Compounds 14-19 were prepared in analogous fashion.

Registry No. 5, 18617-38-4; (*E*)-6, 87155-48-4; (*Z*)-6, 87155-49-5; 7, 87155-50-8; 8, 769-54-0; 9, 87155-51-9; 10, 87155-52-0; 11, 70-34-8; (*E*)-14, 87155-53-1; (*Z*)-14, 87155-54-2; (*E*)-15, 87155-55-3; (*Z*)-15, 87155-56-4; 16, 87155-57-5; 17, 87155-58-6; 18, 87155-59-7; 19, 87155-60-0; methyl 2-butynoate, 23326-27-4; 3-amino-1,2-propanediol, 616-30-8; ethyl (*E*)-3-amino-2-butenoate, 41867-20-3; ethyl (*Z*)-3-amino-2-butenoate, 626-34-6.

Supplementary Material Available: Full NMR, IR, and mass spectral data for compounds 14-19 (2 pages). Ordering information is given on any current masthead page.

A Simple Photochemical Conversion of Perfluoroalkyl Hydrides to Perfluoroalkyl Bromides Using Interhalogen Compounds

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It is an accepted principle that the inductive effects of halogen substituents reduces the reactivity of hydrogen to radical abstraction by chlorine[1-3] or bromine atoms.[4] Furthermore it is accepted that resonance effects of halogen substituents have an effect on geminal-hydrogen reactivity that is opposite that of their inductive effects.[3] Copp and Tedder have shown that substitution of hydrogen by chlorine lowers the activation energy for radical abstraction of geminal hydrogen by bromine, while substitution of hydrogen or chlorine by fluorine raises the activation energy for radical abstraction by bromine.[4] The increase in activation energy for hydrogen abstraction on fluorinated and chlorofluorinated methanes for bromination would seem to apply to direct fluorinations as well. For example, fluorine substitution of neopentanes tends to produce preferentially the symmetrically substituted polyfluoroneopentanes.[5]

Despite the deactivation of hydrogens toward radical abstraction in fluorocarbons, photochemical bromination and chlorination of hydryl-*F*-alkanes have been previously reported in early work by Haszeldine[6] and by Benning and Park.[7] Thermal brominations of hydryl-*F*-alkanes have been studied by Amphlett and Whittle at temperatures in excess of 400 °C.[8] They have also shown increases in the activation energies in hydrogen abstraction by bromine in the fluoromethane series: CFH_3, CF_2H_2, CF_3H, and also document the reversibility of the bromination reaction due to its inhibition by HBr.[8]

As part of a research effort directed at the construction of highly branched fluorocarbon networks, we sought convenient ways to introduce reactive groups onto hydryl-*F*-neopentanes and other fluorocarbons. This led us to attempt several photochemical bromination schemes. We were able to confirm the very facile room-temperature, gas-phase photochlorination of hydryl-*F*-alkanes but were not able to achieve significant photobromination of these molecules at ambient temperatures. Thermal bromination was unsuccessful at 250 °C, and higher temperatures resulted in significant fluorocarbon skeletal fragmentation. Efforts were then directed toward interhalogen compounds as potential bromination reagents. It is the results of those investigations that are the basis of this report.

Results and Discussion

Because the reactivity of chlorine with hydryl-*F*-neopentane was high and that for bromine was so low, the first interhalogen that suggested itself was bromine chloride. A search of the literature produced many instances where bromine chloride was used as a reactive electrophilic brominating agent but far fewer instances where it was used as a free-radical brominating agent. These examples have been reviewed in some detail by Mills and Schneider.[9] Among the free-radical reaction examples was a reference to the bromination of fluoroform by bromine chloride, which reportedly produced exclusively bromotrifluoromethane.[10]

Bromine chloride (mp −66 °C, bp 5 °C) is approximately 40% dissociated at 25 °C ($k_d° = 0.34$) into bromine (mp −7.2 °C, bp 58.8 °C) and chlorine (mp −103 °C, bp −34.6 °C).[11] It is a polar, reactive electrophile and its selectivity as a brominating agent is apparently due to the attraction of the electron-rich radical to the positive (bromine) end of the molecular dipole of BrCl.[9] Given this hypothesis, the more electrophilic the radical, the less selective will be the bromination.

The reaction of hydryl-*F*-neopentane with bromine chloride was much slower (100 h) than the ambient temperature chlorination of that compound (10 min). The reaction was followed by gas-phase infrared spectroscopy. Although bromo-*F*-neopentane formed much faster initially than chloro-*F*-neopentane, the latter compound was negligible in yields only for overall conversions of less than 10%. As the reaction reached completion (304 h) the percentages of bromo- to chloro-*F*-neopentane was 48-43%. A slight excess of bromine to chlorine and a slightly shorter (254 h) reaction time slightly increases the yield of bromo-*F*-neopentane. The ^{19}F NMR data (Table I) are characteristic and easily interpretable.

The reactions of 1,3-dihydryl-*F*-neopentane under similar conditions are summarized in Table II. All possible products were produced. For example in reaction 1, 1,3-dibromo (31.5%), 1-bromo-3-chloro (18.6%), 1-bromo-3-hydryl (29.2%), 1,3-dichloro (6.5%), and 1-chloro-3-hydryl (11.4%) were produced. The overall ratio of chlorination to bromination was 1:2.6. Increases in chlorine concentration (reaction 2) and increases in overall reaction time (reaction 3) markedly increased the yield of 1-bromo-3-chloro-*F*-neopentane (29.4% and 32%, respectively). Decreases in chlorine concentration (or increases in bromine concentration), reaction 4, significantly increased the yield of 1-bromo-3-hydryl-*F*-neopentane (48%) and recovered starting material (10%). The optimum reaction (reaction 1) for making 1,3-dibromo-*F*-neopentane produced 2.6 times as much bromination as chlorination products; however, optimal bromination (4.4:1) occurred for reaction 4, which produced predominately 1-bromo-3-

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Table I. ^{19}F NMR[a] Data and Elemental Analyses of Substituted *F*-Neopentanes

		CF_3	CF_2Br	CF_2Cl	remarks	elem anal. theor	elem anal. obsd
(1)	$CF_3C(CF_3)_2CF_2Br$	−63.84 ppm (t), J_{FF} = 10.5 Hz	−47.94 ppm (dectet)		mp 51.5–52.0 °C	*b*	
(2)	$CF_3C(CF_3)_2CF_2Cl$	−64.18 ppm (t), J_{FF} = 10.7 Hz		−52.29 ppm (dectet)	mp 77.5–78.0 °C	C, 19.72 F, 68.63	C, 19.67 F, 68.60
(3)	$CF_3C(CF_2Br)(CF_3)CF_2Br$	−62.29 ppm (p), J_{FF} = 9.77 Hz	−46.56 ppm (hept)			C, 14.65 F, 46.35	C, 14.76 F, 46.66
(4)	$CF_3C(CF_2Cl)(CF_3)CF_2Br$	−63.35 ppm (p), J_{FF} = 11.4 Hz	−47.30 ppm (m)	−51.35 ppm (m)			
(5)	$CF_3C(CF_2Cl)(CF_3)CF_2Cl$	−62.95 ppm (p), J_{FF} = 10.5 Hz		−51.05 ppm (hept)		C, 18.71 F, 59.20	C, 18.85 C, 58.91
(6)	$CF_3C(CF_2Br)(CF_3)CF_2H$	−63.45 ppm (p), J_{FF} = 9.77 Hz	−47.95 ppm (m)		Φ_{CF_2H} = −125.36 ppm (dm) δ_{CF_2H} = 6.29 ppm (t) J_{CF_2H} = 51.0 Hz (^1H), 53.7 Hz (^{19}F)		
(7)	$CF_3C(CF_2Cl)(CF_3)CF_2H$	−63.85 ppm (p), J_{FF} = 9.77 Hz		−52.44 ppm (m)	Φ_{CF_2H} = −125.51 ppm (dm) δ_{CF_2H} = 6.28 ppm (t) J_{CF_2H} = 50.9 Hz (^1H), 48.8 Hz (^{19}F)		

[a] Relative to $CFCl_3$ (1.0% internal) ≡ 0.0 ppm, $CDCl_3$. [b] See ref 12.

Table II. Reaction of 1,3-Dihydryl-*F*-neopentane with BrCl: Product Distributions vs. Reaction Conditions

rxn no.	1,3-diH, g	mole ratios[a] Cl_2	mole ratios[a] Br_2	rxn time, h	H, H[b]	1,3 product distrib (mol %) H, Cl	Cl, Cl	H, Br	Br, Cl	Br, Br	bromination to chlorination ratio[c]
1	0.663	1.113	1.165	186	2.7	11.4	6.5	29.2	18.6	31.5	2.6
2	0.302	1.311	1.315	180	2.0	9.8	9.8	24.6	29.4	24.5	1.75
3	0.608	0.975	0.980	302	1	7	9	35	32	16	1.74
4	0.354	0.93	1.75	173	10	8	3	48	9	22	4.4

[a] Relative to 1,3-dihydryl-*F*-neopentane. [b] Recovered 1,3-dihydryl-*F*-neopentane. [c] Calculated as millimoles of C-Br bonds to millimoles of C-Cl bonds in 1,3 product distribution.

hydryl-*F*-neopentane (48%).

It is apparent from these results that the proportion of chlorination to bromination increases both with the concentration of chlorine and with overall reaction time. Conversely, the proportions of brominated to chlorinated products decreased with reaction time.

In a set of control experiments *F*-neopentyl bromide and chlorine gas irradiated for 30 h produced approximately 8% *F*-neopentyl chloride, 90% recovered *F*-neopentyl bromide, and 2% *F*-pivaloyl chloride. The converse reaction of *F*-neopentyl chloride with bromine did not occur. Furthermore *F*-neopentyl bromide plus hydrogen (and also deuterium) did not react. The reaction of *F*-neopentyl bromide with mercury, however, produced 20% *F*-2,2,5,5-tetramethylhexane (*F*-dineopentyl) after 47 h of irradiation. The chloride produced only a trace of the coupled product under similar conditions.

These experiments suggest that although the bromides are produced faster, they are more reactive and are gradually consumed, i.e., converted to the chlorides in the interhalogen reactions.

The reaction of 2-(difluoromethyl)-2-(trifluoromethyl)-4,4,5,5-tetrafluoro-1,3-dioxolane with BrCl produced much higher yields of perhalogenated products: 59.5% bromo- and 37.5% chloro-*F*-dioxolanes. This is likely a result of increased reactivity and shorter reaction time. The reaction of BrCl and 1-hydryl-*F*-2,5-dioxohexane (hydryl-*F*-glyme, $CF_3OCF_2CF_2OCF_2H$), however, does not go to completion but "equilibrates" at 37.1% chloro, 34.5% bromo, and 28.4% starting material.

The reactions of BrCl with 2-hydryl-*F*-dioxane and 4-hydryl-*F*-2,2-dimethyl-1,3-dioxolane result in extensive decomposition of both fluorocarbons. Neither reaction produced identifiable amounts of the chloro or bromo analogues nor were significant amounts of starting material recovered in either case.

The "chlorobromination" reaction is a significant improvement over the metalation–bromination of hydryl-*F*-

neopentane, the only previously reported route to bromo-*F*-neopentane.[12] The metalation route, however, remains the preferred route to iodo-*F*-neopentane. Photolysis of ICl and hydryl-*F*-neopentane produced chloro-*F*-neopentane, HCl, and I_2. This failure is not surprising because of the photolability of *F*-alkyl iodides and the low reactivity of iodine atoms.

Despite the improvement in convenience of the chlorobromination over the metalation route, it is still slow and produces considerable amounts of undesired chlorofluorocarbons. In search of a faster, more efficient brominating agent, we immediately began to investigate the possibility of using bromine fluoride, BrF. Bromine monofluoride (mp −33 °C, bp 20 °C) is not stable but disproportionates extensively [55% at 55 °C (55 torr)] to bromine (mp −7.2 °C, bp 58.8 °C) and bromine trifluoride (mp 9 °C, bp 126 °C). Dissociation to the elements is not appreciable at room temperature ($K°_d = 8 \times 10^{-3}$). Because of the disproportionation of BrF to BrF_3 and Br_2, special techniques were required to minimize contact between the hydryl fluorocarbons and BrF_3 and to prevent the liquid BrF_3 from attacking the quartz reactor. The net reaction $BrF + R_FH \rightarrow R_FBr + HF$ also requires a hydrogen fluoride scavenger to prevent HF attack on the quartz. These conditions were met relatively easily by placing a 9 mm × 50 mm Teflon FEP[14] test tube vertically in the bottom of the cylindrical quartz reactor (170 mL) surrounded by anhydrous sodium fluoride pellets to absorb HF and support the Teflon tube. A threefold stoichiometric amount of BrF_3 was syringed into the Teflon test tube. The tube was cooled and evacuated. Then the stoichiometric amount of hydryl fluorocarbon and a threefold stoichiometric amount of bromine were introduced. Photolysis began as soon as frost cleared the tube and the fluorocarbon and bromine evaporated. The much lower vapor pressure of BrF_3 and the large vapor-phase excess of bromine maintained the disproportionation substantially toward BrF. Some BrF and BrF_3 evidently form adducts with the NaF because at the completion of the reaction (24 h) all of the volatile BrF_3 had been consumed.

"Fluorobromination" of hydryl-*F*-neopentane produced 78.6% bromo-*F*-neopentane and 6.6% *F*-neopentane. The remainder consisted of recovered starting material plus, occasionally, an unidentified *F*-acid fluoride probably formed by contaminant oxygen from attack by BrF_3 on the quartz. "Fluorobromination" of 1,3-dihydryl-*F*-neopentane produced 20% 1,3-dibromo-*F*-neopentane and 15% 1-bromo-3-hydryl-*F*-neopentane with 60% of the starting material recovered. No traces of bromo-*F*-neopentane or *F*-neopentane were found.

Experimental Section

Hydryl-*F*-neopentane, 1,3-dihydryl-*F*-neopentane, 4-hydryl-*F*-2,2-dimethyl-1,3-dioxolane, 2-(difluoromethyl)-2-(trifluoromethyl)-*F*-1,3-dioxolane, and 2-hydryl-*F*-1,4-dioxane were major products isolated from nonphotochemically finished, aerosol direct fluorinations of neopentane, 2,2-dimethyl-1,3-dioxolane, and 1,4-dioxane, respectively.[5] Some 2-hydryl-*F*-1,4-dioxane and 1-hydryl- and 1,3-dihydryl-*F*-neopentanes and all of the 1-hydryl- and 3-hydryl-*F*-2,5-dioxahexanes [hydryl-*F*-(ethylene glycol dimethyl ethers)] were produced by LTG direct fluorination techniques.[12,15] Bromine (Fisher), chlorine (Linde), and bromine trifluoride (Matheson) were commercial products, which were purified by vacuum-line fractionation, using flexible Teflon PTFE tubing as traps in the case of BrF_3. Photolysis reactions were conducted in a 170-mL cylindrical quartz vessel (~40 mm × ~135 mm) fitted with a Kontes 0–4-mm Hivac stopcock through a graded seal. Contents were irradiated with a 125-W Hanovia medium-pressure mercury-vapor arc lamp. Ambient temperature inside the enclosure was approximately 35 °C during operation. The reaction was monitored at half-day intervals by withdrawing some of the gas-phase products into a 10-cm gas infrared cell (KCl windows). Following the reaction, excess halogens were absorbed by condensation of the product into a tube containing a filter paper wet with oleic acid. Nonreactive products were vacuum transferred and subjected to a workup that consisted of vacuum-line fractionation, infrared assay of fractions, gas chromatographic separation of components using either a 7 m × $^3/_8$ in. 13% Fluorosilicone QF-1 (Analabs) stationary phase on 60–80-mesh, acid-washed, Chromosorb P conditioned at 225 °C (12 h) or a 4 m × 3/8 in. 10% SE-52 phenylmethylsilicone rubber on acid washed, 60–80-mesh Chromosorb P conditioned at 225 °C (12 h). Following gas chromatographic separation (Bendix Model 2300, subambient multicontroller), all products of "significance" were collected, transferred to the vacuum line, assayed, and characterized by vapor-phase infrared spectrophotometry (PE1330), electron impact (70 eV) and chemical ionization (CH_4 plasma) mass spectrometry (Hewlett-Packard GC/MS, 5710A GC, 5980A MS, 5934A computer), and ^1H and ^{19}F nuclear magnetic resonance (JEOL FX90Q, omniprobe) in $CDCl_3$ with 1% $CFCl_3$ internal standard. Elemental analyses, where necessary, were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Hydryl-*F*-neopentane: BrCl. Hydryl-*F*-neopentane (0.508 mmol, 0.1371 g), chlorine (0.480 mmol, 0.340 g), and bromine (0.572 mmol, 0.0915 g) were condensed into the evacuated quartz cylindrical bulb. The contents of the bulb were warmed to ambient temperature, until all reactants were evaporated. The contents were then irradiated for a total of 254 h. The irradiation was interrupted at half-day intervals for infrared examination. Workup of the products produced 52% bromo-*F*-neopentane and 45% chloro-*F*-neopentane with 3% recovered starting material. See Table I for characterization.

1,3-Dihydryl-*F*-neopentane: BrCl. 1,3-Dihydryl-*F*-neopentane was reacted with bromine chloride under several sets of conditions that are outlined in Table II. The effect on product distributions by changes in Cl_2/Br_2 ratios and reaction times are tabulated. Reactions were performed in a manner similar to the hydryl-*F*-neopentane reactions. Characterizations of products are also given in Table I.

***F*-Neopentyl Bromide: Cl_2.** Bromo-*F*-neopentane (0.03 mmol, 0.010 g) and chlorine (0.09 mmol, 0.0064 g) were condensed into the evacuated quartz cylindrical bulb. The contents were warmed to ambient temperature and then irradiated with the 125-W mecury-vapor lamp for a total of 30 h. The irradiation was interrupted three times at 2-h intervals and at 6-h intervals thereafter for infrared examination. The CCl band of *F*-neopentyl chloride at 860 cm^{-1} was noticeable after 2 h as a shoulder on the CBr band of *F*-neopentyl bromide at 840 cm^{-1}. Gas chromatographic assay of the total product indicated 90% *F*-neopentyl bromide, 8% *F*-neopentyl chloride, and 2% *F*-pivaloyl chloride.

***F*-Neopentyl Bromide: Hg.** Bromo-*F*-neopentane (0.04 mmol, 0.014 g) and mercury (0.5 mmol, 0.1 g) were combined in the evacuated quartz cylindrical bulb and irradiated for 47 h with the 125-W mercury lamp. Gas chromatographic assay of the total product indicated a mixture of 20% dimer, *F*-2,2,5,5-tetramethylhexane identified by its infrared spectra.[12,16] The remainder consisted of unchanged starting material.

***F*-Neopentyl Chloride: Hg.** Chloro-*F*-neopentane (0.20 mmol 0.062 g) and mercury (1 mmol, 0.2 g) were combined in a second quartz vessel, and the reaction was carried out simultaneously with the bromo-*F*-neopentane reaction. Only a trace of dimer was produced in this reaction. Identification was made by GLC retention time comparison of products with the bromo-*F*-neopentane run.

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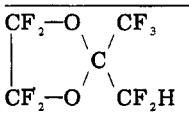
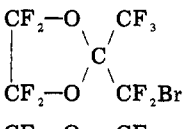
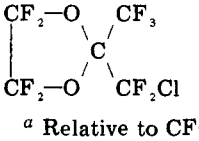
Table III. ^{19}F NMR Data[a] for 1-Substituted-*F*-2,5-dioxahexanes

CF_3-O-CF_2-CF_2-O-CF_2X
a b c d e

deriv	CF_3 (a)	CF_2 (b)	CF_2 (c)	CF_2 (d)	X (e)
1-hydryl[b]	−59.23 ppm (t)	−93.63 ppm (q)	−92.47 ppm (t)	−88.36 ppm (dt)	3.74 ppm (t)
	J_{ab} = 9.4 Hz	$J_{bc} \simeq 0$ Hz	J_{cd} = 4.5 Hz	J_{de} = 68.9 Hz	
1-bromo[c]	−55.75 ppm (t)	−91.06 ppm (q)	−90.13 ppm (t)	−19.19 ppm (t)	
	J_{ab} = 8.79 Hz	$J_{bc} \simeq 0$ Hz	J_{cd} = 10.74 Hz		
1-chloro	−55.74 ppm (t)	−91.06 ppm (q)	−90.52 ppm (t)	−27.46 ppm (t)	
	J_{ab} = 8.79 Hz	$J_{bc} \simeq 0$ Hz	J_{cd} = 10.74 Hz		

[a] Relative to $CFCl_3$ (1.0% internal) ≡ 0.0 ppm, $CDCl_3$. [b] See ref 15. [c] Anal. Calcd for $C_4F_9O_2Br$: C, 14.52; F, 51.67. Found: C, 14.38; F, 51.31.

Table IV. ^{19}F NMR[a] Data for Some *F*-1,3-Dioxolane Derivatives

F-1,3-dioxolane	CF_2	CF_3	CF_2(X)	X
	−83.35 ppm (hexet) [4][c]	−82.35 ppm (tpd) [3]	−138.01 ppm (dqp) [2]	δ_{CF_2H} = 5.996 ppm (t)[b]
	$J_{CF_2X-CF_2} = J_{CF_3-CF_2}$ = 2.0 Hz		J_{HF} = 53.1 Hz (^{19}F)	J_{HF} = 52.2 Hz (^1H)
			$J_{CF_3-CF_2H}$ = 7.8 Hz	
	−81.40 ppm (s)[d] [4]	−78.76 ppm (t) [3]	−63.71 ppm (q) [2]	
	−81.78 ppm (s)[d] [4]	−79.43 ppm (t) [3]	−68.54 ppm (q) [2]	

[a] Relative to $CFCl_3$ (1.0% internal) ≡ 0.0 ppm, $CDCl_3$. [b] See ref 15. [c] [Integral]. [d] $J_{CF_2CF_2}$ and $J_{CF_3-CF_2} < 2$ Hz. [e] Anal. Calcd for $C_5F_9O_2Br$: C, 17.51; F, 49.86. Found: C, 17.52; F, 49.35.

1-Hydryl-*F*-2,5-dioxahexane: BrCl. 1-Hydryl-*F*-2,5-dioxahexane (0.3077 mmol, 0.075 g), chlorine (0.318 mmol, 0.0225 g), and bromine (0.3206 mmol, 0.0521 g) were condensed into the quartz bulb. On warming, the mixture was irradiated for 302 before coming to equilibrium. Workup produced 1-bromo-*F*-2,5-dioxahexane (34.5%), 1-chloro-*F*-2,5-dioxahexane (37.1%), and recovered starting material (28.4%). Characterizations are given in Table III.

2-(Difluoromethyl)-2-(trifluoromethyl)-4,4,5,5-tetrafluoro-1,3-dioxolane:[17] **BrCl.** The starting material (0.563 mmol, 0.150 g), chlorine (0.588 mmol, 0.0417 g), and bromine (0.588 mmol, 0.0939 g) were condensed into the quartz bulb. On warming, the mixture was irradiated for 192 h. Workup produced 2-(bromodifluoromethyl)-2-(trifluoromethyl)-4,4,5,5-tetrafluoro-1,3-dioxolane (59.5%), the analogous chloro-*F*-dioxolane (37.5%),[17] and recovered starting material (2.3%). Characterizations are given in Table IV.

Hydryl-*F*-neopentane: BrF. The quartz bulb used in the BrCl reactions was fitted with a 9 mm × 50 mm Teflon FEP test tube, supported vertically in the bottom and charged with approximately 25 g of sodium fluoride, $^1/_8$ in. pellets (Harshaw). Approximately 1.80 mmol (0.10 mL, 0.25 g) of bromine trifluoride was syringed into the test tube under a nitrogen atmosphere. The quartz bulb was cooled with liquid nitrogen and evacuated, and 0.167 g (0.620 mmol) of hydryl-*F*-neopentane and 0.290 g (1.80 mmol) of bromine were condensed into the bulb. On warming, the mixture was irradiated for a total of 108 h, although infrared assay showed little change after 24 h. Workup produced bromo-*F*-neopentane (78.6%), *F*-neopentane (6.6%), and recovered starting material (14%). See Table I for characterization.

1,3-Dihydryl-*F*-neopentane: BrF. 1,3-Dihydryl-*F*-neopentane (0.345 mmol, 0.0868 g) and bromine 0.313 mmol, 0.050 g) were condensed into the quartz bulb containing the bromine trifluoride (0.90 mmol, 0.05 mL, 0.12 g). On warming, the mixture was irradiated for 64 h with most of the reaction occurring within the first 24 h. Workup of the product produced 1,3-dibromo-*F*-neopentane (20%), 1-bromo-3-hydryl-*F*-neopentane (15%), hydryl-*F*-neopentane (trace), and unreacted starting material (60%). See Table I for characterization.

Registry No. BrCl, 13863-41-7; BrF, 13863-59-7; hydryl-*F*-neopentane, 2993-15-9; bromo-*F*-neopentane, 71076-46-5; chloro-*F*-neopentane, 87136-72-9; 1,3-dihydryl-*F*-neopentane, 71076-43-2; 1,3-dibromo-*F*-neopentane, 87136-73-0; 1-bromo-3-chloro-*F*-neopentane, 87136-74-1; 1,3-dichloro-*F*-neopentane, 87136-75-2; 1-bromo-3-hydryl-*F*-neopentane, 87136-76-3; 1-chloro-3-hydryl-*F*-neopentane, 87136-77-4; *F*-pivaloyl chloride, 13027-23-1; *F*-2,2,5,5-tetramethylhexane, 71076-47-6; 1-hydryl-*F*-2,5-dioxahexane, 40891-98-3; 1-bromo-*F*-2,5-dioxahexane, 87136-78-5; 1-chloro-*F*-2,5-dioxahexane, 87136-79-6; 2-(difluoromethyl)-2-(trifluoromethyl)-4,4,5,5-tetrafluoro-1,3-dioxolane, 87136-80-9; 2-(bromodifluoromethyl)-2-(trifluoromethyl)-4,4,5,5-tetrafluoro-1,3-dioxolane, 87136-81-0; 2-(chlorodifluoromethyl)-2-(trifluoromethyl)-4,4,5,5-tetrafluoro-1,3-dioxolane, 64499-70-3.

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Intramolecular Wittig Cyclization: A Novel Route to Previously Unknown 3-Thia and 3-Sulfinyl Analogues of Testosterone

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As a result of our ongoing interest in thiasteroid analogues as potential therapeutic agents,[1] we became interested in the synthesis of 3-sulfinyltestosterone analogue 1. As depicted in Scheme I, consideration of an intramolecular Wittig cyclization in our retrosynthetic analysis was prompted by the results of Bertin and Perronnet[2] in

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