MIXED ORGANOFLUORINE - ORGANOSILICON CHEMISTRY: REACTION OF PERFLUOROORGANOMETALLIC REAGENTS WITH BENZOYLSILANE

Charles Portella* and Boniface Dondy

Laboratoire des Réarrangements Thermiques et Photochimiques, associé au CNRS, Faculté des Sciences, BP 347, 51062 REIMS (France)

Summary: Reaction of a perfluoroorganometallic (Mg or Li) reagent with benzoylsilanes gives, depending on the metal, the substituents and the reaction conditions, the F-alkyl phenyl trialkylsilyl carbinol 3, the F-alk-1-enyl phenyl ketone 4 or the 1-phenyl-1-trialkylsilyloxy-F-alk-1-ene 7.

The energy of the silicon-fluorine bond ($\approx 590 \text{ kJ.mol}^{-1}$) accounts for the very high reciprocal affinity of these two elements. Widely used in classical organic chemistry², this property has rarely been exploited in organofluorine chemistry. Except for the fluoride induced reaction between trifluoropropene and disilane³, the literature affords only examples exhibiting conventional reactivity such as generation of carbanions from silylated organofluorine substrates by nucleophilic substitution by fluoride⁴. We assumed that, owing to the easy β -elimination of a fluoride ion (from fluorinated carbanions) and its high affinity for silicon (in organosilicon molecules), new reactions and/or products would occur in reactions of organofluorine substrates with organosilicon substrates. Such chemistry would constitute a frontier area between organofluorine and organosilicon chemistry.

To test this concept, we chose as starting materials acylsilanes and iodoperfluoroalkanes. The choice of acylsilane arose from the reports of Reich and co-workers, who combined the Brook rearrangement⁵ of an α -silyl alkoxide (1,2-C to O migration of silicon), with the β -fragmentation of a leaving-group, to regiospecifically synthesize silyl enol ethers⁶. Our key hypothesis was that, if the leaving-group had been a fluoride, further steps would have occurred involving nucleophilic attack on the silicon by the fluoride. We report here preliminary results obtained by reaction of perfluoroorganometallic reagents on benzoylsilane. The latter was chosen as a model because it was a simple, non enolizable silylketone, and because the phenyl group would favour the Brook rearrangement. Magnesium and lithium derivatives were considered.

When F-hexylmagnesium bromide, prepared by halogen-metal exchange⁷ from F-hexyliodide <u>1</u> ($R_F = C_4F_9$), was reacted with benzoyltrimethylsilane <u>2</u> in ether at -45°C, a slow reaction took place leading, after hydrolysis at this temperature, to the corresponding alcohol <u>3</u>⁸ in 78% isolated yield⁹ (scheme 1). This conventional addition reaction leads to a new class of alcohols, which can be conveniently named by the old nomenclature: aryl perfluoroalkyl trialkylsilyl carbinol. The course of the reaction of $\underline{2}$ with a perfluoroorganolithium reagent was completely different (scheme 2). Owing to its low stability ¹⁰, the lithium derivative was generated in situ by

$$R_{F} - CF_{2} - CF_{2} - I \xrightarrow{i-iii} R_{F} - CF_{2} - CF_{2} - CF_{2} - CF_{2} - SiMe_{3}$$

$$Ph$$

$$\frac{1}{2}$$

$$\frac{3}{2} (78\%)$$

i, EtMgBr, Et2O, -45°C, 30 min.; ii, PhCOSiMe3 2, -45°C, 15h; iii, aq. HCl.

Scheme 1

$$\underline{1} + \underline{2} \xrightarrow{i,ii} R_{F} - CF = CF - C - Ph + R_{F} - CF = CF - C - Ph + R_{F} - CF = CF - C - Ph + R_{F} - CF = CF - C - Ph + CH_{3}$$

$$\underline{4} (67\%) \qquad \underline{5} (21\%)$$

i, MeLi (Ether solution of MeLi, LiBr), Et₂O, -80°C, 45 min.; ii, aq. HCl.

Scheme 2

adding methyllithium to a solution of $\underline{1}$ and $\underline{2}$ in ether at -80°C. A fast reaction yielded the enone $\underline{4}$ as the major product (67% isolated yield) accompanied by the alcohol $\underline{5}^{11}$ arising from a secondary 1,2-addition of methyllithium to $\underline{4}$, as was verified in a separate experiment. Owing to the very fast formation of the enone $\underline{4}$, the best conditions for restricting the secondary reaction was to add the methyllithium quickly to the mixture of reactants.

The enone $\underline{4}$ was obtained as a mixture of isomers in which the Z configuration was the major one, as shown by gas chromatographic analysis of the crude product (Z/E=75/25). Contact with silicagel isomerized the Z to the E isomer and the latter could be isolated almost exclusively after chromatographic purification.

Perfluoroalkenyl ketones are interesting compounds which can be considered as starting materials of choice for the synthesis of various derivatives such as α -fluoro- β -diketones and fluorinated heterocycles. Alkyl analogs have previously been synthesized by addition of perfluoro-alkenyl magnesium bromide to acyl chlorides with moderate isolated yields ($\leq 50\%$)¹².

Although other hypotheses could be made, a mechanism involving a Brook rearrangement at the lithium alkoxide level accounts best for the formation of the enone (scheme 3). According to our initial assumption, the intermediate silyl enol ether (from LiF elimination) reacts with the fluoride and gives, after a formal 1,4 elimination of Me_3SiF , the enone <u>4</u>.



This mechanism accounts for the influence of the metal on the course of the reaction. At low temperature, only the lithium alkoxide rearranges, whereas the more covalent magnesium analog is stable giving, after hydrolysis at the reaction temperature (-45° C), the corresponding alcohol 3.

All these mechanistic considerations were confirmed by two experiments. The enone $\underline{4}$ was prepared in high yield from the perfluoroorganomagnesium reagent if the reaction mixture was allowed to warm and was kept for several hours at room temperature before hydrolysis (scheme 4). Under these conditions, the Brook rearrangement took place giving $\underline{4}$ as the unique product (86% yield)⁹ In the second experiment, the last step leading to enone formation was slowed by substituting a methyl group on silicon by a bulky t-butyl group. Addition of methyllithium to an ether solution of $\underline{1}$ and benzoyl-t-butyldimethylsilane $\underline{6}$ at -80°C (45 min.) gave $\underline{4}$ and the silyl enol ether $\underline{7}^8$ in 28% and 51% yield respectively (scheme 5). The secondary addition product $\underline{5}$ was now limited to less than 3%.

$$R_{F} - CF_{2} - CF_{2} - MgBr + 2 \xrightarrow{i} R_{F} - CF_{2} - CF_{2}$$

Scheme 4

Ph- CO- SitBuMe₂ +
$$1 \xrightarrow{i_{1}i_{1}} 4 + 5 + C_{5}F_{11} - CF = C$$

6 (28%) (<3%) 7 (51%)
6 (28%) (<3%) 7 (51%)

i, MeLi, LiBr, Et₂O, -80°C, 45 min.; ii, aq. HCl.

Scheme 5

Thus the nature of the metal, of the substituents, and the reaction conditions strongly affect the successive steps and consequently the results. Research is in progress to explore the scope of this new reaction and the chemical applications of these new fluorinated derivatives.

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- 8 All new compounds reported here gave spectral and analytical data consistent with assigned sructures. Selected NMR data (δ ppm, internal reference: CFCl₃ and TMS for ¹⁹F and ¹³C spectra respectively): <u>3</u>: -106.3 (CF₂α); 76 (t, C(OH), J=33 Hz). <u>4</u> Z isomer: -121.7 (Fα), -148.2 (Fβ); E isomer: -142.2 and -154.9 (F_α and F_β, AB type system, J=142 Hz). <u>7</u>: 135.6 (CF, dt, J=241 and 30 Hz), 145.7 (C(Ph), d, J12 Hz).
- 9 based on converted benzoylsilane <u>2</u>. Reaction with the magnesium reagent yielded a minor amount of unreacted <u>2</u>: 11% in the preparation of alcohol <u>3</u>, 14% in the preparation of enone <u>4</u>.
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