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Fluoride-induced proto- and carbodesilylation of S,S-, O,O- and O,Ssilylated acetals: an insight into the chemical and stereochemical reaction outcome

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### SHORT COMMUNICATION

## Fluoride-induced proto- and carbo-desilylation of S,S-, O,Oand O,S-silylated acetals: an insight into the chemical and stereochemical reaction outcome<sup>†</sup>

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A general overview on the chemical and stereochemical behavior of a wide range of stereodefined 2-silyl-1,3-dithianes, -1,3-dioxanes, -1,3-dioxolanes and -1,3-oxathiolanes is reported, when subjected to fluoride ion-induced proto- and carbo-desilylation. Retention of configuration or epimerization appears to depend not only on the kind of the substituents on the aromatic ring, but also on the nature of heteroatoms in the silyl acetals, leading to envisage the occurence of a free carbanion or of an hypervalent-silylated species.



Keywords: silyl acetals; fluoride ion; proto-desilylation; carbo-desilylation; stereocontrol

#### 1. Introduction

Organosilanes have been widely used in the search for new synthetic methodologies and in this context, the fluoride ion-induced reactivity of the C–Si bond has for long time been used for the generation under mild conditions of nucleophilic species suitable to react with electrophiles (1). Of particular interest are 1,3-dithiane anions generated by fluoride-induced desilylation and widely used in umpolung reactivity as masked acyl carbanions and examples of silyl dithiane functionalization have been reported in (2). However, in the past fluoride-induced proto- or carbodesilylation of such molecules has never been applied to stereoselective synthesis. Only recently several investigations (3) have uncovered interesting examples of proto- and carbo-desilylation

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<sup>&</sup>lt;sup>†</sup>Dedicated to the memory of our colleague and friend Professor Alessandro Degl'Innocenti.

of sterically defined silyl dithianes occurring with retention of configuration. In order to obtain a deeper insight into the origin and the limits of this stereochemical outcome, which poses the premises for the development of a synthetically interesting stereoconservative synthetic methodologies, a wider range of S,S-, O,O- and O,S-silylated acetals has been subjected to both protoand carbo-desilylation and the results are reported in this paper.

#### 2. Results and discussion

When both 4c,6c-r-2- (**1a**) and 4t,6t-r-2-trimethylsilyl-2,4,6-trimethyl-1,3-dithiane (**1b**) were subjected to fluoride-induced desilylation with 0.4 equiv tetrabutylamonium fluoride (TBAF) at r.t. for 4 h, they reacted smoothly to afford the corresponding 1,3,5-trimethyl dithianes **2a** and **2b**, respectively, in good yields and with clean retention of configuration (Scheme 1) (3a, b).



Scheme 1. Fluoride-induced desilylation of 4c,6c-r-2- (1a) and 4t,6t-r-2-trimethylsilyl-2,4,6-trimethyl-1,3-dithianes (1b).

With 4*c*,6*c*-r-2-trimethylsilyl-2-phenyl-4,6-dimethyl-1,3-dithiane **3**, however, the results of the desilylation were less straightforward appearing as a function of the temperature and of the equivalents of TBAF used. So far under the same conditions used in Scheme 1, the sole product deriving from the inversion of configuration was observed. On the other hand, when the desilylation of **3** is carried out at  $-5^{\circ}$ C with 0.02 equiv of TBAF for 15 min, proto-desilylation occurs with clean retention of the configuration albeit with very low yields, whereas an increased amount of TBAF (0.2 equiv) led to complete desilylation after 2 h but with substantial epimerization (Scheme 2).

On these premises, a stereoconservative behavior emerges in the TBAF-induced protodesilylation, though an increased acidity of the C-2 hydrogen  $\alpha$  to the aromatic ring can favor epimerization (4). Furthermore, these results highlight the concept that the reported reactions are likely to proceed via a pentacoordinated silicon intermediate rather than through a free carbanion, which should be expected to undergo easy epimerization.

Extension to more synthetically useful carbo-desilylation reactions confirmed this trend with stereochemically defined silyl dithianes bearing H or a Me<sub>3</sub>Si group as substituents at C-2 leading to the expected products in satisfactory yields but with an excellent stereoconservative outcome (*3*). However, again the carbo-desilylation of the phenyl substituted derivative **3** performed with 4-anysaldehyde led to a less straightforward reaction behavior. Only under strictly controlled conditions, the expected carbo-desilylation product **5** was obtained (Scheme 3, route *a*) in good yield (83%) besides minor amounts (16%) of the proto-desilylation product **4a**, both with retention of configuration. On the other hand, when the reaction was performed at r.t. with higher amounts



Scheme 2. Fluoride-induced desilylation of 4c,6c-r-2-trimethylsilyl-2-phenyl-4,6-dimethyl-1, 3-dithiane (**3**) under different reaction conditions.

of TBAF only the product of proto-desilylation (**4b**) with inversion of configuration was detected (Scheme 3, route b) in the reaction mixture.



Scheme 3. Carbo-desilylation of 3 under different reaction conditions.

A fragility of the carbo-desilylation product **5** has been detected in the presence of an exceeding amount of TBAF, most likely due to a retro-aldol reaction, and accounts for this behavior.

With the aim of establishing the role of the heteroatom in driving the stereochemistry in the proto- and carbo-fluorodesilylations of the silylated cyclic compounds, the 2-trimethylsilyl-2-phenyl-4,6-dimethyl-1,3-dioxane **6a**, the oxygenated counterpart of **3**, was considered. To the best of our knowledge, no example appeared in the literature, but an analogue reaction was reported on 4-silyl-1,3-dioxane functionalization (5). Thus, **6a** was subjected to proto-desilylation under the same conditions employed in Scheme 1. Remarkably, a low tendency to epimerize could be noticed for the oxygen derivative with respect to the sulfur analogous. The absence in the dioxanes **6a–c** of a heteroatom that can provide a  $\sigma^*$  orbital suitable to host as in the case of the sulfurated derivative **3**, the electrons generated by H extraction by the F<sup>(-)</sup> ion would certainly make the deprotonation more difficult and any putative carbanion less stabilized. Both these facts may account for the minor epimerization. However, a sizeable effect of the aromatic ring substituents

on the epimerization is noticed, which increased with the stabilization of the carbanionic species generated by desilylation (Scheme 4).



\*Reaction conditions in the carbo-desilylation of 6b: 1.5 eq. TBAF, 24 h r.t.

Scheme 4. Proto- and carbo-desilylation of dioxanes **6a–c**.

Moreover, regarding the stereoisomeric ratio in Scheme 4, one possibility is that the observed epimerization might take place at the level of the desilylated acetals by proton extraction, to some extent reasonable in the case of the more acidic **7a** and **7c**. This assumption, however, can be ruled out in the case of **7b**. Due to the high-energy difference between the two diastereoisomers, an exceeding, if not the sole, amount of the more stable compounds **8a–c** should be generated, which contrasts with the experimental findings. The formation of balanced mixtures in which the less stable stereoisomers **7a–c** prevail should be conversely ascribed to the formation of a not carbanionic intermediate, even though a slower epimerization with respect to the quench of the carbanion by the electrophilic proton remains a viable hypothesis.

In the carbo-desilylation with 2-furylaldehyde of dioxanes **6a–c** (Scheme 4), several interesting features can be noticed. Again the amount of epimerization is strongly affected by the nature of the substituent in the aromatic ring and increases from 33% (R = p-OMe–C<sub>6</sub>H<sub>4</sub>–) to 40% ( $R = C_6H_5$ –) up to 55% (R = p-CF<sub>3</sub>–C<sub>6</sub>H<sub>4</sub>–) with the possibility that an intermediate carbanion could be stabilized. Moreover, whereas the proto-desilylation of dioxanes **6a–c** takes place at comparable rates, in the corresponding carbo-desilylation **6b** results to be poorly reactive. Since for a reaction occurring via a highly destabilized free carbanion species a high reactivity is expected, the low reactivity observed in this case can be justified only with the formation in the rate-determining step of an hypervalent silicon species on which the attack of the C-electrophile would be prevented by the high steric hindrance.

The mechanism that can be proposed for the formation of a silicon intermediates is described in Figure 1 on the basis of already reported hypervalent silicon as the reactive site in bond formations (6). Nonetheless, for the reactions described in this communication, no definitive evidence for an unambiguous mechanicistic pathway can be assumed. In fact, it is commonly recognized that it is difficult to accurately assess the precise nature, coordination and conformation of the active catalyst and transition state orientation in this kind of reactions.

Along the lines previously envisaged for the dioxanes, the proto- and carbo-desilylations of the less conformationally rigid 2-silyl-1,3-dioxolanes **11a–c** take place. An almost complete retention



Figure 1. Proposed mechanisms for the fluoride induced desilylation.

of configuration (96%) is found in the proto-desilylation of **11b** (Scheme 5). Such an excellent stereoconservative stereochemistry might be ascribed to the occurrence of an intermediate hypervalent-silylated species in the case of **11b** whereas the increasing amounts of epimerized products found in the corresponding reaction of **11a,c** might be accomplished with the formation of a more free carbanionic species. Worth noting only in the case of the dioxolane **11c**, the expected diastereomeric acetals are obtained with a high degree of epimerization (from 43% to 53.6%) but in very low yields, the main product (85%) being an oligomeric species (Scheme 6) derived by a combination of different monomeric quinoidic bis-fluorinated units coming from  $F^{(-)}$  ion delivery from a free stabilized carbanionic species. This finding supports, therefore, the concept that a carbanionic-like species must be highly effective in the proto-desilylation of this compound and in general in all the cases in which a high stabilization of a negative charge occurs.



\*In the proto-desilylation of **11b** 1 eq. TBAF has been used. \*\*The carbo-desilylation of **11b** has been performed for 160 h and 2 eq. TBAF.

Scheme 5. Proto- and carbo-desilylation of dioxolanes 11a-c.

It is worth noting that the extent of the observed oligomerization could be slightly diminished by running the proto-desilylation reaction in the presence of one equiv. CH<sub>3</sub>COOH.

The carbo-desilylation of dioxolanes follows once more the trend previously observed, the extent of epimerization being however slightly larger than that observed in the proto-desilylation.



Scheme 6. Oligomerization of dioxolane11c.

This can be ascribed to the lower energy difference between the stereochemically different carbodesilylated products with respect to the corresponding acetals. Interestingly in the case of **11c** by using the separate diastereoisomers or their mixture in a 3:1 ratio in the crude reaction mixture, the ratio between the diastereomeric alcohols is the same (Scheme 7).



Scheme 7. Carbo-desilylation of dioxolanes diastereoisomers11c and 11'c.

This points out again toward a free carbanion-like mechanism viable in those cases in which a stabilization of the negative charge is made possible. In line with this assumption **11b** results to be highly unreactive in the carbo-desilylation even in the presence of an excess of TBAF and after long reaction time, which may suggest again a difficult formation of an hypervalent silicon species due to the severe steric crowding. Finally, the absence of the oligomerization previously observed in the proto-desilylation reaction outlines an intriguing aspect of the reactivity of dioxolanes, which opens the route to hypothetical mechanistic differences occurring between the proto- and carbo-desilylation of these compounds, at present under investigation.

To evaluate the replacement of an oxygen atom with sulfur on the fluoride-promoted desilylation reaction and on the stereochemical outcomes, oxathiolanes 16a-c have been taken into consideration and subjected to proto- and carbo-desilylation. As a general trend, the epimerization in both the proto- and carbo-desilylation of oxathiolanes **16a–c** appears higher with respect to that observed in the case of dioxolanes (Scheme 8).



\*The carbo-desilylations of **16a,b,c** were performed at 0°C / r.t.: 60 min. for **a**, 105 min. for **b** and 15 min for **c**. \*\*The proto-desilylation of **16c** has been performed at r.t. for 15 min.

Scheme 8. Proto- and carbo-desilylation of oxathiolanes 16a-c.

So far in the case of proto-desilylation of **16a**, a 40.5% epimerization is detected versus a 27.5% found in the case of **11a**. In the same way 7.9% and 62.9% of epimerization obtained for **16b** and **16c** outlines the influence of the sulfur atom in the stereochemical outcome. Worth noting in the case of **16c**, the reaction performed with 1 equiv TBAF after only 15 min leads to the product of proto-desilylation in a 46.5% yield together with the 53% yield of oligomerization, which is substantially lower than 85% obtained in the case of **11c**, but still in line with the intermediacy of free carbanion-like species. The lesser oligomerization can be accounted for by the different nature of the carbanionic species, since in **16c** the negative charge can be delocalized also into the  $\sigma^*$  orbital of sulfur, thus preventing to some extent the F<sup>(-)</sup> ion delivery and the generation of the monomeric reactive intermediate (Scheme 9).

The carbo-desilylation trend confirms again the differences between **11a–c** and **16a–c**, and as in the case of dioxolanes no oligomerization is observed in the carbo-desilylation reaction. A remarkable difference in the reaction behavior between dioxolanes and oxathiolanes occurs in the case of the carbo-desilylation of compound **16b**, which takes place with a much higher rate with respect to **11b**. The presence of the sulfur atom in the five-membered ring makes **16b** much more reactive, probably due to the higher Lewis acidity of the silicon atom, but the still low epimerization is in line with the intermediacy of a hypervalent organosilicon species.

An interesting insight into the nature of the reactive intermediate in the reaction of 16c is provided by the use of the two pure diastereoisomers of 16c and 16'c (Scheme 10) in both the proto- and carbo-desilylation reactions. Under the same reaction conditions, the composition of the diastereomeric mixtures of the acetals and of the carbo-desilylated products appears very similar and this means that the epimerization is different for the single diastereoisomers. This finding can be ascribed to the intermediacy of a free carbanion or to the formation of the thermodynamic mixture at the level of products. This latter possibility, in principle viable due to the presence of TBAF in the case of acetals (17c/18c) obtained by proto-desilylation, can be ruled out in the case



Scheme 9. Oligomerization of oxathiolane 16c.

of the carbo-desilylation products (19c/20c), thus supporting the intermediacy in this case of a classical carbanionic species.

#### 3. Conclusions

In summary, a general overview has been provided on the chemical and stereochemical outcome of a wide range of S,S-O,O- and O,S-silylated acetals subjected to proto- and carbo- fluoride-induced desilylation. The extent of retention of configuration or of the epimerization appears clearly dictated by the substituents in the aromatic moiety as well as by the nature of the heteroatoms in the silylated acetals. These structural features are likely to affect the reaction mechanisms that range between the occurrence of a free carbanion to the intermediacy of an hypervalent-silylated species. The observed oligomerization in the case of the proto-desilylation of p-CF<sub>3</sub>-substituted dioxolane and oxathiolane, in line with the presence of a highly delocalized negative charge, seems to not have its counterpart in the carbo-desilylation reaction. This intriguing aspect, which reinforces the hypothesis of a substantial change of mechanism between these two reactions, is nowadays under investigation.

#### 4. Experimental section

#### 4.1. General remarks

 Silylated acetals were prepared according to the previously described procedures (3). Proto-desilylation reactions (proto-desilylation reactions were performed under anhydrous conditions as the cardo-desilylation reactions. The proton sources can be: not-dry products,



Scheme 10. Proto- and carbo-desilylation of oxathiolanes diastereoisomers 16c and 16'c.

enolizable electrophiles or dry TBAF. The GC-MS analysis of the crude proto-desilylation reaction mixtures revealed the presence of tributylamine derived by Hofmann elimination. On the other hand, tributylamine was not revealed in carbo-desilylation reactions (7)) are performed as described in ref. (3a). All compounds showed spectroscopical and analytical data consistent with the assigned structure. NMR spectra were recorded at 400, 300 and 600 MHz for <sup>1</sup>H and 75.45 and 150.8 MHz for <sup>13</sup>C. Full assignments of <sup>1</sup>H and <sup>13</sup>C signals were obtained by bi-dimensional experiments (edited-gHSQC (8) and gHMBC (9) sequences). Structural assignment of the diastereoisomers was deduced from NOE experiments acquired at 600 MHz, by means of the double pulsed field gradient spin echo-NOE (10) sequence. To selectively irradiate the desired signal of each diastereoisomer, a 20 Hz-wide shaped pulse was calculated with a refocusing-selective excitation for biochemical application shape (11)and a pulse width of 92.5 ms. Mixing time was set to 1.25/1.75 s. In the case of 11'c, the NOE spectra obtained by saturation of the SiMe<sub>3</sub> signal showed NOE on the aromatic ortho hydrogens. This enhancement can be used as a "control" NOE enhancement that is valuable to evaluate the position of the methyl group in position four of the dioxolane ring. The saturation of the SiMe<sub>3</sub> signal showed also a strong NOE effect on the signal of the H in position four and a weak enhancement on the methyl signal. These data suggested that the methyl and the SiMe<sub>3</sub> lie on the opposite side of the dioxolane ring in 11'c. The same approach was used to assign the relative stereochemistry of the other compounds.

#### 4.2. Typical Procedure

*Proto-desilylation.* Silylated acetal (1 mmol) was dissolved in 10 mL of dry THF and added portion wise every 1 h with 0.5 mL of TBAF solution (0.2 M in THF). The progress of the reaction was monitored by TLC (petroleum ether/diethyl ether 98:2). After the addition of the required amount of TBAF (reported in the related schemes), a complete proto-desilylation was observed (7). The mixture was then treated with a 5% solution of NH<sub>4</sub>Cl, extracted with diethyl ether and dried over MgSO<sub>4</sub>. Filtration and evaporation of solvent gave crude acetals, whose NMR spectra were identical with an authentic sample.

*Carbo-desilylation.* Two 5 mL round bottom flasks equipped with a magnetic stirring bar were separately charged with 0.5 mmol of the two diastereoisomers 11c and 11'c under N<sub>2</sub> atmosphere. Dry THF (1 mL for each flask) was then added followed by 1.0 mmol of 2-furaldehyde. Dry TBAF 0.5 M in dry THF (aliquots of 0.1 mmol) was added at r.t. in each flask to the homogenized solutions. After the addition of only 0.2 eq. of TBAF, 11c and 11'c were not detectable (TLC eluent petroleum ether/ $Et_2O: 4/1$ ), nevertheless the addition of 1.0 eq. of TBAF was completed in order to avoid the presence of O-SiMe<sub>3</sub> derivatives along with alcohols 14c and 15c. After an hour of stirring at r.t., the reactions were quenched by the addition 0.5 mL of a saturated solution of NH<sub>4</sub>Cl. After extraction with Et<sub>2</sub>O and evaporation of solvents, the residues were separately purified by flash chromatography on silica gel. A first fraction containing the two diastereoisomers of 14c in a 1:1 ratio (<sup>1</sup>H-NMR) was obtained using petroleum ether/ $Et_2O:4/1$  as the eluent, next a second fraction containing the two diastereomers of **15c** in a 1:1 ratio (<sup>1</sup>H-NMR) was obtained using petroleum ether/Et<sub>2</sub>O:7/3 as the eluent. From **11c** (0.207 g of crude product), it was obtained a first fraction (0.0633 g) of 14c/14'c and a second fraction (0.0761 g) of 15c/15'c; from 11'c(0.223 g of crude product), it was obtained a first fraction (0.0617 g) of 14c/14'c and a second fraction (0.0760 g) of 15c/15'c.

*I4c/14'c. Mixture of isomers.* <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 1.33 (d, 3H, J = 6 Hz), 1.35 (d, 3H, J = 6 Hz), 2.58–2.82 (bs, 2H), 3.52 (app t, 2H), 3.91–4.03 (m, 2H), 4.07–4.15 (m, 2H), 4.87 (s, 1H), 4.88 (s, 1H), 6.17 (dd, 2H, J = 7 Hz, J = 1 Hz), 6.27 (bs, 2H), 7.32 (bs, 2H), 7.48–7.54 (m, 8H). <sup>13</sup>C NMR (75.45 MHz, CDCl<sub>3</sub>):  $\delta = 17.9$ , 18.0, 71.7, 72.0, 72.5, 72.6, 72.8, 73.0, 108.9, 109.2, 109.5, 109.6, 110.4, 124.7 (q,  $J_{C-F} = 285$  Hz), 124.77, 124.82, 124.86, 127.0, 127.1, 142.0, 142.1, 144.0, 151.5, 151.5.

**15***c*/**15**′*c*. *Mixture of isomers*. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 1.18 (d, 3H, J = 6 Hz), 1.20 (d, 3H, J = 6 Hz), 2.42–2.58 (bs, 2H), 3.33 (dd, 2H, J = 15, 7 Hz), 4.23 (dd, 1H, J = 15, 4 Hz), 4.24 (dd, 1H, J = 15, 4 Hz), 4.32–4.41 (m, 2H), 4.83 (s, 1H), 4.87 (s, 1H), 6.14 (bd, 2H, J = 1 Hz), 6.26–6.28 (m, 2H), 7.32 (bd, 2H, J = 6 Hz), 7.42–7.55 (m, 8H). <sup>13</sup>C NMR (75.45 MHz, CDCl<sub>3</sub>):  $\delta = 18.3$ , 18.4, 71.6, 71.9, 72.9, 74.8, 75.1, 108.9, 109.0, 110.4, 124.6 (q,  $J_{C-F} = 284$  Hz), 124.7, 124.76, 126.89, 126.98, 142.1, 142.2, 144.5, 151.5. **MS** (*m*/*z*): 328 (0.08) [M<sup>+</sup>]; 254 (3); 331 (88); 225 (6); 173 (100); 145 (20); 95 (8).

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