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Synthesis, Characterization, and Reaction Chemistry of *tert*-Butyl Hypofluorite

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Abstract: *tert*-Butyl hypofluorite ($(CH_3)_3COF$) can be synthesized by the low-temperature reaction of elemental fluorine with *tert*-butyl alcohol dissolved in propionitrile or acetonitrile. The isolated compound, which melts around -94 °C and has an extrapolated boiling point of about +40 °C, has been characterized by mass, NMR, and IR spectrometry. The ^{19}F NMR shift of +67 ppm lies between the corresponding shifts of HOF and CH_3OF and implies a rather high O–F bond energy. Although sterically crowded, *tert*-butyl hypofluorite adds to olefins to form β-fluoro-*tert*-butoxy compounds. Addition is mainly in an anti mode, and the regioselectivity corresponds to the action of a hitherto unknown *tert*-butoxylium electrophile. Also formed are adducts containing F and CH_2CN, the latter deriving from the acetonitrile solvent.

Although hypofluorites—compounds containing the OF moiety—have been known for many decades, in most of these compounds the OF group is bonded either to a fully fluorinated residue (CF_3OF, SF_5OF) or to the residue of an inorganic or perfluoroorganic oxyacid (O_2NOF, $CF_3C(O)OF$). In particular, hypofluorites containing hydrogen have only recently been synthesized. An unstable, incompletely fluorinated alkyl hypofluorite (HCF_2CF_2OF) was identified by NMR spectroscopy in the 1960s,[1] but the first well-characterized hydrogen-containing hypofluorite was the archetypal hypofluorous acid (HOF),[2] followed a decade later by acetyl hypofluorite ($CH_3C(O)OF$).[3,4] In recent years, several higher acyl hypofluorites have been reported to result from fluorination of the corresponding carboxylates at low temperatures,[5] but these latest compounds have yet to be isolated or fully characterized.

Unfluorinated alkyl hypofluorites have been particularly resistant to synthesis, until the simplest member of the group, methyl hypofluorite (CH_3OF), was prepared in 1990 and subsequently isolated and characterized.[6,7] Methyl hypofluorite, as expected, decomposes by evolution of HF with concomitant formation of a C=O double bond

$$CH_3OF \rightarrow H_2C{=}O + HF$$

Attempts to prepare higher homologs of CH_3OF by fluorination of ethanol, propanol, or 2,2,2-trifluoroethanol have proven unsuccessful, presumably because an analogous decomposition proceeds even more readily when an O–F group is attached to the same carbon atom as active methylenic hydrogen atoms. Inasmuch as this mode of decomposition would be unavailable to *tert*-butyl hypofluorite ($(CH_3)_3COF$), it would seem reasonable to expect that this compound would be at least as stable as CH_3OF. In the present paper we report on the synthesis and characterization of *tert*-butyl hypofluorite along with an investigation of some of its reactions with olefins.

Results and Discussion

tert-Butyl hypofluorite may be prepared by reaction of elemental fluorine with solutions of *tert*-butyl alcohol in propionitrile at -78 °C and may be isolated by fractional distillation at low temperature. Dilute solutions suitable for fluorinating organic substrates may be prepared by reaction of fluorine with *tert*-butyl alcohol solutions in acetonitrile at -45 °C. At low temperatures, *tert*-butyl hypofluorite is a white solid, melting around -94 °C to a colorless liquid. The liquid and solid show no evidence of decomposition at temperatures of -78 °C or lower, while gradual decomposition is observed as the temperature of the liquid is raised to the ice point. Decomposition of the vapor in a Kel-F vessel or in an IR cell at room temperature is slow, requiring several days for completion. In contrast, the $(CH_3)_3COF$ in the original relatively concentrated propionitrile reaction mixture decomposes completely within 1 min at room temperature. On the other hand, the more dilute solutions in acetonitrile used for reaction with olefins exhibited a half-life of about 1 h at 0 °C. We have been unable to characterize the decomposition products completely. Acetone appears to be formed, along with an oily product of low volatility. Formation of methyl fluoride is not observed.

The vapor pressure of the crude product was found to be 0.28 Torr at -79.1 °C, 0.55 Torr at -72.1 °C, 1.25 Torr at -63.9 °C, 2.6 Torr at -55.6 °C, 5.8 Torr at -45.8 °C, 13.5 Torr at -33.9 °C, and 27.5 Torr at -24 °C. Extrapolation of a plot of ln P vs $1/T$ indicates a normal boiling point of about +40 °C. These results, along with the observed melting point, must be considered highly tentative, however, in view of the uncertain purity of the material.

The mass spectrum of the compound was observed from liquid held at -78 °C, after volatile impurities had been pumped away. The principal mass peaks are at m/e (assignment, relative intensity) 77 ($(CH_3)_2COF^+$, 23%), 58 ($(CH_3)_2CO^+$, 37%), 43 (CH_3CO^+, 100%), 42 ($(CH_3)_2C^+$ and CH_2CO^+, 19%), 41 ($CHCO^+$ and $CH_3CCH_2^+$, 26%), 29 (HCO^+ (?), 20%), 27 (CH_3C^+, 19%), and 15 (CH_3^+, 20%).

The principal bands in the mid-infrared spectrum of *tert*-butyl hypofluorite (4 Torr, AgCl) are seen at cm^{-1} (intensity): 3008/3002/2994 (s), 1479 (mw), 1468 (mw), 1390/1384/1374 (s), 1252/1246/1244 (s), 1201 (ms), 1159 (m), 1088 (m), 948 (w), 932 (w, br), 857/855 (ν_{OF} (?), s), 751 (w), and 517 (mw). The principal bands of propionitrile and *tert*-butyl alcohol were not detected. After the sample had remained in the cell for several days at room temperature, the residual spectrum was essentially that of acetone.

The ^{19}F NMR spectrum of *tert*-butyl hypofluorite shows a broadened singlet at low field (+67 ppm, $\Delta\nu_{1/2} = 7$ Hz), as might be expected for a relatively deshielded fluorine coupled to remote protons. The ^1H NMR spectrum also shows a broadened singlet (1.26 ppm, $\Delta\nu_{1/2} = 9$ Hz), while the ^{13}C spectrum displays two doublets, a relatively intense one at 24 ppm ($^3J_{CF} = 8$ Hz), which

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Table I. Physical Properties of Methyl and *tert*-Butyl Hypofluorites

	CH_3OF	$(CH_3)_3COF$
mp (°C)	ca. −142	ca. −95
bp (°C extrap)	−32.6	ca. 40
ν_{O-F} (cm^{-1})	824.5 (?)^a	855/857 (?)^a
NMR parameters		
δ_H (vs $(CH_3)_4Si$)	4.51	1.26
δ_F (vs $CFCl_3$)	120.3	67
δ_C (vs $(CH_3)_4Si$)	70.3	24, 88
$^2J_{CF}$(Hz)	11	15
$^3J_{CF}$ (Hz)		8
$^3J_{HF}$ (Hz)	45.2	

^{a} Assignment uncertain.

we assign to the methyl carbon atoms of *tert*-butyl hypofluorite, and a much weaker one at 88 ppm ($^2J_{CF}$ = 15 Hz), which we assign to the tertiary carbon atom. As expected, the second of these carbon resonances disappears in the DEPT-135 spectrum. The assignment of all of these resonances to $(CH_3)_3COF$ was confirmed by observing their disappearance as the compound decomposed.

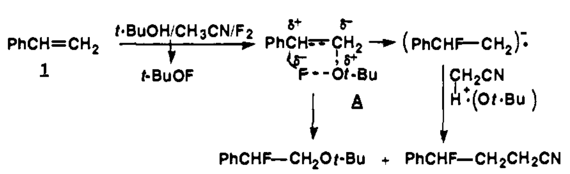
tert-Butyl hypofluorite is the second alkyl hypofluorite to be synthesized, and it may be of some interest to compare its properties with those of its predecessor, methyl hypofluorite. This is done in Table I. The variation in melting and boiling points is more or less what we might expect, while the frequency that we assign to the O–F stretching vibration of *tert*-butyl hypofluorite is considerably higher than that of the methyl compound but fairly close to the O–F stretching frequencies of other hypofluorites.[8]

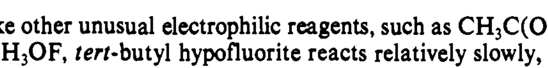
The absence of an observable molecular ion in the mass spectrum of *tert*-butyl hypofluorite is similar to what is seen in the mass spectra of most such compounds. Of the hypofluorites for which mass spectra have been reported, only CH_3OF and HOF show substantial molecular ion intensities, and they should probably be regarded as anomalies. The case of CH_3OF is particularly anomalous, inasmuch as one fragmentation path requires less energy than does simple ionization.[9] This fragmentation, however, involves formation of the fragment ion CH_2OH^+ and thus involves substantial atomic rearrangement.

The ^{19}F NMR chemical shift of the *tert*-butyl compound is substantially less positive than that of CH_3OF; in fact, the only hypofluorite with a less positive shift is HOF itself (+21 to +27 ppm).[10] A negative correlation has been established between ^{19}F shift and O–F bond energy in the hypofluorites,[11] and on the basis of this correlation we may predict that the O–F bond energy in *tert*-butyl hypofluorite will be found to be second only to that in HOF.

Comparison of the chemistry of *tert*-butyl hypofluorite with that of other hypofluorites allows us to attach additional significance to the ^{19}F NMR shifts. Most hypofluorites have shifts greater than +130 ppm[8] and act as electrophilic fluorinating agents.[12] Only three such compounds have smaller shifts (HOF, $(CH_3)_3COF$, and CH_3OF), and in none of these three compounds is the fluorine atom the electrophile. Hypofluorous acid acts as an electrophilic hydroxylating agent,[13] while in the case of methyl and *tert*-butyl hypofluorites, we observe a most unusual electrophilic alkoxylating species—a virtual alkoxylium cation.[7,14] While the *tert*-butoxide anion has, of course, been long known and often used, its counterpart, the *tert*-butoxylium cation, "*t*-BuO$^+$",[15] has never before been described, simply because no group attached to the butoxy moiety has been sufficiently electronegative to withdraw electron density from the oxygen. The hypofluorite fluorine atom has this capability, and *tert*-butyl hypofluorite therefore provides a rare glimpse of the chemistry of the unusual *tert*-butoxylium electrophile.

When *tert*-butyl hypofluorite was reacted with styrene (**1**), a single regioisomer (1-fluoro-1-phenyl-2-*tert*-butoxyethane, **2**) was formed in good yield, underscoring the electrophilicity of the *tert*-butoxyl oxygen atom. However, it should be pointed out that unlike other unusual electrophilic reagents, such as $CH_3C(O)OF$ or CH_3OF, *tert*-butyl hypofluorite reacts relatively slowly, presumably because of the large steric effects associated with the *tert*-butoxyl group. It was thus necessary to use a 5-fold or greater excess of the *tert*-butyl hypofluorite in order to achieve complete reaction before the reagent had decomposed. In addition to the expected product **2**, however, we also observed formation of small quantities of 1-fluoro-1-phenyl-3-cyanopropane (**3**), which incorporates part of the acetonitrile solvent molecule. Although we do not yet know the exact mechanism involved in the formation of this minor product, it is reasonable to assume that both **2** and **3** originate from the same transition state **A**, in which as a result of the strong steric hindrance only weak carbon–oxygen interactions are formed. One relaxation pathway for this transition state is the expected collapse to **2**, but an alternative is the attack of the radical anion on a nearby solvent molecule to form **3** and *tert*-butyl alcohol. Such a mechanism seems more likely than a purely radical one, since all the cyano derivatives are known to have excellent regiospecificity, and the CH_2CN group is always vicinal to the fluoride atom. What is more, addition of nitrobenzene or other radical scavengers does not change the reaction rate or the final result. A similar reaction was observed with 1,1-diphenylethylene (**4**), producing 1-fluoro-1,1-diphenyl-2-*tert*-butoxyethane (**5**) along with 1-fluoro-1,1-diphenyl-3-cyanopropane (**6**).





With somewhat more hindered olefins, such as *trans*-1-phenyl-1-propene (**7**), the reaction proceeds even more slowly, and we were compelled to use up to a 10-fold excess of *tert*-butyl hypofluorite to accomplish a reasonable 60% conversion. Although in this case only traces of the corresponding cyano derivative were formed, two stereoisomers, *erythro*- and *threo*-1-fluoro-1-phenyl-2-*tert*-butoxypropane (**8**), were obtained in a ratio of 3:1. The stereoisomers originate respectively from anti and syn mode addition. Taking the gauche effect into consideration, **8A** and **8B** are the respective conformers of the erythro (anti addition) and threo isomers that make the greatest contributions. The vicinal HH coupling constant in the erythro isomer should therefore be smaller than in the threo one, while $^3J_{HF}$ should be larger.[16] The

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(15) Describing an electrophile in such a way is well accepted by now. It is important to note, however, that a designation such as "*t*-BuO$^+$" does not imply that a free positive *tert*-butoxylium ion is floating around nor even that the *tert*-butoxyl group in the reagent molecule has a partial positive charge. What it does mean is that the *tert*-butoxyl group is the part of the reagent molecule with the greatest electron affinity. This point has been discussed in detail in Lerman, O.; Tor, Y.; Hebel, D.; Rozen, S. *J. Org. Chem.* **1984**, *49*, 806–813 (note 12, p 807).

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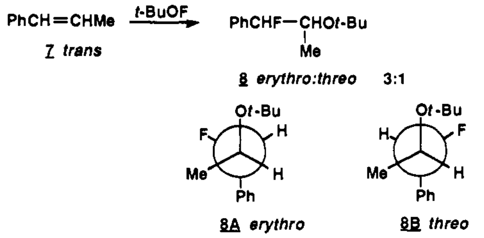
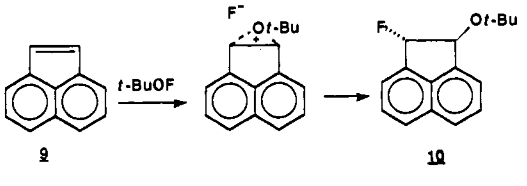


dominant anti addition, which is typical of a stable, epoxide-like oxonium transition state, appears in sharp contrast to the addition to olefins of the more orthodox hypofluorites, such as CF_3OF, CF_3CF_2OF, and $CH_3C(O)OF$. The latter proceed in a syn mode, since in these cases the electrophilic fluorine reacts to form the extremely unstable α-fluorocarbocation.[17,18]

In the case of acenaphthylene (**9**), the rigid double bond provides an extra stabilization to the intermediate oxonium bridge, and only the anti adduct *threo*-1-fluoro-2-*tert*-butoxyacenaphthene (**10**) is formed, along with traces of the corresponding cyano derivative.



Conclusion

In this paper we have described the synthesis and characterization of *tert*-butyl hypofluorite, the second member of a new family of alkyl hypofluorites. We have demonstrated that the compound can be easily made and that it is relatively stable, perhaps more so than we might have anticipated. Very recent studies with methyl hypofluorite, the first member of this new family, indicate that it may prove to be a useful reagent for electrophilic methoxylation.[14] Although we have only begun to elucidate the chemical behavior of the *tert*-butyl hypofluorite, we have already shown that it can serve as a source of the unique *tert*-butoxylium electrophile, and we are confident that future investigations will bring to light new applications for this promising reagent.

Experimental Section

CAUTION: The synthesis described here entails the use of elemental fluorine, a toxic, highly reactive, and extremely corrosive gas, and anyone undertaking to repeat this work should be thoroughly familiar with the proper procedures for its safe handling. (See, for example, ref 19.) In particular, adequate ventilation should be assured at all times, and all contact with readily oxidizable materials should be avoided. Passage of fluorine through solutions of *tert*-butyl alcohol in acetonitrile or propionitrile can itself lead to combustion, and appropriate precautions should be taken. After preparation, solutions of *tert*-butyl hypofluorite in acetonitrile or propionitrile are powerful oxidants but are otherwise not particularly hazardous. *Neat tert*-butyl hypofluorite, however, must be regarded as a substance the hazards of which have not yet been fully defined. Simple prudence dictates that the neat compound be prepared in no greater quantities than are absolutely required and that use be made of face shields, gloves, and explosion barriers when working with it.

Reagents. Elemental fluorine was obtained from Air Products and Chemicals as a 20% v/v mixture with argon or from Kali Chemie as the neat (95%) material. Commercially available solvents and organic substrates were used without additional purification.

Vapor Pressure and Melting Point Measurements. The vapor pressure of $(CH_3)_3COF$ was measured in a small vacuum line equipped with an MKS Baratron pressure gauge. During these measurements the liquid was contained in a Kel-F tube, while the vapor came in contact with stainless steel, Monel, nickel, and Kel-F. The melting point of $(CH_3)_3COF$ was measured on a sample contained in a Kel-F tube immersed in an ethanol bath in an unsilvered Dewar flask. Temperatures for melting point and vapor pressure measurements were determined to ±0.1 °C with a copper–constantan thermocouple calibrated against a platinum resistance thermometer.

Mass, Infrared, and NMR Spectrometry. The 70-eV electron-impact mass spectra of $(CH_3)_3COF$ and its decomposition products were determined with a Finnigan 400 quadrupole mass spectrometer equipped with a Kel-F inlet tube and using a data system provided by Shrader Analytical Labs. The infrared spectrum of $(CH_3)_3COF$ vapor was measured at ambient temperature at 1 cm^{-1} resolution with a Nicolet 510P FTIR spectrometer. Samples were contained in a Kel-F cell of 10-cm path length, fitted with AgCl windows. NMR spectra of $(CH_3)_3COF$ solutions in CD_2Cl_2 were measured in glass tubes (10-mm o.d. for ^{13}C, 5-mm o.d. for ^1H and ^{19}F) on a Bruker AM300 spectrometer. The sample probe was cooled to −80 °C. The ^{19}F spectra, measured at 282.4 MHz, were referenced to internal $CFCl_3$. The ^1H spectra, measured at 300.1 MHz, were referenced to the $CDHCl_2$ solvent proton, which was taken to have a shift of 5.32 ppm vs $(CH_3)_4Si$. The broadband proton-decoupled ^{13}C spectra were measured at 75.5 MHz with respect to the carbon of the CD_2Cl_2 solvent, taken as 53.8 ppm vs $(CH_3)_4Si$. The ^{13}C measurements were made both with and without the DEPT-135 pulse sequence. Assignment of NMR resonances to $(CH_3)_3COF$ was confirmed by noting their disappearance after a sample had been warmed to room temperature, recooled, and the NMR spectrum remeasured.

The NMR spectra of the products of reaction of *tert*-butyl hypofluorite with olefins were recorded in $CDCl_3$ at ambient temperature on a Bruker AM-360 WB spectrometer. Proton spectra were measured at 360 MHz and referenced to internal $(CH_3)_4Si$. The ^{19}F spectra were measured at 338.8 MHz and referenced to internal $CFCl_3$. The broadband proton-decoupled ^{13}C spectra were recorded at 90.5 MHz and also referenced to internal $(CH_3)_4Si$; only the C–F couplings were observed. Mass spectra (70-eV electron-impact) and IR spectra (KBr pellets) of these reaction products were measured respectively with a Du Pont 21-491B and a Perkin-Elmer 177 spectrometer.

Preparation and Isolation of $(CH_3)_3COF$. Apparatus and fluorine handling procedures are similar to those that we have described previously.[7] Fluorine (20% v/v in argon) was passed at a rate of ca. 100 cm^3/min through 4 cm^3 of a 20% v/v solution of dry *tert*-butyl alcohol in propionitrile contained in a Teflon-brand vessel at −78 °C. The buildup of oxidizing power in the solution was monitored by adding samples to an acidified solution of KI and titrating the resulting iodine with thiosulfate. An oxidant concentration of ca. 1.8 N (3.6 mmol $(CH_3)_3COF$) was reached after about 1 h. The solution was then warmed to about −45 °C while a stream of nitrogen at 100 cm^3/min was passed through it to transfer a portion of the hypofluorite into a Kel-F U-tube fitted with Kel-F valves and cooled with liquid nitrogen. The U-tube was then connected to a Kel-F vacuum manifold, and the nitrogen was pumped away, after which the tube was warmed to about −78 °C and pumped on for ca. 15 min to remove relatively volatile impurities. Less volatile impurities were removed by fractionation from a $CHCl_3$ slush bath at ca. −64 °C.

To prepare samples for ^1H and ^{13}C NMR measurements, a nitrogen stream was passed through the original mixture at −45 °C and then into a tube containing CD_2Cl_2 cooled to −78 °C. In this way a sample was obtained that was about 0.08 M in $(CH_3)_3COF$. Samples for ^{19}F NMR were prepared by adding 75 mm^3 of the propionitrile reaction mixture to ca. 0.5 cm^3 of CD_2Cl_2.

Larger-Scale Preparation of *tert*-Butyl Hypofluorite Solutions and Reactions with Olefins. Since no isolation of the hypofluorite is needed when the reagent is to be used for reactions with organic substrates, a somewhat different procedure was adopted for such cases. Typically 10 cm^3 of *tert*-butyl alcohol was dissolved in 230 cm^3 of cold (−45 °C) acetonitrile in a glass vessel, and F_2 (15 vol % in N_2) was bubbled through it until ca. 50 mmol of oxidizing *tert*-butyl hypofluorite was formed. The organic substrate (10–20 mmol), dissolved in cold (0 °C) CH_2Cl_2, was added in one portion, and the temperature was then allowed to rise to 0 °C. The progress of the reaction was monitored by following the disappearance of the oxidizing power (iodometric titration) and of the starting material (GC). Reaction appeared complete after about 30 min, and the mixture was poured into 400 cm^3 of dilute $NaHCO_3$ solution and stirred until neutral. It was then dried over anhydrous $MgSO_4$, and the solvent was removed. The crude product was purified in most cases by vacuum flash chromatography, using Silicagel 60-H (Merck) and eluting with mixtures of petroleum ether and ethyl acetate.

Reaction of *tert*-Butyl Hypofluorite with Styrene (1). One gram of **1** (10.6 mmol) was reacted with the oxidizing solution containing 50 mmol of *tert*-butyl hypofluorite. Two compounds were isolated by chromatography. The less polar one proved to be 1-fluoro-1-phenyl-2-*tert*-butoxyethane (**2**), oil, 60% yield: ^1H NMR (ppm) 7.35–7.20 (5 H,

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1382 *J. Am. Chem. Soc.* **1993**, *115*, 1382–1396

m), 5.55 (1 H, ddd, $J_1 = 48$ Hz, $J_2 = 8$ Hz, $J_3 = 2$ Hz), 3.4–3.8 (2 H, m), 1.2 (9 H, s); ^{19}F NMR −149.3 ppm (m); ^{13}C NMR (ppm) 128–125 (C_{arom}), 93.6 (d, $^1J_{CF} = 180$ Hz), 73.5 (s, $(CH_3)_3C$), 66.4 (d, $^2J_{CF} = 25$ Hz), 27.3 (s); MS *m/e* 123 ($PhCHFCH_2^+$), 109 ($PhCHF^+$). Anal. Calcd for $C_{12}H_{17}FO$: C, 73.47; H, 8.67. Found: C, 73.69; H, 8.90. The more polar fraction proved to be 1-fluoro-1-phenyl-3-cyanopropane (**3**), oil, 15% yield: IR 2248 cm^{-1}; ^{1}H NMR (ppm) 7.45–7.24 (5 H, m), 5.59 (1 H, ddd, $J_1 = 48$ Hz, $J_2 = 8$ Hz, $J_3 = 4$ Hz), 2.52 (2 H, dd, $J_1 = 15$ Hz, $J_2 = 9$ Hz), 2.28–2.10 (2 H, m); ^{19}F NMR −180.1 ppm (m); ^{13}C NMR (ppm) 136–125 (C_{arom}), 118 (*C*N), 92.05 (d, $^1J_{CF} = 172$ Hz), 32.7 (d, $^2J_{CF} = 26$ Hz), 13.2 (s); MS *m/e* 163 (M^+), 143 [$(M - HF)^+$], 109 ($PhCHF^+$). Anal. Calcd for $C_{10}H_{10}FN$: C, 73.62; H, 6.13; N, 8.59; F, 11.66. Found: C, 73.36; H, 6.37; N, 8.42; F, 12.09.

Reaction of *tert*-Butyl Hypofluorite with 1,1-Diphenylethene (4). When 1.8 g of **4** (10 mmol) was reacted with 50 mmol of *tert*-butyl hypofluorite, the less polar compound isolated by chromatography proved to be 1-fluoro-1,1-diphenyl-2-*tert*-butoxyethane (**5**), oil, 70% yield: ^{1}H NMR (ppm) 7.45–7.26 (10 H, m), 3.99 (2 H, d, $J = 20$ Hz), 1.14 (9 H, s); ^{19}F NMR −152.0 ppm (t, $J = 20$ Hz); MS *m/e* 252 [$(M - HF)^+$], 195 [$(M - HF - (CH_3)_3C)^+$], 185 (Ph_2CF^+). The compound tends to decompose at room temperature, and no analytically pure sample could be obtained. The more polar fraction proved to be 1-fluoro-1,1-diphenyl-3-cyanopropane (**6**), mp 48 °C, 15% yield: IR 2246 cm^{-1}; ^{1}H NMR (ppm) 7.40–7.27 (10 H, m), 2.86–2.69 (2 H, m), 2.37 (2 H, M); ^{19}F NMR −152 ppm (t, $J = 22.5$ Hz); MS *m/e* 239 (M^+), 219 [$(M - HF)^+$], 185 (Ph_2CF^+). Anal. Calcd for $C_{16}H_{14}FN$: C, 80.33; H, 5.85; Found: C, 79.87; H, 5.50.

Reaction of *tert*-Butyl Hypofluorite with *trans*-1-Phenyl-1-propene (7). When 0.6 g of **7** (5 mmol) was reacted with the oxidizing solution containing 50 mmol of *tert*-butyl hypofluorite, the only compound isolated by chromatography proved to be 1-fluoro-1-phenyl-2-*tert*-butoxypropane (**8**), oil, 80% yield (60% conversion). This adduct, however, is a 3:1 mixture of the corresponding erythro and threo isomers. For the erythro isomer: ^{1}H NMR (ppm) 7.36–7.27 (5 H, m), 5.24 (1 H, dd, $J_1 = 47$ Hz, $J_2 = 4.5$ Hz), 3.85 (1 H, m), 1.1 (9 H, s), 0.96 (3 H, d, $J = 8$ Hz); ^{19}F NMR −190.5 ppm (dd, $J_1 = 47$ Hz, $J_2 = 16$ Hz); ^{13}C NMR (ppm) 128–126 (C_{arom}), 96.6 (d, $^1J_{CF} = 192$ Hz), 73.8 (s, (CH_3C), 70.6 (d, $^2J_{CF} = 25$ Hz), 28 (s), 18 (CH_3CH, s); MS *m/e* 190 [$(M - HF)^+$], 133 [$(M - Ph)^+$], 109 ($PhCHF^+$). Anal. Calcd for $C_{13}H_{19}FO$: C, 74.29; H, 9.05; F, 9.05. Found: C, 74.09; H, 9.08; F, 8.64. For the minor threo isomer: ^{1}H NMR (ppm) 5.19 (1 H, dd, $J_1 = 46$ Hz, $J_2 = 6$ Hz); ^{19}F NMR −182.3 ppm (dd, $J_1 = 46$ Hz, $J_2 = 13$ Hz); ^{13}C NMR (ppm) 95.5 (d, $^1J_{CF} = 185$ Hz), 69.4 (d, $^2J_{CF} = 25$ Hz), 19.6 (CH_3CH, s).

Reaction of *tert*-Butyl Hypofluorite with Acenaphthylene (9). When 1.5 g of **9** (10 mmol) was reacted with the oxidizing solution containing 50 mmol of *tert*-butyl hypofluorite, the only product isolated by chromatography proved to be *threo*-1-fluoro-2-*tert*-butoxyacenaphthene (**10**), oil, 90% yield (60% conversion); ^{1}H NMR (ppm) 7.79–7.37 (6 H, m), 6.2 (1 H, dd, $J_1 = 54$ Hz, $J_2 = 1.5$ Hz), 5.54 (1 H, dd, $J_1 = 22$ Hz, $J_2 = 1.5$ Hz), 1.45 (9 H, s); ^{19}F NMR −173.7 ppm (dd, $J_1 = 54$ Hz, $J_2 = 22$ Hz); ^{13}C NMR (ppm) 128–120 (C_{arom}), 102.6 (d, $^1J_{CF} = 182$ Hz), 80.7 (d, $^2J_{CF} = 26$ Hz), 75.1 (s, $(CH_3)_3C$, 28.5 (s); MS *m/e* 244 (M^+), 187 [$(M - (CH_3)_3C)^+$]. Anal. Calcd for $C_{16}H_{17}FO$: C, 78.69; H, 6.97; F, 7.79. Found: C, 78.13; H, 6.41; F, 7.60.

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Metal-Promoted Higher-Order Cycloaddition Reactions. Stereochemical, Regiochemical, and Mechanistic Aspects of the [6π + 4π] Reaction

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Abstract: Transition-metal-promoted higher-order cycloaddition reactions are described. (η^6-1,3,5-Cycloheptatriene)tricarbonylchromium(0) and various substituted derivatives undergo photochemically or thermally initiated [6π + 4π] cycloaddition with a range of substituted butadiene partners. Electron-rich and electron-deficient dienes participate equally well in the transformation, and in every case examined only the endo diastereomer was produced. The reaction displays little regioselectivity for 2- and 3-substituted cycloheptatriene complexes; however, most yields of products exceed 85%. Chiral auxiliaries appended to the diene partner can provide very good stereoinduction in the resultant bicyclo[4.4.1]undecane adducts. Tropone and 1-substituted tropone complexes also undergo photoinduced cycloadditions with hydrocarbon dienes but not with oxygen-substituted partners. Azepine and thiepin 1,1-dioxide complexes engage dienes to provide high yields of the corresponding heterocyclic adducts. Molybdenum- and tungsten-based complexes are inferior to Cr(0) complexes as 6π partners in the [6 + 4] cycloaddition, and tungsten has been totally ineffective for promoting the cycloadditions studied to date. Possible mechanistic schemes are presented, and the implications of each are discussed with regard to the scope and limitations of the cycloaddition reaction. Optimization of the reaction conditions on the basis of the aspects of these mechanisms is also outlined. The [6 + 4] cycloaddition of cycloheptatrienechromium(0) complexes can also be effected by heating in various ether solvents, and the cycloadducts produced in this fashion are identical in all respects with those prepared photochemically. The [6 + 4] reaction can also be carried out with modest efficiency employing only catalytic quantities of chromium(0) catalysts.

Introduction

The application of so-called higher-order cycloaddition reactions (i.e., those involving 6π + 4π, 4π + 4π, and 6π + 2π combinations (Figure 1)) to problems in organic synthesis has been of relatively limited scope, although most known examples of these transformations exhibit many features that are considered attractive from a synthetic perspective.[1] In general, higher-order cycloaddition reactions proceed with very high levels of predictable stereoselectivity and can accommodate substantial functionalization in the participating addends. Furthermore, these processes are in-

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(1) For recent reviews of higher-order cycloaddition chemistry as applied to synthesis, see: (a) Hosomi, A.; Tominaga, Y. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 5, pp 593–615. (b) Rigby, J. H. *Ibid.*; Vol. 5, pp 617–643. (c) Wender, P. A.; Siggel, L.; Nuss, J. M. *Ibid.*; Vol. 5, pp 645–673.

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