tert-Butyl Hypofluorite—An Electrophilic *tert*-Butoxylation Agent

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tert-Butyl hypofluorite, *t*-BuOF, easily synthesized from *t*-BuOH and F_2, is a unique source of the novel electrophilic *tert*-butoxylium moiety *t*-BuO^+. It was added to several benzylic double bonds to form vicinal fluoro-*tert*-butoxide derivatives. Not surprisingly, this bulky reagent is quite sensitive to steric hindrance. The process is electrophilic in nature, but since the reaction is relatively slow (20−60 min) formation of various radical species can take place, forming eventually several distinct byproducts. *t*-BuOF was also reacted with a number of enols, producing the corresponding α-*tert*-butoxy ketone derivatives in moderate to good yields. The best results were obtained with benzylic enol derivatives.

While the chemistry of the negatively charged *tert*-butoxide is well-established, the chemistry of the *tert*-butoxylium species is practically nonexistent. A few years ago we developed the HOF·CH_3CN complex,[1] in which the fluorine-bound hydroxylium moiety—HO^+—reacts as an electrophile and is used for powerful oxidations, fast epoxidations, and various hydroxylation reactions.[2] More recently, we have demonstrated that the elusive CH_3OF, the smallest unknown organic molecule at the time, could be synthesized and serve as a source of the methoxylium species, MeO^+, used in electrophilic methoxylations.[3] *t*-BuOF was the second member[4] of the alkyl hypofluorite family to be prepared, isolated, and fully characterized.[5] As with CH_3OF, the fluorine-bound *tert*-butoxylium moiety, *t*-BuO^+,[6] seems to possess an electrophilic nature, a feature which is demonstrated here in its reactions with various π centers.

tert-Butyl hypofluorite can be easily prepared by the reaction of fluorine with *tert*-butyl alcohol using acetonitrile as a solvent. Its isolation and purification are quite tedious, but these steps are usually unnecessary, since it can be used in situ as generated. *t*-BuOF adds smoothly across unhindered benzylic double bonds such as in styrene (**1**) or 1-vinylnaphthalene (**2**), forming 1-fluoro-1-phenyl-2-*tert*-butoxyethane (**4**) or 1-fluoro-1-naphthyl-2-*tert*-butoxyethane (**3**) in 60% yield each. The regiochemistry of the reaction (we have not detected any 1-aryl-1-*tert*-butoxyethane derivatives) strongly suggests an initial electrophilic attack of the *tert*-butoxylium moiety. A somewhat better yield was obtained with the more electron rich double bond of 4-methoxystyrene (**5**), which gave the corresponding adduct 1-fluoro-1-(4-methoxyphenyl)-2-*tert*-butoxyethane (**6**) in 70% yield. When a mixture of **1** and **5** was reacted with less than 1 mol equiv of *t*-BuOF, twice as much **6** was obtained compared to **3**, in accordance to the electrophilic nature of the reagent (Scheme 1). The mainly anti addition mode could be easily discerned from the reaction with indene (**7**), which formed 1α-fluoro-2*β*-*tert*-butoxyindan (**8**) in good yield. This stereochemistry is in sharp contrast to the syn addition of all reactions involving electrophilic fluorine.[7] The difference is attributed to the geometry of the electrophile, where, unlike with the small fluorine atom, the oxygen is capable of forming an oxonium bridge such as in **8a**.

The lower electron density of nonbenzylic double bonds was responsible for generally more sluggish reactions. Thus when cyclohexene was reacted with *t*-BuOF, only a low yield of a stereoisomeric mixture of 2-fluoro-*tert*-butoxycyclohexanes (**9**) was obtained. This result prompted us to examine the reactions of *t*-BuOF with more electron rich double bonds such as various enol derivatives.

α-*t*-Butoxy ketones are known and usually prepared with the aid of metal catalysts.[8] The electrophilic *tert*-butoxylium moiety in *t*-BuOF, by attacking the electron rich pole of the π regions of various enols, should offer a novel way to introduce the *tert*-butoxy group into the α-position of ketones without the use of heavy metal agents.

When the enol acetate or the trimethylsilyl enol ether of 1-indanone (**10a** or **10b**) was treated with *t*-BuOF, 2-*tert*-butoxy-1-indanone (**11**) was isolated in 45% and 40% yield, respectively. Similarly, tetralone trimethylsilyl enol ether **12b** or its methyl enol ether **12c** afforded the expected 2-*tert*-butoxy-1-tetralone (**13**) in good yields. The reaction seems to proceed through an addition elimination pathway, associated with most electrophilic reagents possessing the OF moiety.[9] Support for this assumption could be found in the reaction of *tert*-butyl

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(3) Rozen, S.; Mishani, E.; Kol, M.; Ben-David, I. *J. Org. Chem.* **1994**, *59***,** 4281. Kol, M.; Rozen, S. *J. Org. Chem.* **1993**, *58*, 1593. Rozen, S.; Mishani, E.; Kol, M. *J. Am. Chem. Soc.* **1992,** *114*, 7643.
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(5) Appelman, E. H.; French, D.; Mishani, E.; Rozen, S. *J. Am. Chem. Soc.* **1993**, *115*, 1379.
(6) It should be noted that as with F^+ and CH_3O^+, the notation *t*-BuO^+ only indicates that in the transition state the *tert*-butoxylium pole acts as an electrophile with the counterpole being a good leaving group. For more detailed discussion, see: Lerman, O.; Tor, Y.; Hebel, D.; Rozen, S. *J. Org. Chem.* **1984**, *49***,** 806.
(7) Rozen, S.; Lerman, O. *J. Org. Chem.* **1980**, *45*, 4122. Rozen, S.; Lerman, O.; Kol, M.; Hebel, D. *J. Org. Chem.* **1985,** *50*, 4753. Rozen, S.; Brand, M. *J. Org. Chem.* **1986,** *51*, 3607. Rozen, S.; Bareket, Y.; Kol, M. *J. Fluorine Chem.* **1993,** *61***,** 141.
(8) a) Takebayashi, M.; Ibata, T.; Kohara, H.; Kim, B. H. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2392. (b) Nakatsuka, T.; Mukaiyama, T. *Chem. Lett.* **1982**, 369.
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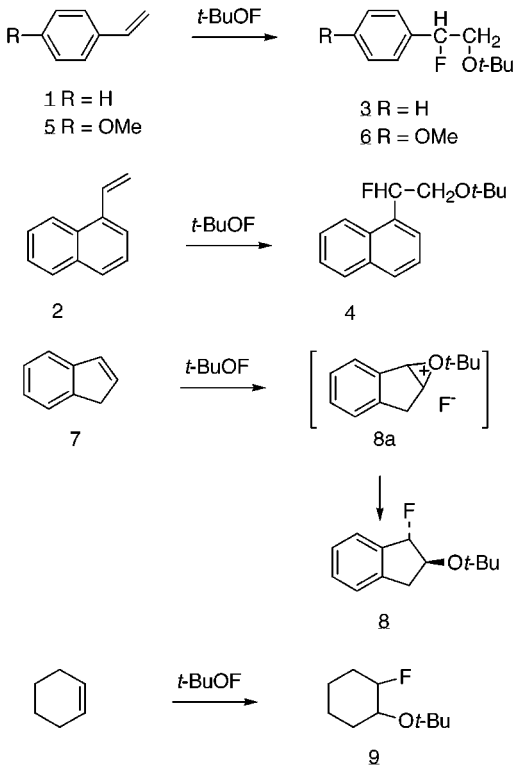
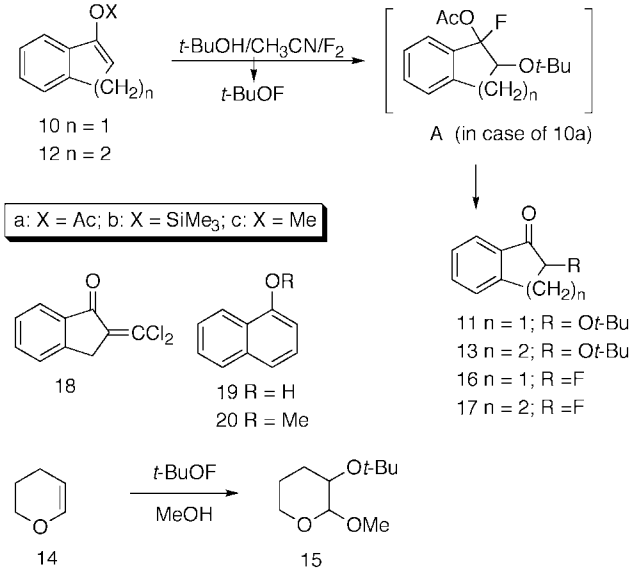
Scheme 1

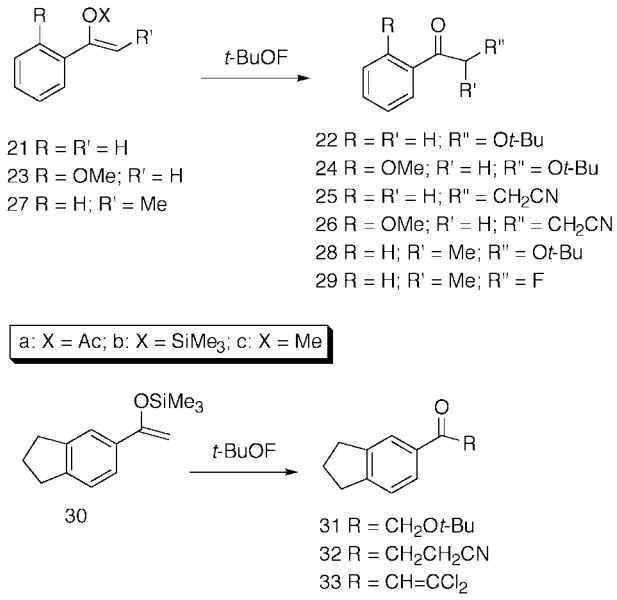


Scheme 2



hypofluorite with **10a**, in which an intermediate **A** was isolated and characterized (Scheme 2). This adduct, however, was unstable and eventually decomposed to the expected **11**. Another question was whether the incorporated *tert*-butoxy group originated from the reagent or from some secondary reaction with *tert*-butyl alcohol, present in the reaction medium. We treated 3,4-dihydropyrane (**14**), an enol ether of an aldehyde, with *tert*-butyl hypofluorite in the presence of methanol as a competitive nucleophile. The only isolated product, 3-*tert*-butoxy-2-methoxytetrahydropyrane (**15**), is in support of the electrophilic attack of the *tert*-butoxylium moiety. Moreover, addition of nitrobenzene or other radical scavengers does not change the reaction rate or the final result.

Scheme 3



It should be noted that in all reactions of **10** and **12** small amounts of 2-fluoro-1-indanone (**16**)[10] and 2-fluoro-1-tetralone (**17**)[11] were formed, as well as 2-dichloromethylene-1-indanone (**18**) in the case of **10**. Small amounts of 1-naphthol (**19**) or 1-naphthyl methyl ether (**20**), from the reaction of **12b** and **12c** respectively, were also detected. We believe that the formation of these byproducts is the outcome of the relatively long reaction times needed for the bulky $(CH_3)_3COF$ to react, inevitably resulting in some radical decomposition of the reagent, whose half-life time at room temperature is about 1 h. In addition to forming small amounts of fluorine radicals, this decomposition also induced the formation of CCl_3 radicals from the chloroform used as a solvent. This competitive radical decomposition was also evident when the electron-poor double bond of 1-hexene was the substrate. With usual reaction conditions, only tars were eventually produced, so we substituted the acetonitrile with propionitrile and added the substrate to the *t*-BuOF solution which was cooled to −78 °C. Warming the reaction mixture slowly did not produce any desired adduct, but we were able to isolate 2,3-dicyanobutane,[12] which apparently resulted from coupling of two α-propionitrile radicals, $CH_3CH^{\bullet}CN$.

Enol derivatives of open chain benzylic ketones also proved to be suitable substrates. Acetophenone trimethylsilyl enol ether (**21b**) gave 2-*tert*-butoxy-acetophenone (**22**)[8a] in 50% yield, while the less sterically hindered methyl enol ether **21c** was converted into **22** in a higher yield of 65% (Scheme 3). Similarly, *o*-methoxyacetophenone methyl enol ether (**23c**) gave 2-*tert*-butoxy-*o*-methoxyacetophenone (**24**) in 50% yield. In both cases, minor byproducts identified as 3-cyanopropiophenone (**25**)[13] and 3-cyano-*o*-methoxypropiophenone (**26**)[14] (15% yield each) were also obtained from solvent (CH_3CN) incorporation, apparently through a radical pathway. We have also

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reacted the more sterically hindered propiophenone trimethylsilyl enol ether (**27**) with *t*-BuOF, resulting in 2-*tert*-butoxypropiophenone (**28**) in moderate yield. Here too, it was possible to detect a small amount of 2-fluoropropiophenone (**29**)[15] as a byproduct. 5-Acetylindan trimethylsilyl enol ether (**30**) was also reacted to give 5-*tert*-butoxyacetylindan (**31**), along with small amounts of 5-(1-cyano-3-propanone)indan (**32**) and 5-(1,1-dichloro-1-en-3-propanone)indan (**33**).

tert-Butoxylation with *tert*-butyl hypofluorite seems to be of limited use with aliphatic and nonbenzylic ketones. The methyl enol ethers of 4-*tert*-butyl cyclohexanone and adamantyl methyl ketone, as well as trimethylsilyl enol ethers of pinacolone and cyclooctanone, did not react satisfactorily and produced either tars or very low yields of the desired α-*tert*-butoxy ketones. This probably reflects the relatively low electron density of the enolic double bond of aliphatic ketones, resulting in insufficient nucleophilicity toward *t*-BuOF.

Experimental Section

^{1}H NMR and decoupled ^{13}C NMR spectra were recorded with 200 and 360 spectrometers, with $CDCl_3$ as solvent and Me_4Si as internal standard. The ^{19}F NMR spectra were measured at 338.8 MHz and are reported in ppm upfield from $CFCl_3$, which also served as internal standard. IR spectra were recorded as neat films, in $CHCl_3$ solution or in KBr pellets.

General Procedure for Working with Fluorine. Fluorine is a strong oxidant and a very corrosive material. An appropriate vacuum line made from copper or monel in a well-ventilated area should be constructed for working with this element. Additional experimental information on how we handle it may be found in ref 16. For the occasional user, however, various premixed mixtures of F_2 in inert gases are commercially available, simplifying the whole process. The reactions themselves can be carried out in glass vessels. If elementary precautions are taken, work with fluorine is relatively simple, and we have had no bad experiences working with it.

Preparation and General Reactions of *t*-BuOF. A mixture of 15% F_2 in N_2 was bubbled for 1 h at a rate of 200 mL/min into a cold (−40 °C) solution of 7.5 mL $(CH_3)_3COH$ in 173 mL of CH_3CN placed in a Teflon vessel. The amount of the $(CH_3)_3COF$ thus obtained could easily be determined by reacting aliquots of the reaction mixture with aqueous KI and titrating the liberated iodine. After the desired concentration of *t*-BuOF was achieved, usually around 0.1−0.2 M, a cold (0 °C) solution of the substrate in $CHCl_3$ was added and the mixture allowed to warm to 0 °C. The reactions were usually carried out on scales of 3−20 mmol using a 5−10-fold excess of *t*-BuOF. It should be noted that although pure liquid *t*-BuOF can explode,[5] it is perfectly safe when diluted with solvents. The progress of the reactions was usually monitored by following the disappearance of the oxidizing power of the reagent (iodometric titration) and starting material (GC). The duration of the reaction was usually 15−60 min, considerably slower than other reactions where electrophilic fluorine or oxygen species, such as $HOF{\cdot}CH_3CN$[2] or CH_3OF,[3] are involved. The term "usual work up" refers to terminating the reaction by pouring it into $NaHCO_3$ solution, extracting with $CHCl_3$, washing the organic layer with water until neutral, drying it over $MgSO_4$, and finally evaporating the solvent. The crude reaction mixture was usually subjected to vacuum flash chromatography using Silica gel 60-H (Merck) and mixtures of ethyl acetate in petroleum ether as eluent.

Synthesis of Enol Derivatives. The enol acetates and silyl enol ethers were prepared from the corresponding ketones by standard procedures (e.g., with isopropenyl acetate/sulfuric acid or trimethylsilyl triflate/triethylamine). The methyl enol ethers were prepared by mixing 1 mol equiv of the appropriate ketone with 1.1 mol equiv of trimethyl orthoformate, in the presence of 0.005 mol equiv of *p*-toluenesulfonic acid at room temperature overnight. The methanol and methyl formate formed were distilled off slowly for at least 4 h until no more methanol was formed. The methyl enol ethers were distilled under reduced pressure. Most of the enol derivatives are known, so spectral data are only reported for the few unknown compounds.

Reaction of *t*-BuOF with styrene (1) was carried out as described to give 1-fluoro-1-phenyl-2-*tert*-butoxyethane (**3**) as an oil, in 60% yield.[5]

Reaction of *t*-BuOF with 1-vinylnaphthalene (2) gave 1-fluoro-1-naphthyl-2-*tert*-butoxyethane (**4**): oil, 60% yield; ^{1}H NMR 7.85−7.43 (7 H, m), 5.73 (1 H, ddd, $J_1 = 48$ Hz, $J_2 = 8$ Hz, $J_3 = 3$ Hz), 3.89−3.5 (2 H, m), 1.18 (9 H, s); ^{19}F NMR −183.98 (m); ^{13}C NMR 132.9−123.4, 93.9 (d, $^1J_{CF} = 174.5$ Hz), 73.6 (s), 66.13 (d, $^2J_{CF} = 25$ Hz), 27.4 (s); MS *m*/*z* 246 (M^+), 173 $(M - t\text{-BuO})^+$. Anal. Calcd for $C_{16}H_{19}FO$: C, 78.04; H, 7.72; F, 7.72. Found: C, 77.56; H, 7.86; F, 7.72.

Reaction of *t*-BuOF with 4-methoxystyrene (5) gave 1-fluoro-1-(4-methoxyphenyl)-2-*tert*-butoxyethane (**6**): oil, 60% yield; ^{1}H NMR 7.35−7.25 (2 H, m), 6.96−6.84 (2 H, m), 5.48 (1 H, ddd, $J_1 = 48$ Hz, $J_2 = 8$ Hz, $J_3 = 3$ Hz), 3.8 (3 H, s), 3.6−3.45 (2 H, m), 1.21 (9 H, s); ^{19}F NMR −131.23 (m); ^{13}C NMR 127.4−113.6, 93.4 (d, $^1J_{CF} = 182$ Hz), 73.5 (s), 65.96 (d, $^2J_{CF} = 25$ Hz), 55.2, 27.4; MS *m*/*z* 206 $(M - HF)^+$.

Reaction of *t*-BuOF with indene (7) was carried out as described, forming 1α-fluoro-2β-*tert*-butoxyindan (**8**): oil, 70% yield; ^{1}H NMR 7.65−7.24 (4 H, m), 5.8 (1 H, dd, $J_1 = 57$ Hz, $J_2 = 4.8$ Hz), 4.6−4.4 (1 H, m), 3.29 (1 H, dd, $J_1 = 16$ Hz, $J_2 = 8$ Hz), 2.82 (1 H, ddd, $J_1 = 16$ Hz, $J_2 = 6.6$ Hz, $J_3 = 4$ Hz), 1.18 (9 H, s); ^{19}F NMR −177.4 (dd, $J_1 = 57$ Hz, $J_2 = 22.3$ Hz); ^{13}C NMR 129.4−124.8, 101.4 (d, $^1J_{CF} = 180.6$ Hz), 78.5 (d $^2J_{CF} = 21$ Hz), 74.25, 38.48 (d, $^3J_{CF} = 5$ Hz), 28.3 (s); MS *m*/*z* 208 (M^+), 151 $(M - t\text{-Bu})^+$, 135 $(M - t\text{-BuO})^+$. Anal. Calcd for $C_{13}H_{17}FO$: C, 75.0; H, 8.17; F, 9.13. Found: C, 74.65; H, 7.75; F, 9.09.

Reaction of *t*-BuOF with cyclohexene was carried out as described, forming *cis*- and *trans*-2-fluoro-*tert*-butoxycyclohexane (**9**) as an oil, in 20% yield. The cis isomer: ^{1}H NMR 4.59 (1 H, dm, $J_1 = 50$ Hz, $W_{h/2} = 10$ Hz), 3.5−3.39 (1 H, m), 2.1−1.2 (8 H, m), 1.18 (9 H, s); ^{19}F NMR −178.9 (m); ^{13}C NMR 92.46 (d, $^1J_{CF} = 173.5$ Hz), 73.7, 70 (d, $^2J_{CF} = 17$ Hz), 30.6 (d, $^2J_{CF} = 18$ Hz), 29.7, 28.4, 23.1, 20.2; MS *m*/*z* 174 (M^+), 159 $(M - Me)^+$, 100 $(M - t\text{-BuOH})^+$. The trans isomer: ^{1}H NMR 4.2 (1 H, dm, $J_1 = 47$ Hz, $W_{h/2} = 26$ Hz), 3.6−3.5 (1 H, m), 2.1−1.2 (8 H, m), 1.18 (9 H, s).

Reaction of *t*-BuOF with 1-indanone enol acetate (10a) formed a mixture of three compounds, which were chromatographically separated. The least polar fraction proved to be 2-dichloromethylene-1-indanone (**18**): mp 122 °C; 15% yield; IR 1702 cm^{-1}; ^{1}H NMR 7.83 (1 H, d, $J = 8$ Hz), 7.62 (1 H, t, $J = 8$ Hz), 7.5−7.35 (2 H, m), 3.87 (2 H, s); ^{13}C NMR 188, 146, 139, 135, 133.5, 130, 128, 126, 124.7, 35; MS *m*/*z* 212 (M^+), 177 $(M - Cl)^+$, 149, 114. The second fraction proved to be 2-*tert*-butoxy-1-indanone (**11**): mp 70 °C (pentane); 45% yield; IR 1730 cm^{-1}; ^{1}H NMR 7.74 (1 H, d, $J = 5$ Hz), 7.59 (1 H, dt, $J_1 = 9$ Hz, $J_2 = 1$ Hz), 7.4−7.2 (2 H, m), 4.38 (1 H, dd, $J_1 = 8$ Hz, $J_2 = 5$ Hz), 3.45 (1 H, dd, $J_1 = 17$ Hz, $J_2 = 8$ Hz), 2.99 (1 H, dd, $J_1 = 17$ Hz, $J_2 = 5$ Hz), 1.34 (9 H, s); ^{13}C NMR 204.9, 150.6, 135.2, 134.7, 127.6, 126.5, 124, 75.0, 74, 36.5, 28.3; MS *m*/*z* 148 $(M - t\text{-Bu} + H)^+$, 147 $(M - t\text{-Bu})^+$, 119, 91, 57. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 75.95; H, 7.85. The most polar fraction proved to be 2-fluoro-1-indanone (**16**):[10] mp 56 °C; 13% yield; IR 1731 cm^{-1}; ^{1}H NMR 7.8 (1 H, d, $J = 8$ Hz), 7.68 (1 H, dt, $J_1 = 8$ Hz, $J_2 = 1$ Hz), 7.5−7.4 (2 H, m), 5.28 (1 H, ddd, $J_1 = 51$ Hz, $J_2 = 8$ Hz, $J_3 = 5$ Hz), 3.64 (1 H, dt, $J_1 = 17$ Hz, $J_2 = 8$ Hz), 3.24 (1 H, ddd, $J_1 = 23$ Hz, $J_2 = 17$ Hz, $J_3 = 5$ Hz); ^{19}F NMR −194.5 (ddd, $J_1 = 51$ Hz, $J_2 = 23$ Hz, $J_3 = 7$ Hz); MS *m*/*z* 150 (M^+), 122 $(M - CO)^+$, 102 $(M - CO - HF)^+$. The adduct **A** was isolated in 6% yield: ^{1}H NMR 7.6 (1 H, d, $J = 7$ Hz), 7.4−7.2 (3 H, m), 4.53 (1 H, ddd, $J_1 = 15$ Hz, $J_2 = 6$ Hz, $J_3 = 7$ Hz), 3.18 (1 H, dd, $J_1 = 16$ Hz,

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(16) Hebel, D.; Rozen, S. *J. Org. Chem.* **1991**, *56*, 6298.

$J_2 = 7$ Hz), 3.0 (1 H, ddd, $J_1 = 16$ Hz, $J_2 = 6$ Hz, $J_3 = 4$ Hz), 2.11 (3 H, s), 1.28 (9 H, s); ^{19}F NMR −101 (dd, $J_1 = 15$ Hz, $J_2 = 4$ Hz).

The reaction with 10b gave, after the usual workup and chromatographic separation, three compounds: the least polar fraction proved to be **18** (10% yield), the second was identified as **11** (40% yield), and the most polar one proved to be **16** (30% yield).

Reaction of *t*-BuOF with Tetralone Trimethylsilyl Enol Ether (12b). After 30 min the reaction was worked up as usual. Chromatographic separation gave three compounds; the least polar fraction proved to be 2-*tert*-butoxy-3,4-dihydronaphthalenone (**13**): oil, 40% yield; IR 1698 cm^{-1}; ^{1}H NMR 8.01 (1 H, d, $J = 9$ Hz), 7.49−7.24 (3 H, m), 4.19 (1 H, t, $J = 8$ Hz), 3.08 (2 H, t, $J = 6$ Hz), 2.21 (2 H, m), 1.28 (9H, s); ^{13}C NMR 197.6, 143−125.8, 75.0, 73.6, 32.4, 28.0. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.06; H, 8.25. Found: C, 76.23; H, 7.80. The next fraction proved to be 2-fluoro-3,4-dihydronaphthalenone (**17**):[11] oil, 5% yield; IR 1704 cm^{-1}; ^{1}H NMR 8.0−7.2 (4 H, m), 5.15 (1 H, ddd, $J_1 = 48$ Hz, $J_2 = 13$ Hz, $J_3 = 6$ Hz), 3.07−3.14 (2 H, m), 2.27−2.58 (2 H, m). The most polar fraction proved to be 1-naphthol (**19**) (10% yield), identical with an authentic sample. A similar reaction was performed with tetralone methyl enol ether **(12c),** giving again three compounds, which were chromatographically separated. The least polar fraction proved to be 1-methoxy naphthalene (**20**) (15% yield), identical to an authentic sample. The next fraction proved to be **13,** formed in 55% yield. The most polar one was identified as **17** (15% yield).

Reaction of *t*-BuOF with 3,4-dihydropyrane (14) was carried out as described in the presence of methanol. The adduct 3-*tert*-butoxy-2-methoxytetrahydropyrane (**15**) was obtained in 30% yield as an oil: ^{1}H NMR 4.28 (1 H, d, $J = 3$ Hz), 3.7 (1 H, m), 3.55−3.45 (2 H, m), 3.40 (3 H, s), 1.90−1.84 (2 H, m), 1.54−1.36 (2 H, m), 1.19 (9 H, s); ^{13}C NMR 102.45, 74.6, 66.67, 61.19, 55.24, 28.28, 27.5, 21.5; MS *m*/*z* 188 (M^+), 115 ($M - Ot\text{-Bu}$)$^+$, 74 ($CH_3OCHOCH_2$)$^+$.

Reaction of *t*-BuOF with Acetophenone Trimethylsilyl Enol Ether (21b). After 40 min reaction time and usual workup, two compounds were chromatographically separated. The least polar fraction obtained in 50% yield proved to be 2-*tert*-butoxy-acetophenone (**22**):[8a] mp 120 °C (pentane/CH_2Cl_2); IR 1706 cm^{-1}; ^{1}H NMR 8.0 (2 H, d, $J = 8$ Hz), 7.6−7.4 (3 H, m), 4.67 (2 H, s), 1.29 (9 H, s); ^{13}C NMR 196.5, 135, 132.7, 128, 127.5, 74.0, 65.6, 26.8; MS *m*/*z* 149 ($M - CO - CH_3$)$^+$, 122, 105, 77, 57 (*t*-Bu)$^+$. The more polar fraction proved to be 3-cyanopropiophenone (**25**),[13] obtained in 15% yield: mp 71 °C (hexane/ethanol); IR 1683, 2251 cm^{-1}; ^{1}H NMR 8.0 (2 H, d, $J = 7$ Hz), 7.7−7.5 (3 H, m), 3.4 (2 H, t, $J = 7$ Hz), 2.8 (2 H, t, $J = 7$ Hz); ^{13}C NMR 195, 135, 134, 129, 128, 119, 34, 12; MS *m*/*z* 105 (PhCO)$^+$, 77. Similarly, the reaction of acetophenone methyl enol ether **(21c)** with *t*-BuOF gave **22** in 65% yield.

***o*-Methoxyacetophenone methyl enol ether (23c)** is unknown and was prepared by the general way described above. ^{1}H NMR 7.46 (1 H, dd, $J_1 = 8$ Hz, $J_2 = 2$ Hz), 7.33−7.24 (1 H, m), 6.98−6.90 (2 H, m), 4.62 (1 H, d, $J = 2$ Hz), 4.42 (1 H, d, $J = 2$ Hz), 3.86 (3 H, s), 3.72 (3 H, s). Its reaction with *t*-BuOF gave, after 20 min reaction time and usual workup, two compounds which were chromatographically separated. The less polar fraction proved to be 2-*tert*-butoxy-*o*-methoxyacetophenone (**24**): oil, 55% yield; IR 1690 cm^{-1}; ^{1}H NMR 7.81 (1 H, dd, $J_1 = 8$ Hz, $J_2 = 2$ Hz), 7.46 (1 H, dt, $J_1 = 8$ Hz, $J_2 = 2$ Hz), 6.99 (2 H, m), 4.64 (2 H, s), 3.91 (3 H, s), 1.27 (9 H, s); ^{13}C NMR 198.6, 158.6, 133.7, 130.4, 125.9, 120.7, 111.3, 73.8, 69.5, 55.4, 27.4; MS *m*/*z* 223 ($M + H$)$^+$, 167, 135 ($M - CH_2CO\text{-}t\text{-Bu}$)$^+$, 57 (*t*-Bu)$^+$. Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 69.70; H, 7.95. The more polar fraction proved to be 3-cyano-*o*-methoxypropiophenone (**26**):[14] oil, 19% yield; ^{1}H NMR 7.84 (1 H, dd, $J_1 = 8$ Hz, $J_2 = 2$ Hz), 7.6−7.45 (1 H, m), 7.07−6.95 (2 H, m), 3.95 (3 H, s), 3.41 (2 H, t, $J = 7$ Hz), 2.73 (2 H, t, $J = 7$ Hz).

Reaction of *t*-BuOF with Propiophenone Trimethylsilyl Enol Ether (27b). After 40 min reaction time and usual workup, two compounds were chromatographically separated. The main fraction (25% yield) was 2-*tert*-butoxypropiophenone (**28**): mp 70 °C; IR 1687 cm^{-1}; ^{1}H NMR 8.14 (2 H, dd, $J_1 = 8$ Hz, $J_2 = 2$ Hz), 7.6−7.4 (3 H, m), 4.73 (1 H, q, $J = 7$ Hz), 1.44 (3 H, d, $J = 7$ Hz), 1.17 (9 H, s); ^{13}C NMR 203, 134.5, 133, 129, 128, 75, 73, 28, 21.3. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.47; H, 8.93. The minor product, although not isolated in pure form, was found to be 2-fluoropropiophenone (**29**):[15] ^{1}H NMR 5.7 (1 H, dq, $J_1 = 49$ Hz, $J_2 = 7$ Hz), 1.66 (3 H, dd, $J_1 = 24$ Hz, $J_2 = 7$ Hz); ^{19}F NMR 181.8 (dq, $J_1 = 49$ Hz, $J_2 = 24$ Hz).

***5*-Acetylindane Trimethylsilyl Enol Ether (30)** is unknown and was prepared as described above: ^{1}H NMR 7.48 (1 H, s), 7.41 (1 H, d, $J = 8$ Hz), 7.18 (1 H, d, $J = 8$ Hz), 4.89 (1 H, d, $J = 2$ Hz), 4.40 (1 H, d, $J = 2$ Hz), 2.91 (4 H, t, $J = 7$ Hz), 2.09 (2 H, quintet, $J = 7$ Hz), 0.30 (9 H, s). It was then reacted with *t*-BuOF as described above. After 40 min reaction time and usual workup, three compounds were chromatographically separated. The less polar fraction proved to be 5-(1,1-dichloro-1-en-3-propanone)indan (**33**): oil, 14% yield; IR 1668 cm^{-1}; ^{1}H NMR 7.77 (1 H, s), 7.71 (1 H, d, $J = 8$ Hz), 7.31 (1 H, d, $J = 8$ Hz), 7.24 (1 H, s), 2.96 (4 H, t, $J = 7$ Hz), 2.12 (2 H, quintet, $J = 7$ Hz); ^{13}C NMR 186.8, 151.3, 145.2, 135.3, 134.3 127.2, 124.6, 124.4, 33.0, 32.5, 25.3; MS *m*/*z* 240 (M^+), 212 ($M - C_2H_4$)$^+$, 177 ($M - C_2H_4 - Cl$)$^+$, 159, 145 ($M - CH{=}CCl_2$)$^+$, 117, 115. The second product was identified as 5-*tert*-butoxyacetylindane (**31**): oil, 22% yield; IR 1698 cm^{-1}; ^{1}H NMR 7.82 (1 H, s), 7.76 (1 H, d, $J = 8$ Hz), 7.29 (1 H, d, $J = 8$ Hz), 4.66 (2 H, s), 2.95 (4 H, t, $J = 7$ Hz), 2.10 (2 H, quintet, $J = 7$ Hz), 1.28 (9 H, s); ^{13}C NMR 197, 150, 145, 134, 126.4, 124.2, 123.9, 74.4, 66, 33, 32.5, 27.4, 25; HRMS calcd for $C_{15}H_{20}O_2$ 232.1463 $(M)^+$, found 232.1469. Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 76.81; H, 8.30. The most polar fraction proved to be 5-(1-cyano-3-propanone)indan (**32**): oil, 7% yield; IR 2250, 1721 cm^{-1}; ^{1}H NMR 3.36 (2 H, t, $J = 8$ Hz), 2.96 (4 H, t, $J = 8$ Hz), 2.76 (2 H, t, $J = 8$ Hz), 2.13 (2 H, quintet, $J = 8$ Hz).

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