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Functionalization of saturated fluorocarbons with and without light

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Abstract

Photochemical transformation of saturated fluorocarbons into tetrabutylammonium enolates has been improved, and a method employing ketyls as reductants has been developed that accomplishes the same chemistry without light. Enolates have been isolated as enol methyl ethers, from which they can be efficiently regenerated with tetrabutylammonium iodide. In other cases, enolates have been isolated as the corresponding ketone or stable enol. Fluorocarbon LUMO energies correlate with their reactivity and serve as a guide to the choice of ketyl. Use of this chemistry for fluoropolymer surface modification is discussed.

Keywords: Fluorocarbon functionalization; Photoreduction; Ketyls; Enolates; Enol ethers; β-Diketonates; Fluoropolymer modification

1. Introduction

Saturated fluorocarbon liquids enjoy a wide variety of uses ranging from vapor phase soldering and heat exchange media to breathing liquids and oxygen carriers in blood substitutes [1,2]. A common requirement of most of their applications is chemical inertness, for which they are famous. Their spectrum of uses could potentially be expanded in new directions if functional groups were introduced [3,4]. The challenge to functionalization that their inertness poses is enhanced by the fact that conditions vigorous enough to attack them often suffice to bring about catastrophic destruction. Because they are highly resistant to acids, bases and oxidizing agents, powerful electron donors are required to attack them, and the intermediates generated in the course of reaction are more susceptible to reduction than the starting materials. Thus, a destructive cascade ensues with wholesale loss of fluoride ions, as illustrated for perfluoromethylcyclohexane (**1**) in Scheme 1. In the case of fluorocarbons containing six-membered rings, like **1**, the cascade can be stopped under certain conditions at the stage when the ring is aromatized because of the relatively strong resistance of benzene (and naphthalene) derivatives to further reduction [5–7]. These results are understandable in terms of the LUMO energies [8] calculated for **1** and intermediates in its reduction (Table 1). The values descend from **1** to perfluoro-1-methylcyclohexene (**2**) to perfluoro-2-methylcyclohexa-1,3-diene (**3**) (and its 1-methyl isomer **3a**, which may also form), indicating that reduction becomes progressively easier until the ring is aromatized as perfluorotoluene (**4**). Then reduction becomes enough slower that it can be interrupted if conditions are right.

Although functionalization without aromatization has been achieved in other ways [3,7,9], several years ago we developed the only general method that introduces a functional group in good yields and without extensive loss of fluoride into saturated fluorocarbons having tertiary sites [10]. Its secret of success is interception by hydroxide ion of an early intermediate in the reduction cascade, with the formation of an enolate ion. The negative charge on the ion protects the molecule from further attack by electrons, as illustrated for the functionalization of fluorocarbon **1** in Scheme 2. The reaction is carried out by irradiating a THF solution of the fluorocarbon containing tetrabutylammonium iodide (TBAI). Iodide ion undergoes a charge-transfer-to-solvent (CTTS) transition [11], producing a solvated electron for the reduction plus an iodine atom.[1] The reaction is regioselective, as the initial loss of fluoride ion occurs exclusively at a tertiary position.

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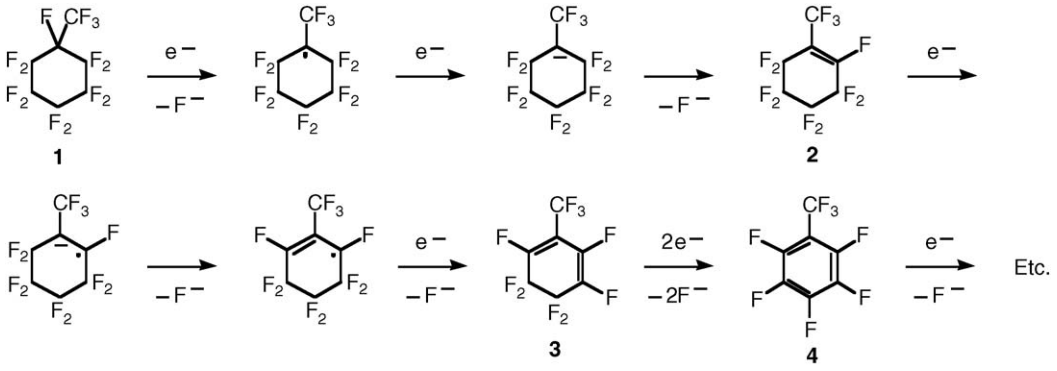
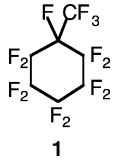
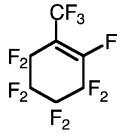
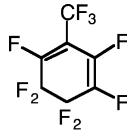
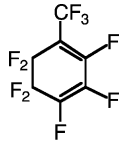
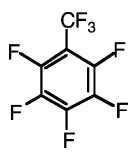
[1] Other applications of photoreduction by iodide ion include the photo-Finkelstein reaction [12] and iododefluorination of perfluoroacid esters [13]. Triiodide ion produced in all these reactions may also serve as a source of electrons upon irradiation.



Scheme 1.

In that work, we found that the presence of too much water lowered yields dramatically by hydrolyzing the enolate ion, **5** for example, to the corresponding β-diketonate ion **7** (Scheme 3). By hydrogen bonding to a fluorine in the γ-position, a water molecule assists loss of fluoride ion to give α,β-unsaturated ketone **6**, which is followed by attack of hydroxide ion and loss of HF. For that reason, the tetrabutylammonium iodide was dried before use, but it was assumed that reduction of residual water was the source of the hydroxide ion necessary for making the enolate.

Table 1
LUMO energies[a] (kcal/mol) of perfluoromethylcyclohexane and degradation products

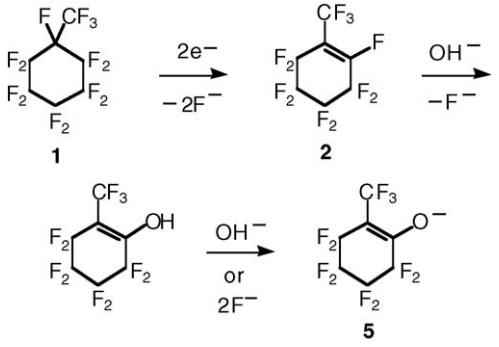
 **1**	−14.75
 **2**	−51.34
 **3**	−62.40
 **3a**	−64.86
 **4**	−35.05

[a] Calculated at the B3LYP/6-31G* level of theory.

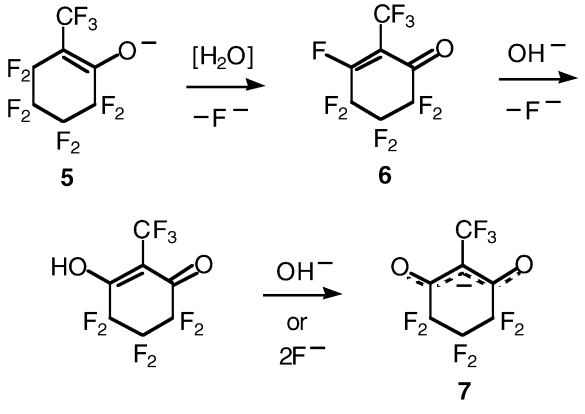
2. Results and discussion

2.1. Photochemical functionalization

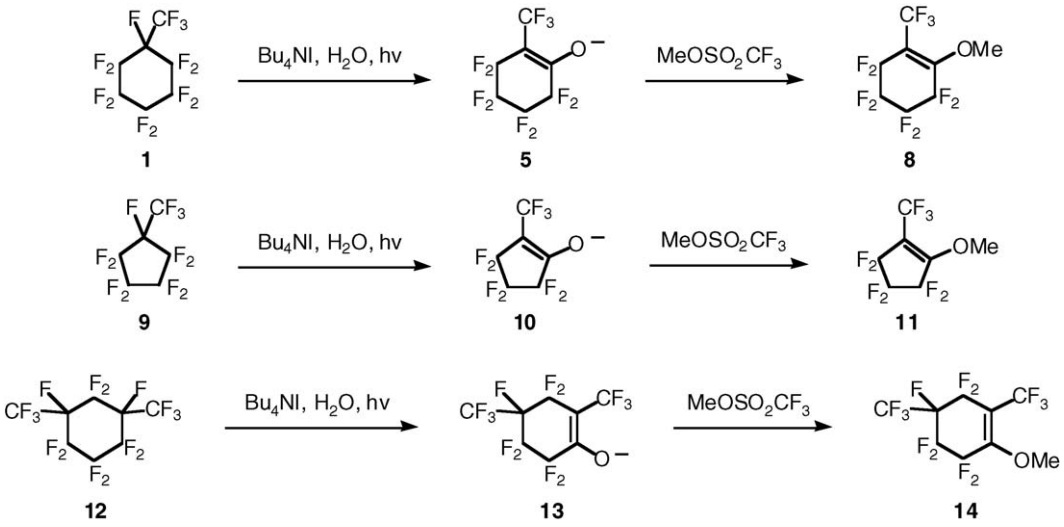
The first task in the present investigation was to establish definitively the source of the oxygen in the enolate product. Integration of the ^{1}H NMR spectrum of a solution of TBAI in D_2O revealed that its water content was too low to provide the necessary hydroxide ion. On the chance that air was not excluded rigorously enough in the earlier work, and that it was the source of the enolate oxygen (e.g., via superoxide ion), dry



Scheme 2.



Scheme 3.



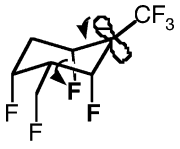
Scheme 4.

air was bubbled into irradiated THF solutions of **1** and dried TBAI. Yields of enolate were only 5–10%, and even that amount may have resulted from adventitious moisture.

In the earlier work, nominally anhydrous magnesium sulfate had been added to assure sufficient dryness to avoid β-diketonate formation. We now discovered that this salt actually contained sufficient water to account for the enolate formed! Addition of "anhydrous" magnesium sulfate to otherwise dry reaction mixtures resulted in enolate yields up to 80% by NMR. The water content varied even in samples of the salt from the same bottle, and sometimes there was enough to make β-diketonate the major product. Obviously, a better controlled source of water was needed. We found that magnesium sulfate monohydrate served that purpose well, giving an 88% NMR yield of enolate **5** at 91% conversion of fluorocarbon **1**. However, the simple expedient of adding a somewhat less than stoichiometric amount of water directly to the reaction mixture was the best solution, affording enolate **5** in 91% yield by NMR at complete conversion.

Enolate **5** reacted nearly quantitatively at RT with methyl triflate to yield enol ether **8** [10,14] (Scheme 4), which was isolated by preparative GC in 52% yield based on fluorocarbon **1**. In similar fashion, perfluoromethylcyclopentane (**9**) was transformed in high yield into enolate **10** [10], which was methylated to give enol ether **11** [15]. Interestingly, β-diketonate ion **7** failed to react at RT with methyl triflate, revealing it to be a remarkably weak nucleophile.

As was found in the earlier work [10], perfluoro-1,3-dimethylcyclohexane (**12**) underwent functionalization only once despite the presence of two tertiary sites. Apparently the enolate's negative charge suffices to protect the ion from attack at the other vulnerable position. Surprisingly, the reaction is regiospecific, yielding only enolate **13**, which was methylated to give **14**. The only abundant species available to assist loss of fluoride ion to form the intermediate alkene is the tetrabutylammonium ion, which may be sufficiently bulky to discriminate on steric grounds between the two possible reaction sites. The situation is depicted in **15**, where most of the fluorines have been omitted for clarity, and where the two axial candidates for extrusion are shown in bold. While the bold fluorine in front has three close neighbors, that in back has only two:



15

The ^{19}F NMR spectrum of **14** comprised nine sets of peaks: δ −59.1 (s, 3F, CF_3); −70.4 (s, 3F, CF_3); −98.5, −105.4 (ABq, J = 307 Hz, 2F); −105.0 (dd, J = 24, 301 Hz, IF); −119.5 (d, 289 Hz, IF);−125.1 (d, 301 Hz, IF);−135.9 (d, 289 Hz, IF); −183.9 (s, IF, C4). Thus, the three pairs of CF_2 fluorines, distinguished by their coupling constants, appeared at −98.5 and −105.4, −105.0 and −125.1, and −119.5 and −135.9. Assignments were made with the help of NOE measurements and are displayed in Fig. 1, which depicts the structure of **14** calculated at the B3LYP/6-31G* level of theory. Irradiation of the tertiary F revealed interaction with one F in each of the CF_2 groups, as well as the geminal CF_3. This measurement sufficed

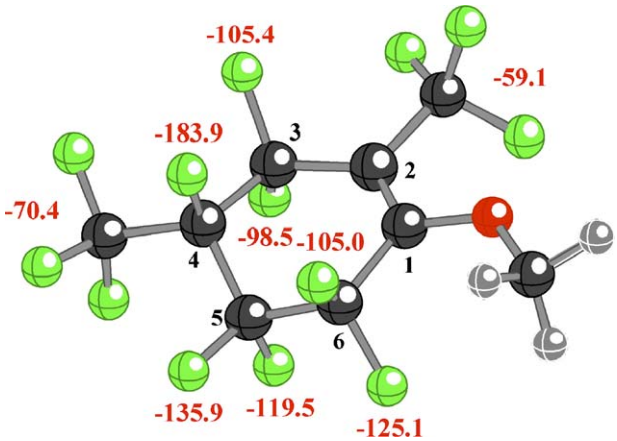


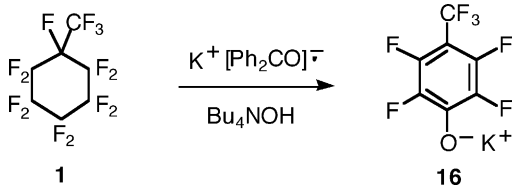
Fig. 1. Calculated structure of 1-methoxyperfluoro-2,4-dimethylcyclohexene (**14**) with ^{19}F NMR assignments.

to complete the assignments, and they were confirmed by the NOEs resulting from irradiation of the two CF_3 groups.

2.2. Functionalization without light

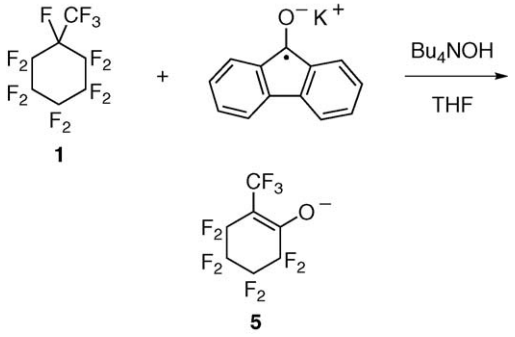
There are potential advantages in being able to accomplish the chemistry described above "thermally." The photoreactions are quite slow, and scale-up by a large factor would be far more practical if the reactions could be carried out without the need for light. We therefore sought electron donors that could substitute for the solvated electrons generated in the photoreactions. Because light from an arc is effectively a dilute reagent, producing solvated electrons slowly, there is time for intermediate alkenes to be trapped by hydroxide ion before suffering further reduction. In the presence of a powerful electron donor in substantial concentration, however, the lifetimes of those alkenes might be too short for trapping. Our plan, therefore, was to find reducing agents with barely enough power to attack the fluorocarbon, so that reaction would be slow enough for efficient capture when the first double bond appears.

Pez et al. found that sodium benzophenone ketyl in THF reduces perfluoromethylcyclohexane (**1**) to carbon and sodium fluoride [6]. When we carried out the reaction of the potassium ketyl with **1** in the presence of dry tetrabutylammonium hydroxide (TBAH), capture of an intermediate was successful, but at too late a stage. Only potassium perfluoro-*p*-cresolate (**16**) was obtained, showing that the hemorrhaging of fluoride ions was not halted until the ring had become aromatized (Eq. (1)):



(1)

Some commercially available aryl ketones (**17**–**21**) with their half-wave potentials are shown in Table 2 in order of decreasing reducing power of their radical anions. Having found the ketyl from **17** too potent, our next attempt was with that from benzil (**21**). No reaction with **1** was observed even at elevated temperatures. With the requisite reducing power bracketed, the potassium ketyl of 4-benzoylbiphenyl (**18**) was tried, and a small amount of the desired enolate (**5**) was obtained. Finally, the potassium ketyl of fluorenone (**19**) gave **5** in 69% NMR yield at 85% conversion (Eq. (2)). Before this reaction was optimized, a better process was developed, as described below:

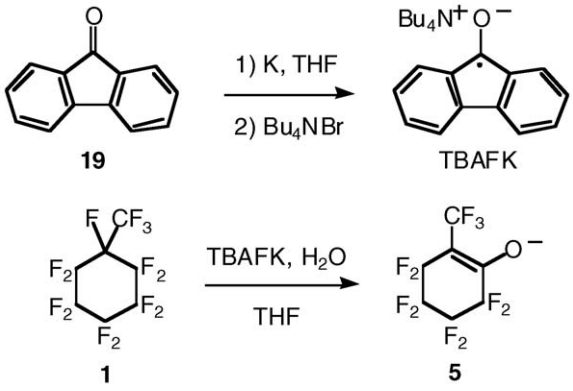


(2)

The use of tetrabutylammonium hydroxide (TBAH) is problematic for a number of reasons. Available as a 40% aqueous solution, it can be dried by azeotropic distillation [17], but the process consumes much time and solvent. TBAH is difficult to obtain in completely anhydrous form. Moreover, several equivalents of it are required in the functionalization reactions because the potassium counterion of the ketyl precipitates hydroxide ion from THF as KOH. Both the use of TBAH and the precipitation problem could be circumvented if the ketyl counterion were tetrabutylammonium and the necessary hydroxide ion were generated in situ from reaction of this ketyl with water.

Tetrabutylammonium fluorenone ketyl (TBAFK) was easily prepared by addition of tetrabutylammonium bromide to a THF solution of the potassium ketyl, and the potassium bromide by-product was removed by filtration (Scheme 5). When water was added to a THF solution of the ketyl, its purple color disappeared in about 5 min, showing the practicality of in situ generation of hydroxide ion. The stoichiometry of the fluorocarbon functionalization requires 1 equiv. of water and 4 equiv. of ketyl, since 2 equiv. are need to reduce the fluorocarbon and 2 equiv. serve as a base to deprotonate the water and enol. Slow addition of the ketyl in THF to fluorocarbon **1** in moist THF afforded enolate **5** in 79% yield by NMR at complete conversion.

As noted above, methylation of the enolate with methyl triflate is nearly quantitative at RT, but separation of the enol ether from by-products and residual reagent is not easy. Though



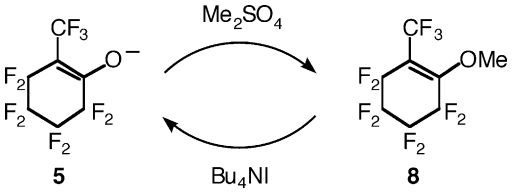
Scheme 5.

Table 2
Half-wave reduction potentials of aryl ketones [16]

Ketone	$E_{1/2}$ (V vs. SCE)	Solvent
Benzophenone (**17**)	−1.97	DMSO
4-Phenylbenzophenone (**18**)	−1.35	46% EtOH
Fluorenone (**19**)	−1.29	DMF
4,4′-Dimethoxybenzil (**20**)	−1.20	DMSO
Benzil (**21**)	−1.04	DMSO

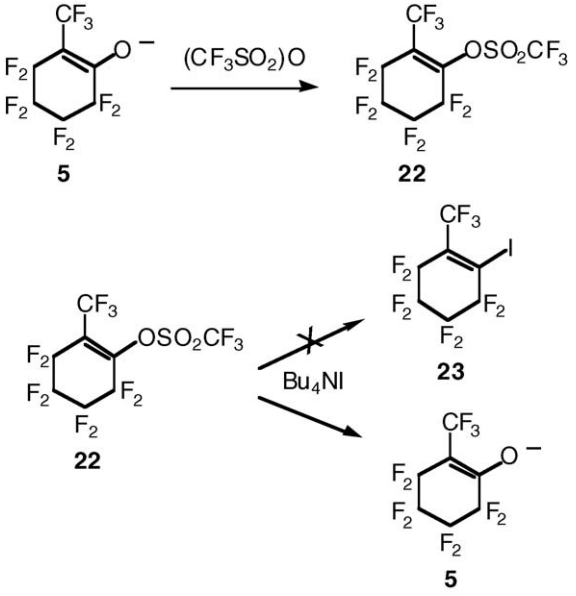
it reacts much more slowly and requires gentle heating, dimethyl sulfate is the better choice for methylation because product isolation is easier, not to mention that it is cheaper and less poisonous. Volatile by-products, notably methanol, can be removed in vacuo before the enolate reacts, and being nonvolatile, excess reagent does not interfere with product purification. Methyl ether **8** was isolated in yields up to 71% (based on starting fluorocarbon) after reaction of enolate **5**, prepared as in Scheme 5, with dimethyl sulfate.

Direct isolation of a tetrabutylammonium enolate such a **5** is not feasible because the reaction mixture contains large amounts of tetrabutylammonium fluoride, etc., and because the enolate is extremely susceptible to hydrolysis to β-diketonate. Enol ether **8** is a convenient storage form for **5** from which the enolate is quantitatively regenerated by treatment with tetrabutylammonium iodide at RT (Eq. (3)). The ether is easily purified and stable to water:

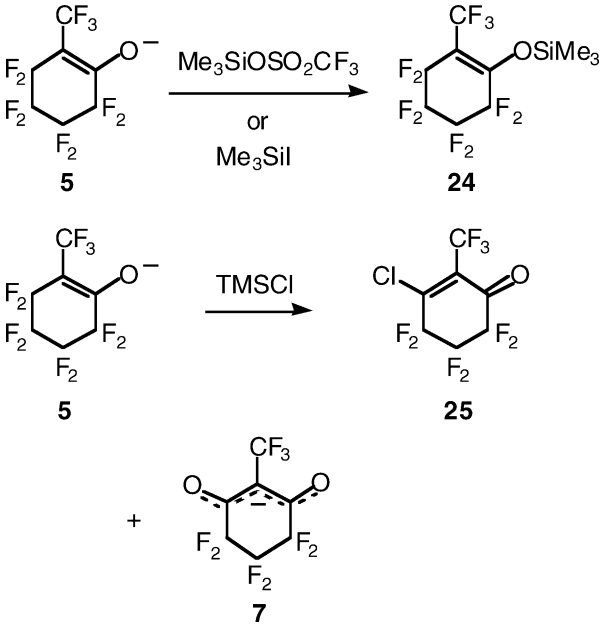


(3)

Enolate **5** reacts readily with triflic anhydride to give enol triflate **22** (Scheme 6). We anticipated that this molecule would serve to introduce other functional groups at C1 via addition–elimination reactions, given the excellence of triflate ion as a leaving group. However, treatment of **22** with TBAI yielded, not iodide **23**, but enolate **5**, testimony to the ability of the enolate to function as a leaving group. As a quintessentially soft nucleophile, iodide was expected to attack the relatively soft center C1, not the hard sulfur atom. Clearly, the negative charge on the enolate ion is very well stabilized, both by negative



Scheme 6.

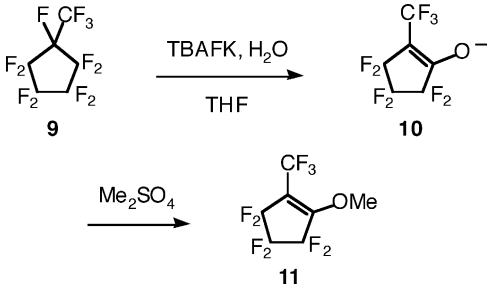


Scheme 7.

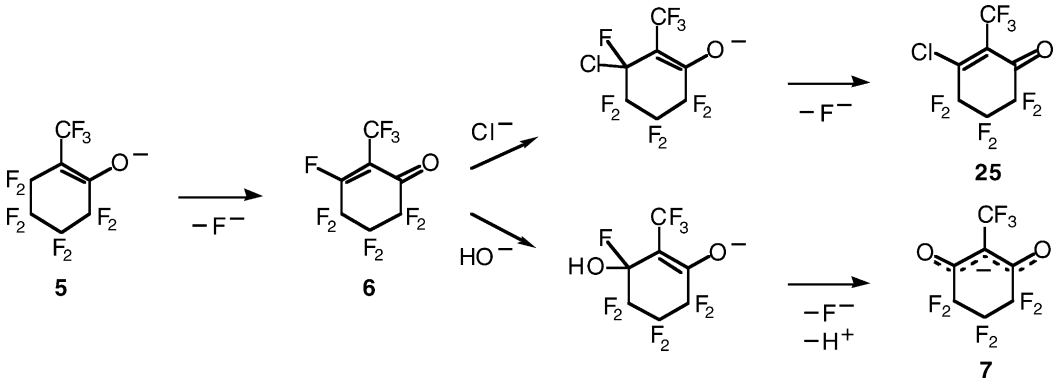
hyperconjugation with the five fluorines β to C2 and by the inductive and field effects of those and other fluorines.

Reaction of enolate **5** with trimethylsilyl iodide or triflate gave the TMS enol ether **24** [10], but trimethylsilyl chloride (TMSCl) afforded instead two products, chloroketone **25** and β-diketonate **7** (Scheme 7). The contrast may be understood in terms of the weaker electrophilicity and thus greater selectivity of TMSCl. Since hydroxide in the reaction mixture is far more nucleophilic than the enolate, the reagent was apparently largely hydrolyzed. This provided chloride ion and a source of protons (trimethylsilanol or water from deprotonation of the silanol by hydroxide) to assist loss of fluoride ion from **5** (Scheme 8). Attack on the resulting α,β-unsaturated ketone **6** by chloride ion gave **25**, and by hydroxide ion gave **7** via addition–elimination reactions. The weak nucleophilicity of enolate **5** is further revealed in its failure to react with the good electrophiles α-bromoacetophenone and chloroacetone.

The ketyl TBAFK was allowed to react with perfluoromethylcyclopentane (**9**), giving enolate **10** in 80% yield by NMR (Eq. (4)). Reduction of this substrate was notably faster than that of **1**, suggesting a lower LUMO energy. At the B3LYP/6-31G* level of theory, it is in fact lower by 5.3 kcal/mol (Table 3). Methylation of enolate **10** with dimethyl sulfate afforded methyl ether **11** in 55% isolated yield, based on **9**:

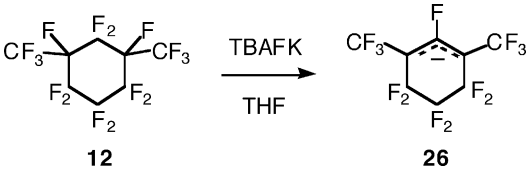


(4)



Scheme 8.

Surprisingly, reaction of 1,3-dimethylcyclohexane (**12**) with TBAFK in moist (or dry) THF gave a very different result from the photochemical functionalization of **12** described above. The product was the tetrabutylammonium salt of allylic anion **26**, a stable, weakly basic species, the origin and nature of which has been discussed elsewhere (Eq. (5)) [18]:

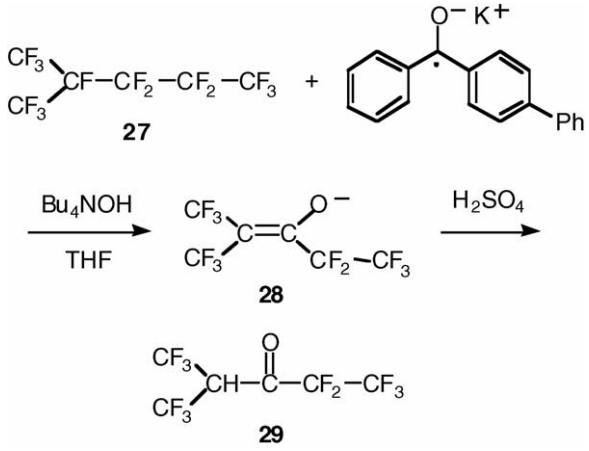


(5)

Table 3
LUMO energies (kcal/mol) of some saturated fluorocarbons calculated at the B3LYP/6-31G* level of theory

1	−14.75
9	−20.05
27	−3.28
30	−10.09
31	−16.63
32	−17.77

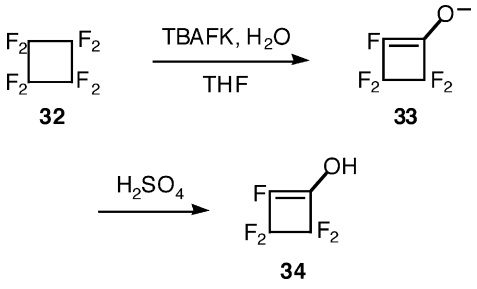
Acyclic substrate perfluoro-2-methylpentane (**27**) was not reduced by TBAFK. Perfluorocycloalkanes are well known to have higher electron affinities than their acyclic counterparts [19], and indeed the LUMO energy calculated for **27**, −3.28 kcal/mol, lies well above those of both **1** and **9**. We therefore attempted to prepare the tetrabutylammonium ketyl of 4-benzoylbiphenyl (**18**), which would have more reducing power than TBAFK (Table 1). Unfortunately, the ketyl anion was apparently basic enough to bring about Hoffmann elimination on the tetrabutylammonium ion, as the deep blue color of the potassium ketyl faded when tetrabutylammonium bromide was introduced. Functionalization of fluorocarbon **27** was successfully accomplished nonetheless using the potassium ketyl (KBBK) of **18**. TBAH was added to a THF solution of the fluorocarbon, and the ketyl was introduced slowly using a syringe pump. Enolate **28** was obtained in 73% yield by NMR, and acidification with concentrated sulfuric acid gave ketone **29** [20], isolated in 62% yield based on **27** (Scheme 9). Monitoring



Scheme 9.

of the reaction revealed that the enolate precipitated initially as the potassium salt, only to slowly return to solution as the tetrabutylammonium salt. The cation exchange was presumably driven by formation of potassium fluoride.

That different substrates require different reducing power is clear from the above examples, and the array of ketyls that are available gives the method flexibility. Since the calculated LUMO energies of the fluorocarbon substrates we have studied correlate nicely with their reactivity under reducing conditions, one should be able to predict the reactivity of other substrates with tertiary fluorines and choose a ketyl accordingly. Fluorocarbons having tertiary sites and thus relatively weak C–F bonds are easier to reduce than those with only primary and secondary fluorines, indicating that bond strength as well as LUMO energy influence the ease of reduction. LUMO energies may well correlate with reactivity for fluorocarbons lacking tertiary fluorine, such as the series perfluorocyclohexane (**30**), perfluorocyclopentane (**31**) and perfluorocyclobutane (**32**) (Table 3), but with a different calibration than for fluorocarbons with tertiary sites. Thanks to its very low lying LUMO, perfluorocyclobutane was readily reduced by TBAFK (Eq. (6)). Protonation of the resulting enolate (**33**) gave the enol (**34**) [21], which we found some years ago to be lower in energy than its keto form [22]. Under our conditions, perfluorocyclohexane (**30**) was reduced very slowly if at all even by potassium benzophenone ketyl.



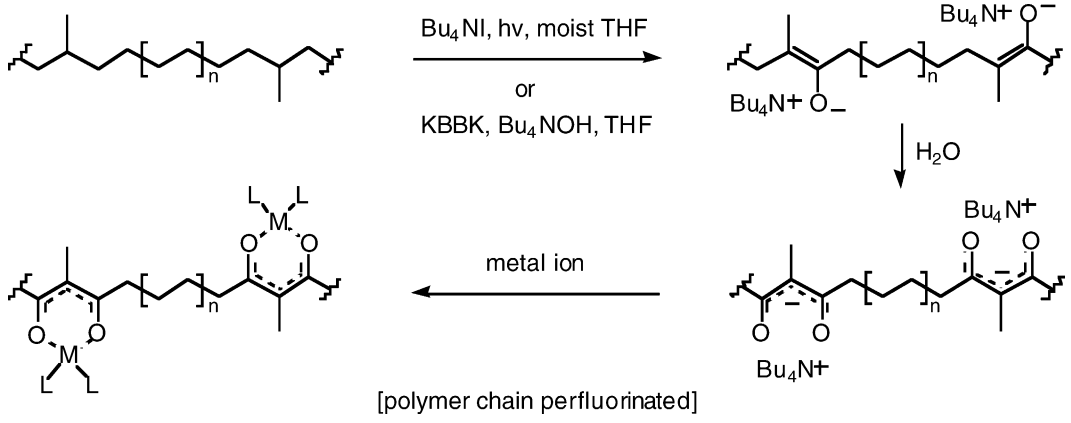
(6)

The inertness and low surface energy of fluoropolymers make them resistant to bonding with other substances, so a variety of methods have been developed to improve adhesion. These techniques include treatments with plasmas [23], X-ray [24], ion beam [25], and UV irradiation [26]; electrochemical reduction [27]; wet chemical etching with solvated electrons in liquid ammonia [28], sodium naphthalene [29], and benzoin dianion [30]. All these methods damage the surface in non-selective ways.

Teflon FEP is a random copolymer of tetrafluoroethylene and hexafluoropropene, typically containing ~8.5 mol% of the latter component [31]. There is a tertiary fluorine at each of the branch points, and our selective reduction chemistry should be capable of introducing β-diketonate functionality precisely at these sites either photochemically or without light (Scheme 10). The resulting polymer with an ionic surface might find some applications. Its wettability and affinity for various coating materials would be enhanced, but the prospect of exploiting the specific functionality that has been introduced is more interesting. In principle, the β-diketonate moieties would be capable of chelating an array of metals. Depending upon the choice of metal and other ligands, it should be possible to modify the properties of the surface in various ways. One could imagine making the surface fluoresce or function as a catalyst, for example.

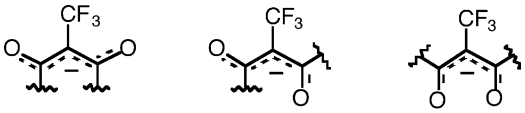
Teflon FEP film was treated with potassium 4-benzoylbiphenyl ketyl (KBBK) in the presence of TBAH, resulting in a dramatic increase in its wettability. Teflon FEP powder, treated similarly, displayed new strong, broad infrared absorption at ~1600 cm^{-1} and new absorptions peaking at 2969 cm^{-1}. Bands in the latter region are attributable to the tetrabutylammonium ion, the counterion of the β-diketonate groups, which are responsible for the ~1600 cm^{-1} absorption. For comparison, the IR spectrum of tetrabutylammonium β-diketonate **7** showed absorptions at 2971 and 1606 cm^{-1} (strong and broad).

Preliminary attempts to prepare metal chelates from the treated film and powder have been unavailing, however. Fluorinated β-diketonates are known to form complexes with a variety of metals [32], but perhaps the polymer-bound β-diketonate moieties exist primarily in the W (**35**) or skew (**36**) configurations instead of the U-shape (**37**) that is required for



Scheme 10.

chelation. We believe that selective surface functionalization of fluoropolymers by our reduce-and-capture method, or a variation thereof, merits further investigation.



35 36 37

3. Conclusions

The photochemical method developed earlier in our laboratory for functionalizing saturated fluorocarbons as tetrabutylammonium enolates has been refined, and derivatives of the enolates have been isolated. The enolates are highly susceptible to hydrolysis, forming β-diketonates, but their methyl ethers serve as stable storage forms from which they can be regenerated cleanly in excellent yield. The same functionalization reactions have been accomplished without light, utilizing ketyls with variable reducing power. Fluorocarbon LUMO energies correlate with ease of reaction, and guide the choice of ketyl to be employed with a particular substrate. Infrared spectra indicate that β-diketonate ions have been introduced on the surface of Teflon FEP using this chemistry.

4. Experimental

NMR spectra were taken on Varian Unity Plus 300 and 500 MHz machines. ^{19}F NMR spectra were recorded at 282.2 and 470.3 MHz, using an internal standard of trichlorofluoromethane. NMR yields were determined using α,α,α-trifluorotoluene as an internal area standard. ^{13}C NMR spectra were recorded at 125.7 MHz. GC was performed on a Hewlett-Packard 5750 gas chromatograph, and GC/MS on a Hewlett-Packard 5890A gas chromatograph with a Hewlett-Packard 5971 series mass detector. IR spectra were measured on a Perkin-Elmer 599 FT-IR instrument. The UV source for photoreaction was a Vycor-filtered 450W Hanovia medium-pressure mercury arc contained in a quartz water jacket. The high resolution mass spectrum was obtained from the Mass Spectrometry Center, University of Massachusetts, Amherst, MA.

THF was distilled from potassium benzophenone ketyl, and acetonitrile from calcium hydride. Preparation of perfluoro-2,4-dimethylcyclohex-1-enolate (**13**) and its methyl ether (**14**) is described elsewhere [18].

4.1. Tetrabutylammonium perfluoro-2-methylcyclohex-1-enolate (*5*) and 1-methoxyperfluoro-2-methylcyclohexene (*8*) [10]

4.1.1. Photochemically

Perfluoromethylcyclohexane (**1**) (0.77 g, 2.2 mmol), water (25 mg, 1.4 mmol), tetrabutylammonium iodide (2.0 g, 5.4 mmol), and THF (10 mL) were added to a 25 mL quartz tube. It was sealed with a septum and attached to the UV source. The whole assembly was immersed in a large beaker, into which cooling water was introduced continuously. A large pan with a draining hose caught the overflow. The mixture was irradiated for 48 h, while it was stirred with a horseshoe magnet attached to a stirring motor. The magnet was mounted outside the beaker, close to the quartz tube. Formation of perfluoro-2-methylcyclohex-1-enolate (**5**) was observed and quantitated by ^{19}F NMR. Yield: 91%.

Tetramethylenesulfone (5 mL) was added to the mixture, and THF and other volatile materials were removed in vacuo. Methyl triflate (300 μL, 2.65 mmol) was added, together with $CaCO_3$ (0.50 g, 5 mmol). The mixture was stirred for 0.5 h, then methyl ether **8** was vacuum transferred to a U-trap cooled by liquid nitrogen. The crude product was purified by preparative GC. Yield: 0.217 g, 52% based on fluorocarbon **1**. ^{1}H NMR ($CDCl_3$): δ 4.18 (t, J = 1.8 Hz, CH_3). ^{19}F NMR ($CDCl_3$): δ −59.2 (s, 3F, CF_3), −108.3 (s, 2F, C3), −114.9 (s, 2F, C6), −134.7 (s, 2F, C4 or 5), −134.9 (s, 2F, C4 or 5). IR (neat, cm^{-1}): 2977, 1657, 1470, 1386, 1255, 1198, 1030, 997.

4.1.2. Without light

The following operations were done under nitrogen protection, and glassware was dried in an oven at 120 °C overnight. Tetrabutylammonium bromide (3.87 g, 12 mmol), fluorenone (2.16 g, 12 mmol), potassium (0.48 g, 12 mmol), and THF (40 mL) were added to a 60 mL dropping funnel with a fritted filter plate. The mixture was magnetically stirred overnight. Then nitrogen pressure was applied to force tetrabutylammonium fluorenone ketyl solution through the filter plate into a 50 mL flask. Potassium bromide was thus removed by filtration. The deep red ketyl solution was transferred to a 50 mL syringe. Water (50 μL, 2.8 mmol) and THF (10 mL) were placed in a 100 mL two-neck round-bottom flask, and one-fourth of the ketyl solution (10 mL) was added. After the mixture had been stirred for 0.5 h, perfluoromethylcyclohexane (**1**) (0.70 g, 2.0 mmol) was added to the mixture. The remaining ketyl was slowly added to the above flask over the course of 8 h, controlled by a syringe pump. Formation of perfluoro-2-methylcyclohex-1-enolate (**5**) was observed and quantitated by NMR. Yield: 79%.

Dimethyl sulfate (10 mL) was added to the mixture. THF and other volatile materials were removed by vacuum transfer. The mixture was then heated to 45 °C, and stirred for 10 h under vacuum. Methyl ether **8** was collected in a U-trap cooled by liquid nitrogen. This crude product was further purified by preparative GC. Yield: 0.36 g, 56% based on fluorocarbon **1**.

4.2. Perfluoro-2-methylcyclohex-1-enolate (*5*) from methyl ether *8*

2-Methoxyperfluoro-1-methylcyclohexene (**8**) (30 mg, 0.093 mmol), tetrabutylammonium iodide (35 mg, 1 equiv.), and THF (0.5 mL) were added to a flame-dried NMR tube. Tetrabutylammonium perfluoro-2-methylcyclohex-1-enolate (**5**) was generated quantitatively, as determined by ^{19}F NMR. ^{19}F NMR (THF): δ −55.6 (s, 3F, CF_3), −93.8 (s, 2F, C3), −122.0 (s, 2F, C6), −133.5 (s, 2F, C4 or 5), −135.7 (s, 2F, C4 or 5).

4.3. 2-Trifluoromethanesulfonyloxyperfluoro-1-methylcyclohexene (22)

To the above solution in the NMR tube was added triflic anhydride (27 mg, 0.095 mmol). Triflate derivative **22** was formed in 88% yield, determined by NMR. ^{19}F NMR (THF): δ −59.5 (s, 3F, CF_3C), −79.2 (s, 3F, CF_3S), −108.2 (s, 2F, C3), −115.2 (s, 2F, C6), −135.3 (s, 2F, C4 or 5), −135.7 (s, 2F, C4 or 5).

Tetrabutylammonium iodide (70 mg, 0.19 mmol) was added to the above solution, and periluoro-2-methylcyclohex-1-enolate (**5**) was regenerated. ^{19}F NMR (THF): δ −55.6 (s, 3F, CF_3), −93.8 (s, 2F, C3), −121.9 (s, 2F, C6), −133.4 (s, 2F, C4 or 5), −135.6 (s, 2F, C4 or 5).

4.4. 3-Chloroperfluoro-2-methylcyclohex-2-enone (25)

Prepared as above from methyl ether **8**, perfluoro-2-methylcyclohex-1-enolate (**5**, ca. 0.32 mmol) in 10 mL THF was added to a 25 mL oven-dried round-bottom flask. Tetramethylenesulfone (4 mL) was added, and then THF was removed under vacuum. Trimethylsilyl chloride (1 mL, freshly distilled) was added, and the mixture was stirred for 0.5 h. Volatile materials were vacuum transferred to a U-trap cooled by liquid nitrogen. The resulting crude 3-chloroperfluoro-2-methylcyclohex-2-enone (**25**) was purified by preparative GC. ^{19}F NMR ($CDCl_3$): δ −60.2 (s, 3F, CF_3), −112.2 (s, 2F), −127.5 (s, 2F), −133.6 (s, 2F). ^{13}C NMR ($CDCl_3$): δ 173.5 (C1); 149.5 (C3); 129.7 (C2); 119.6 (CF_3); 108.2, 108.0, 105.5 (C4-6). IR (neat, cm^{-1}): 1751, 1610, 1333, 1291, 1258, 1179, 1068, 992, 902, 835. HRMS: 305.9486 found, 305.9494 calculated for C_7F_9ClO.

4.5. Perfluoro-2-methylcyclopent-1-enolate (10) and 1-methoxyperfluoro-2-methylcyclopentene (11)

4.5.1. Photochemically

According to the procedure for fluorocarbon **1**, perfluoromethylcyclopentane (**9**) (0.500 g, 1.67 mmol) was photoreduced to perfluoro-2-methylcyclopent-1-enolate (**10**) [10] in 80% yield, measured by NMR. Perfluoro-2-methylcyclopent-1-enol methyl ether (**11**) was obtained by treating **10** with methyl triflate, as described for enolate **5**, and the crude product (with ca. 10% mechanical loss) was purified by preparative GC. Yield: 0.176 g, 43% based on **9**. ^{1}H NMR ($CDCl_3$): δ 4.19 (narrow m, CH_3). ^{19}F NMR ($CDCl_3$): δ −59.1 (s, 3F, CF_3), −106.9 (s, 2F, C3), −114.2 (s, 2F, C5), −130.2 (s, 2F, C4). IR (neat, cm^{-1}): 1678, 1480, 1416, 1296, 1155, 1059, 1005, 931, 875.

4.5.2. Without light

Perfluoromethylcyclopentane (**9**) (0.60 g, 2.0 mmol) was functionalized as described for **1**, and the formation of perfluoro-2-methylcyclopent-1-enolate (**10**) was quantitated by NMR. Yield: 80%. Treatment with dimethyl sulfate at 35 °C according to the procedure for **5** gave pure methyl ether **11**. Yield: 0.30 g, 55% based on **9**.

4.6. Perfluoro-2-methylpent-2-en-3-olate (28) and 2H-Perfluoro-2-methyl-3-pentanone (29) [10]

Under nitrogen protection, potassium (0.80 g, 20 mmol), THF (40 mL), and *p*-phenylbenzophenone (5.16 g, 20 mmol) were placed in a 100 mL round-bottom flask. After the mixture had been stirred overnight, it was transferred to a 50 mL syringe. Tetrabutylammonium hydroxide solid (2.08 g, 8.0 mmol, prepared from the commercial 40% aqueous solution by azeotropic concentration using benzene, 3 × 10 mL), perfluoro-2-methylpentane (**27**) (0.67 g, 2.0 mmol), and THF (10 mL) were added to a 100 mL round-bottom flask. The ketyl solution was added dropwise via syringe pump to the above mixture over the course of 8 h. Formation of perfluoro-2-methylpent-2-en-3-olate (**28**) was quantitated by NMR. Yield: 81%.

Freshly distilled triglyme (10 mL) was added to the mixture, and THF was removed under vacuum. Concentrated sulfuric acid (10 mL) was added, and the resulting 2*H*-perfluoro-2-methyl-3-pentanone (**29**) was vacuum transferred to a U-trap cooled by liquid nitrogen. Yield: 0.37 g, 62% based on **27**. ^{1}H NMR ($CDCl_3$): δ 4.71 (m, 1H). ^{19}F NMR ($CDCl_3$): δ −63.4 (narrow m, 6F, *gem* CF_3s), −81.8 (s, 3F, C5), −122.7 (s, 2F, C4).

4.7. Perfluorocyclobut-1-enol (33)

The following operations were done under nitrogen, and glassware was dried in an oven at 120 °C overnight. Tetrabutylammonium bromide (3.87 g, 12 mmol), fluorenone (2.16 g, 12 mmol), potassium (0.48 g, 12 mmol), and THF (40 mL) were added to a 60 mL dropping funnel with a fritted filter plate. The mixture was magnetically stirred overnight, then nitrogen pressure was applied to force the tetrabutylammonium fluorenone ketyl solution through the filter plate into a 50 mL flask. The deep red ketyl solution was transferred to a 50 mL syringe. Water (50 μL, 2.8 mmol) was placed in a 100 mL two-neck round-bottom flask together with THF (10 mL) and one-fourth of the ketyl solution (10 mL). After the mixture had been stirred for 0.5 h, it was cooled to −31 °C in a bromobenzene/Dry Ice bath. Perfluorocyclobutane (**32**, 0.38 g, 1.9 mmol) was condensed into the mixture from a balloon, the quantity determined by the weight difference before and after the condensation. The remaining ketyl was slowly added to the above flask via syringe pump over the course of 5 h. Formation of perfluorocyclobut-1-enolate was observed by NMR.

1,2,4-Trichlorobenzene (40 mL) was added, then THF and other volatile materials were removed by vacuum transfer. Concentrated sulfuric acid (10 mL) was added to the mixture. With vigorous stirring, perfluorocyclobut-1-enol was vacuum transferred into a series of two traps. The first trap at −13 °C (ethylene glycol/Dry Ice bath) collected solvent; the second trap, cooled to −78 °C (acetone/Dry Ice), collected the enol (0.21 g, 69%). ^{19}F NMR ($CDCl_3$): δ −116.2 (m, 2F), −120.3 (m, 2F), −141.8 (m, IF).

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