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Mixed Organofluorine-Organosilicon Chemistry. 5. Reactivity of 1-aryl (or alkyl)-1-trialkylsilyl perfluoroalkanols

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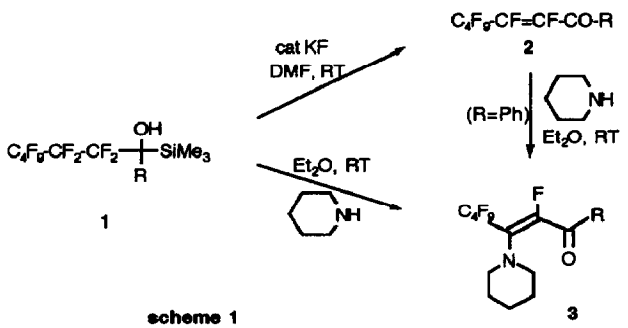
Key Words : 1-trialkylsilyl perfluoroalkanols, polyfluoroenaminones, polyfluoropyrazoles, 1-perfluoroalkyl -1-trialkylsilyloxyalkane.

Abstract : The title alcohols react with amines and hydrazines to yield perfluoro-β-enaminones and pyrazoles respectively. With ammonia, they lead either to the β-enaminone or to the silylether of the corresponding secondary alcohol, depending on the ammonia concentration.

Previously reported papers in this series have exhibited the versatility of the reaction of perfluoroorganometallic reagents with acylsilanes[1-4] which can lead to various compounds in high yield and selectivity. The most simple application is obviously the preparation of alcohols **1**, which can be isolated in fair to excellent yields providing that magnesium reagents are employed and that the alkoxide adduct is quenched at low temperature before a Brook rearrangement can take place.[2] These new alcohols have very interesting properties and the purpose of this paper is to illustrate some of their applications.

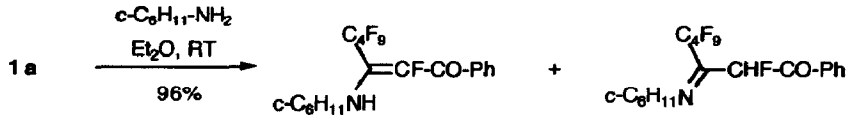
The hydroxylic proton of alcohol 1 is very labile, due to the withdrawing effect of the perfluoroalkyl group. Thus, simple treatment of **1a** with a catalytic amount of potassium fluoride in dimethylformamide yielded quantitatively the enone **2** (scheme 1). The details of this reaction have been reported elsewhere.[3] What we would like to emphasize here is that the alcohols **1** can be used directly as equivalents of enones **2**



scheme 1

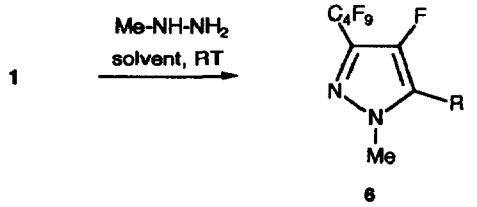
	R	2(%)	3 (%)
a	Ph	95	88
b	C_5H_{11}	-	81

Treatment of **1a** with piperidine (3 eq.) in ether at room temperature gave cleanly the β-enaminone **3a**[4] with 88% yield. The same product was obtained in 93% yield from the enone **2a**. Although much slower, the aliphatic alcohol **1b** reacted similarly, giving the enaminone **3b**[4] in 81% yield (Scheme 1). A primary amine reacted in the same way giving a tautomeric mixture of β-enamino and β-iminoketones **4** and **5**[4] (Scheme 2).



scheme 2

More interesting is the direct and convenient synthesis of heterocycles as exemplified in the scheme 3. Treatment of **1a** with methylhydrazine (3 eq) in ether at room temperature yielded quantitatively the polyfluorinated pyrazoles **6a**[5]. This reaction is as efficient as that from the corresponding enone **2** generated from corresponding enolphosphates.[5] Here too, the aliphatic alcohol **1b** is much less reactive: the reaction is inefficient in ether, but the corresponding pyrazole **6b** was obtained in DMF, although with only partial conversion.



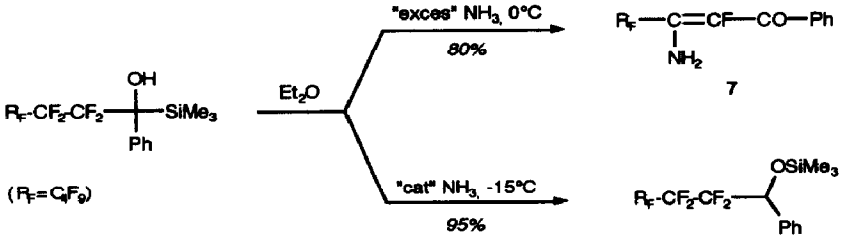
	R	solvent	prod. (%)	
1a	Ph	Et_2O	**6a** (95)	(isol., 100% conv)
1b	C_5H_{11}	DMF	**6b** (57)	(GLC, 60% conv.)

scheme 3

All these reactions proceed by a multistep pathway beginning with the formation of the alkoxide and involving, via a Brook rearrangement, the intermediate enoxysilane which in turn reacts with the amine to yield the enone.[1,4] An addition-elimination process yields the final substitution product. Despite the rather complex pathway, the reaction is remarkably clean, efficient and convenient, especially in the aromatic series. The aliphatic analogues are less reactive: the corresponding enoxysilanes are better substrates for carrying out such reactions.[4]

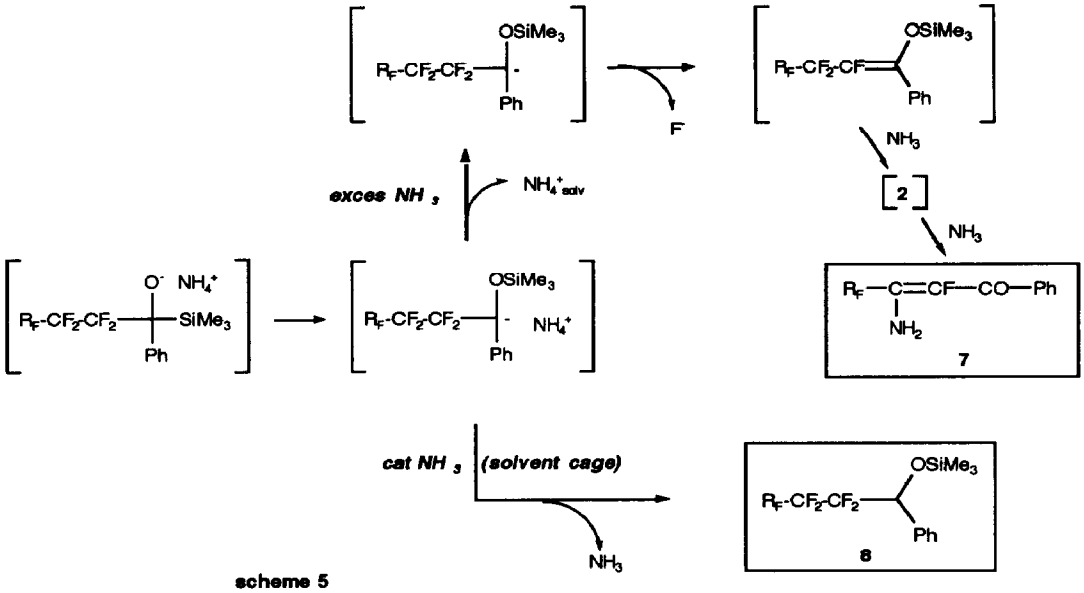
The reaction of alcohols 1 with ammonia is both similar and different than with amines, the product of the reaction depending on the experimental conditions . Bubbling ammonia into a solution of **1a** in ether gave either the β-enaminone **7**[6] or the silyl ether **8**[6] according to the flow of ammonia and the reaction temperature (Scheme 4). Saturation of the solution by vigorous bubbling (excess ammonia) led to the enaminone **7** as the major product, accompanied by a small amount of a new product, the silyl ether **8**. With very gentle bubbling of

ammonia (catalytic NH_3) and cooling to -15°C, the silyl ether **8** was formed quantitatively. Silyl ether **8** is in fact the result of a clean Brook rearrangement without β-elimination of fluoride. Compound **8** was not observed when a catalytic amount of piperidine was added to **1a** in the same conditions.



scheme 4

A tentative explanation of this dual reactivity with ammonia could be the following (Scheme 5). With ammonia in catalytic concentration and at low temperature, the rearrangement takes place in a solvent cage, and a reverse proton transfer to the rearranged anion occurs before β-elimination. In contrast an excess of ammonia favors the solvation of the ammonium cation and hence charge separation occurs, followed by fluoride elimination. The specificity of the rection with ammonia could be due to a better reverse proton transfer from the more acidic ammonium ion. On the other hand, aliphatic alcohol **1b** is not a good starting material for the reaction with ammonia. Whereas the corresponding enoxysilanes gave quantitatively the β-enaminone[4], no reaction was observed under catalytic conditions and only a partial conversion to enaminone was obtained after a long reaction time in saturated ammonia.



scheme 5

In conclusion, alcohols **1** are useful synthons acting essentially as synthetic equivalents of the corresponding enones **2**. Hence, they are excellent building blocks (in particular aromatic analogues of **1**) for the synthesis of fluorinated heterocycles. Furthermore, their reactivity with ammonia can be modulated: the fluoride elimination subsequent to the Brook rearrangement either occurs or can be avoided by adjusting the base concentration.

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6. Selected data:

   -compound **7**: ^{1}H NMR 6.5 (NH_2); ^{13}C NMR 140.7 (d, J = 244 Hz, Cα); ^{19}F NMR -81.5 (3F), -116.7 (2F), -123.7 (2F), -126.7 (2F), -162.1 (Fα); MS m/z (%) 383 (M^+,10), 105 (100).

   -compound **8**: ^{1}H NMR 0.10 (s, 9H), 5.14 (dd, $^{3}J_{HF}$ = 22.5 and 4.5 Hz); ^{13}C NMR -0.4 ($Si(CH_3)_3$), 73.0 (m, CH($OSiMe_3$)); ^{19}F NMR -81.4 (CF_3), -108.5 ($2F_\alpha$), -115.8 and -119.7 ($2F_\beta$, J_{AB} = 282 Hz), -122.6 ($2F_\gamma$), -123.2 ($2F_\delta$), -126.7 ($2F_\varepsilon$). Analysis Calcd. for $C_{16}H_{15}F_{13}OSi$: C, 38.56; H, 3.03. Found: C 38.88, H 2.95.

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