), ethanol, and ethylene chlorohydrin. The mixture was dissolved in ether which was washed with water, dried ($CaCl_2$), and then added to a twofold excess of allylmagnesium chloride in ether. Stirring was continued overnight after which the mixture was treated with a saturated solution of ammonium chloride until the ether layer clarified as a precipitate deposited. The ether layer was dried ($MgSO_4$) and filtered. Evaporation of the solvent and distillation of the residue afforded the alcohol **15** (5.6 g, 41%): bp 150–152 °C; n_D^{20} 1.4258; IR (neat) 3350 (OH), 1680 (C=C), 915 (HC=CH) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.9–6.2 (m, 3 H, 1-H and 6-H), 4.68 (dd, 1 H, J = 17, 3 Hz, *trans*-CH=CF), 3.95–4.4 (m, 2 H, 3-H and 5-H), 2.46 (t, 2 H, J = 6.5 Hz, CH_2), 2.28 (s, 1 H, exch, OH); mass spectrum *m/e* 116 (M^+). Anal. Calcd for C_6H_9FO: C, 62.07; H, 7.76. Found: C, 61.95; H, 7.64.

1-Fluorobicyclo[2.1.1]hexan-2-one (17). To a vigorously stirred solution of 2-fluorohexa-1,5-dien-3-ol (**15**) (5.5 g, 0.047 mol) in ether (50 mL) was added in one portion a 0.33 M solution of chromic acid (300 mL), and the mixture was allowed to reflux for 30 min at which stage 90% conversion to **16** had been achieved (GC analysis). The organic layer was separated and the aqueous phase extracted with fresh solvent (2 × 30 mL). The combined extracts were washed with saturated sodium hydrogen carbonate (2 × 20 mL) and then dried ($MgSO_4/K_2CO_3$). The ketone **16** was not generally isolated because it polymerized on standing; ^{1}H NMR ($CDCl_3$) δ 5.2–5.8 (m, 5 H, vinyl protons), 3.4 (dd, 2 H, J = 17, 2.8 Hz, 4-H); mass spectrum *m/e* (relative intensity) 114 (M^+, 81), 86 (29), 73 (100); IR (neat) 1700 (C=O), 1640 (C=C), 915 (HC=C-H) cm^{-1}.

The solution of **16** in ether was diluted to 350 mL with fresh solvent and the solution irradiated with a 450-W Hanovia lamp placed in a water-cooled Pyrex well. The extent of cyclization was monitored by GC. After being irradiated for 10 h the solution was concentrated carefully with cooling, and the residue distilled to give 1-fluorobicyclo[2.1.1.]-hexan-2-one (**17**) (1.5 g, 27%): bp 72 °C (13 mmHg); IR (neat) 1780 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.9–3.2 (m); mass spectrum *m/e* 114 (M^+). Anal. Calcd for C_6H_7FO: C, 63.16; H, 6.14. Found: C, 63.19; H, 6.09. 1-Fluorobicyclo[2.1.1]hexan-2-one tosylhydrazone had mp 189.5–190.5 °C; mass spectrum *m/e* 282 (M^+). Anal. Calcd for $C_{13}H_{15}FN_2O_2S$: C, 55.32; H, 5.32. Found: C, 55.21; H, 5.61.

1-Fluorobicyclo[2.1.1]hexane (5). A stirred mixture of potassium hydroxide (3.5 g), hydrazine (2.5 g), and 1-fluorobicyclo[2.1.1]hexan-2-one (**17**) (0.5 g) in diethylene glycol (10 mL) was heated at 110 °C for 30 min. As the temperature was raised to 180 °C and held there for 2 h, the apparatus was purged with a steady stream of nitrogen which passed through two traps—one cooled to 0 °C and the other to −70 °C. The contents of the second trap proved to be the fluoride **5**; ^{1}H NMR ($CDCl_3$) δ 2.2 (d, 1 H, J = 20.5 Hz, 4-H), 1.50–1.83 (m, 8 H); mass spectrum *m/e* 100 (M^+). Anal. Calcd for C_6H_9F: C, 71.96; H, 9.06. Found: C, 71.83; H, 9.33.

1-Fluorobicyclo[3.1.1]heptan-2-one (19). To a solution of 1-fluorobicyclo[2.1.1]hexan-2-one (**17**) (0.6 g) and potassium hydroxide (1 g) in methanol (40 mL) was added a solution of *p*-tolylsulfonylmethylnitrosamide (3.5 g) in ether (20 mL). The solution was stirred overnight at room temperature, after which the excess diazomethane was destroyed by addition of 10% hydrochloric acid (4 mL). The mixture was diluted with water, neutralized with sodium hydroxide, and extracted with ether (3 × 20 mL) and the combined ether extracts were then dried ($MgSO_4$). Analysis of the product (GC–MS) indicated the predominance of the fluoroketone **19** together with a small quantity of the isomer **18** (ratio ca. 19:1) as well as smaller quantities of what appeared to be higher homologues. Preparative GC enabled separation of the major constituent, **19**: mp 60–62 °C; ^{1}H NMR ($CDCl_3$) δ 1.89–2.88 (m); mass spectrum *m/e* 128 (M^+); ^{13}C NMR ($CDCl_3$) δ 207.35 (C2), 93.95 (C1), 37.25 (C6,C7), 32.95 (t, C3), 25.09 (t, C4), 24.73 (d, C5). Anal. Calcd for C_7H_9FO: C, 65.61; H, 7.08. Found: C, 65.50; H, 6.84.

1-Fluorobicyclo[3.1.1]heptane (4). The above procedure employed for reduction of fluoroketone **17** to **5** was used to convert **19** into the fluoride **4**; ^{1}H NMR ($CDCl_3$) δ 1.41–2.35 (m); mass spectrum *m/e* 114 (M^+, 4), 99 (12), 86 (16), 84 (100), 82 (80), 77 (24).

1-Fluorobicyclo[1.1.1]pentane (7). 1-Fluorobicyclo[2.1.1]hexan-2-one (**17**) (0.2 g) and a small drop of mercury were placed in a 26 cm × 6 cm quartz cylindrical vessel (capacity, 750 mL) which had been rinsed first with aqueous potassium hydroxide then with water prior to being flame dried and purged with nitrogen. The container was cooled with liquid nitrogen, evacuated (0.01 mmHg), and then stoppered. The vessel was placed in a sand bath (preheated to 110 °C) located at the base of a Rayonet-type photochemical reactor containing 16 8-W germicidal lamps (254 nm) arranged circularly around the apparatus. After 30 min the lamps were activated and the ketone **17** irradiated for 1 h. The reaction vessel was allowed to cool to ambient temperature and the volatile constituents were removed under vacuum (10 mmHg) and condensed into one (0 °C) or other (−196 °C) of two traps. The contents of the latter were transferred in a stream of nitrogen via an aqueous potassium permanganate solution into a cold trap (−196 °C). Analysis (GC–MS, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR) showed this product to be essentially pure fluoride **7** (ca. 15 mg); ^{1}H NMR ($CDCl_3$) δ 2.01–2.07 (m); mass spectrum *m/e* (relative intensity) 86 (M^+, 100), 85 (95), 71 (23), 65 (30), 59 (45). The residue in the quartz vessel appeared to be a mixture of polymeric compounds.

Acknowledgment. This work was supported in part by the Australian Research Grants Committee which also provided access to the National NMR Centre, Canberra (Director Dr. Alan Jones).