a result of heavy atom catalysis of intersystem crossing. Finally, the photohydrodechlorination reaction of pentachlorobenzene can be carried out successfully in an aerated aqueous micellar solution of CTAB in the sunlight wavelength range, which augers well for use of the photohydrodehalogenation process as a basis for toxic waste disposal systems.

Experimental Section

Materials. Pentachlorobenzene (Aldrich) was recrystallized twice from ethanol. The purity was checked by gas chromatography and was greater than 99.9%. Hexadecyltrimethylammonium bromide (CTAB) (Aldrich) was washed with pentane twice and recrystallized from ethanol. Deionized water was distilled from potassium permanganate.

General Procedure for Photolysis and Analysis. Samples (1.0 mL) were placed in quartz tubes (Ace Glass, 170 × 15 mm) and degassed twice by using freeze–pump–thaw cycles. The samples were sealed under vacuum using resealable nylon/glass stopper valves. The photolyses of the samples were carried out in a Rayonet merry-go-round reactor (The Southern New England Co.) equipped with eight 2537-Å Rull lamps. The temperature in the reactor was 50 °C and constant under a stream of air. After photolysis of 2 min, the samples were extracted several times with pentane. The efficiency of extraction with pentane was greater than 90%. Dodecane as an internal standard was added to the extracts, and most of the pentane was removed by using a rotary evaporator to get more concentrated reaction mixtures. The photolysis mixtures were analyzed by GLC on a Varian 3300 capillary gas chromatograph equipped with an FID and Varian 4290 integrator. A 30-m × 0.25-mm DB-225 capillary column (J and W Scientific Inc.) was used. The temperature of the column was held at 60 °C for 5 min and increased to 180 °C at a rate of 5 °C/min. The carrier gas was helium, and the flow rate was 30 mL/min. Azoxybenzene was used as an actinometer according to the procedure of Bunce et al.[7] A Finnigan 4023 mass spectrometer equipped with a Finnigan 9610 gas chromatograph was also used to identify the reaction mixtures. Byproduct, bromotetrachlorobenzene, was analyzed by GC–MS using a 15-m × 0.20-mm OV-225 capillary column (temperature programming: 60–150 °C, 5 °C/min, 150–180 °C, 2 °C/min).

Photolysis of Pentachlorobenzene in the Presence of KBr. (a) Pentachlorobenzene (2.18×10^{-2} M) in CH_3CN/H_2O (8:2) with 0.100 M KBr was degassed and irradiated at 254 nm for 5 min in a quartz tube under the conditions described in the general procedure for photolysis. After photolysis, the reaction mixture was analyzed by GLC: C_6HBrCl_4; 44.5% (5:6:7 = 11.3:66.8:21.9%), $C_6H_2Cl_4$; 55.5% (2:3:4 = 48.4:40.6:11.0%). (b) Pentachlorobenzene (4.70×10^{-3} M) in CH_3CN/H_2O (8:2) with 0.104 M KBr was degassed and irradiated in the presence of 0.526 M of Et_3N at 254 nm for 5 min. No bromotetrachlorobenzene was observed. Only tetrachlorobenzene was produced (2:3:4 + 25.9:69.5:4.7%). (c) Pentachlorobenzene (3.91×10^{-3} M) was dissolved in aqueous CTAB solution (0.200 M) with 8.16×10^{-2} M Et_3N and degassed. After irradiation for 30 min at 300 nm, the reaction mixture was extracted with pentane and analyzed by GLC. Only tetrachlorobenzene was observed (2:3:4 = 43.7:43.2:13.0%).

Photolysis of an Aerated Sample of Pentachlorobenzene. Pentachlorobenzene (3.91×10^{-3} M) was dissolved in 0.200 M aqueous CTAB medium, and 1 mL of the solution was transferred into each Pyrex tube. The Pyrex tube was not sealed and was open to the atmosphere. The temperature of the reaction mixture was kept constant by providing a stream of fresh air. The sample was irradiated with a 275-W Westinghouse sun lamp held at approximately 10 cm from the sample tube. After photolysis for a certain period, the reaction mixture was extracted with pentane and analyzed by GLC. Dodecane was used as an internal standard.

Acknowledgment. Support of this research by the National Institute of Environmental Health Sciences (Grant ES00040) is gratefully acknowledged.

Registry No. 1, 608-93-5; 2, 634-90-2; 3, 95-94-3; 4, 634-66-2; 5, 1125-52-6; 6, 139606-99-8; 7, 81067-39-2; CTAB, 57-09-0; KBr, 7758-02-3; tetrachlorobenzene, 12408-10-5; trichlorobenzene, 12002-48-1; dichlorobenzene, 25321-22-6.

Synthesis of Bridgehead Fluorides by Fluorodeiodination

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Fluorodeiodination is found to be an attractive procedure for the synthesis of bridgehead fluorides. Thus, treatment of the corresponding iodide with xenon difluoride in dichloromethane at ambient temperature generally leads to high yields of the fluoride. Evidence suggests the intermediacy of the bridgehead cation in this reaction, and accordingly the substrates which are unfavorably disposed to fluorodeiodination are the bicyclo[*n*.1.1]alkyl iodides. In this context the isolation of a small quantity of methyl 4-fluorobicyclo[2.1.1]hexane-1-carboxylate (46, R = COOMe) is significant because it represents the first occasion on which the elusive 1-bicyclo[2.1.1]hexyl cation has been trapped. We have also demonstrated that synthesis of the iodides themselves can be accomplished efficiently both by Barton halodecarboxylation and by treatment of the carboxylic acid with lead tetraacetate and iodine.

Introduction

An important feature of our studies into the chemistry of strained bicycloalkanes and polycycloalkanes has been to develop convenient procedures for the synthesis of their bridgehead halide derivatives. Thus, we have shown that Barton halodecarboxylation methodology[1] involving radical decomposition of thiohydroxamic esters in the presence of the appropriate halogen donor represents a broadly-based high-yielding route to bridgehead chlorides and bromides[2] of the range of systems depicted in Chart I. Synthesis of the corresponding iodides has also been accomplished by *tert*-butyl hypoiodite-mediated iododecarboxylation.[3]

The analogous conversion of bridgehead acids into the corresponding fluorides has not been described, however.

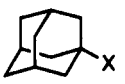
(1) Barton, D. H. R.; Lacher, B.; Zard, S. Z. *Tetrahedron* **1987**, *43*, 4321. Barton, D. H. R.; Crich, D.; Motherwell, W. B. *Tetrahedron Lett.* **1983**, *24*, 4979.

(2) Della, E. W.; Tsanaktsidis, J. *Aust. J. Chem.* **1989**, *42*, 61.

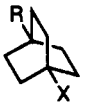
(3) Abeywickrema, R. S.; Della, E. W. *J. Org. Chem.* **1980**, *45*, 4226.

0022-3263/92/1957-2850$03.00/0

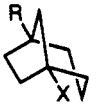
Chart I



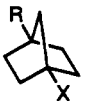
1 , X = F
24 , X = I
25 , X = IF_2



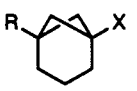
2 , X = F , R = H
10 , X = CO_2H , R = CO_2Me
17 , X = F , R = CO_2Me
20 , X = H , R = CO_2Me
27 , X = H , R = CO_2H
32 , X = I , R = H
41 , X = I , R = CO_2Me



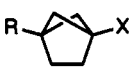
28 , X = CO_2H , R = CO_2Me
33 , X = I , R = CO_2Me
42 , X = F , R = CO_2Me



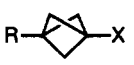
3 , X = F , R = H
11 , X = CO_2H , R = CO_2Me
18 , X = F , R = CO_2Me
21 , X = H , R = CO_2Me
29 , X = H , R=CO_2H
34 , X = I , R = H
35 , X = I , R = CO_2Me
43 , X = Cl , R = CO_2Me
55 , X = Cl , R = H



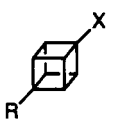
4 , X = F , R = H
30 , X = CO_2H , R = CO_2Me
36 , X = I , R = CO_2Me
44 , X = F , R = CO_2Me



5 , X = F , R = H
12 , X = CO_2H , R = CO_2Me
15 , X = H , R = CO_2Me
37 , X = I , R = CO_2Me
46 , X = F , R = CO_2Me



6 , X = F , R = H
8 , X = Ph , R = CO_2H
13 , X = CO_2H , R = CO_2Me
16 , X = H , R = CO_2Me
38 , X = I , R = CO_2Me



7 , X = F , R = H
14 , X = CO_2H , R = CO_2Me
19 , X = F , R = CO_2Me
22 , X = H , R = CO_2Me
23 , X = Cl , R = CO_2Me
26 , X = H , R = IF_2
31 , X = H , R = CO_2H
39 , X = I , R = H
40 , X = I , R = CO_2Me
47 , X = Cl , R = H

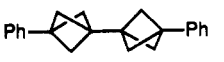
Table I. Products of Reaction of the Carboxylic Acids 10–14 with Xenon Difluoride[a]

reactant	product[b] (%)
10	17 (77[c]), 20 (12[c])
11	18 (65), 21 (4), 43 (7)
12	15 (69)
13	16 (84)
14	19 (51), 22 (15), 23 (4)

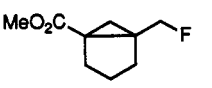
[a] 1.5 equiv of XeF_2 in CH_2Cl_2 overnight. [b] Yields in parentheses. [c] Corrected for recovered starting material.

The major obstacle which has precluded extension of the above process to the transformation RCOOH → RF has been the lack of a suitable fluorine atom donor and the necessity to retain favorable thermodynamics. Accordingly, access to the fluorides 1–6 described in our earlier ^{19}F NMR study,[4] for example, was restricted to methods which were essentially unique to each substrate.

In the search for a procedure which would be generally applicable to the synthesis of bridgehead fluorides, we were attracted to a recent report[5] which described how fluorodecarboxylation could be effectively accomplished by treatment of carboxylic acids with xenon difluoride. This seemed very promising considering its successful application to the synthesis of 1 from adamantane-1-carboxylic acid. On a discouraging note, however, the authors reported[5] that 3-phenylbicyclo[1.1.1]pentane-1-carboxylic acid 8, the other bridgehead acid investigated, gave only the dimeric product 9.



9



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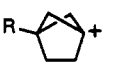

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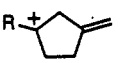

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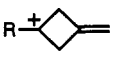
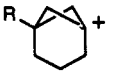
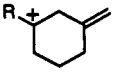


51



52



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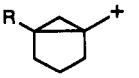


54

(4) Della, E. W.; Cotsaris, E.; Hine, P. T. *J. Am. Chem. Soc.* **1981**, *103*, 4131.
(5) Patrick, T. B.; Johri, K. K.; White, D. H.; Bertrand, W. S.; Mokhtar, R.; Kilbourn, M. R.; Welch, M. J. *Can. J. Chem.* **1986**, *64*, 138.

Table II. Iododecarboxylation of the Bridgehead Carboxylic Acids 11–14, 27–31

reactant	procedure[a]	product[b]
27	A	32 (69)
28	A	33 (71)
29	A	34 (73)
11	A	35 (74)
30	A	36 (78)
12	B	37 (79)
	C	(91)
13	B	38 (81)
	C	(91)
31	A	39 (74)
	C	(83)
14	A	40 (75)
	C	(96)

[a] A ≡ reaction of the acid chloride with sodium salt of *N*-hydroxypyridine-2-thione in boiling benzene containing CF_3CH_2I (5 equiv). B ≡ reaction using the preformed Barton ester. C ≡ $Pb(OAc)_4/I_2$. [b] Isolated yields in parentheses.

In view of the relevance[6] of organo fluorides as physiologically active compounds and as strategic materials, the design of a practical route to bridgehead fluorides was considered of some importance. We report here details of a synthetic method which is generally applicable to the synthesis of bridgehead fluorides from their readily accessible iodides and is superior to the fluorodecarboxylation process cited above. We present strong evidence for the intermediacy of carbocations in this reaction, and the only systems which fail to respond favorably to the conversion are the 1-bicyclo[*n*.1.1]alkyl iodides in which the derived cations are highly prone to rearrangement.

Results and Discussion

Despite the failure encountered with the acid **8**,[5] we decided to test the applicability of Patrick's fluorodecarboxylation procedure to a range of bridgehead acids available from our earlier work. The reaction conditions are mild and the reported yields satisfactory, and there was always the possibility that **8** represented an isolated recalcitrant substrate and that the method may be more generally applicable. In order to facilitate the analysis and isolation of otherwise volatile fluorides, we have examined the behavior of the half-esters **10–14** with xenon difluoride. Reactions were performed using 1.5 equiv of XeF_2 in dichloromethane solution at room temperature overnight, and as the data in Table I illustrate, the yield of fluoride varies considerably, depending upon the system. For example, both 3-carbomethoxybicyclo[2.1.1]hexane-1-carboxylic acid (**12**) and 3-carbomethoxybicyclo[1.1.1]-pentane-1-carboxylic acid (**13**) gave the corresponding reduced products **15** and **16** only,[7] and in neither case was the presence of the target fluoride even detected in the product. On the other hand, the remaining half esters, **10**, **11**, and **14**, were converted into the corresponding fluorides **17**, **18**, and **19** in reasonable yields although the products were contaminated with significant quantities of the parent ester **20**, **21**, and **22**, respectively; furthermore, in the case of the bicycloheptyl and cubyl systems some of the bridgehead chloride **43** or **23**, respectively, was also present. Formation of the reduced product, in particular, is unfortunate because its separation from the fluoride represents a very difficult assignment; this procedure, therefore, has a serious drawback if the latter is required in a reasonable state of purity.

Exclusive production of the protio analogue in the case of the bicyclo[*n*.1.1]alkyl acids **12** and **13** is surprising, although it is instructive to consider the likely reaction mechanism involved.

Patrick and his colleagues[5] considered several possible mechanisms for the fluorodecarboxylation process (Scheme I), the first step of which is formation of the xenon ester (eq 1).

Scheme I

$$RCOOH + XeF_2 \rightarrow RCOOXeF + HF \quad (1)$$

$$RCOOXeF + F^- \rightarrow RF + CO_2 + Xe + F^- \quad (2)$$

$$RCOOXeF \rightarrow R^\bullet + CO_2 + \dot{X}eF \quad (3)$$

$$R^\bullet + \dot{X}eF \rightarrow RF + Xe \quad (4)$$

$$R^\bullet + \dot{X}eF \rightarrow R^+ + Xe + F^- \quad (5)$$

$$R^+ + F^- \rightarrow RF \quad (6)$$

The latter is thermally labile and is believed to decompose to give the fluoride in one of several possible pathways: (a) an S_N2 process (eq 2), the preferred route for primary and secondary carboxylic acids; (b) a dissociation mechanism in which the ester homolyses to the radical and $\dot{X}eF$ (eq 3) which either interact directly to produce the fluoride (eq 4) or are involved in electron transfer yielding the carbocation (eq 5) which then combines with fluoride to give the observed product (eq 6). The process depicted in eqs 5 and 6 is suggested to apply to systems such as benzyl and tertiary alkyl which produce stable carbocations.

The S_N2 pathway can be discarded as far as the caged compounds under study here are concerned, and the mechanism involving cationic intermediates is unlikely for compounds **12** and **13**. For these substrates, production of the hydrocarbon is best accomodated on the basis of transfer of a hydrogen atom from methylene chloride to the bridgehead radical. The exclusive formation of reduced product can be ascribed to the highly reactive nature of the radicals. Formation of the bridgehead cation would have been expected in the case of the bicyclooctyl acid **10** to lead to the fluoride as well as some of the chloride as a byproduct by reaction with methylene chloride, and to rearranged products from the acids **12** and **13** because the bicyclo[*n*.1.1]alkyl carbocations are extraordinarily susceptible to rearrangement, requiring little activation.[8]

The mechanism of reaction of the bicycloheptyl and cubyl acids **11** and **14** with XeF_2 is more complicated and may involve both radical and cationic intermediates because of the production of some of the chloride byproduct.

Concomitant production of the hydrocarbon, either exclusively from **12** and **13** or in lesser but undesirable amounts from **10**, **11**, and **14**, led us to direct our attention to the search for an alternative procedure for generating bridgehead fluorides. We were inclined to retain XeF_2 as reagent, if at all possible, firstly in the belief that any disadvantage it possessed on the basis of cost would likely be offset by its ease of handling, its reactivity, and its

(6) See: (a) Davis, F. A.; Han, W. *Tetrahedron Lett.* **1991**, *32*, 1631. (b) Uneyama, K.; Kanai, M. *Tetrahedron Lett.* **1991**, *31*, 3583 for leading references.

(7) This is consistent with the recent observation (Kaszynski, P.; McMurdie, N. D.; Michl, J. *J. Org. Chem.* **1991**, *56*, 307) that treatment of the acid **8** with XeF_2 actually gives 1-phenylbicyclo[1.1.1]pentane and not **9**.

(8) The 1-bicyclo[1.1.1]pentyl cation: (a) Wiberg, K. B.; Williams, V. Z. *J. Am. Chem. Soc.* **1967**, *89*, 3373. (b) Della, E. W.; Taylor, D. K. *Aust. J. Chem.* **1990**, *43*, 945. (c) Della, E. W.; Schiesser, C. H. *J. Chem. Res., Synop.* **1989**, 172. The bicyclo[2.1.1]hexyl cation: (a) Wiberg, K. B.; Lowry, B. R. *J. Am. Chem. Soc.* **1963**, *85*, 3188. (b) Della, E. W.; Schiesser, C. H. *Tetrahedron Lett.* **1987**, *28*, 3869.

Table III. Reaction of the Bridgehead Iodides 24, 32–41 with Xenon Difluoride

reactant	temp (°C)	products (%)
24	20	**1** (85)
32	20	**2** (88)
41	20	**17** (75)
33	20	**42** (87)
34	45	**3** (76), **55** (22[a])
35	45	**18** (60), **43** (12[a])
36	20	**44**[b] and **45**[b] (50)
37	20	**46** (5)
38	20	*c*
39	20	**7** (80), **47** (5[a])
40	45	**19** (58)

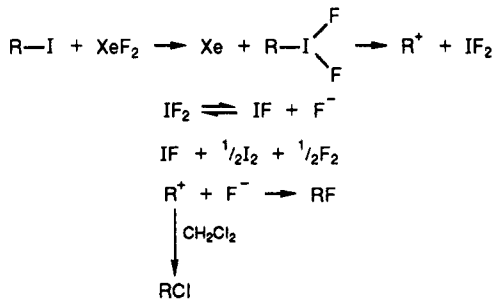
[a] GC yield, not isolated. [b] Tentative assignments. [c] No volatile product detected.

modest requirements in terms of the simplest of glass apparatus. Secondly, one of the interesting properties of XeF_2, observed some time ago, is its reaction with aryl iodides to yield kinetically stable compounds of the type $ArIF_2$[9] in which the derived functional group, $-IF_2$, is described as a supernucleofuge. In an extension to alicyclic chemistry an analogous intermediate **25** has been postulated by Rozen and Brand[10] in the reaction of 1-iodoadamantane (**24**) with fluorine en route to 1-fluoroadamantane (**1**). Furthermore, Tsanaktsidis and Eaton[11] recently referred to the formation of the corresponding hypervalent cubyl derivative **26** from treatment of iodocubane with xenon difluoride. The species **26** was thought to be the precursor to fluorocubane. Encouraged by these observations we decided to investigate the process of fluorodeiodination as a potential source of bridgehead fluorides. The first objective, therefore, was to convert the readily available bridgehead carboxylic acids **11–14**, **27–31** into the corresponding iodides.

Although we have observed previously[3] that this transformation can be effected by *tert*-butyl hypoiodite, the recent synthesis of both iodocubane[12] and 1-iodobicyclo[1.1.1]pentane[13] in high yield by Barton halodecarboxylation methodology[1] employing CF_3CH_2I as the iodine atom donor seemed more attractive. In practice, we find that the Barton procedure can be extended generally to the synthesis of bridgehead iodides from the corresponding acids (Table II). The products were purified by sublimation and were obtained in very good yield. At the same time we have observed that bridgehead RCOOH → RI interconversion is also expeditiously accomplished by treatment of the acid with $Pb(OAc)_4/I_2$ in boiling benzene under illumination. This method was described some years ago,[14] and we recommend it as an alternative to the Barton reaction above; indeed, in many ways it possesses considerable advantages because of its simplicity, ease of operation, and the fact that it is a one-step procedure.

Exposure of the iodides **24**, **32–35**, and **39–41** to XeF_2 (1.5 equiv[15]) in dichloromethane either at ambient temperature or in several cases at reflux furnished the corresponding fluorides **1–3**, **7**, **17–19**, **42** smoothly and in impressive yield, generally without contamination (Table III). Only the bicyclo[2.2.1]heptyl fluorides **3** and **18** and fluorocubane **7** were found to be accompanied by small amounts of the chloride. However, in these cases the more volatile fluoride could be easily purified by sublimation.

Scheme II



As the data in Table III illustrate, this procedure is a convenient, high-yielding route to bridgehead fluorides. The notable exceptions are the bicyclo[*n*.1.1]alkyl iodides **36**, **37**, and **38**. In the case of **37** a small quantity (ca. 5%) of the fluoride **46** was isolated but the predominant product consisted of intractable, unidentified material. A similar nonvolatile tarry substance was produced exclusively from the bicyclo[1.1.1]pentyl iodide **38**. The higher homologue **36** gave a mixture of volatile fluoro esters (combined yield 50%) which on the basis of ^1H and ^{13}C NMR and GC/MS analysis are tentatively identified as the fluorides **44** and **45**.

These observations are consistent with a mechanism involving cationic intermediates (Scheme II). We and others[8] have noted previously the kinetic instability of bridgehead cations such as **48** (R = H) and **49** which rearrange to the respective isomers **50** (R = H) and **51** (R = H) so rapidly as to defy interception by nucleophile. Isolation of **46** is highly significant inasmuch as it represents the first reported occasion on which a 1-bicyclo[2.1.1]hexyl cation **48** has been trapped. No doubt the presence of the ester function at the bridgehead tends to inhibit the otherwise facile rearrangement **48** (R = COOMe) → **50** (R = COOMe). On the other hand, the cation **52** (R = H) has a higher activation for rearrangement[16] and, when generated in protic media, some of it survives long enough to be trapped, while the remainder is transformed into the isomeric species **53** (R = H) and **54** (R = H). The bicyclic cations **52** (R = COOMe) and **54** (R = COOMe) react with fluoride ion to give the observed products **44** and **45**, respectively. Fluorides produced by the corresponding reaction of the alkenyl cations **50** (R = COOMe), **51** (R = COOMe), and **53** (R = COOMe) were not detected, which is not surprising in view of the rapid reaction of alkenes with XeF_2, especially in the presence of catalytic amounts of HF[17].

In a similar way, the mechanism depicted in Scheme II is consistent with the type of products obtained with the remaining substrates (Table III). We suggest that the stable, less reactive bridgehead cations are converted by F^- into the desired products, whereas intermediates such as the highly energetic cubyl and norbornyl cations are less

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(15) An excess of XeF_2 is required in order to effect complete consumption of the iodide, particularly in the case of the more highly strained systems. We ascribe this, in part, to the fact that the reagent decomposes slowly in dichloromethane, and also because of the loss of fluorinating agent in the open vessel. We find it convenient to use 1.5 equiv for this reason.
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discriminate in their reactivity and participate in a competing reaction with solvent CH_2Cl_2 to give small amounts of the chloride.

Experimental Section

General experimental details were described previously.[18] The carboxylic acids **10–14**, **27–31**,[19] the esters **15**, **16**, **20**, and **21**,[19] 1-iodoadamantane (**24**), and methyl 4-iodobicyclo[2.2.2]octane-1-carboxylate (**41**)[20] were available from previous work.

General Procedure for Treatment of the Bridgehead Acids 10–14 with XeF_2. To a solution of the carboxylic acid in dichloromethane (ca 0.1 M) under a nitrogen atmosphere was added grannular XeF_2 (1.5 equiv). The mixture was stirred overnight and then washed with 5% sodium bicarbonate solution, after which the organic layer was dried ($MgSO_4$) and the solvent evaporated.

4-Carbomethoxybicyclo[2.2.2]octane-1-carboxylic Acid (10) with XeF_2. Sublimation (100–150 °C (2 mm)) of the product obtained from treatment of the acid **10** (103 mg) with XeF_2 (123 mg) gave, besides some starting material (24 mg), a product (62 mg) which by GC/MS analysis proved to be an 86:14 mixture of methyl 4-fluorobicyclo[2.2.2]octane-1-carboxylate (**17**) and methyl bicyclo[2.2.2]octane-1-carboxylate (**20**).

4-Carbomethoxybicyclo[2.2.1]heptane-1-carboxylic Acid (11) with XeF_2. The half ester **11** (96 mg) was exposed to XeF_2 (123 mg) as described; sublimation (100–150 °C (2 mm)) gave a product (64 mg) which was shown by GC/MS analysis to be a 17:1:2 mixture of methyl 4-fluorobicyclo[2.2.1]heptane-1-carboxylate (**18**), methyl bicyclo[2.2.1]heptane-1-carboxylate (**21**), and methyl 4-chlorobicyclo[2.2.1]heptane-1-carboxylate (**43**).

4-Carbomethoxybicyclo[2.1.1]hexane-1-carboxylic Acid (12) with XeF_2. The crude product obtained from the reaction of **12** (84 mg) with XeF_2 (123 mg) was distilled (Kugelrohr, 120–130 °C (20 mm)) to give methyl bicyclo[2.1.1]hexane-1-carboxylate (**15**) (44 mg, 69%) the spectral properties of which were identical with those of the authentic material.

3-Carbomethoxybicyclo[1.1.1]pentane-1-carboxylic Acid (13) with XeF_2. Reaction between the half ester **13** (82 mg) and XeF_2 (123 mg) and distillation of the product furnished methyl bicyclo[1.1.1]pentane-1-carboxylate (**16**) (51 mg, 84%) which was identified by comparison with an authentic sample.

4-Carbomethoxycubanecarboxylic Acid (14) with XeF_2. The acid **14** (100 mg) was treated with XeF_2 (123 mg) in the manner outlined. Sublimation (100–150 °C (2 mm)) afforded a 12:3:1 mixture (61 mg) of methyl 4-fluorocubanecarboxylate (**19**), methyl cubanecarboxylate (**22**), and methyl 4-chlorocubanecarboxylate (**23**) which were identified by GC/MS.

General Procedures for the Conversion of the Bridgehead Acids 11–14, 27–31 into the Iodides 32–40. Method A. A mixture of the carboxylic acid (36.4 mmol) and thionyl chloride (80 mL) was heated under reflux for 2 h and the excess thionyl chloride removed. The crude acid chloride was dissolved in benzene or CH_2Cl_2 (75 mL) and then added, under a nitrogen atmosphere and with irradiation (300-W tungsten lamp), to a stirred suspension of sodium *N*-hydroxypyridine-2-thione (40 mmol, 1.1 equiv) in benzene or CH_2Cl_2 (100 mL) containing 4-(dimethylamino)pyridine (several mg) and CF_3CH_2I (18.2 mmol, 5 equiv). After 1 h the mixture was cooled, washed with water (2 × 100 mL), and concentrated HCl (2 × 100 mL), and then dried ($MgSO_4/K_2CO_3$) and evaporated.

Method B. A solution of the carboxylic acid (2.7 mmol) and *N*-hydroxypyridine-2-thione (1.05 equiv) in CH_2Cl_2 (10 mL) at 0 °C under a nitrogen atmosphere and protected from light by aluminium foil was treated with dicyclohexylcarbodiimide (1.01 equiv). The mixture was stirred at 0 °C for 15 min and then at room temperature for 2 h. The mixture was filtered and the precipitate (dicyclohexylurea) washed with CH_2Cl_2 (3 × 3 mL). The combined filtrate and washings were evaporated at 25 °C and the residue added to benzene (15 mL) and CF_3CH_2I (3 equiv). The mixture was heated to reflux under nitrogen and irradiated with a tungsten lamp (300 W) for 30 min. The workup procedure was identical with that described under Method A.

Method C. Lead tetraacetate (1.24 equiv) and iodine (5 equiv) were added to a solution of the carboxylic acid (1 mmol) in dry, deoxygenated benzene (45 mL). The mixture was stirred at room temperature for 15 min and then heated to reflux while under irradiation (300-W tungsten lamp). After 2.5 h the solution was cooled, filtered, and washed with sodium metabisulfite solution (3×) followed by aqueous sodium bicarbonate (1×). The organic layer was dried ($MgSO_4$) and the solvent evaporated in vacuo.

1-Iodobicyclo[2.2.2]octane (32). Sublimation (100 °C (5 mm)) of the product obtained from treatment of the acid **27** (0.50 g, 3.2 mmol) as described (Method A, CH_2Cl_2) gave 1-iodobicyclo-[2.2.2]octane (**32**) (0.53 g, 69%), mp 27 °C (lit.[21] mp 27.5–28.5 °C).

Methyl 5-Iodobicyclo[3.2.1]octane-1-carboxylate (33). Distillation (Kugelrohr, 60 °C (0.005 mm)) of the product obtained from the above treatment (Method A, benzene) of the half ester **28** (0.30 g, 1.4 mmol) gave the title iodide **33** (0.29 g, 71%): ^1H NMR ($CDCl_3$) δ 3.68 (s, 3 H), 1.40–2.90 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 175.42, 55.04, 51.90, 50.17, 46.59, 33.48, 32.67, 22.16, 0.98; mass spectrum *m/z* (relative intensity) 235 (5.5), 167 (64), 107 (100); HRMS calcd for $C_{10}H_{15}O_2$ (M − I) 167.1072, found 167.1069. Anal. Calcd for $C_{10}H_{15}IO_2$: C, 40.8; H, 5.1. Found: C, 40.6; H, 4.9.

1-Iodobicyclo[2.2.1]heptane (34). Bicyclo[2.2.1]heptane-1-carboxylic acid (**29**) (0.31 g, 2.2 mmol) was exposed to the conditions described in method A (CH_2Cl_2). The product was distilled (Kugelrohr, 70 °C (10 mm)) and gave 1-iodobicyclo[2.2.1]heptane (**34**) (0.35 g, 73%) which had spectral properties identical with those of a specimen prepared previously.[3,22]

Methyl 4-Iodobicyclo[2.2.1]heptane-1-carboxylate (35). The half ester **11** (0.63 g, 3.2 mmol) when treated as outlined in method A (benzene) yielded a product which was distilled (Kugelrohr, 75–80 °C (0.1 mm)) affording the iodide **35** (0.66 g, 74%): ^1H NMR ($CDCl_3$) δ 3.70 (s, 3 H), 1.60–2.30 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 173.79, 53.42, 51.79, 49.79, 43.18, 35.27, 34.83. Anal. Calcd for $C_9H_{13}IO_2$: C, 38.6; H, 4.7. Found: C, 38.9; H, 4.4.

Methyl 5-Iodobicyclo[3.1.1]heptane-1-carboxylate (36). Distillation (Kuhelrohr, 50–55 °C (0.01 mm)) of the product obtained from exposure of 5-carbomethoxybicyclo[3.1.1]heptane-1-carboxylic acid (**30**) (0.48 g, 2.4 mmol) to the above conditions (method A, benzene) gave the iodide **36** (0.53 g, 78%): mp 35–37 °C; ^1H NMR ($CDCl_3$) δ 3.70 (s, 3 H), 1.75–3.20 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 173.03, 51.99, 49.16, 49.09, 42.65, 30.82, 27.83, 18.90. Anal. Calcd for $C_9H_{13}IO_2$: C, 38.6; H, 4.7. Found: C, 38.5; H, 4.6.

Methyl 4-Iodobicyclo[2.1.1]hexane-1-carboxylate (37). Method B. The half ester **12** (0.50 g, 2.7 mmol) was treated as described above. Distillation (Kugelrohr, 100 °C (2 mm)) of the crude product yielded the title iodide **37** (0.57 g, 79%): ^1H NMR (CCl_4) δ 3.58 (s, 3 H), 1.70–2.40 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 170.54, 52.01, 51.84, 51.74, 39.93, 30.72, 23.57. Anal. Calcd for $C_8H_{11}IO_2$: C, 36.1; H, 4.2. Found: C, 36.0; H, 4.2.

Method C. Treatment of **12** (0.19 g) with $Pb(OAc)_4/I_2$ as outlined and distillation of the product yielded methyl 4-iodobicyclo[2.1.1]hexane-1-carboxylate (**37**) (0.25 g, 91%).

Methyl 3-Iodobicyclo[1.1.1]pentane-1-carboxylate (38). Method B. Distillation (Kugelrohr, 100 °C (3 mm)) of the product obtained from treatment of the acid **13** (1.14 g, 6.7 mmol) as discussed furnished the title iodide **38** (1.36 g, 81%): ^1H NMR ($CDCl_3$) δ 3.65 (s, 3 H), 2.55 (s, 6 H); ^{13}C NMR ($CDCl_3$ δ 166.80, 60.51, 52.01, 45.89. Anal. Calcd for $C_7H_9IO_2$: C, 33.4; H, 3.6. Found: C, 33.2; H, 3.4.

Method C. Following the conditions referred to above, the half ester **13** (205 mg) was converted into the corresponding iodo ester **38** (278 mg, 91%).

Iodocubane (39). Method A (CH_2Cl_2). Treatment of cubanecarboxylic acid (**31**) (0.43 g, 2.9 mmol) as described and distillation (Kugelrohr, 85 °C (6 mm)) of the product yielded iodocubane (**39**) (0.49 g, 74%), mp 32–33 °C (lit.[3] mp 31 °C), having spectral data in accord with those reported previously.[3]

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Method C. Cubanecarboxylic acid (**31**) (1.0 g, 6.76 mmol) was exposed to $Pb(OAc)_4/I_2$ as discussed. Concentration of the solution using a column packed with glass helices and distillation of the product gave the iodide **39** (1.28 g, 83%).

Methyl 4-Iodocubanecarboxylate (40). Method A (Benzene). Treatment of 4-carbomethoxycubanecarboxylic acid (**14**) (7.5 g, 36.4 mmol) in the manner described above and sublimation (70 °C (0.05 mm)) of the product furnished the title iodide **40** (7.85 g, 75%), mp 123–125 °C (lit.[23] mp 112–114 °C).

Method C. Exposure of the half ester **14** (6.3 g) to the specified conditions and purification of the product by sublimation gave the iodo ester **40** (8.4 g, 96%)

General Procedure for Reaction of the Bridgehead Iodides 24, 32–41 with XeF_2. Xenon difluoride (1.5 equiv) was added in one portion to a 0.15 M solution of the bridgehead iodide in dichloromethane under a nitrogen atmosphere and the solution stirred until the starting iodide was no longer present (GC). The mixture was washed with aqueous sodium metabisulfite (4 × 40 mL) and then dried ($MgSO_4$) before the solvent was evaporated. The residue was purified as outlined.

1-Fluoroadamantane (1). Treatment of 1-iodoadamantane (**24**) (20 mg, 0.08 mmol) as described followed by sublimation gave the fluoride **1** (10.0 mg, 85%) mp 228 °C (lit.[24] mp 225 °C) whose ^{13}C NMR spectrum was in accord with that reported;[24] ^1H NMR ($CDCl_3$) δ 1.15–2.55 (m).

1-Fluorobicyclo[2.2.2]octane (2). In a similar way the iodide **32** (340 mg, 1.4 mmol) gave, upon sublimation (60 °C (1 mm)), 1-fluorobicyclo[2.2.2]octane (**2**) (162 mg, 88%), mp 150 °C (lit.[25] mp 152 °C), whose ^{13}C spectrum was consistent with that reported;[25] ^1H NMR ($CDCl_3$) δ 1.50–1.80 (m).

Methyl 4-Fluorobicyclo[2.2.2]octane-1-carboxylate (17). Methyl 4-iodobicyclo[2.2.2]octane-1-carboxylate (**41**) (115 mg, 0.39 mmol) was exposed to XeF_2 in dichloromethane. Sublimation (110 °C (2.5 mm)) of the product into a cold trap (−100 °C) yielded the fluoride **17** (55 mg, 75%), mp 66 °C (lit.[25] 66.5 °C), which had spectral properties as reported.[25]

Methyl 5-Fluorobicyclo[3.2.1]octane-1-carboxylate (42). Reaction of the iodo ester **33** (197 mg, 0.67 mmol) with XeF_2 and distillation (Kugelrohr, 120 °C (2 mm)) of the product afforded the title fluoride **42** (108 mg, 87%): ^1H NMR ($CDCl_3$) δ 3.68 (s, 3 H), 1.45–2.65 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 176.18, 100.47 (^1J(CF) = 191.7 Hz), 49.46 (^3J(CF) = 7.56 Hz), 45.45 (^2J(CF) = 19.07 Hz), 36.24 (^2J(CF) = 21.71 Hz), 33.43, 32.94 (^2J(CF) = 22.91 Hz), 29.85 (^3J(CF) = 7.82 Hz), 19.67 (^3J(CF) = 11.08 Hz); mass spectrum m/z (relative intensity) 186 (14), 158 (54), 127 (100); HRMS calcd for $C_{10}H_{15}FO_2$ 186.1056, found 186.1062. Anal. Calcd for $C_{10}H_{15}FO_2$: C, 64.5; H, 8.1. Found: C, 64.3; H, 8.5.

1-Fluorobicyclo[2.2.1]heptane (3). 1-Iodobicyclo[2.2.1]-heptane (**34**) (433 mg, 1.95 mmol) was treated with XeF_2 as outlined except that the mixture was heated under reflux for 2.5 h. Workup yielded a product which was shown (GC/MS, ^{13}C NMR) to consist of a 3:1 mixture of 1-fluorobicyclo[2.2.1]heptane (**3**) and 1-chlorobicyclo[2.2.1]heptane (**55**). Careful sublimation gave the pure fluoride **3** (170 mg, 76%), mp 92–94.5 °C (lit.[25] mp 95–98 °C) which had spectral properties consistent with those reported.[26]

Methyl 4-Fluorobicyclo[2.2.1]heptane-1-carboxylate (18). The iodide **35** (350 mg, 1.25 mmol) was treated with XeF_2 as described for reaction of **34** and afforded a product which analyzed as a 4:1 mixture of the fluoride **18** and chloride **43**. Distillation (Kugelrohr, 70–85 °C (1.0 mm)) furnished pure fluoride **18** (125 mg, 60%) which was identified by comparison of its spectral properties with those reported.[26]

Methyl 4-Fluorobicyclo[2.1.1]hexane-1-carboxylate (46). Methyl 4-iodobicyclo[2.1.1]hexane-1-carboxylate (**37**) (450 mg, 1.69 mmol) was treated with XeF_2 as discussed except that a further quantity (ca. 1 equiv) of reagent was required to effect consumption of all the iodide **37**. Workup yielded a viscous dark-brown product which when heated under vacuum (120 °C (20 mm)) gave a small quantity (ca. 8 mg) of the fluoride **46**: ^1H NMR ($CDCl_3$) δ 3.70 (s, 3 H), 1.75–2.50 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 179.44, 91.95 (^1J(CF) = 259.5 Hz), 51.84, 46.48 (^2J(CF) = 19.53 Hz), 29.42 (^3J(CF) = 4.89 Hz), 28.50 (^2J(CF) = 19.51 Hz); HRMS calcd for $C_8H_{11}FO_2$ 158.0743, found 158.0741.

Fluorocubane (7). Exposure of iodocubane (**39**) (340 mg, 1.48 mmol) to XeF_2 as above gave a product consisting of a 94:6 mixture of fluorocubane (**7**) and chlorocubane (**47**). Sublimation (110 °C (2.5 mm)) into a cold trap (−100 °C) yielded the fluoride **7** (144 mg, 80%): mp 116–118 °C; ^1H NMR ($CDCl_3$) δ 3.63–4.43 (m); ^{13}C NMR ($CDCl_3$) δ 103.54 (^1J(CF) = 329.4 Hz), 56.25 (^2J(CF) = 24.35 Hz), 48.62 (^4J(CF) = 13.54 Hz), 39.90 (^3J(CF) = 4.87 Hz); mass spectrum m/z (relative intensity) 122 (4.8), 121 (45), 96 (100); HRMS calcd for C_8H_7F 122.0532, found 122.0523.

Methyl 4-Fluorocubanecarboxylate (19). Methyl 4-iodocubanecarboxylate (**40**) (1.3 g, 4.5 mmol) was heated under reflux with XeF_2 in methylene chloride for 6.5 h. Workup and sublimation (110–120 °C (2 mm)) of the product furnished the title fluoride **19** (470 mg, 58%): mp 97–99 °C; ^1H NMR ($CDCl_3$) δ 3.85–4.55 (m, 6 H), 3.71 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 172.15, 102.65 (^1J(CF) = 327.9 Hz), 56.50 (^4J(CF) = 13.55 Hz), 53.89 (^2J(CF) = 25.45 Hz), 51.37, 42.11 (^3J(CF) = 5.46 Hz); mass spectrum m/z (relative intensity) 180 (7), 149 (13), 121 (100); HRMS calcd for $C_{10}H_9FO_2$ 180.0587, found 180.0585. Anal. Calcd for $C_{10}H_9FO_2$: C, 66.7; H, 5.0. Found: C, 67.0; H, 5.4.

Reaction of Methyl 5-Iodobicyclo[3.1.1]heptane-1-carboxylate (36) with XeF_2. The iodide **36** (300 mg, 1.07 mmol) was treated with XeF_2 in the usual manner. Workup gave an oil which was distilled (Kugelrohr 65–70 °C (2 mm)) giving a 5:2 mixture (90 mg) of what are tentatively assigned (^{13}C NMR, GC/MS) methyl 5-fluoromethylbicyclo[3.1.0]hexane-1-carboxylate (**45**) [mass spectrum m/z (intensity) 172 (16), 152 (27), 144 (18), 141 (31), 140 (16), 113 (55), 112 (46), 100 (30), 99 (21), 97 (22), 93 (100)] and methyl 5-fluorobicyclo[3.1.1]heptane-1-carboxylate (**44**) [mass spectrum m/z (intensity) 172 (18), 152 (20), 141 (28), 140 (24), 125 (12), 113 (42), 112 (49), 100 (36), 99 (34), 97 (32), 93 (100)]. The residue which remained in the distillation flash was a viscous intractable substance.

Reaction of Methyl 3-Iodobicyclo[1.1.1]pentane-1-carboxylate (38) with XeF_2. Treatment of the iodide **38** with XeF_2 as outlined above afforded a dark intractable viscous product which could not be induced to distill or sublime under high vacuum and could not be identified.

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