and H-20). Tosylation of 0.02 g of **8j** in 0.5 mL of pyridine by stirring with 0.012 g of tosyl chloride and 0.01 g of DMAP at room temperature for 48 h (the solution became dense and dark red), dilution with water, acidification, extraction with ether, and chromatography of the washed and dried ether extract over silica gel gave a pale yellow semisolid which was immediately reduced with excess $LiAlH_4$ in dry ether by refluxing for 1 h. The usual workup followed by chromatography over silica gel gave in the hexane eluates, 6 mg (31%) of **8b**.

15-Isobutyl-*ent*-isocopalane (8c). To a solution of 0.3 g of **8e** in 10 mL of THF was added at −20 °C with stirring 1.4 mL of a 1.5 M solution of methyllithium in ether. After 30 min the temperature was allowed to rise to 0 °C and maintained there for 2 h. The mixture was decomposed with ice-cold H_2O and extracted with ether. The usual workup and purification by preparative TLC (hexane–ether, 3:2) furnished as the less polar product 0.04 g (14%) of **8i** as a pale yellow solid: mp 67–68 °C; IR 1705 cm^{-1}; ^1H NMR δ 2.13 ($-COCH_3$), 0.87 (d, J = 7 Hz, H-16), 0.84, 0.83, 0.81, and 0.79 (H-17, H-18, H-19, and H-20); M_r calcd for $C_{23}H_{40}O$ 332.3077, found 332.3065. The more polar product was 0.15 g (48%) of **8k**: mp 95–96 °C; IR 3300, 1220, 1150, 1005, 975, 955, 925 cm^{-1}; ^1H NMR δ 1.22 (H-23 and H-24), 0.88 (d, J = 7 Hz, H-16), 0.86, 0.83, 0.82, and 0.81 (H-17, H-18, H-19, and H-20); M_r calcd for $C_{24}H_{44}O$ 34,.3390, found 348.3370; ^{13}C NMR spectrum is listed in Table III.

Dehydration of 0.1 g of **8h** with 0.2 mL of $POCl_3$ in 2 mL of pyridine by stirring for 6 h at −5 °C, decomposition with crushed ice, extraction with ether, and purification by preparative TLC (hexane–ether, 19:1) after the usual workup gave 0.085 g (90%) of an olefin mixture whose ^1H NMR spectrum indicated that it contained approximately equal amounts of the Δ^{21} and the Δ^{22} isomer; M_r calcd for $C_{24}H_{42}$ 330.3287, found 330.3293. Hydrogenation of 0.075 g of this material (PtO_2, MeOH–EtOAc, 4.1) in a Parr hydrogenator at room temperature and purification of the product by preparative TLC gave 0.06k g (85%) of **8c** as a waxy solid: mp 58–59 °C; IR 2950, 1465, 1390, 1370, 1050, 1025, 980 cm^{-1}; ^1H NMR 0.88, 0.87, and 0.86 (all d, J = 7.5 Hz, H-16, H-23, and H-24), 0.83, 0.83, 0.81, and 0.79 (H-17, H-18, H-19, and H-20); M_r calcd for $C_{24}H_{44}$ 332.3443, found 332.3423.

Preparation of the C_{22} and C_{23} Hydrocarbon Mixtures. A solution of 0.2 g of **6c** in 20 mL of glacial acetic acid was reduced in a Parr hydrogenator using PtO_2 as catalyst. After 6 h the product was worked up as described earlier for the synthesis of **8d** from **6c**. The ^1H NMR spelctrum of the gummy material (0.12 g) exhibited two $-CO_2Me$ signals at δ 3.67 (**8d**) and 3.64 (**3g**) in ca. 10:1 ratio but was otherwise identical with that of pure **8d**. $LiAlH_4$ reduction of the mixture and purification as described for pure **8d** yielded 0.10 g of a mixture containing **8f** and its stereoisomers, which was converted to a tosylate mixture, purified in the same manner as pure **8g** in 0.085-g yield. A 0.025-g portion of this material on reduction with excess $LiAlH_4$ followed by chromatography gave 0.01 g of the mixture of C_{22} hydrocarbons. GLC analysis on column 2 indicated the presence of four components, **8a** (R_f 27.58 min, 78%), **3h** (R_f 26.64 min, 17%), **4a** and **20a** (R_f 25.95 and 25.54 min, 4% and 1%). CGCMS analysis at the Chevron Oil Research Laboratory on a 7070H VG micromass mass spectrometer at 70 eV using a 60-m DB1 capillary column, temperature programmed at 150–300 °C at 2 °C/min, indicated the presence of four isomeric components with retention times of 52:57 (**8a**), 51:09 (**3h**), and 49:27 and 48:27 min, (**4a** and **20a**), respectively, whose mass spectra were indistinguishable and essentially identical with that given for **8a** in Table I.

Coupling of 0.02 g of the tosylate mixture with CH_3MgCl in the presence of Li_2CuCl_4 as described for pure tosylate **8g** and chromatography of the crude product gave 0.012 g of the mixture of C_{23} hydrocarbons. GLC analysis on column 2 indicated the presence of mainly two components, **8b** (R_f 32.96 min, 85%) and **3e** (R_f 32.04 min, 13%); the two minor constituents were represented by very weak peaks only. CGCMS analysis at the Chevron Oil Research Laboratory at 70 eV using a 60-m DB1 capillary column, a Finnigan mass spectrometer, and the INCOS data handling system revealed the presence of four isomeric components with retention times of 63:30 (**8b**), 61:57 (**3e**), and 60:00 and 58:24 min (**4b** and **20b**). Isomer 3 represented about 1.5% of the total mixture, isomer 4 less than 0.5%. The mass spectra of all four components were indistinguishable and essentially identical with that of pure **8b**.

Acknowledgment. We thank Dr. P. Sundararaman and Ms. Cathy Y. Lee, Chevron Oil Field Research, Richmond, CA, for carrying out CGCMS analyses of the C_{22} and C_{23} *ent*-isocopalane mixtures described in this article.

Registry No. **3g**, 87953-79-5; **3h**, 87953-80-8; **4b**, 87953-78-4; **6a**, 87953-40-0; **6b**, 59909-34-1; **6c**, 87953-41-1; **6d**, 87953-42-2; **3d** (12,13-dihydro derivatives), 87953-77-3; **7a**, 87953-43-3; **7b**, 88034-05-3; **7d**, 87953-44-4; **8a**, 87953-45-5; **8b**, 87953-46-6; **8c**, 87953-47-7; **8d**, 87953-48-8; **8e**, 87953-49-9; **8f**, 87953-50-2; **8g**, 87953-51-3; **8h**, 87953-52-4; **8i**, 87953-53-5; **8j** (*R* alcohol), 87953-54-6; **8j** (*S* alcohol), 87953-81-9; **8k**, 87953-55-7; **9a**, 88034-06-4; **9b**, 87953-56-8; **9c**, 87953-57-9; (*E*)-**9d**, 87969-50-4; (*Z*)-**9d**, 87953-82-0; **10a**, 87953-58-0; **10b**, 87953-59-1; (*E*)-**11**, 87953-60-4; (*E*)-**12a**, 87953-61-5; (*Z*)-**12a**, 88034-07-5; **12b**, 87953-62-6; **12c**, 87953-63-7; (*E*)-**12d**, 87953-64-8; (*Z*)-**12d**, 87953-65-9; **13a** (α-C_5H_{11}), 87953-66-0; **13a** (β-C_5H_{11}), 88034-11-1; **13b**, 87953-67-1; **14a**, 57672-83-0; **14b**, 57672-84-1; **15**, 88034-08-6; **16a**, 17633-79-3; **16b**, 38237-44-4; **17a**, 10395-43-4; **17b**, 10395-38-7; **18a**, 87953-68-2; **18b**, 88034-09-7; **18c**, 87953-69-3; **18d**, 88034-10-0; **19a**, 87953-70-6; **19b**, 87953-71-7; **20a**, 87953-72-8; **20b**, 87953-73-9; (*E*)-7,13-labdadiene, 87953-74-0; (*Z*)-7,13-labdadiene, 87953-75-1; (*Z*)-8,13-labdadiene, 87953-76-2; sclareol, 515-03-7; manool, 596-85-0; trimethyl phosphonoacetate, 5927-18-4; triethyl phosphono-2-butyrate, 17145-91-4.

Stereochemistry of Fluorination and Halofluorination of 1-Phenyl-4-*tert*-butylcyclohexene

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Acid-catalyzed liquid-phase fluorine addition with xenon difluoride to 1-phenyl-4-*tert*-butylcyclohexene (1) resulted in equal amounts of cis and trans adducts, while introduction of a methoxy group into the phenyl ring had no effect on the stereochemistry of addition. Bromofluorination and chlorofluorination of 1 with *N*-bromosuccinimide or *N*-chlorosuccinimide in the presence of a mixture of hydrogen fluoride–pyridine followed Markovnikov-type regioselectivity and proceeded stereospecifically anti, thus forming two pairs of vicinal halofluorides.

It is known that the stereochemistry of halogen addition to alkenes depends on the reagent, the structure of the alkene, and the reaction conditions.[1] Stereochemical information on the addition pathway is important for further

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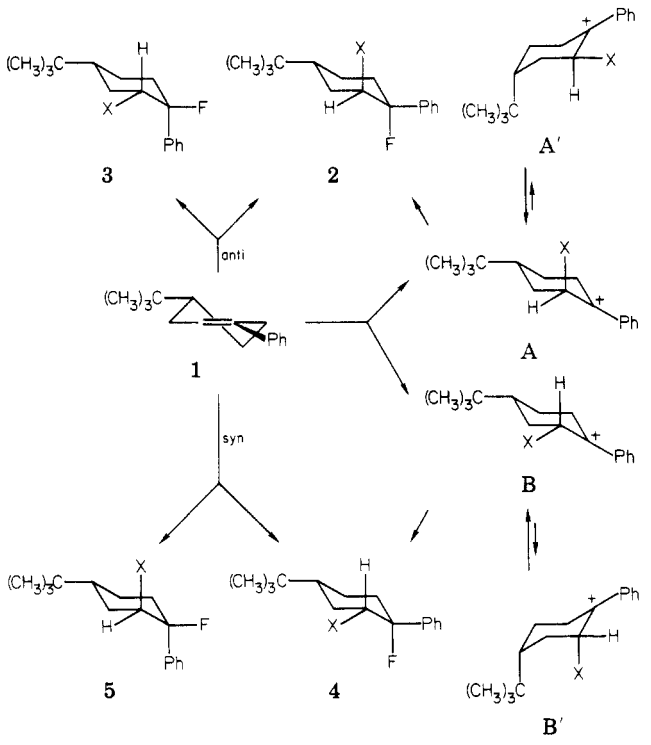
Scheme I



elucidation of the reaction mechanism. Many halogenating reagents have been tested on acyclic alkenes, but the great disadvantage of such a study is the possibility of rotation about the newly formed C–C single bond in the β-halo carbonium ion. Such rotation could be diminished by using cycloalkenes but eliminated only in the case of the cyclopentene ring, while in the case of cyclohexene the primarily formed β-halo carbonium ion with the halogen in the axial position could also be transformed into a carbonium ion with the halogen in the equatorial position. We now report that such isomerization of the primarily formed halo carbonium ion could be avoided when the stereochemistry of halogenation is studied with 1-phenyl-4-*tert*-butylcyclohexene.

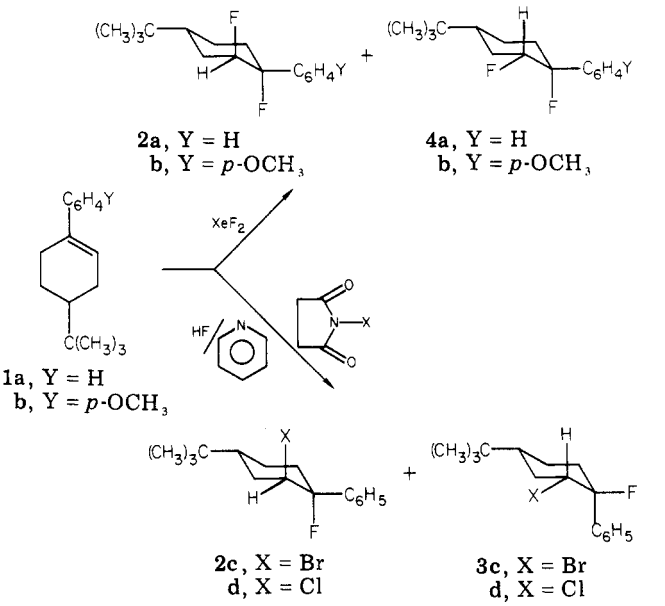
Results and Discussion

Fluorination or halofluorination of 1-phenyl-4-*tert*-butylcyclohexene (1) could occur, depending on the reagent, via syn or anti addition or through β-halo carbonium ions. Anti addition which occurs through a transition state or complex of rigid nature will result in the formation of products **2** and **3** (Scheme I), with the presence of thermodynamically unfavorable product **3** with the phenyl group in the axial position, proving the concerted nature of the reaction. Similarly, syn addition to **1** can result in products **4** and **5** while the presence of product **5** with the phenyl group in the axial position will again confirm the concerted path of the reaction. However, if the reaction occurs through formation of β-halo carbonium ions A or B, their ratio depending on the site of attack of the reagent, the presence of the *tert*-butyl group will prevent their isomerization to ions A′ or B′, and further attack of the nucleophile on both ions will occur in such a way that products (**2** and **4**) with the phenyl substituent in the equatorial position will result.

Table I. Effect of Substituent, Reagent, and Catalyst on Fluorination and Halofluorination of 1

		rel yields, %		
reagent/catalyst	1 (Y)	2	3	4
XeF_2/HF	H	51		49
XeF_2/HF-C_5H_5N	H	49		51
XeF_2/BF_3	H	52		48
XeF_2/	H	54		46
XeF_2/Nafion-H	H	61		39
XeF_2/HF	*p*-OCH_3	55		45
NBS-HF-C_5H_5N	H	64	36	
NCS-HF-C_5H_5N	H	60	40	

Scheme II



The stereochemistry of fluorine addition with xenon difluoride to phenyl-substituted cycloalkenes depends on ring magnitude, and the reaction with cyclohexene derivatives results in equal amounts of syn and anti adducts.[2] Introduction of a methoxy group in the para position of the phenyl ring changed the product distribution, the syn product being preferred, which was explained by secondary isomerization of the primarily formed β-fluoro carbonium ion, with fluorine in the axial position, to a carbonium ion with fluorine in the equatorial position.[2] If introduction of a *tert*-butyl group in the cyclohexene derivative prevents isomerization of carbonium ion A to A′ or B to B′, the presence of a methoxy group in the phenyl ring should not produce any appreciable effect. Room-temperature fluorination of 1-phenyl-4-*tert*-butylcyclohexene (1) in the presence of hydrogen fluoride with xenon difluoride gave two products in nearly equal amounts, which were isolated by preparative GLC (Scheme II, Table I). The structures of the products **2a** and **4a** were determined on the basis of spectroscopic data and assigned as *r*-1-phenyl-1-fluoro-*c*-2-fluoro-*t*-4-*tert*-butylcyclohexene and *r*-1-phenyl-1-fluoro-*t*-2-fluoro-*t*-4-*tert*-butylcyclohexane, respectively.

It is also known that the catalyst used in the fluorination with xenon difluoride plays an important role,[3,4] and for

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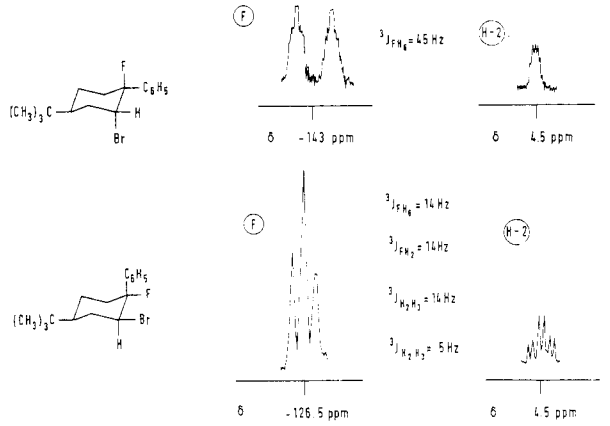
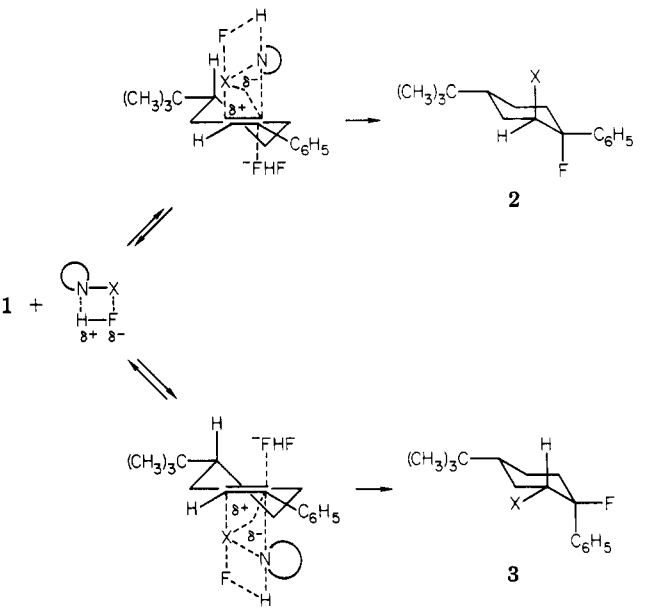


Figure 1. NMR spectra of the two products from bromofluorination of 1-phenyl-4-*tert*-butylcyclohexene.

this reason we have studied the effect of various catalysts, i.e., hydrogen fluoride–pyridine, boron trifluoride, boron trifluoride supported on cross-linked polystyrene–4-vinylpyridine and Nafion-H. We found that change of catalyst has no significant influence on the stereochemistry of fluorine addition (Table I). Introduction of a methoxy group into the para position of the phenyl ring (**1b**, y = p-OCH_3, Scheme II) also has no significant effect on the stereochemistry of fluorine addition, indicating that the presence of a *tert*-butyl group in the cyclohexene ring has prevented isomerization of the β-fluoro carbonium ion, as has been observed[2] in the fluorination of 1-(4-methoxyphenyl)cyclohexene.

Olah and co-workers[5] have found that the use of a mixture of hydrogen fluoride–pyridine can simplify the experimental technique for the preparation of vicinal halofluorides from alkenes, formed in the presence of *N*-bromosuccinimide (NBS), *N*-chlorosuccinimide (NCS), or *N*-iodosuccinimide (NIS). We have found that the reaction of phenyl-substituted alkenes[6] and phenylcyclohexene[7] withNBS in the presence of HF–pyridine follows the Markovnikov-type regioselectivity, and is stereospecifically anti for *trans*- and nonstereospecific for *cis*-alkenes. Bromofluorination of 1-phenyl-4-*tert*-butylcyclohexene with NBS in HF–pyridine gave a crude reaction mixture containing two products which were isolated by preparative TLC. In Figure 1 NMR spectra of both products are shown, which also have very similar mass spectra. On the basis of the spectroscopic data the major products, formed (**2c**, Table I) were assigned as *r*-1-phenyl-1-fluoro-*c*-2-bromo-*t*-4-*tert*-butylcyclohexane and **3c** as *r*-1-phenyl-1-fluoro-*c*-2-bromo-*c*-4-*tert*-butylcyclohexane. Chlorofluorination of **1** also gave two products with NMR data very similar to those of the vicinal bromofluorides. The formation of product **3** with a phenyl group in the axial position in bromo- and chlorofluorination could be explained by the formation of two complexes (Scheme III) in a way similar to that already suggested.

Scheme III[a]



[a] X = Cl, Br.

Experimental Section

IR spectra were recorded by using a Perkin-Elmer 727B spectrometer and ^1H and ^{19}F NMR spectra by a JEOL JNM-PS 100, with Me_4Si or CCl_3F as an internal reference. Mass spectra and high-resolution measurements were taken on a CEC 21-110 spectrometer. Gas–liquid partition chromatography was carried out on a Varian Aerograph, Model 1800, and TLC on Merck PSC-Fertigplatten silica gel F-254. 1-Phenyl-4-*tert*-butylcyclohexene and 1-(4-methoxyphenyl)cyclohexene were prepared by known methods.[8] Hydrogen fluoride and boron trifluoride of Fluka Purum quality were used without further purification. Solvents were purified[9] and stored over molecular sieves. Xenon difluoride was prepared by a photosynthetic method, and its purity was better than 99.5%.

Fluorination of 1-Phenyl-4-*tert*-butylcyclohexene (1a). To a solution of 1 mmol of alkene in methylene chloride (2 mL) in a Kel-F vessel was added 1 mmol of xenon difluoride at room temperature, and the catalyst was introduced under stirring into the reaction mixture (trace amounts of hydrogen fluoride, 20 mg of hydrogen fluoride–pyridine, trace amounts of boron trifluoride, 25 mg of the complex of boron trifluoride with cross-linked polystyrene–4-vinylpyridine, or 25 mg of Nafion-H). Reaction was complete in 1 h and in the case of Nafion-H in 3 h. The reaction mixture was diluted with methylene chloride (15 mL), the solid catalyst was filtered off, the reaction mixture was washed with aqueous $NaHCO_3$ and water and dried over anhydrous sodium sulfate, and the solvent was evaporated in vacuo. The crude reaction mixture was analyzed by NMR spectroscopy, and the product distributions are presented in Table I. Products were isolated by preparative GLC (30% FFAP–Chromosorb 80/100, temperature 240 °C).

***r*-1-Phenyl-1,*c*-2-difluoro-*t*-4-*tert*-butylcyclohexane (2a)**: yield 57 mg (23%); white crystalline compound; mp 55–57 °C; NMR $\delta(F_1)$ −162.8 (dm, $^3J_{F_1H_6}$ = 42 Hz), $\delta(F_2)$ −192.5 (ddm, $^2J_{F_2H_2}$ = 48 Hz, $^3J_{F_2H_3}$ = 48 Hz), $\delta((CH_3)_3)$ 1.0 (s, 9 H), δ(H) 1.6–2.1 (m, 7 H), $\delta(H_2)$ 4.6 (d, 1 H, $^2J_{F_2H_2}$ = 48 Hz), $\delta(C_6H_5)$ 7.2 (m, 5 H); mass spectrum (mol wt calcd for $C_{16}H_{22}F_2$ 252.1689, found 252.1690), m/e (relative intensity) 253 (M^+ + 1, 2), 252 (M^+, 10), 232 (2), 196 (24), 135 (10), 122 (14), 109 (8), 91 (13), 86 (9), 85 (10), 84 (15), 83 (14), 57 (100), 47 (13), 41 (26).

***r*-1-Phenyl-1,*t*-2-difluoro-1-*t*-4-*tert*-butylcyclohexane (4a)**: yield 54 mg (21%); white crystalline compound; mp 62–63.5 °C; NMR $\delta(F_1)$ 181.5 (m), $\delta(F_2)$ −187.7 (dm, $^2H_{F_2H_2}$ = 48 Hz), $\delta((CH_3)_3)$ 0.9 (s, 9 H), δ(H) 1.6–2.1 (m, 7 H), $\delta(H_2)$ 4.6 (dddd, 1 H, $^2J_{F_2H_2}$ = 48 Hz, $^3J_{F_1H_2}$ = 24 Hz, $^3J_{H_2H_{3a}}$ = 10 Hz, $^3J_{H_2H_{3e}}$ = 4.5 Hz), $\delta(C_6H_5)$ 7.2 (m, 5 H); mass spectrum (mol wt calcd for $C_{16}H_{22}F_2$ 252.1689, found 252.1685), m/e (relative intensity) 253 (M^+ + 1, 2), 252 (M^+, 10), 232 (1), 196 (24), 135 (10), 122 (15), 109 (8), 91 (10), 86 (5),

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85 (4), 84 (9), 83 (6), 57 (100), 41 (24).

Fluorination of 1-(4-Methoxyphenyl)-4-*tert*-butylcyclohexene (1b). To a solution of 1 mmol of alkene in methylene chloride (2 mL) in a Kel-F vessel was added 1 mmol of xenon difluoride at room temperature, and under stirring, trace amounts of hydrogen fluoride were introduced into the reaction mixture. The reaction was complete in 1 h, the reaction mixture was diluted with methylene chloride, and after the usual workup procedure, the crude reaction mixture was analyzed by NMR spectroscopy (product distribution is presented in Table I). Products were isolated by preparative TLC (SiO_2; chloroform–cyclohexane, 4:6).

***r*-1-(4-Methoxyphenyl)-1,*c*-2-difluoro-*t*-4-*tert*-butylcyclohexane (2b):** yield 53 mg (19%); white crystalline compound: mp 138–140 °C; NMR $\delta(F_1)$ −159.1 (dm, $^3J_{F_1H_6}$ = 42 Hz), $\delta(F_2)$ −190.5 (ddm, $^2J_{F_2H_2}$ = 48 Hz, $^3J_{F_2H_3}$ = 48 Hz), $\delta((CH_3)_3)$ 1.0 (s, 9 H), δ(H) 1.6–2.1 (m, 7 H), $\delta(OCH_3)$ 3.9 (s, 3 H), $\delta(H_2)$ 4.7 (d, 1 H, $^2J_{F_2H_2}$ = 48 Hz), $\delta(C_6H_4)$ 7.2 (m, 4 H); mass spectrum (relative intensity) (mol wt calcd for $C_{17}H_{24}OF_2$ 282.1795, found 282.1790), *m/e* (relative intensity) 283 (M^+ + 1, 4), 282 (M^+, 14), 262 (6), 246 (19), 225 (15), 185 (15), 184 (100), 169 (31), 165 (33), 152 (11), 147 (20), 141 (29), 139 (14), 121 (15), 115 (24), 57 (49).

***r*-1-(4-Methoxyphenyl)-1,*t*-2-difluoro-*t*-4-*tert*-butylcyclohexane (4b):** yield 73 mg (26%); white crystalline compound; mp 87–89 °C; NMR $\delta(F_1)$ −178.7 (m), $\delta(F_2)$ −186.8 (dm $^2J_{F_2H_2}$ = 48 Hz), $\delta((CH_3)_3)$ 1.0 (s, 9 H), δ(H) 1.6–2.1 (m, 7 H), $\delta(OCH_3)$ 3.9 (s, 3 H), $\delta(H_2)$ 4.7 (dddd, 1 H, $^2J_{F_2H_2}$ = 48 Hz, $^3J_{F_1H_2}$ = 24 Hz, $^3J_{H_2H_{3a}}$ = 10 Hz, $^3J_{H_2H_{3e}}$ = 4.5 Hz), $\delta(C_6H_4)$ 7.3 (m, 4 H); mass spectrum (mol wt calcd for $C_{17}H_{24}OF_2$ 282.1795, found 282.1800), *m/e* (relative intensity) 283 (M^+ + 1, 10), 282 (M^+, 70), 262 (22), 225 (17), 185 (20), 184 (50), 169 (14), 165 (100), 152 (20), 147 (10), 141 (11), 139 (11), 121 (15), 115 (13), 57 (80).

Halofluorination of 1-Phenyl-4-*tert*-butylcyclohexene (1a). A 0.6-mmol sample of *N*-chlorosuccinimide or *N*-bromosuccinimide, 1 mL of diethyl ether, and 1 mL of a 70% mixture of HF–pyridine were stirred at 0 °C until the *N*-halosuccinimide was dissolved, and then at room temperature 0.5 mmol of 1-phenyl-4-*tert*-butylcyclohexene was added. After being stirred 2 h at room temperature, the reaction mixture was poured onto ice, and the products were extracted with diethyl ether. The diethyl ether extract was washed with water, aqueous KOH (10%), and water and dried over Na_2SO_4, and the solvent was evaporated in vacuo. The crude reaction mixture was analyzed by NMR, and the product distribution is presented in Table I. Products were isolated by preparative TLC with cyclohexane.

***r*-1-Phenyl-1-fluoro-*c*-2-bromo-*t*-4-*tert*-butylcyclohexane (2c):** yiLd 41 mg (26%); white crystalline compound; mp 84–86 °C; NMR $\delta(F_1)$ −143.0 (dm, $^3J_{F_1H_6}$ = 45 Hz), $\delta((CH_3)_3)$ = 1.0 (s, 9 H), δ(H) 1.6–2.3 (m, 7 H), $\delta(H_2)$ 4.5 (br s, 1 H), $\delta(C_6H_5)$ 7.3 (m, 5 H); mass spectrum (mol wt calcd for $C_{16}H_{22}BrF$ 312.0889, found 312.0880), *m/e* (relative intensity) 314 (M^+ + 2, 2) 312 (M^+, 2), 258 (2), 256 (2), 212 (12), 156 (30), 155 (100), 154 (44), 153 (10), 91 (10), 77 (16), 57 (33), 41 (14).

***r*-1-Phenyl-1-fluoro-*c*-2-bromo-*c*-4-*tert*-butylcyclohexane (3c):** yield 42 mg (27%); oily compound; NMR $\delta(F_1)$ −126.5 (ddm, $^3J_{F_1H_6}$ = 14 Hz $^3J_{F_1H_2}$ = 14 Hz), $\delta((CH_3)_3)$ 1.0 (s, 9 H), δ(H) 1.3–2.6 (m, 7 H), $\delta(H_2)$ 4.5 (ddd, 1 H, $^3J_{H_2H_{3e}}$ = 5 Hz, $^3J_{H_2H_{3a}}$ = 14 Hz, $^3J_{F_1H_2}$ = 14 Hz), $\delta(C_6H_5)$ 7.3 (m, 5 H); mass spectrum (mol wt calcd for $C_{16}H_{22}BrF$ 312.0889, found 312.0900), *m/e* (relative intensity) 314 (M^+ + 2, 2), 312 (M^+, 2), 258 (2), 256 (2), 212 (11), 156 (31), 155 (100), 154 (35), 91 (12), 83 (10), 77 (18), 57 (70), 41 (19).

***r*-1-Phenyl-1-fluoro-*c*-2-chloro-*t*-4-*tert*-butylcyclohexane (2d):** yield 17 mg (13%); white crystalline compound; mp 48–50 °C; NMR $\delta(F_1)$ −146.9 (dm, $^3J_{F_1H_6}$ = 45 Hz), $\delta((CH_3)_3)$ 1.0 (s, 9 H), δ(H) 1.7–2.3 (m, 7 H), $\delta(H_2)$ 4.3 (br s, 1 H), $\delta(C_6H_5)$ 7.3 (m, 5 H); mass spectrum (mol wt calcd for $C_{16}H_{22}ClF$ 268.1394, found 268.1390 ;, *m/e* (relative intensity) 270 (M^+ + 2, 4), 268 (M^+, 10), 212 (18), 156 (21), 155 (63), 154 (36), 135 (15), 91 (19), 85 (13), 83 (20), 77 (16), 57 (100), 41 (25).

***r*-1-Phenyl-1-fluoro-*c*-2-chloro-*c*-4-*tert*-butylcyclohexane (3d):** yield 18 mg (13%); oily compound; decomposed on heating; NMR $\delta(F_1)$ −129.7 (ddm, $^3J_{F_1H_6}$ = 14 Hz, $^3J_{F_1H_2}$ = 14 Hz), $\delta((CH_3)_3)$ 0.9 (s, 9 H), δ(H) 1.2–2.4 (m, 7 H), $\delta(H_2)$ 4.3 (ddd, 1 H, $^3J_{H_2H_{3e}}$ = 5 Hz, $^3J_{H_2H_{3a}}$ = 14 Hz, $^3J_{F_1H_2}$ = 14 Hz), $\delta(C_6H_5)$ 7.2 (m, 5 H); mass spectra (mol wt calcd for $C_{16}H_{22}ClF$ 268.1394, found 268.1400), *m/e* (relative intensity) 270 (M^+ + 2, 3), 268 (M^+, 10), 212 (16), 156 (15), 155 (43), 154 (14), 135 (18), 91 (13), 77 (11), 57 (100), 41 (20).

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Hydroxyalkylation with α-Hydroperoxydiazenes. Alcohols from Olefins and Carbonyl Compounds from Enol Ethers

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Alkyl(1-hydroperoxy-1-methylethyl)diazenes **2a–f** [$(CH_3)_2C(OOH)N{=}NR$: **a**, R = CH_2CF_3; **b**, R = CH_2CH_2CN; **c**, R = $CH_2CH(CH_3)CN$; **d**, R = $CH_2CH_2OCH_3$; **e**, R = $CH_2CH_2OC_6H_5$; **f**, R = $CH_2CH_2CH_2OC_6H_5$)] were prepared in solution by autoxidation of the corresponding hydrazones of acetone. Thermolysis of the diazenes at 50–80 °C in alkenes leads to alcohols. For example, **2b** decomposes in 1,1-diphenylethene to afford 5-hydroxy-5,5-diphenylpentanenitrile. Alkenes with abstractable allylic hydrogens gave analogous products, but in very low yield. Thermolysis of a diazene **2** in an enol ether solvent leads to an aldehyde or a ketone. Thus, **2a** decomposes in 1-ethoxyethene and in 2-methoxypropene to afford, respectively, 4,4,4-trifluorobutanal and 5,5,5-trifluoro-2-pentanone. Yields lie in the range from 50% to 70%. The thermolysis of **2** in alkenes involves radical intermediates and radical chain hydroxyalkylation of alkene double bonds. In one chain-propagating step, R·, generated from **2**, adds to the alkene. The adduct radical so formed propagates by inducing decomposition of **2** by attack at hydroxyl oxygen. According to this mechanism, initial products from enol ethers are hemiacetals or hemiketals which do not survive the reaction conditions but decompose to the corresponding carbonyl compounds. Preliminary evidence for this mechanism is presented.

Although α-hydroperoxydiazenes (α-azo hydroperoxides, **1**) have been known for many years as the products of inadvertent or deliberate autoxidation of hydrazones[1] (eq 1), relatively little is known about their chemistry. Their

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