dition of 0.7 ml of a 1.5 M THF solution of 10-undecenylmagnesium chloride (1 mmol) to 1 mmol of this copper acetylide at -78° gave a red-orange solution of a copper ate complex. Warming this solution to room temperature resulted in no color changes other than some slight darkening. In alkylation reactions, the alkyl halide was added by syringe at -78 to this copper ate complex. After stirring at  $-78^{\circ}$  for 0.5 hr, these solutions were allowed to gradually warm to room temperature. The reactions were hydrolyzed with 0.1 ml of hydrochloric acid after 2-3 hr of stirring at room temperature and analyzed by GLC on an 8-ft, SE-30 column.

Registry No.-11-Chloroundecene, 872-17-3; 10-undecenol, 112-43-6; carbon tetrachloride, 56-23-5; ethyl 11-iodoundecanoate, 53821-20-8; 11-bromoundecanoic acid, 2834-05-1; methyl 11-iodoundecanoate, 929-33-9; methyl 6-iodohexanoate, 14273-91-7; 6bromohexanoic acid, 4224-70-8; 6-benzoxy-1-chlorohexane, 53821-21-9; 1-chloro-6-hydroxyhexane, 2009-83-8; benzyl chloride, 100-44-7; ethyl 21-docosenoate, 53821-22-0; 21-docosenoic acid, 53821-23-1; ethyl 17-benzoxyheptadecanoate, 53821-24-2; ethyl heptacosanoate, 53821-25-3; methylcopper(I), 1184-53-8; diethyl tetratriacontanedioate, 53821-26-4; dimethyl tetracosanedioate, 26134-71-4; methyl 12-methylheptadecanoate, 2490-24-6; 2,2-dimethylbutynylcopper(I), 53821-27-5.

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# The Mechanism of the Reaction of Alkyl Bromides and Iodides with Mercury(II) and Silver(I) Fluorides<sup>1</sup>

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The conversion of representative alkyl bromides and iodides to alkyl fluorides by mercury(II) and silver(I) fluoride has been shown to involve generation of intermediate alkyl carbonium ions by comparison of the product distributions obtained on conversion with those observed on solvolysis of related alkyl derivatives. Treatment of exo-2-bromo-endo-2-chloronorbornane (1) and endo-2-bromo-exo-2-chloronorbornane (2) with either mercury(II) or silver(I) fluoride yields endo-2-chloro-exo-2-fluoronorbornane (8) as the only fluorine-containing epimer. The extensive elimination observed in the reaction of cis- and trans-4-tert-butylcyclohexyl bromide (3 and 4) with both mercury(II) and silver(I) fluoride, as well as the substantial fraction of cis- and trans-3-tert-butylcyclohexyl fluorides produced, parallels the related product ratios observed from the solvolysis of cis- and trans-4-tert-butylcyclohexyl arenesulfonates. Treatment of 1-iodo-2-phenylethane- $2,2-d_2$  (5) with mercury(II) or silver(I) fluoride produces a 1:1 mixture of 1-fluoro-2-phenylethane- $2,2-d_2$  and 1-fluoro-2-phenylethane- $1,1-d_2$ . Similar treatment of 1-iodo- or 1-bromooctane produces a mixture of 1- and 2-fluorooctane while conversion of 2-iodo- or 2-bromooctane yields 2-fluorooctane, exclusively. The C-F bond-forming step in these reactions is suggested as proceeding by the intermolecular transfer of fluoride from a halometallo-ate complex to a carbonium ion center.

The biological activity<sup>2</sup> of organic compounds containing isolated fluorine atoms and the utility of the <sup>19</sup>F nucleus as a probe of molecular structure<sup>3</sup> are in large part responsible for the continuing interest in monofluoro-substituted organic compounds. The introduction of a single fluorine atom into an organic molecule is, therefore, a reaction of some importance and a variety of reagents are useful for this purpose.<sup>4,5</sup> For complex molecules, however, the direct replacement of an isolated halogen atom, particularly bromine or iodine, by reaction with mercury(II) or silver(I) fluoride has frequently proven the procedure of choice for such syntheses, since these reactions proceed under mild conditions.<sup>5</sup>

The major fraction of evidence pertinent to the mechanism of the reaction of halocarbons with mercury(II) or silver(I) fluoride is stereochemical in nature. Conversion of  $16\beta$ -bromo- $17\alpha$ , 20:20, 21-bis(methylenedioxy)- $\Delta^4$ -pregnen-3-one into  $16\beta$ -fluoro- $17\alpha$ , 20:20, 21-bis(methylenedioxy)- $\Delta^4$ -pregnen-3-one and of  $\alpha$ -1-bromo-2,3,4,6-tetraacetyl-Dgalactose into  $\beta$ -1-fluoro-2,3,4,6-tetraacetyl-D-galactose by silver(I) fluoride are reported to proceed, respectively, with predominant retention<sup>6</sup> and inversion<sup>7</sup> of configuration. A concerted reaction<sup>8</sup> might be expected to lead to products with retained or inverted stereochemistry while a nonconcerted process might be expected to yield, in general, products with loss of stereochemistry. Without complementary

Reaction of Alkyl Bromides and Iodides with HgF2 and AgF

	Table I
F	Reaction of exo-2-Bromo-endo-2-chloronorbornane (1)
	and endo-2-Bromo-exo-2-chloronorbornane (2) with
	Silver(I) and Mercury(II) Fluoride at 0° in Pentane

		Product rel y	ield, <sup>a,b</sup> %
MF <sub>x</sub>	Substrate	84	9e
Ag F <sup>f</sup>	1ª	>97	с
$\operatorname{HgF}_{2}^{h}$	1	>97	с
AgF	<b>2</b> <sup><i>i</i></sup>	>97	c
$\operatorname{Hg} F_2$	2	>97	С

<sup>a</sup> As determined by <sup>19</sup>F nmr;<sup>10</sup> estimated accuracy ± 3%. <sup>b</sup> Absolute yields ranged between 10 and 20%. <sup>c</sup> None observed. Under the conditions of analysis a relative yield of <3% would not have been detected. <sup>d</sup> Registry no., 49633-61-6. <sup>e</sup> Registry no., 49633-64-9. <sup>f</sup> Registry no., 7775-41-9. <sup>g</sup> Registry no., 21690-94-8. <sup>h</sup> Registry no., 7783-39-3. <sup>l</sup> Registry no., 21690-95-9.

examination of the stereochemical course of the reaction of the second diastereomer, no convincing stereochemical or mechanistic generalizations can be drawn from these studies.

Our interest in this class of reactions has prompted us to resolve the stereochemical and mechanistic ambiguities posed by previous studies by examination of the reactions of mercury(II) and silver(I) fluoride with exo-2-bromoendo-2-chloronorbornane (1) and endo-2-bromo-exo-2chloronorbornane (2), cis- and trans-4-tert-butylcyclohexyl bromide (3 and 4), 1-iodo-2-phenylethane-2,2-d<sub>2</sub> (5), and 1- and 2-iodo- and -bromooctane (6 and 7). Here we wish to report that the product distributions observed on conversion of these halides are consistent with a nonconcerted mechanism involving intermediate carbonium ions.



# Results

Reaction of exo-2-Bromo-endo-2-chloronorbornane (1), endo-2-Bromo-exo-2-chloronorbornane (2), and cis- and trans-4-tert-Butylcyclohexyl Bromide (3 and 4). As a first step in establishing the mechanism of the reaction of mercury(II) and silver(I) fluoride with alkyl halides, we have examined the reaction of exo-2-bromo-endo-2-chloronorbornane (1) and endo-2-bromo-exo-2-chloronorbornane (2) with these reagents (Table I). Studies of the solvolysis of norbornyl derivatives have established the nearly exclusive preference of the norbornyl cation for exo product formation.<sup>9</sup> Thus, the production of endo-2chloro-exo-2-fluoronorbornane (8) as the only fluorine-containing epimer from reaction of both 1 and 2 would suggest the possibility that these reactions involve intermediate carbonium ions.

Treatment of 1 or 2 with mercury(II) or silver(I) fluoride in pentane at 0° yielded, within the limits of detection, *exo*-2-fluoro-*endo*-2-chloronorbornane, exclusively. To make certain that these results do not simply reflect loss of stereochemistry in the starting halide, these reactions were carried to  $\sim$ 50% completion. Comparison of the ir spectra



of the recovered starting material established that in these reactions no loss of stereochemistry in the starting material accompanies reaction. The stereochemical integrity of the potential product exo-2-chloro-endo-2-fluoronorborane<sup>10</sup> (9) under reaction conditions was similarly established.

The conversion of both 1 and 2 to 8 implicates a carbonium ion intermediate in these reactions. However, in view of the recognized nature of 2-substituted norbornyl derivatives to participate in carbonium ion processes when such processes are not always observed in more general systems, a parallel stereochemical study was carried out.

Solvolysis studies performed on *cis*- and *trans*-4-*tert*butylcyclohexyl derivatives do not reveal a preferred product stereochemistry but are characterized by significant loss of stereochemistry at the 1 carbon, giving rise to epimeric product mixtures. Moreover, appreciable yields of *cis*and *trans*-3-*tert*-butylcyclohexyl derivatives occur, presumably as the result of Wagner-Meerwein rearrangement. Significantly, the predominant products in all instances are olefins, produced by competing elimination reactions.<sup>11</sup>

The relative yields of fluorine-containing products from the reaction of 3 and 4 with silver(I) fluoride are summarized in Table II. Product ratios were determined by <sup>19</sup>F NMR using the characteristic assignments identified by Eliel and Martin.<sup>12</sup> A similar product distribution was observed in the reaction of 3 and 4 with mercury(II) fluoride. The principal product in all instances was *tert*-butylcyclohexene. These results, summarized in Table II, are clearly consistent with the reaction of 3 and 4 with mercury(II) and silver(I) fluoride as involving an intermediate carbonium ion. The origin of the considerable differences between the relative yields of products 10 and 11 and 12 and 13 pro-



duced from 3 and 4 is not entirely evident, but may reflect ion-pairing effects.

Reaction of 1-Iodo-2-phenylethane-2,2-d<sub>2</sub> (5), 1- and 2-Iodooctane and 1- and 2-Bromooctane (6 and 7). Solvolysis studies of  $\beta$ -phenethyl derivatives have shown that 1,2-aryl migration proceeds concomitantly with ionization.<sup>13</sup> Thus, the presence of rearranged product from the reaction of 5 with mercury(II) and silver(I) fluoride can only imply the intermediacy of a carbonium ion pathway in these reactions.

1-Iodo-2-phenylethane- $2,2-d_2$  (5) was obtained by treating 2-phenylethanol- $2,2-d_2$  (14) with N-methyl-N,N'-dicyclohexylcarbondiimidium iodide.<sup>14</sup> Reduction of 5 with tri-

Table IIRelative Yields of tert-Butylcyclohexyl Fluorides fromthe Reaction of cis- and trans-4-tert-ButylcyclohexylBromide (3 and 4) with Silver(I) and Mercury(II)Fluoride in Pentane

				Product re	l yield, % <sup>a</sup>	, % <sup>a</sup>
MF x	Substrate	Temp, °C	10°	$\mathfrak{U}^d$	12 <sup>e</sup>	13 <sup>f</sup>
AgF	3 <sup>g</sup>	-20	6	13	19	62
AgF	$4^{h}$	$-20^{b}$	40	35	13	12
$HgF_2$	3	0	15	6	5	74
$\operatorname{HgF}_{2}$	4	0	60	7	13	20

<sup>a</sup> Analysis performed by <sup>19</sup>F NMR. The extensive decomposition of compounds 10-13 under analysis conditions prevented their determination by GLC. Product balances of fluorine-containing products as determined by <sup>19</sup>F NMR ranged between 10 and 20%. *tert*-Butylcyclohexenes comprised the predominant products in these reactions. <sup>b</sup> Reactions carried out at 25 and 0° yielded no detectable fluorine-containing products. <sup>c</sup> Registry no., 20259-37-4. <sup>d</sup> Registry no., 20259-36-3. <sup>e</sup> Registry no., 20272-31-5. <sup>f</sup> Registry no., 20272-35-9. <sup>g</sup> Registry no., 5009-36-9. <sup>h</sup> Registry no., 5009-37-0.

*n*-butyltin hydride yielded exclusively and quantitatively phenylethane- $2,2-d_2$ , thereby confirming the position of isotopic substitution.

$$C_{6}H_{5}CH_{2}CO_{2}CH_{3} \xrightarrow{CH_{3}ONa} C_{6}H_{5}CD_{2}CO_{2}CH_{3} \xrightarrow{\text{LiAlH}_{4}} C_{6}H_{5}CD_{2}CO_{2}CH_{3} \xrightarrow{\text{LiAlH}_{4}} C_{6}H_{5}CD_{2}CH_{2}OH$$

$$14 + [C_{6}H_{11}N = C = N(CH_{3})C_{6}H_{11}]I \longrightarrow C_{6}H_{5}CD_{2}CH_{2}I$$

$$5$$

$$5 \xrightarrow{(n-C_{4}H_{9})_{3}SnH} C_{6}H_{5}CD_{2}CH_{3}$$

Examination of the <sup>1</sup>H NMR spectrum of the 1-fluoro-2-phenylethane- $d_2$  isolated from the reaction of 5 with mercury(II) and silver(I) fluoride revealed equal amounts of 1-fluoro-2-phenylethane- $1,1-d_2$  and  $-2,2-d_2$  (Table III).

$$C_{6}H_{5}CD_{2}CH_{2}I \xrightarrow{MF_{x}} C_{6}H_{5}CD_{2}CH_{2}F + C_{6}H_{5}CH_{2}CD_{2}F$$

Control experiments established that the starting halide 5 did not isomerize in the presence of mercury(II) fluoride under reaction conditions. Similar experiments indicated that 5 is partially isomerized ( $\sim$ 20%) by silver(I) fluoride under corresponding reaction conditions.

To determine if, in fact, product isomerism was occurring during the course of the reaction, authentic 2-phenyl-1-fluoroethane- $2,2-d_2$  was prepared as outlined below and

$$C_6H_5CD_2CH_2OTs \xrightarrow{KF-DEG} C_6H_5CD_2CH_2F$$

subjected to the influence of reaction conditions. The recovered material showed no evidence, as determined by <sup>1</sup>H NMR, of having undergone rearrangement.

In complementary experiments, 1-iodo- and 1-bromooctane were both treated with mercury(II) and silver(I) fluoride. The results, summarized in Table IV, show that, inter alia, a substantial quantity of 2-fluorooctane is produced in these reactions. To exclude the possibility that this product arises via readdition of hydrogen fluoride to 1-octene, the products produced by  $\beta$ -elimination of hydrogen fluoride from initially formed 1-fluorooctane, these reactions were repeated in the presence of 1-decene. The failure to observe any 2-fluorodecane in the reaction products demonstrates

Table III
Yield and Composition of 1-Fluoro-2-phenylethane-d <sub>2</sub>
Obtained on Reaction of 1-Iodo-2-phenylethane-2, $2-d_2$
with Silver(I) and Mercury(II) Fluoride in Pentane

			Product re		
MF <sub>X</sub>	Temp,°C	Reaction time, hr	PhCD <sub>2</sub> - CH <sub>2</sub> F <sup>c</sup>	PhCH <sub>2</sub> - CD <sub>2</sub> F <sup>d</sup>	Product abs yield, <sup>b</sup> %
AgF	36	1			94
	25	2			70
	0	3	50	50	87
	-20	5			88
$HgF_{2}$	36	3			73
	25	7	50	50	25
	0	20			30
	-20	60			30

<sup>a</sup> Determined by <sup>1</sup>H NMR. <sup>b</sup> Analysis performed by GLC on 10 ft × 0.25 in. column of SE-30 on Chromosrob G. <sup>c</sup> Registry no., 50561-93-8. <sup>d</sup> Registry no., 53907-37-2.

that readdition of eliminated hydrogen fluoride is not taking place in these and by inference in similar reactions described above. Furthermore, the formation of 2-fluorooctane suggests that a Wagner-Meerwein rearrangement is occurring. Taken together, these results further implicate a carbonium ion pathway in these reactions.

Several additional features of the data of Table IV are noteworthy. First, it is apparent that reaction temperature significantly affects product distribution and overall yields in the reaction of 1-iodo-, but not 2-iodooctane, with both mercury(II) and silver(I) fluoride. Lower reaction temperatures clearly favor a higher yield of 1-fluorooctane from silver(I) fluoride while the same reaction with mercury(II) fluoride appears to proceed in higher yields at higher temperatures. Second, comparison of these results and those in Tables I–III suggests that silver(I) fluoride is superior overall to mercury(II) fluoride for the preparation of simple monofluorinated organic compounds from the corresponding alkyl iodide or bromide.

Finally, a comparison of the different product ratios resulting from the reaction of 1- and 2-bromo- and 1- and 2iodooctane with mercury(II) and silver(I) fluoride and those recently reported by Liotta and Harris<sup>4</sup> for the reaction of 1- and 2-bromooctane with potassium fluoride in the presence of 18-crown-6 ether merits brief attention. These limited data suggest that the 18-crown-6 ether complex of potassium fluoride may be superior to mercury(II) and silver(I) fluoride for the conversion of a primary alkyl halides to the corresponding alkyl fluoride but that mercury(II) and silver(I) fluorides provide higher yields of secondary alkyl fluorides from the corresponding alkyl bromides and iodides. Moreover, in our hands, potassium fluoride reacted with 1-iodo-2-phenylethane in benzene solution in the presence of 18-crown-6 ether to yield styrene exclusively, while treatment of the same substrate with either mercury(II) or silver(I) fluoride results in high yields of 1-fluoro-2-phenylethane. These facts suggest that, while the KF-18-crown-6 ether reagent may be useful for certain conversions, further studies of this system need to be carried out before any definitive statement regarding the scope of this reagent can be made.

### Discussion

The fact that the production of alkyl fluorides by reaction of alkyl iodides and bromides with mercury(II) and silver(I) fluorides involves a heterogeneous reaction makes a detailed investigation of this reaction difficult. This diffi-

## Reaction of Alkyl Bromides and Iodides with HgF2 and AgF

						Product, <sup>a</sup>		
MF <sub>x</sub>	x Alkyl halide	Registry no.	Reaction time, hr. Temp, $^\circ {\cal C}$		Solvent	n∙ Alkyl fluoride	sec-Alkyl fluoride	€lefin <sup>b</sup>
	1.0.11.1	690 97 6		26	Dontono	20		95
Agr	$1 - C_8 n_{17}$	029-27-0	2	20	Pentane	30	33 34	20
			10	20	Pentane	40	24	24
			10	-20	Pentane	49 50	14	14
Uar	1001		24 5	-20	Pentane	55 41	14	4
Hgr <sub>2</sub>	$1 - C_8 n_{17}$		5	25	Pontane	21	11	1
			24	23	Pentane	25	17	1 9
			24	-20	Pentane	14	16	1
Amt	9041	557 26 9	40	-20	Pentane	· 1	56	34
Agr	2-C <sub>8</sub> n <sub>17</sub> 1	001-00-0	2	20	Pontane	~1	65	32
			2		Pontane	< 1	63	92 90
			10	-78	Pentane	- 1	56	20 30
II.~E	осчт		10	25	Pentane	< 1	48	28 28
ngr <sub>2</sub>	$2 - C_8 n_{17}$		2	20	Pentane	2 1 2 1	57	20
			4	-20	Pentane	< 1	65	26
			10	-78	Pentane	<1	57	11
AcrE	1 CH Br	111_83_1	24	36	Pentane	9	59	14
Agr	1-C <sub>8</sub> II <sub>17</sub> D1	111-00-1	48	25	Pentane	8	46	13
Har	1-C.H. By		24	36	Pentane	23	27	2
11g,1 2	1-C81117D1		48	25	Pentane	10	25	3
AcrF	2-C.H.Br	557-35-7	5	36	Pentane	< 1	65	16
AG1	2-08117D1	001 00 1	6	25	Pentane	< 1	55	20
			24	0	Pentane	<u></u>	58	23
			48	-20	Pentane	< 1	61	23
HoF.	2-C-H-Br		1	36	Pentane	< 1	54	18
1161 2	- 08-11/21		2	25	Pentane	<1	61	22
			5	0	Pentane	< 1	68	18
			24	-20	Pentane	< 1	58	8
KF <sup>e</sup> -	$1-C_8H_{17}Br$		128 <sup>c, d</sup>	90	Benzene	92°	<1°	8°
18-crown-6 KF-	$2-C_8H_{17}Br$		240 <sup>c, d</sup>	90	Benzene	< 1°	32°	68 <sup>c</sup>
18-crown-6 KF- 18-crown-6	$C_6H_5CH_2CH_2I$	17376-04-4	96 <sup>d</sup>	90	Benzene	< 1	<1	99

 Table IV

 Products from the Reaction of Silver(I) and Mercury(II) Fluorides with

 1-Iodo-, 1-Bromo-, 2-Iodo-, and 2-Bromooctane

<sup>a</sup> As determined by GLC on a 20 ft  $\times$  0.25 in. column of SE-30 on Chromosorb G. <sup>b</sup> No effort was made to distinguish between 1- and 2octene, which had identical retention times under the conditions of analysis. <sup>c</sup> Taken from ref 4. <sup>d</sup> Time for one-half conversion of starting materials to products. <sup>e</sup> Registry no., 7789-23-3.

culty is compounded by the sometime instability of the alkyl fluoride product. Nonetheless, the stereochemical and product studies presented above establish that the production of alkyl fluorides in these reactions proceeds through intermediate carbonium ions. The detailed nature of the C-F bond-forming step in these reactions has not been delineated, although it could conceivably proceed by the intermolecular transfer of fluoride from a halometallo-ate complex to a carbonium ion center.

In conclusion, it should be recalled that the influence which heteroatom-containing neighboring groups play in determining product stereochemistry in solvolysis reactions is well known and provides a satisfactory explanation for the apparent conflict in stereochemical conclusions reached in earlier work,<sup>6,7</sup> since both results are consistent with the involvement of a carbonium ion intermediate accompanied by neighboring group participation.<sup>15</sup>

# **Experimental Section**

All melting points and boiling points are uncorrected. Infrared spectra were determined within sodium chloride cells on a Perkin-Elmer Model 225 grating spectrophotometer. NMR (<sup>1</sup>H and <sup>19</sup>F) spectra were determined with a Varian T-60 NMR spectrometer at 60 and 56.4 MHz, respectively. <sup>1</sup>H chemical shifts are reported in parts per million relative to internal tetramethylsilane. All coupling constants are in hertz. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-7E mass spectrometer. Samples for spectral and elemental analyses were purified on a Hewlett-Packard Model 700 thermal conductivity gas chromatograph. Analytical GLC analyses were performed on a Hewlett-Packard Model 5750 flame ionization instrument. Absolute yields of products were calculated from peak areas using internal standard techniques with response factors obtained from authentic samples.

Several commercial sources of mercury(II) and silver(I) fluoride were used in this study. No obvious differences in results were observed when reasonable caution was taken to exclude moisture during storage and handling. Pentane was deolefinated and deoxygenated prior to use.

**exo-2-Bromo-***endo-2***-chloronorbornane** (1) and *exo-2***-chloro-***endo-2***-bromonorbornane** (2), bp 41-42 (1.0 Torr) and  $83-85^{\circ}(9.0 \text{ Torr})$ , respectively [lit.<sup>16</sup> bp 42-49° (0.06 Torr)], were prepared by treating 2-chloronorborn-2-ene and 2-bromonorborn-2-ene with anhydrous hydrogen bromide and hydrogen chloride, respectively, as described by Fry.<sup>16</sup>

endo-2-Chloro-exo-2-fluoronorbornane (8) and exo-2-Chloro-endo-2-fluoronorbornane (9). Authentic samples of these substances were prepared by literature procedures.<sup>10</sup>

cis- and trans-4-tert-butylcyclohexyl bromide (3 and 4) were prepared according to the procedures described by Eliel and Martin <sup>12b</sup> Tri-*n*-butyltin hydride was prepared by a modification<sup>17</sup> of the literature procedure.<sup>18</sup>

Methyl-1-phenyl- $2/2-d_2$  Acetate. Under a flush of nitrogen, sodium (150 mg, 6.5 mg-atoms) was placed into a flame-dried, three-necked, 250-ml flask equipped with a reflux condenser. All remaining arms were stoppered with serum caps and methanol-O-d (100 g, 99% d) and methyl phenylacetate (7.5 g, 50 mmol) were added by syringe. This mixture was refluxed for 12 hr under a static head of nitrogen, then neutralized by addition of aqueous deuterium chloride (240 mg of a 30% solution of deuterium chloride in deuterium oxide). The resulting mixture was concentrated at reduced pressure to yield 6.5 g (87%) of crude methyl-1-phenyl-2,2 $d_2$  acetate: <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  7.20 (5 H, s), 3.58 (3 H, s).

2-Phenylethanol-2,2- $d_2$ . Into a three-necked, 250-ml flask equipped with a Teflon-coated magnetic stirrer bar, an addition funnel, and a condenser and containing a solution of 0.91 g (24 mmol) of lithium aluminum hydride in 100 ml of anhydrous ether was added a solution of crude methyl-1-phenyl-2,2- $d_2$  acetate (6.0 g, 40 mmol) in 40 ml of anhydrous ether. The rate of addition was such that a gentle reflux was maintained. This mixture was subsequently refluxed for 2 hr, cooled, and poured into 70 ml of cold, 15% sulfuric acid. The ether layer was separated and the aqueous phase extracted with three 50-ml portions of ether. The combined organic layers were extracted with a solution (50 ml) of saturated aqueous sodium bicarbonate followed by a final extraction with 50 ml of water, then dried (MgSO<sub>4</sub>) and concentrated under reduced pressure to yield 4.5 g (91%) of crude 2-phenylethanol-2,2- $d_2$ : <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  7.20 (5 H, s), 3.65 (2 H, s), 3.10 (1 H, s).

N-Methyl-N,N'-dicyclohexylcarbodiimidium iodide was synthesized as described by Scheffold and Saladin,<sup>14</sup> mp 109.5– 111.5° (lit.<sup>14</sup> mp 111–113°).

1-Iodo-2-phenylethane- $2,2-d_2$  (5). Crude 2-phenylethanol- $2,2-d_2$  (4.5 g, 36 mmol) was added to a stirred solution of 25.1 g (72.0 mmol) of freshly prepared N-methyl-N,N'-dicyclohexylcarbodiimidium iodide in 400 ml of anhydrous THF contained in a 500-ml flask. The resulting solution was stirred at  $35^\circ$  for 3 hr and the volatile components were subsequently removed under reduced pressure. The remaining brown oil was taken up in 400 ml of hexane which was then extracted with three 200-ml portions of methanol-water (4:1). The combined aqueous washings were extracted with three 150-ml portions of hexane. All hexane layers were combined, dried over Na<sub>2</sub>SO<sub>4</sub>, and percolated through 80 g of silica gel (40-140 mesh), before concentrating at reduced pressure. Distillation of the residual oil yielded 6.7 g (78% based on crude 2-phenylethanol-2,2- $d_2$ , 57% overall from methyl phenylacetate) of 1-iodo-2-phenylethane-2,2- $d_2$ : bp 65–68° (0.5 Torr) [lit.<sup>19</sup> (undeuterated) bp 95° (3 Torr)]; <sup>1</sup>H NMR (CCl<sub>4</sub>) & 7.21 (5 H, s), 3.27 (2 H, s); 96%  $d_2$  as indicated by mass spectral analysis.

Reduction of 1-Iodo-2-phenylethane-2,2- $d_2$  (5) with Tri-*n*butyltin Hydride. Into a flame-dried, 40-ml centrifuge tube was placed 0.50 g (2.1 mmol) of 1-iodo-2-phenylethane-2,2- $d_2$  and 10 mg of AIBN. The vessel was capped with a rubber septum and flushed with nitrogen before adding 2 ml of pentane and 0.87 g (3.0 mmol) of tri-*n*-butyltin hydride by syringe. The mixture was photolyzed at 25° for 1 hr with a hand scanner. Excess tri-*n*-butyltin hydride was destroyed by the addition of 0.46 g of carbon tetrachloride and the resulting phenylethane-1,1- $d_2$  analyzed by glpc on a 6-ft, 10% SE-30 column. Analysis of the <sup>1</sup>H NMR of a collected sample indicated >97% phenylethane-1,1- $d_2$ .

Preparation of 2-Phenylethyl *p*-Toluenesulfonate-2,2- $d_2$ . *p*-Toluenesulfonyl chloride (4.80 g; 25.2 mmol) was added to an ice-cooled, stirred solution of 2.50 g (20.0 mmol) of freshly distilled 2-phenylethanol-2,2- $d_2$  in 7.0 ml of pyridine over a 15-min period. The resulting mixture was stirred for an additional 15 min at 0° and then for 6 hr at room temperature before pouring it into 100 ml of water. The mixture was then extracted with four 100-ml portions of ether. The combined ether layers were washed with two 100-ml portions of water, dried (CaSO<sub>4</sub>), and concentrated. The oily residue was recrystallized from pentane, yielding 2.58 g, mp 38-39°; second crop (0.14 g), mp 38.5-39.5° [lit.<sup>20</sup> (undeuterated) mp 39-40°] (total yield 50%); <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  7.8-7.0 (9 H, m) 4.11 (2 H, s), 2.37 (3 H, s).

Preparation of 2-Phenyl-1-fluoroethane<sup>21</sup> and 2-Phenyl-1fluoroethane-2,2-d<sub>2</sub>. Into a 25-ml, two-necked flask containing a Teflon-coated stirrer bar was placed 1.00 g (3.62 mmol) of 2-phenylethyl-*p*-toluenesulfonate-2,2-d<sub>2</sub> and 1.05 g (18.1 mmol) of anhydrous potassium fluoride. One neck was capped with a rubber septum and the other connected to a flame-dried cold trap. The apparatus was flushed with nitrogen as the trap was cooled to  $-78^{\circ}$ . Anhydrous diethylene glycol (5.0 ml) was added by syringe and the mixture allowed to stir for 3 hr at 110° (15 Torr). The trap was allowed to warm to room temperature under a nitrogen atmosphere and found to contain 0.37 g of a liquid which GLC analysis indicated to be 4% styrene and 96% 2-phenyl-1-fluoroethane-2,2- $d_2$  (81% overall yield): <sup>1</sup>H NMR (2-phenyl-1-fluoroethane-2,2- $d_2$ ) (CCl<sub>4</sub>)  $\delta$  7.17 (5 H, s), 4.46 [2 H, d, J(HCF) = 47 Hz]; 95%  $d_2$  as indicated by mass spectral analysis.

**General Procedures.** Similar procedures were used in carrying out the reaction of all alkyl halides with mercury(II) and silver(I) fluorides. Representative examples are given below.

Reaction of endo-2-Bromo-exo-2-chloronorbornane (2) with Mercury(II) Fluoride. Into a flame-dried, nitrogen-flushed, 25-ml flask equipped with a condenser and a Teflon-coated stirrer bar was placed 0.14 g (0.59 mmol) of mercury(II) fluoride. A solution of 0.10 g (0.48 mmol) of endo-2-bromo-exo-2-chloronorbornane in dry pentane (10 ml) was added by syringe. The mixture was stirred for 12 hr at 25° at which time GLC analysis of an aliquot indicated the complete consumption of 2. The resulting mixture was filtered through diatomaceous earth and the product, endo-2-chloro-exo-2-fluoronorbornane, was collected by preparative GLC using a 40 ft  $\times$  0.25 in. column of 7% Zonyl E-7 on Chromosorb W. Its ir spectrum and GLC retention time were identical with those of authentic endo-2-chloro-exo-2-fluoronorbornane (8).<sup>10</sup>

Reaction of exo-2-Bromo-endo-2-chloronorbornane (1) with Silver(I) Fluoride. Under a flush of nitrogen, silver(I) fluoride (0.14 g, 1.1 mmol) was placed into a flame-dried 25-ml flask equipped with a Teflon-coated stirrer bar and condenser. A solution of 0.10 g (0.49 mmol) of exo-2-bromo-endo-2-chloronorbornane in 10 ml of dry pentane was added by syringe. The resulting mixture was stirred until GLC analysis indicated the complete disappearance of starting halide (12 hr at  $25^{\circ}$ ). The resulting mixture was gravity filtered and subjected to preparative GLC on a 40 ft × 0.25 in. column of Zonyl E-7. The collected product, endo-2chloro-exo-2-fluoronorbornane (8), had ir and GLC retention time identical with those of an authentic sample.<sup>10</sup>

**Reaction of** *cis*-4-*tert*-Butylcyclohexyl Bromide (3) with Silver(I) Fluoride. Into a chilled  $(-20^{\circ})$ , flame-dried flask equipped with a condenser and a Teflon-coated stirrer bar and containing 1.5 g (12 mmol) of silver(I) fluoride, was injected by syringe a cold  $(-20^{\circ})$  solution of 1.0 g (4.6 mmol) of *cis*-4-*tert*-butylcyclohexyl bromide in 10 ml of dry pentane. The mixture was stirred at  $-20^{\circ}$  for 12 hr, gravity filtered, and concentrated under reduced pressure. GLC analysis could not be carried out because of extensive product decomposition under analysis conditions. Product ratios were determined by <sup>19</sup>F NMR using the chemical shift values for *cis*- and *trans*-4- and -3-*tert*-butylcyclohexyl fluoride reported by Eliel and Martin.<sup>12a</sup>

**Reaction of 1-Iodo-2-phenylethane-** $2,2-d_2$  (5) with Silver(I) Fluoride. Anhydrous silver(I) fluoride (1.4 g, 11 mmol) was placed in a 50-ml flame-dried flask containing a Teflon-coated stirrer bar. The flask was capped with a rubber septum, flushed with nitrogen, and cooled to 0° before adding by syringe a cold (0°) solution of 1.2 g (5.1 mmol) of 1-iodo-2-phenylethane- $2,2-d_2$  in 10 ml of dry pentane. The resulting mixture was stirred under a static head of nitrogen for 3 hr and gravity filtered and the clear solution was distilled, bp 65–66° (35 Torr) [lit.<sup>21</sup> bp 55–56° (12 Torr)], to yield 0.31 g of a 1:1 mixture of 1-fluoro-2-phenylethane- $1,1-d_2$  and  $-2,2-d_2$ : <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  7.14 (5 H, s), 4.50 [2 H, d, J(HCF) = 47 Hz], 2.94 [2 H, d, J(H-C-CF) = 21 Hz).

Reaction of 1-Iodooctane with Silver(I) Fluoride. Into a 25ml flame-dried flask equipped with a condenser and a Teflon-coated stirrer bar was placed 1.2 g (9.5 mmol) of silver(I) fluoride. The condenser was capped with a rubber septum and a solution of 1.00 g (4.20 mmol) of 1-iodooctane and 0.504 g of *n*-decane (GLC standard) in 10 ml of dry pentane was added by syringe. The resulting mixture was stirred at 25° for 4 hr, at which time GLC analysis indicated that consumption of the starting halide was complete. The reaction mixture was gravity filtered and the product distribution determined by GLC analysis on a 20 ft  $\times$  0.25 in. column of 7.5% SE-30 on Chromosorb G. The principal components in order of increasing elution time were octene(s), 2-fluorooctane, and 1-fluorooctane. The GLC retention time, <sup>1</sup>H NMR, ir, and mass spectra of collected samples of 1-fluorooctane were identical with those of an authentic sample of 1-fluorooctane. $^{22}$  The spectral properties of a collected sample of the second component were consistent with its assignment as 2-fluorooctane: ir (CCl<sub>4</sub>) 870 cm<sup>-1</sup> (vs, C-F); <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  4.50 [1 H, d of multiplets, J(H-C-F) = 48 Hz], ~1.4 [10 H, br, complex multiplet,  $(CH_2)_5$ ], 1.26 [3 H, d of d,  $J(CH_3-CHF) = 23$  Hz,  $J(CH_3-CHF) = 7.0$  Hz], 0.96 (3 H, t).

Reaction of Alkyl Bromides and Iodides with HgF2 and AgF

No attempt was made to separate the possible isomers of octene. Reaction of sec-Octyl Iodide with Mercury(II) Fluoride. Mercury(II) fluoride (1.2 g, 5.0 mmol) was placed in a 25-ml, flame-dried flask equipped with a condenser and a Teflon-coated stirrer bar. The condenser was capped with a rubber septum and the flask cooled to  $-20^{\circ}$  under a flush of nitrogen. A cold (-20°) solution of 1.00 g (4.16 mmol) of sec-octyl iodide and 0.502 g of decane (GLC internal standard) in 10 ml of dry pentane was injected by syringe. The disappearance of sec-octyl iodide was followed by glpc. After 5 hr at  $-20^{\circ}$  consumption of starting halide was complete. The resulting mixture was filtered through diatomaceous earth and the clear solution analyzed by GLC using a 20 ft  $\times$ 0.25 in. column of 7.5% SE-30 on Chromosorb G.

Reaction of 1-Bromooctane with Silver(I) Fluoride. Into a flame-dried, 25-ml flask equipped with a condenser and a Tefloncoated stirrer bar was placed 1.4 g (11 mmol) of silver(I) fluoride. The condenser was capped with a rubber septum and the vessel flushed with nitrogen before injecting by syringe a solution of 1bromooctane (1.0 g, 5.16 mmol) and 0.512 g of n-decane (GLC internal standard) in 10 ml of pentane. This mixture was stirred at 25° until GLC analysis indicated the complete disappearance of starting halide (~48 hr). The solution was gravity filtered and product distribution determined by GLC analysis on a 20 ft  $\times$  0.25 in, column of 7.5% SE-30 on Chromosorb G.

Reaction of 2-Bromooctane with Mercury(II) Fluoride. Mercury(II) fluoride (1.5 g, 6.3 mmol) was placed in a 25-ml, flame-dried flask equipped with a condenser and a Teflon-coated stirrer bar. The condenser was capped with a rubber septum and the vessel flushed with nitrogen before injecting by syringe a solution of 2-bromooctane (1.01 g, 5.20 mmol) and 0.492 g of n-decane (GLC internal standard) in 10 ml of dry pentane. The resulting mixture was stirred at room temperature until the disappearance of starting halide was complete as indicated by GLC ( $\sim 2$  hr). The suspended solids were removed by filtration through diatomaceous earth and the solution components analyzed by GLC on a 20 ft  $\times$ 0.25 in. column of 7.5% SE-30 on Chromosorb G.

Reaction of 1-Iodo-2-phenylethane with Potassium Fluoride in the Presence of 18-Crown-6 Ether. Into a two-necked, 25-ml flask equipped with a Teflon-coated stirrer bar was placed 1.0 mmol of 18-crown-6 ether<sup>23</sup> and 0.58 g (10 mmol) of anhydrous potassium fluoride<sup>24</sup> which had been previously dried at 110° for 12 hr. One neck was stoppered with a rubber septum and to the other neck was attached a small distilling head. Anhydrous benzene (11 ml) was added by syringe and reaction vessel heated under a static head of nitrogen until 1 ml of distillant had been collected. The distillation head was replaced with a flame-dried condenser and 1-iodo-2-phenylethane (1.16 g, 5.00 mmol) added by syringe. The resulting mixture was heated with vigorous stirring at 90°. The extent of reaction was monitored periodically by GLC analysis. After 96 hr, ~50% of the starting halide had been consumed. GLC analysis indicated the presence of <1% 1-fluoro-2phenylethane. The resulting mixture was gravity filtered and concentrated by distillation. Distillation of the residue afforded 0.20 g of styrene, identical by GLC retention time, ir, and nmr with a commercial sample.

Recovery of cis-4-tert-Butylcyclohexyl Bromide (3) from Partial Conversion Using Mercury(II) and Silver(I) Fluoride. Into a flame-dried, nitrogen-flushed, 40-ml centrifuge tube equipped with a Teflon-coated stirrer bar was placed 0.063 g (0.50 mmol) of silver(I) fluoride. The tube was capped with a rubber septum, flushed with nitrogen, and cooled to  $-20^{\circ}$  before adding by syringe a cold  $(-20^{\circ})$  solution of 0.22 g (1.0 mmol) of 3 in 2 ml of dry pentane. The mixture was stirred at  $-20^{\circ}$  for 12 hr and gravity filtered, and the solution components were separated and analyzed by GLC using a 40 ft  $\times$  0.25 in. column of Zonyl E-7 on Chromosorb G.

The equivalent procedure was carried out using mercury(II) fluoride. In both instances, GLC analysis of the unreacted starting bromide indicated that no (<1%) isomerism had occurred.

Recovery of 1-Iodo-2-phenylethane- $2,2-d_2$  (5) from Partial Conversion Using Mercury(II) and Silver(I) Fluoride. A chilled (0°) solution of 5 (1.00 g, 4.30 mmol) in 10 ml of dry pentane was added by syringe to a 25-ml flask equipped with a Tefloncoated stirrer bar and a serum-capped condenser and containing 0.50 g (2.1 mmol) of mercury(II) fluoride. This mixture was stirred for 4.5 hr at 0°, then gravity filtered and concentrated in vacuo. Distillation of the residual liquid afforded ~0.1 g of 1-fluoro-2phenylethane-1,1- and -2,2-d2, bp 58-61° (25 Torr), and 0.51 g of 1-iodo-2-phenylethane-d<sub>2</sub>, bp 95° (3.0 Torr), the <sup>1</sup>H NMR spectrum of which revealed that no (<3%) isomerism to 1-iodo-2-phenvlethane- $1, 1-d_2$  had occurred. Repetition of this experiment using silver(I) fluoride revealed that  $\sim 20\%$  of the recovered starting halide had isomerized to 1-iodo-2-phenylethane- $1, 1-d_2$ .

Reaction of 1-Iodooctane with Mercury(I) and Silver(I) Fluoride in the Presence of 1-Decene. Silver(I) fluoride (1.4 g, 11 mmol) was placed in a flame-dried, 25-ml flask equipped with a Teflon-coated stirrer bar and a condenser capped with a rubber septum. The vessel was flushed with nitrogen before adding by syringe a solution of 1-iodooctane (1.20 g, 5.00 mmol) and 1-decene (0.50 ml) in 10 ml of dry pentane. The resulting solution was stirred for 4 hr at 25° and gravity filtered and the solution components were determined by GLC analysis on a 20 ft  $\times$  0.25 in. column of 7.5% SE-30 on Chromosorb G. The equivalent reaction was repeated using mercury(II) fluoride. In both instances no (<1%) 2-fluorodecane was observed.

Recovery of 2-Phenyl-1-fluoroethane-2,2-d2 from Treatment with Mercury(II) and Silver(I) Fluoride. 2-Phenyl-1-fluoroethane (0.10 g, 0.80 mmol) was placed in a flame-dried 25-ml flask equipped with a Teflon-coated stirrer bar and containing 0.24 g (1.0 mmol) of mercury(II) fluoride suspended in 2.0 ml of pentane under an atmosphere of nitrogen. After 24 hr, the mixture was gravity filtered. Examination of the recovered starting material by <sup>1</sup>H NMR showed no evidence of any rearrangement. Likewise, the material recovered from a similar reaction using silver(I) fluoride was unchanged from that of authentic 2-phenyl-1-fluoroethane  $-2, 2 - d_2$ .

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