Silyl-substituted Diazoacetic Esters in Superacid Media—A Stable Ion and Solvolysis Study†

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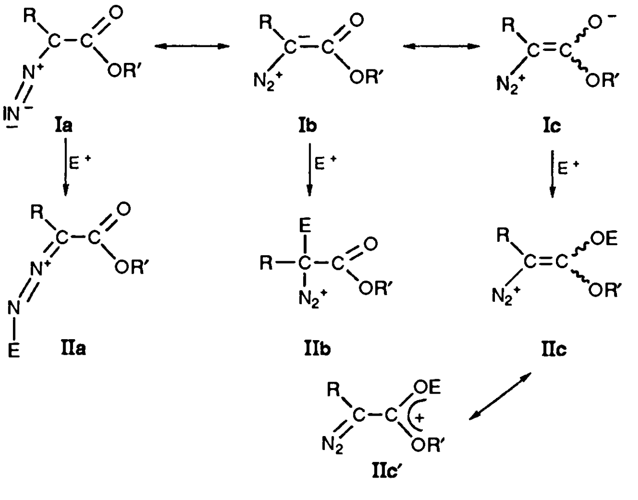
For methyl diazo(triisopropylsilyl)acetate (**1**) and methyl diazo(pentamethyldisilanyl)acetate (**2**), the protonation and subsequent chemistry in superacids, as well as the solvolysis reactions with non-aqueous acids (FSO_3H, CF_3SO_3H, HF) have been studied. Upon solvolysis of **1** by FSO_3H or CF_3SO_3H, protonation, dediazoniation and gegenion addition occur without concomitant desilylation, whereas with HF, partial desilylation takes place. Upon solvolysis of **2**, only desilylated esters are obtained. When **1** is allowed to react with the superacid $FSO_3H{\cdot}SbF_5(1:1)/SO_2$ at $\leqslant -75$ °C, five major ions are formed, among them the silyl-substituted enoldiazonium ions (*Z*)- and (*E*)-**9** (corresponding to *O*-protonated **1** and the protonated (fluorosulfonyloxy)acetate **4**-H^+. In the lower-acidity superacid FSO_3H/SO_2 the *O*-protonated silyldiazoesters [(*Z*)-**9**, (*E*)-**9**] and the *C,O*-diprotonated (**14**-H^+) silyldiazoesters are present. Ion **14**-H^+ is slowly transformed into **3**-H^+ by N_2 loss and gegenion addition. In the reaction mixture from **2** and $FSO_3H{\cdot}SbF_5$ (1:1)/SO_2, the *O*-protonated silyldiazoester [enoldiazonium ion (*Z*)-**15**] as well as the desilylated ions **4**-H^+ and **10** (or **11**) can be identified in relative yields that are temperature dependent (−75 or −85 °C). The silyl-substituted ions **9** and **15** are the first enoldiazonium ions derived from a diazoacetic ester that have been observed, and **16** is the first alkanediazonium ion of this type.

α-Diazocarbonyl compounds display ambident reactivity towards electrophiles. As is shown in Scheme 1 for α-diazoesters, the three important resonance structures **Ia** (a diazocarbonyl compound), **Ib** (a diazonium ylide) and **Ic** (a diazonium enolate) suggest three sites for electrophilic attack, and consequently, a diazenium ion **IIa**, an alkanediazonium ion **IIb** or an alkenediazonium ion **IIc** may be generated.



Scheme 1 Possible sites of electrophilic attack in diazoacetic esters

Whereas numerous examples of electrophilic attack at the diazo carbon exist,[1] trapping of the diazonium enolate has been observed less frequently, and no examples of electrophilic addition at the terminal nitrogen atom are known. For instance, reaction of ethyl diazoacetate with triethyloxonium salts yields isolable, thermally stable 2,2-dialkoxyethenediazonium salts.[2,3] Similarly, *O*-alkylation of ω-diazoacetophenone generates an alkenediazonium salt.[4] Spectroscopic and chemical evidence,[2,3] as well as high-level calculations and a crystal structure analysis,[5] all point to dominant diazocarbenium and diazooxonium character (Scheme 1, **IIc** ⟷ **IIc′**) of the stable alkenediazonium salts obtained from diazoacetic esters by *O*-alkylation. The chemistry of these diazonium species is characterized by β-S_N2 reactions rather than by monomolecular loss of N_2 leading to a vinyl cation.

Previous work by one of us[6] showed that the diazonium enolate form of α-diazoketones can be trapped by acyl triflates at −70 °C. *In situ* dediazoniation of the generated alkenediazonium salts at higher temperatures (*ca.* −40 to +10 °C, depending on the substituents) accompanied by cyclization provides access to 1,3-dioxolium salts. In the same vein, *O*-sulfonylation by triflic anhydride generates alkenediazonium ions that lose N_2 at low temperature; trapping of the derived vinyl cation moieties by the gegenion yields alkene-1,2-bis(triflates).[7]

Under persistent ion conditions in superacid media ($FSO_3H{\cdot}SbF_5/SO_2$ or $HF{\cdot}SbF_5/SO_2$) primary and secondary diazoketones are protonated at the carbonyl oxygen atom to give a mixture of *syn* and *anti* enoldiazonium ions.[8,9] Under normal solvolytic conditions, no evidence for either *O*-protonation (with the exception of the HCl-catalysed methanolysis of 2-diazo-1,2-diphenyl-1-ethanone[10]) or *N*-protonation was found. Decomposition in acidic D_2O leads to H/D exchange in primary diazoketones, indicative of reversible *C*-protonation.[11]

In general, protonated diazoesters are much less stable than protonated diazoketones; for ethyl diazoacetate, loss of dinitrogen occurred even at −60 °C upon reaction with $HF{\cdot}SbF_5/SO_2$ or $FSO_3H{\cdot}SbF_5/SO_2$; in the latter case, only $EtO_2C{-}CH_2{-}OSO_2F$ was isolated.[9] Therefore, the site of protonation of diazoesters has not yet been determined. When α-silyldiazoacetic esters are treated with aqueous acids, both dediazoniation and desilylation occurs.[12] The kinetics of the solvolysis of ethyl diazo(trimethylsilyl)acetate in aqueous perchloric acid point to initial *C*-protonation followed

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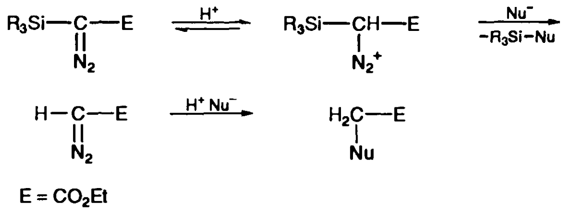


Scheme 2 Possible decomposition pathways of a (silyl)diazoacetate during acid-catalysed solvolysis

by nucleophile-assisted cleavage of the Si–C bond (Scheme 2).[12,*]

Recently, the interaction of silyl groups with positively charged carbon has been elucidated both experimentally and theoretically.[13] A carbenium centre is inductively stabilized by an α-silicon relative to α-H, and the stabilizing effect of an α-pentamethyldisilanyl group is similar to that of α-Me; on the other hand, hyperconjugative stabilization accounts for the β-effect of silyl groups.[13] Whereas a number of α-silyl-substituted carbenium ions have been directly observed in superacids,[14,†] observation of β-silyl-substituted carbenium ions in these media is still rare,[15,16] since even the anions present in superacids can undergo nucleophilic attack at silicon thereby initiating Si–C bond cleavage. The latter complication can be circumvented by the use of bulky silyl groups. With these facts in mind, we decided to study the protonation of α-silyl-α-diazoacetic esters **1** and **2** in superacid media in the hope that cations such as **IIb** and **IIc/c′** (E = H, R = silyl group) would become directly observable. For comparison, we also investigated the decomposition of **1** and **2** in non-aqueous acids under normal solvolysis conditions.

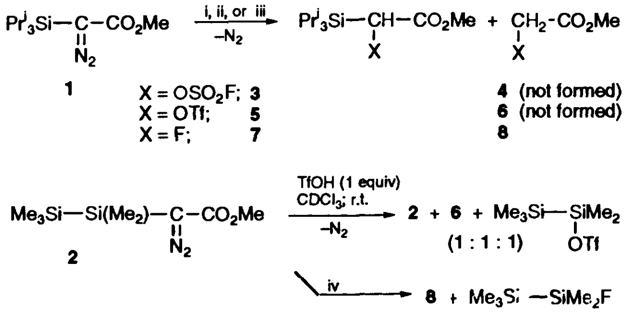
$$\begin{aligned} \text{R-C(N}_2\text{)-CO}_2\text{Me} \quad \mathbf{1}: \text{R} &= \text{Si(Pr}^i)_3 \\ \mathbf{2}: \text{R} &= \text{SiMe}_2\text{-SiMe}_3 \end{aligned}$$

Results

Solvolysis of **1** *and* **2** *by the Non-aqueous Acids.*—When diazoester **1** was treated with one equivalent of fluorosulfuric acid or triflic acid in CH_2Cl_2 at 0 °C, ready dediazoniation occurred. (Triisopropylsilyl)acetates **3** and **5** were isolated in significant yields (74 and 60% respectively), but products of Si–C cleavage such as the (fluorosulfonyloxy)acetate **4** or the (trifloxy)acetate **6** were not found. In contrast, solvolysis by excess HF in CD_2Cl_2 furnished fluoro(triisopropylsilyl)acetate **7** and fluoroacetate **8** in nearly equal amounts (Scheme 3).

Solvolysis of **2** by triflic acid (1 equiv.) in $CDCl_3$ at room temperature was subsequently investigated. Under these conditions, nearly half of **2** remained unreacted. Pentamethyldisilanyl triflate and (trifloxy)acetate **6** were obtained in 1:1 ratio; a dediazoniation/trapping product with the Si–C bond intact (**5**) was not observed. Solvolysis of **2** in excess HF/CH_2Cl_2 gave methyl fluoroacetate (**8**, *ca.* 75% by NMR spectroscopy) and pentamethyldisilanyl fluoride in a 1:1 ratio; again, no dediazoniation/trapping product containing an intact Si–C bond (*e.g.* **7**) was detected.

The results described above show that acid-induced dediazoniation/trapping of α-silyl-α-diazoesters without concomitant desilylation is possible when the following two conditions



Scheme 3 Solvolysis of **1** and **2** by FSO_3H, CF_3SO_3H and HF. *Reagents and conditions:* i, FSO_3H (1 equiv.) CH_2Cl_2, 0 °C; ii, TfOH (1 equiv.), CH_2Cl_2, 0 °C; iii, HF (excess), CD_2Cl_2, -75 °C ⟶ room temp.; $FSO_3H{\cdot}SbF_5$ (1:1)/SO_2, -70 °C

are met: (a) the silicon atom is shielded by bulky substituents and (b) the nucleophilicity of the reaction medium is low. In the reaction of **1** with HF, the formation of the strong Si–F bond [E_{dis}(Si–F) = 590 kJ mol^{-1}][17] is certainly the driving force for attack of F^- at the sterically shielded silicon atom and Si–C cleavage.

Protonation of **1** *in Superacids.*—Careful addition of a clear homogeneous solution of $FSO_3H{\cdot}SbF_5$ (1:1) (magic acid^R) in liquid SO_2 to a solution of **1** in SO_2 at *ca.* -98°C (ethanol/liquid nitrogen bath) gave a yellow, highly viscous solution with no noticeable loss of dinitrogen. The temperature was then raised slowly to *ca.* -75 °C (dry ice/acetone) to reduce viscosity and to allow efficient mixing, during which time some loss of N_2 was noted. The ^1H NMR spectrum of the resulting dark yellow solution, recorded at -75 °C, is reproduced in Fig. 1. A virtually identical spectrum was obtained in the less nucleophilic solvent SO_2ClF. Thus, SO_2 complexation need not be considered in the assignments, and the more readily available SO_2 was used in all subsequent experiments.

The spectrum (Fig. 1) showed five major signals that were attributed to deshielded methoxy groups (δ 4.27, 4.42, 4.75, 4.80 and 5.10) thus indicating the presence of at least five major species. The identity of the OMe signals were confirmed by the ^1H NMR spectrum obtained in deuteriated magic acid^R; in this case, the OMe signals remained unchanged, whereas the intensity of the signals at lower field, assigned to CH_2 and OH absorptions, were dramatically reduced.

The ^{13}C NMR spectrum of **1** in $FSO_3H{\cdot}SbF_5$ (1:1)/SO_2 was also recorded at -75 °C, using a more concentrated solution of **1** than for the proton spectrum. Only three sets of signals were clearly recognizable all of which showed signals between 61–67 (OMe), 52–53 (quaternary carbon), 63–69 (assigned to methylene carbon atoms), and 169–183 ppm (carbonyl region). The multiplicities could not be readily deduced in the proton-coupled ^{13}C NMR spectrum owing to extensive overlap. Moreover, the quaternary carbon region overlapped with the CD_2Cl_2 multiplet. The assignments made are shown in Scheme 4 and Fig. 2. About 50% of the ion mixture consists of enoldiazonium ions (*Z*)-**9** and (*E*)-**9** (*i.e.* *O*-protonated **1**) in a 4:1 ratio. They account for the most upfield pair of methoxy singlets and the two enolic OH singlet absorptions (OMe:OH = 3:1 for both species, Fig. 1). Assignment of the two stereoisomers is based on the assumption that the OH proton in (*Z*)-**9** is deshielded because of its closer proximity to the diazonio group as compared to the *E* isomer. This argument has been put forward before for *O*-protonated diazoketones.[9] The presence of a desilylated enoldiazonium ion (**9**, H instead of $Pr^i{}_3Si$) was ruled out since no signal of the required intensity is found in the ^1H NMR spectrum; furthermore, the expected[9] ^4J coupling with the enolic OH proton was not observed. The ^{13}C NMR signals at

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[*] The detailed mechanism of the nucleophilic substitution at silicon (S_N2-like or addition–elimination) in these cases is not known. In any case, the neutral ethyl diazoacetate is a good leaving group.

[†] Although carbocations are destabilized with respect to alkyl groups by α-silyl group, the cation Ph-C$^+$(Me)($SiMe_3$) has been observed in superacid media under appropriate conditions: H.-U. Siehl, personal communication.

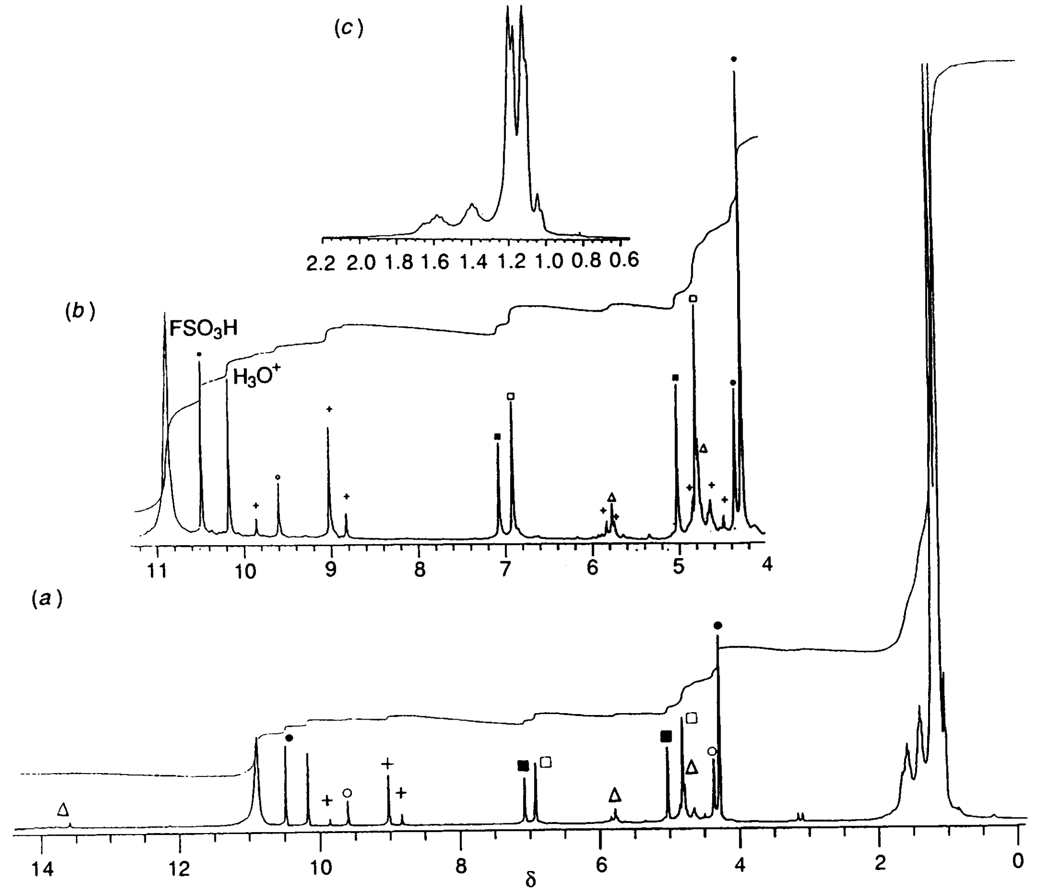
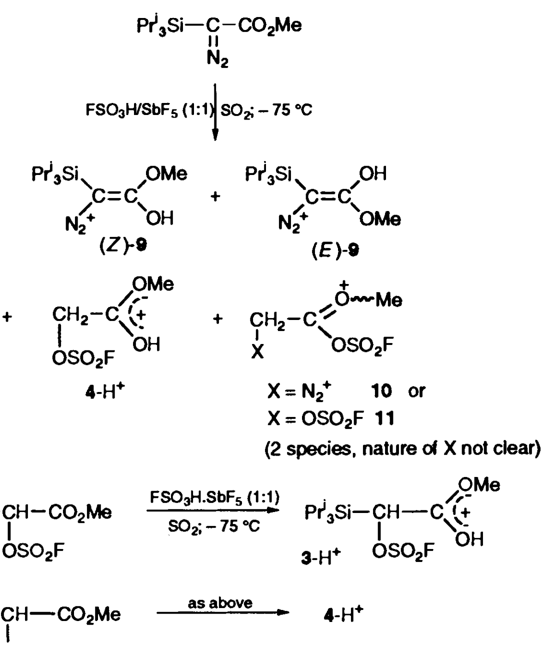


Fig. 1 ^{1}H NMR spectrum (300 MHz) of 1 in $FSO_3H{\cdot}SbF_5$ (1 : 1)/SO_2 at −75 °C; (*a*) the entire spectrum; (*b*) and (*c*) expansions [● = (*Z*)-9; ○ = (*E*)-9; △ = 4-H$^+$; ■ and □ = two isomers of either 10 or 11; + = unknown species]



Scheme 4 Low-temperature protonation of 1 in $FSO_3H{\cdot}SbF_5$ (1 : 1)/SO_2 and independent protonation of 3 and 4

53.3 and 182.1 were assigned to the sp^2 carbons of the major isomer [(*Z*)-9]; they are in close correspondence to the values found in the 2,2-diethoxyethenediazonium ion[5] (δ 55.7 and 177.8).

In order to establish the presence or absence of the dediazoniation products 3 and 4 (as their *O*-protonated forms 3-H$^+$ and 4-H$^+$) among the remaining constituents of the ion mixture, we recorded the NMR spectra of authentic 3 (see above) and 4 (obtained from methyl diazoacetate and FSO_3H) under identical conditions [$FSO_3H{\cdot}SbF_5$(1 : 1)/SO_2, −75 °C]. In this manner, the presence of 4-H$^+$ and the absence of 3-H$^+$ in the ion mixture resulting from 1 were clearly established. It should be noted that the opposite result was obtained when 1 was treated with FSO_3H under normal solvolysis conditions (see above, Scheme 3). Among the three products that are present in a 3 : 2 : 1 ratio besides (*Z*)- and (*E*)-9 as the major constituents of the ion mixture, 4-H$^+$ is the minor component. The remaining two species are characterized by significantly deshielded methoxy (^{1}H: 4.80, 5.10; ^{13}C: *ca.* 67; CH_2:OMe = 2 : 3 by ^{1}H NMR spectroscopy in both cases). By comparison with the other data in Fig. 2, the two sets of signals are tentatively assigned to the *syn*/*anti* pair of either 10 or 11. The close similarity of the corresponding chemical shifts appears to be in agreement with stereoisomerism at the C=O$^+$Me bond, but not with one set of signals belonging to 10 and the other to 11 [compare the chemical shift difference between $CH(N_2^+)$ and $CH(OSO_2F)$ in 3-H$^+$ and 14-H$^+$, Fig. 2]. If 11 represents the correct structure, it should be noted that it is not derived from 4-H$^+$ under stable ion conditions, since the independent protonation of 4 shows 4-H$^+$ to be persistent.

The Pr^i_3Si region of the ion mixture shows two doublets of almost equal size, the more upfield one of which is distinctly broader [Fig. 1(*c*)]. Comparison with the spectrum of an authentic sample of Pr^i_3SiF (obtained from triisopropylsilyl triflate and sodium fluoride) suggests that the broader, more upfield doublet at δ 1.20 stems from Pr^i_3SiF formed as a by-product.

In a control experiment, carbon monoxide was bubbled

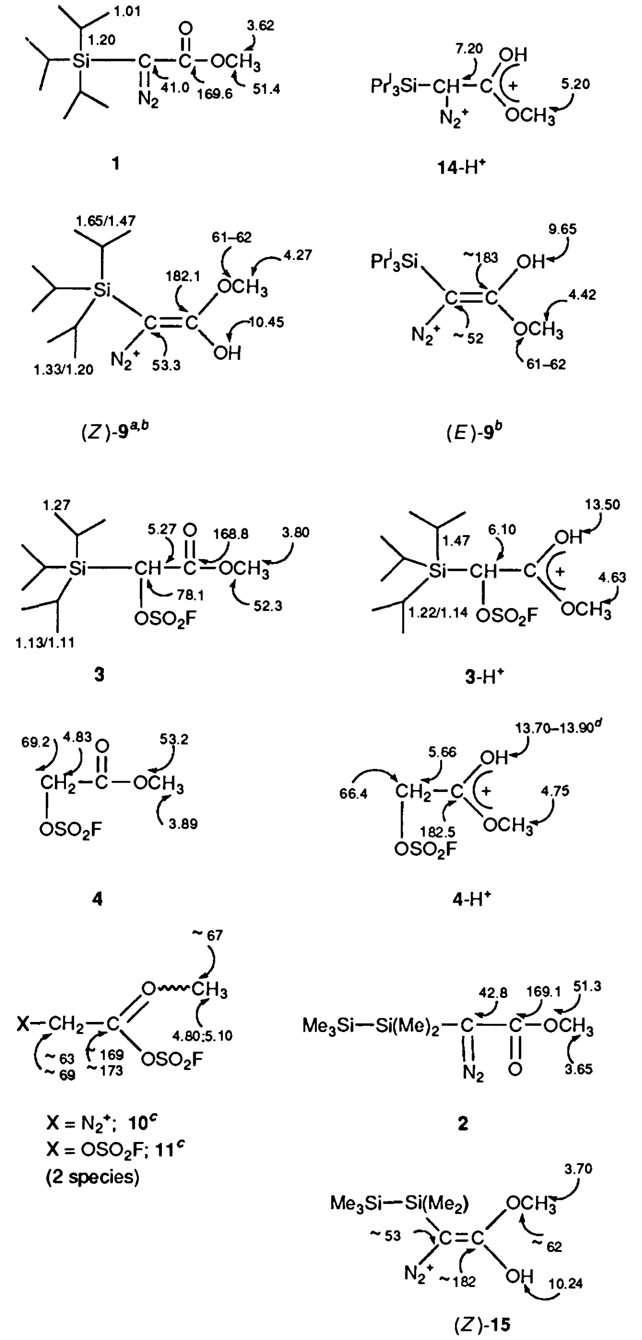


Fig. 2 NMR data (^{1}H and ^{13}C, δ values) of **1** and **2** and their persistent ions formed in superacid media. [a] The two sets of values given for the Pr^i groups refer to both (*E*)- and (*Z*)-**9**. [b] For assignments of the (*Z*) and (*E*) isomers of **9**, see text. [c] Nature of X not established; the two sets of signals are assigned to a *syn*/*anti* pair. [d] Variable depending on sample temperature and concentration.

through the cold ion solution resulting from protonation of **1** in magic acid^R/SO_2. The ^{1}H NMR spectrum remained virtually unchanged. The lack of reaction with CO points to substantial oxonium ion (rather than carbenium ion) character of species **4**, **9**, **10** and **11**. Furthermore, it suggests that species such as α-acylcarbenium ion **12** or vinyl cation **13** are not present.

$Pr^i_3Si\text{-}C^+H\text{-}CO_2Me$ **12** $Pr^i_3Si\text{-}C^+{=}C(OH)OMe$ **13**

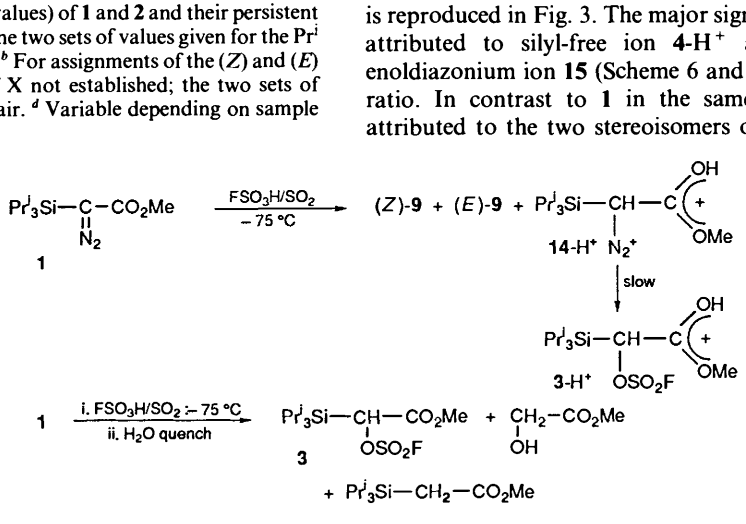
In order to explore whether the acidity (H_0) and nucleophilicity of the superacid medium has an impact on the low temperature protonation, **1** was reacted with the lower acidity superacid FSO_3H/SO_2 at dry ice/acetone temperature (Scheme 5). *O*-Protonation to give enoldiazonium ions (*Z*)- and (*E*)-**9** as well as *C*,*O*-diprotonation to form **14**-H$^+$ were observed. In the ^{1}H NMR spectrum, no OH signal showed up for any of these ions. This fact must be attributed to rapid exchange of the OH protons with the solvent acid, this process being also responsible for the broadening of the acid peak. The alkanediazonium ion **14**-H$^+$, which was not present in magic acid^R/SO_2, showed two deshielded singlets at δ 5.20 and 7.20 (relative intensity 3 : 1) for the OMe and the CH groups.

In agreement with the structural assignment for **14**-H$^+$, it is slowly converted by dediazoniation and gegenion addition into **3**-H$^+$ which was identified by NMR comparison with a solution of authentic **3** in magic acid^R/SO_2 (see above).

The ^{1}H NMR spectrum of protonation of **1** in FSO_3H/SO_2 recorded at −60 °C indicated that *ca.* 30% of **14**-H$^+$ had been converted to **3**-H$^+$ without a noticeable decrease in the more upfield OMe absorptions assigned to stereoisomeric **9**. The spectrum recorded after one week's storage of the sample at −25 °C showed that **3**-H$^+$ had increased to *ca.* 75% of the ion mixture; the enoldiazonium OMe singlets were greatly reduced (*ca.* 22% of the mixture), and **14**-H$^+$ was present only in 1–2%.

When the ion solution resulting from **1** in FSO_3H/SO_2 was quenched with water (Scheme 5), fluorosulfate **3** was obtained as the major product (80%; identification by ^{1}H and ^{19}F NMR spectroscopy) besides minor amounts of methyl (hydroxymethyl)acetate (GC; GC–MS: *m*/*z* 89) and methyl (triisopropylsilyl)acetate [GC–MS: *m*/*z* 230 (68%, M$^+$), 182 (100%), 123 (90%, 182–CO_2Me)]. The mode of formation of the latter product, formally requiring a hydride transfer, is not clear.

Protonation of **2**.—Slow addition of magic acid^R/SO_2 to **2** in liquid SO_2 at −75 °C (dry ice/acetone) gave a yellow-brown solution, the ^{1}H NMR spectrum of which (recorded at −75 °C) is reproduced in Fig. 3. The major signals of the spectrum were attributed to silyl-free ion **4**-H$^+$ and to silyl-substituted enoldiazonium ion **15** (Scheme 6 and Fig. 2), present in a 3 : 2 ratio. In contrast to **1** in the same superacid, the signals attributed to the two stereoisomers of **10** or **11** were present



Scheme 5 Low-temperature protonation of **1** in FSO_3H/SO_2 and quenching with H_2O

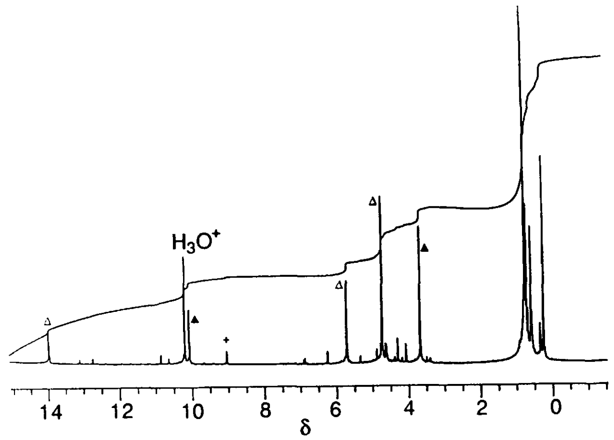


Fig. 3 ^{1}H NMR spectrum (300 MHz) of **2** in $FSO_3H{\cdot}SbF_5$ (1 : 1)/SO_2 at −75 °C [△ = **4**-H$^+$; ▲ = (*Z*)-**15**; + = unknown species]

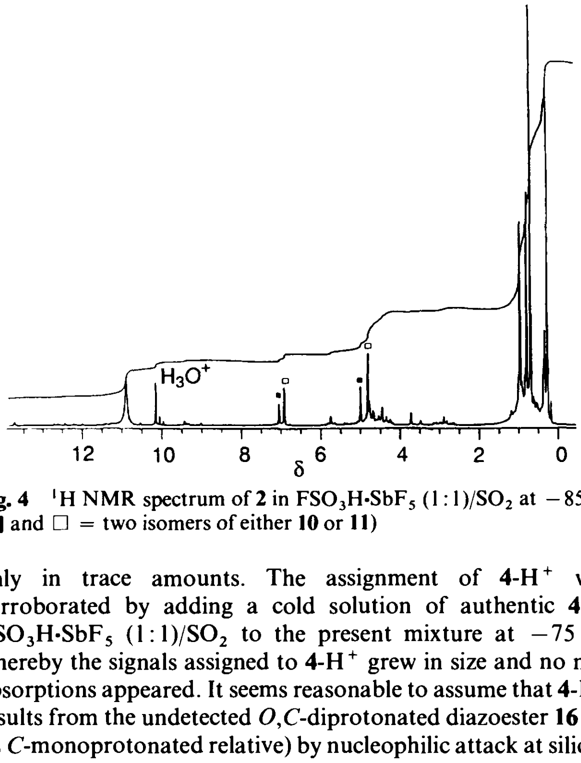
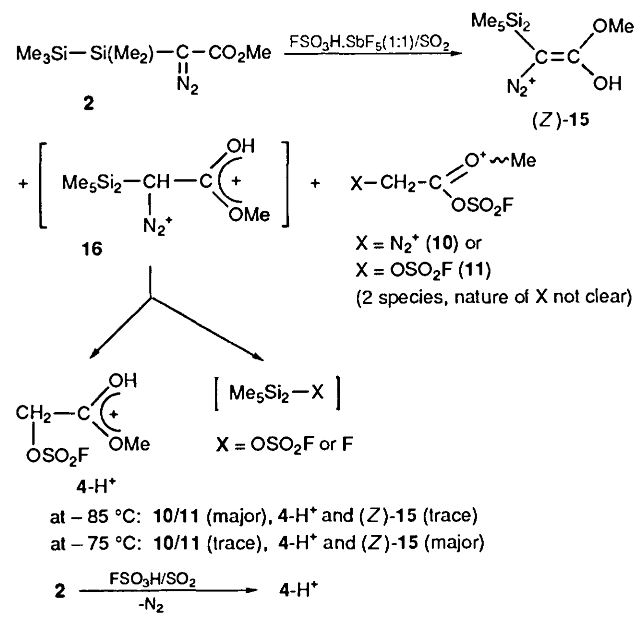


Fig. 4 ^{1}H NMR spectrum of **2** in $FSO_3H{\cdot}SbF_5$ (1 : 1)/SO_2 at −85 °C (■ and □ = two isomers of either **10** or **11**)

only in trace amounts. The assignment of **4**-H$^+$ was corroborated by adding a cold solution of authentic **4** in $FSO_3H{\cdot}SbF_5$ (1 : 1)/SO_2 to the present mixture at −75 °C, whereby the signals assigned to **4**-H$^+$ grew in size and no new absorptions appeared. It seems reasonable to assume that **4**-H$^+$ results from the undetected *O*,*C*-diprotonated diazoester **16** (or its *C*-monoprotonated relative) by nucleophilic attack at silicon and Si–C cleavage. The expected silicon-containing by-product, pentamethyldisilanyl fluorosulfate (or fluoride, see Discussion), is likely to undergo subsequent reaction with the superacid, as the following observations show. The aliphatic region of the NMR spectrum under discussion shows four major singlets at 0.22 ($SiMe_3$), 0.58 ($Me_3Si{-}OSO_2F$), 0.70 and 0.77 (deshielded $SiMe_2$?), a broad hump centred at *ca.* 0.95 ppm, and a tiny triplet at 0.33 ppm. When pentamethyldisilanyl triflate was independently dissolved in magic acid^R/SO_2 at −75 °C, the signals at δ 0.35, 0.77 and 0.95 appeared in the NMR spectrum, thus indicating a reaction of the pentamethyldisilanyl ester with the superacid.

Enoldiazonium ion **15** has ^{1}H NMR signals at δ 3.70 (OMe) and 10.24 (=COH) in the expected 3 : 1 ratio. For the reasons discussed below (see Discussion), the *Z* geometry is proposed for this ion. The other stereoisomer is either absent or present only in minor amounts [in the latter case, one of the tiny signals at 4.05 and 4.28 would belong to (*E*)-**15**, see Fig. 3]. For (*Z*)-**15**, a possible explanation for magnetic shielding of the OMe protons as compared to (*Z*)-**9** is intramolecular association with the $SiMe_3$ group *via* a five-membered chelate-type geometry.



Scheme 6 Low-temperature protonation of **2** in superacids

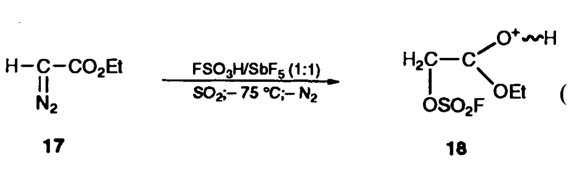
The spectral assignments of **4**-H$^+$ and (*Z*)-**15** were again supported by control experiments. In the ^{1}H NMR spectrum of **2** in deuteriated magic acid^R, the CH_2 (**4**-H$^+$) and the OH (**15**) signals were drastically reduced, whereas the OMe signals remained unchanged. When CO was bubbled through the solution of **2** in magic acid^R/SO_2, no change in the ^{1}H NMR spectrum was noted, suggesting the absence of highly reactive carbenium ions analogous in structure to **12** and **13**.

A dramatic change was observed when **2** was reacted with $FSO_3H{\cdot}SbF_5$ (1 : 1)/SO_2 at −85 °C instead of −75 °C. The ^{1}H NMR spectrum (Fig. 4), also recorded at −85 °C, showed **10** or **11** (two isomers) to be the major constituents, whereas **4**-H$^+$ and (*Z*)-**15** were present only in traces. Formation of the former ions from both **1** and **2** is a clear indication that these species do not contain a silyl group.

Protonation of **2** was also studied in FSO_3H/SO_2 at dry ice/acetone temperature. Extensive evolution of N_2 was observed, and **4**-H$^+$ was the only product detectable in the ^{1}H NMR spectrum. Again, the OH proton of this species was not observable due to fast exchange with the solvent acid.

Protonation of Methyl and Ethyl Diazoacetate.—The preceding experiments have shown that there is an influence of the silyl substituent on the outcome of protonation of diazoesters, as compared to the observations that have been made[9] for low temperature protonation of methyl diazoacetate in magic acid^R/SO_2. The latter results could be fully confirmed by us. Slow addition of a cold solution of magic acid^R/SO_2 to a solution of methyl diazoacetate in liquid SO_2 at −75 °C led to extensive dediazoniation. The ^{1}H NMR spectrum of the resulting yellow solution showed only **4**-H$^+$, with no enoldiazonium ion being observed.

In situ dediazoniation and gegenion addition were also the major events in the reaction of ethyl diazoacetate (**17**) with magic acid^R/SO_2 at −75 °C [reaction (1)]. After a vigorous reaction, the ^{1}H NMR spectrum of the sample at −70 °C showed one major (δ 1.60) and two minor (δ 1.50, 1.75)



(1)

OCH_2CH_3 triplets as well as a cluster of OCH_2CH_3 multiplets between δ 4.50–5.60, the most intense ones being at δ 4.70 and 5.60. Presence of two CH_2 singlets (δ 5.68 and 5.70, *ca.* 70:30) and two COH^+ absorptions (δ 13.28 and 13.50) indicated the formation of two geometrical isomers of protonated (fluorosulfonyloxy)acetate **18** as the major product. Formation of geometrical isomers was previously observed for *O*-protonated ethyl formate and ethyl acetate.[18] The positions of the COH^+ and OCH_2CH_3 protons in **18** are in close agreement with those of the *O*-protonated esters mentioned.

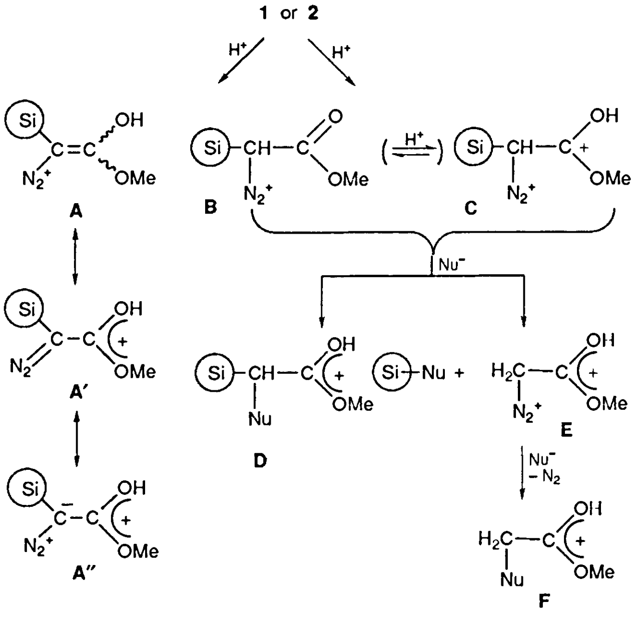
Discussion

Protonation of **1** *and* **2**.—Upon low-temperature protonation of silyldiazoesters **1** and **2** in superacid media, enoldiazonium ions **9** and **15** (species **A**, Scheme 7) and ion **14**-H^+ (species **C**) have been directly observed, but not the *C*-protonated diazoesters (species **B**). Whereas **A** corresponds to the direct protonation of the diazonium enolate form of the silyldiazoesters, it cannot be said *a priori* whether **C** results from either **A** or **B**. Whereas ions of type **A** were persistent in all low-temperature protonation experiments [with **1** or **2**, in $FSO_3H{\cdot}SbF_5(1:1)/SO_2$ and in FSO_3H/SO_2], a species of type **C** (namely **14**-H^+) was observed only when diazoester **1** was reacted with FSO_3H/SO_2. Two reasons may account for the absence of **14**-H^+ in the magic acid^R/SO_2 reaction and its presence in the FSO_3H/SO_2 reaction:

(a) In the higher acidity superacid, *O*-protonation of **1** is fast and irreversible whereas it is reversible in FSO_3H/SO_2 (note the absence of the OH proton in the ^1H NMR spectrum because of fast exchange with the solvent acid), thus allowing for subsequent *C*-protonation of **1** followed by *O*-protonation (**B** ⟶ **C**). The observation that slow conversion of **14**-H^+ to **3**-H^+ was accompanied by significant reduction in **9** appears consistent with this possibility.

(b) Ions of type **A** and **C** (*via* **B**) are formed independently and simultaneously, but ions of type **C** (and/or **B**, if the equilibrium **B** $\rightleftharpoons$ **C** exists) are prone to facile Si–C cleavage that is assisted by nucleophilic attack at silicon. In fact, since enoldiazonium ions **9** and **15** coexist with the products of Si–C cleavage (**4**-H^+) under stable ion conditions (Schemes 5 and 6), the former ones cannot be precursors of the latter. This argument also implies that they cannot be precursors of a *C,O*-diprotonated species **C** which then gives **4**-H^+, causing gradual disappearance of **9** or **15** at the expense of **4**-H^+. The fluoride ion is a highly suitable candidate for the Si–C cleavage reaction taking place in $FSO_3H{\cdot}SbF_5$ system, since it can attack even the strongly shielded silicon atom in **14**-H^+ (compare solvolysis of **1** with HF, Scheme 3). Previous ^{19}F NMR studies of the magic acid^R system[19] have established the presence of the following gegenions: $SbF_5(OSO_2F)^-$ (70%), $Sb_2F_{10}(OSO_2F)^-$ (5%), FSO_3^- (12%) and SbF_6^- (7%). The system is, therefore, a highly effective fluoride ion source. On the other hand, with purified FSO_3H the F^--mediated Si–C cleavage is not competitive at low temperature, although FSO_3H is a fluoride ion source in its own right. Moreover, the FSO_3^- ion is less suited for promoting Si–C cleavage in **14**-H^+ due to a combination of reduced affinity for silicon and steric crowding in its approach to the silicon atom. For this reason, **14**-H^+ undergoes slow nucleophilic substitution of the diazonio group rather than Si–C cleavage.

According to this mechanistic scenario (Scheme 7), initial *O*- and *C*-protonation of silyldiazoesters **1** and **2** are identified as independent pathways. Enoldiazonium ions **4** and **15** are persistent in the chosen superacids at low temperature. The (α-silyl)alkanediazonium species **B** and **C**, on the other hand, are more labile: if a nucleophile is present that has a high affinity for silicon, Si–C cleavage occurs to give alkanediazonium ion **E** which is rapidly transformed into **F** by nucleophilic substitution. If no suitable nucleophile for attack at silicon is present and if the silicon atom is sterically shielded, species **C** can be observed at low temperature, but even under these conditions the diazonio group is slowly substituted to give **D** (no Si–C cleavage). These mechanistic pathways are also suited to explain the outcome of the reactions of **1** and **2** with the non-aqueous acids FSO_3H, CF_3SO_3H and HF (Scheme 3) under normal solvolysis conditions. However, the decomposition pathways of enoldiazonium ion **A** (deprotonation, desilylation, dediazoniation) at room temperature are not known.



Scheme 7 Competing *O*- and *C*-protonation of silyldiazoesters

We also wish to discuss briefly the possible mode of formation of the ions to which we have assigned structures **10** or **11**. If the assignment is correct, formation of these species requires addition of FSO_3^- at the carboxonium group $[-C^+(OH)OMe]$ and dehydration at some stage of the reaction sequence. We have demonstrated that this does not happen with ion **F** (Nu = OSO_2F). Absence of **10**/**11** from the ion mixture observed in the magic acid^R reaction of methyl diazoacetate, where ion **E** is a likely short-lived intermediate, suggests that **E** is not the precursor of **10**/**11**. Therefore, the replacement of OH by OSO_2F should occur in ion **C**. This would also account for the temperature effect described in Scheme 6, *i.e.* at sufficiently low temperatures, the addition–elimination step at the carboxonium group of ion **C** is faster than the Si–C cleavage reaction.

When methyl or ethyl diazoacetate were protonated in superacids, no ions of type **A**–**C** (H instead of silyl group) could be observed by NMR spectroscopy, but rather the products of dediazoniation and gegenion attack (ref. 9 and this work). It has been concluded[9] that if such ions are formed, they are decomposed extremely rapidly. Thus, it is not clear whether *O*- and/or *C*-protonated diazoesters account for product formation in these cases. Nevertheless, one may speculate on the stability difference between silyl-substituted enoldiazonium ions **A** and alkanediazonium ions **C** and their non-silylated congeners. If the dediazoniation of **A**–**C** were to occur by an S_N1 process, *i.e.* if ions **12**, **13** (or their *O*-protonated forms) were formed, one would expect them to be stabilized inductively by the silyl group relative to H, *i.e.* ions **A**–**C** would still be more prone to dediazoniation than the non-silylated analogues. Obviously, this is not the case at low temperature. The dediazoniation/trapping of protonated diazoacetates in superacids seems to occur by an S_N2 process with FSO_3^- as nucleophile.[9] We may, therefore, assume that the transformation of alkanediazonium ion **14**-H^+ into **3**-H^+ is also an S_N2 reaction, and that this process is somewhat retarded because of steric shielding of the reaction centre by the $SiPr^i_3$ group. For (α-silyl)enoldiazonium ion **A**, the remarkable stability in superacids is probably due to a ground-state stabilization. Resonance structures **A′**, **A″** should contribute considerably to the bond state of this ion in analogy to experimental and theoretical results obtained for 2,2-diethoxyethenediazonium ion.[3,5] These resonance structures assign a considerable negative charge to the silyl-substituted carbon, in agreement with the magnetic shielding of the latter (Fig. 2). Stabilization of the negative charge by an α-silyl group is a well-known fact, and the phenomenon described here merely reflects the significantly enhanced thermal stability of (α-silyl)diazo compounds as compared to their non-silylated analogues.[1]

If the silyl groups were to stabilize the positive charge in the carboxonium moiety of ions **A′** and **C**, the hyperconjugative nature of the β-silicon effect would require the Si–C bond to align with the π-system of the carboxonium group. In **C**, this is in fact possible, but the importance of the β-silyl effect is considered low since the positive charge is already delocalized in the $C^+(OH)(OMe)$ group. As far as **A′** is concerned, resonance **A** $\longleftrightarrow$ **A′** requires the molecular skeleton to be planar, and the β-silyl effect cannot operate.

On the Stereochemistry of the Enoldiazonium Ions.—^1H NMR assignments for the (*E*)- and (*Z*)-**9** (Fig. 2) are in accord with previous studies on diazoketones;[8,9] the more deshielded OH and the more shielded OMe signals are assigned to the preferred (*Z*)-isomer (corresponding to the *syn* conformation of the diazocarbonyl moiety in **1**). Preference for the *syn* isomer formation was previously also observed for *O*-protonated diazoacetone.[8]

Dynamic NMR studies on methyl diazoacetate itself showed near equal population of the *s-cis* and *s-trans* isomers.[20] However, with the secondary diazoketones, 3-diazobutan-2-one and 3-diazo-4-methylpentan-2-one the isomer ratios of 4 : 1 and 9 : 1 were observed (although the preferred isomer could not be assigned).[20] High level theoretical studies by Glaser *et al.*[21] showed that the *syn* isomer in β-(carboxyvinyl)diazonium ions was preferred. A recent X-ray analysis[22] of $Me_3SnC(N_2)CO_2Et$ revealed that this diazoacetic ester is fixed in a *Z* conformation with a linear CNN group. It is conceivable that **1** similarly exists in a preferred *s-Z* conformation, and that upon *O*-protonation to give **9**, the conformer ratio is retained.

Regarding enoldiazonium ion formation from **2**, very predominant formation of one conformation was observed. In line with the arguments given above for predominant formation of (*Z*)-**9** from **1**, it is proposed that enoldiazonium ion **15** is present in the *Z* configuration, preference for which may again have its origin in preferential trapping of the *s-Z* conformation of the diazocarbonyl moiety of **2**; Si participation (chelate formation *via* $Me_3Si\cdots OMe$) could further contribute to stabilize the *Z* configuration of **15**.

Conclusions

In superacids at low temperature (α-silyl)diazoacetic esters are *O*-protonated and *C,O*-diprotonated. The (α-silyl)enoldiazonium ions resulting from *O*-protonation are stable at −75 °C in both $FSO_3H{\cdot}SbF_5$ (1 : 1)/SO_2 and in FSO_3H/SO_2. In contrast, the (α-silyl)methanediazonium ions resulting from *C,O*-diprotonation are prone to nucleophile-assisted Si–C cleavage even in the superacid. This cleavage reaction can be prevented only if both of the following conditions are met: (a) the silicon atom is shielded by bulky substituents ($SiPr^i_3$ instead of $SiMe_2SiMe_3$) and (b) the superacid is not an efficient fluoride ion source (purified FSO_3H/SO_2 instead of magic acid^R/SO_2). In this case, the *C,O*-diprotonated diazoester is persistent in the superacid at −75 °C, but slowly undergoes dediazoniation/gegenion (FSO_3^-) attack. No *O*-protonation or *C,O*-diprotonation products can be observed when methyl or ethyl diazoacetate are dissolved in superacids at low temperature, but rather the products of dediazoniation and gegenion attack. Thus the experiments described here with (α-silyl)diazoesters have allowed for the first time direct observation of *O*-protonated and *C,O*-diprotonated diazoacetic esters under stable ion conditions.

Experimental

Materials.—FSO_3H, CF_3SO_3H ('TfOH') and SbF_5 (all Aldrich) were freshly distilled in an all-glass distillation unit under a dry nitrogen atmosphere prior to use. HF and SO_2 (anhydrous; Linde) were used without further purification. FSO_3D was prepared by reacting FSO_3H with excess D_2SO_4 (Aldrich) and subsequent direct distillation of FSO_3D under nitrogen. The process was repeated twice in order to achieve a *ca.* 70% H–D exchange (estimated by NMR spectroscopy using CH_2Cl_2 as internal standard).

Preparative Reactions.—These were carried out under an argon atmosphere in dried solvents and in dried glassware.

The NMR Spectra.—Ambient NMR spectra were recorded on a Bruker AM 400 (^1H: 400 MHz, ^{13}C: 100.6 MHz), a GN-300 (^1H 300 MHz, ^{13}C: 75.57 MHz), and a Varian EM 390 (^1H: 90 MHz) using $CDCl_3$ as solvent (unless stated otherwise) and TMS as internal standard. *J* values are in Hz. The low temperature NMR spectra were all recorded on a GN-300 instrument with CD_2Cl_2 as internal lock and reference. Typically, the probe was cooled while spinning with a 5 mm [$^2H_6$] acetone sample. Owing to potential danger resulting from loss of nitrogen and pressure build up in NMR samples, the cold samples (5 mm tubes) were briefly dipped into liquid nitrogen prior to insertion into the cold probe. The samples were spun for 5 min at −75 °C prior to data collection. To avoid potential explosions during sample ejection, the probe was first cooled to −90 °C, the sample was quickly ejected and immersed into a dry ice/acetone bath.

Synthesis.—Methyl α-diazo-α(triisopropylsilyl)acetate **1** was synthesized according to a literature procedure.[23] δ_H 1.01 (d, *J* 12), 1.20 (m) and 3.62 (s); δ_C 11.2 ($CHMe_2$), 18.0 ($CHMe_2$), 41.0 (CN_2), 51.4 (OMe) and 169.6 (CO).

Methyl α-diazo-α-(pentamethyldisilanyl)acetate **2**. Pentamethyldisilanyl triflate[24] (2.80 g, 10 mmol) was added dropwise at 0 °C to a solution of methyl diazoacetate (1.00 g, 10 mmol) and ethyldiisopropylamine (1.74 cm^3, 10 mmol) in diethyl ether (50 cm^3). After 20 min at 0 °C, the mixture was stirred for 15 h at room temperature. Filtration over $MgSO_4$ (15 g) and evaporation of the filtrate at 20 °C/12 torr gave an oil which was purified by column chromatography [silica gel; eluent light petroleum/diethyl ether (8 : 2)] to give **2** (1.90 g; 82%) as a yellow oil (Found: C, 41.4; H, 7.8; N, 12.2. $C_8H_{18}N_2O_2Si_2$ (230.4) requires: C, 41.70; H, 7.87; N, 12.16%). ν_{max}(film)/cm^{-1} 2080 (CN_2) and 1685 (CO); δ_H 0.01 (s), 0.20 (2) and 3.65 (2); δ_C −4.4 ($SiMe_2$), −2.5 ($SiMe_3$), 42.8 (CN_2), 51.3 (OMe) and 169.1 (CO).

Methyl α-(fluorosulfonyloxy)-α-(triisopropylsilyl)acetate **3**. A solution of **1** (1.00 g, 3.9 mmol) in CH_2Cl_2 (5 cm^3) was added dropwise at 0 °C to FSO_3H (0.22 cm^3, 3.9 mmol) diluted in CH_2Cl_2 (5 cm^3). A vigorous gas evolution started immediately; when it had ceased, the solvent was removed *in vacuo* and the residue was subjected to bulb-to-bulb distillation; yield 0.90 g (74%); b.p. 120 °C/0.08 torr [Calc. for $C_{12}H_{25}FO_5SSi$ (328.5): C, 43.88; H, 7.67. Found: C, 45.45; H, 7.85%]; δ_H(400 MHz) 1.11, 1.13 (2 d, 6 H each, $CHMe_2$), 1.27 (sept, 2 H, $CHMe_2$), 3.80 (s, OMe) and 5.27 (s, CH); δ_C 10.7 (CH*Me*$_2$), 18.0 (*C*HMe$_2$), 52.3 (OMe), 78.1 (*C*HCO) and 168.8 (CO).

Methyl α-(fluorosulfonyloxy)acetate **4**. A solution of methyl diazoacetate[25] (1.00 g, 10 mmol) in CH_2Cl_2 (10 cm^3) was added dropwise to FSO_3H (1.00 g, 0.57 cm^3, 10 mmol) in dichloromethane (10 cm^3). When the vigorous gas evolution ceased, the solvent was removed *in vacuo*, and **4** was isolated by bulb-to-bulb distillation of the liquid residue at 70 °C/0.15 torr; yield 1.69 g (74%) [Calc for $C_3H_5FO_5S$ (172.1): C, 20.93; H, 2.93. Found: C, 20.95; H, 2.8%]; δ_H 3.89 (s, OMe) and 4.83 (s, CH$_2$). δ_C 53.2 (OMe), 69.2 (CH$_2$) and 165.6 (CO).

Methyl α-(trifluoromethylsulfonyloxy)-α-(triisopropylsilyl)-acetate **5**. This compound was obtained from **1** and TfOH using the procedure described for the synthesis of **3**. Bulb-to-bulb distillation at 130 °C/0.015 torr yielded **5** (0.22 g, 60%) [Calc. for $C_{13}H_{25}F_3O_5SSi$ (378.5): C, 41.25; H, 6.65. Found: C, 39.0; H, 6.5%]; δ_H(90 MHz) 0.95–1.10 (m, 21 H, CH*Me*$_2$), 3.75 (OMe) and 5.25 (CHCO); δ_C(C_6D_6) 10.6 (CH*Me*$_2$), 17.9, 18.7 (*C*HMe$_2$), 51.8 (OMe), 77.2 [d, ^1J(C,H) 144.7, *C*HCO], 119.7 [q, ^1J (C, F) 321.6, CF$_3$] and 169.0 (CO).

Reaction of **2** *with Triflic Acid*.—A solution of **2** (0.230 g, 1 mmol) in $CDCl_3$ (1 cm^3) was added *via* a syringe to a solution of triflic acid (0.150 g, 0.08 mmol, 1 cm^3) and trichloroethylene (0.131 g, 1 mmol) in $CDCl_3$ (2 cm^3). After N_2 evolution was over (*ca.* 11 cm^3, *ca.* 50% of the theoretical amount), the reaction mixture could not be separated by bulb-to-bulb distillation. The following products were identified based on the ^{1}H NMR spectrum of the reaction mixture, either by peak enhancement or by comparison with published δ values (yields were determined by integration *versus* trichloroethylene as internal standard): unreacted **2** (40%), pentamethyldisilanyl triflate (50%), **6**[26] (50%).

Preparation of Pr^i_3SiF.—To a solution of triisopropylsilyl triflate (1.14 g, 1.0 cm^3, 3.7 mmol) in dry ether (5 cm^3) was added NaF (0.50 g, 12 mmol). After stirring for 24 h, the mixture was filtered and the solid was rinsed with pentane. The solvent of the combined filtrates was removed at 20 °C/15 torr, and the product obtained as a colourless liquid (0.50 g; 77% yield) (Calc. for $C_9H_{21}FSi$: C, 61.4; H, 11.93. Found: C, 61.7; H, 11.8%); δ_H(400 MHz) 1.08 (d, CH*Me*$_2$) and 1.10 (mc, CH).

Reaction of **1** *and* **2** *with* HF.—In a typical experiment, the silyldiazoester (0.5 cm^3) was placed inside a Nalgene bottle equipped with a teflon-coated magnetic stirrer bar, and was diluted with CD_2Cl_2 (*ca.* 3 cm^3). The bottle was cooled to dry ice/acetone temperature and kept under a dry nitrogen atmosphere. Excess HF (10 cm^3) was condensed from a lecture bottle into a graduated teflon cold finger inside an efficient fume-hood, and was subsequently poured slowly into the Nalgene bottle under nitrogen with efficient mixing, whereupon a vigorous reaction occurred. After *ca.* 5 min, the cold bath was removed and the temperature allowed to rise slowly to ambient. After a total of 45 min reaction time, excess HF was vented with a stream of dry nitrogen and the residue was transferred *via* a pipette into a 5 mm quartz NMR tube and examined by NMR spectroscopy at room temperature. Product ratios were determined directly from the NMR integration. **7**: δ_H 1.05–1.15 (Pr^i), 3.74 (s, OMe) and 5.32 (d, CHF); δ_C 8–9 (CH*Me*$_2$), 14.5–15.5 (*C*HMe$_2$), 51.0 (OMe), 52.9 [d, CHF, ^1J (C, F) 179]. **8**:[27] δ_H 3.77 (s, OMe) and 4.80 [d, CH$_2$, ^1J (H, F) 46.6]; δ_C 55.3 (d, CHF), 54.1 (OMe). Me_3Si-$Si(Me_2)F$: δ_H 0.12 (s, Me$_3$Si) and 0.31 [d, SiMe$_2$, ^3J (H, F) 8.6].

Low Temperature Stable Ion Generation.—To the diazoester (20–25 mg) charged into a 10 mm NMR tube, diluted with *ca.* 0.5 cm^3 SO_2, was carefully added a clear homogeneous solution of $FSO_3H{\cdot}SbF_5$ (1 : 1) (*ca.* 0.7 cm^3) diluted in *ca.* 0.5 cm^3 of SO_2, initially at EtOH/liquid nitrogen bath temperature, followed by vigorous vortex mixing while allowing the temperature to rise slowly to dry ice/acetone bath temperature; during mixing, loss of N_2 was noticed. The resulting homogeneous sample was carefully poured directly into a precooled 5 mm NMR tube which was carefully immersed in a dry ice/acetone bath (*ca.* −75 °C) under a dry nitrogen atmosphere; *ca.* 5 drops of precooled CD_2Cl_2 was then added *via* a cold pipette. After vortex mixing, the sample was immediately examined by NMR spectroscopy as described above.

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