"Advances in Silicon Chemistry"
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CHEMISTRY OF TRIALKYLSILYL PERFLUOROALKANE SULFONATES

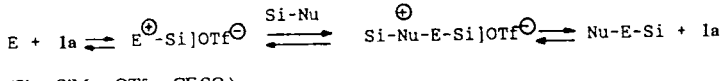
PART II.

TRIALKYLSILYL PERFLUOROALKANE SULFONATES AS LEWIS CATALYSTS IN ORGANIC SYNTHESIS

1. GENERAL ASPECTS OF CATALYSIS BY TRIALKYLSILYL PERFLUOROALKANE SULFONATES

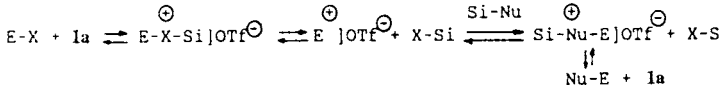
Because of its high electrophilicity, which is not affected by steric hindrance as in **1b**, trimethylsilyltriflate (**1a**) has found the broadest application as a Lewis acid catalyst. More seldom trimethylsilylnonafluorobutane sulfonate (**1r**), which is just as effective as **1a**, is used in this regard.

The hard Lewis acid **1a** activates polar multiple bonds in aldehydes, ketones, esters, imines and iminoesters (**E**) as well as polar single bonds in acetals, orthoesters, ethers, aminals, or C–Cl bonds in α-heterosubstituted chloroalkanes (**EX**). After bond formation between the reactive center activated by **1a** and a silylated nucleophile such as silylethers, silyl enol ethers, silylketene acetals, silylamines, allylsilanes, or hydrosilanes **1a** is regenerated (Schemes 1,2). So all processes including the interaction between the reaction products and **1a** are reversible at low temperatures with 0.1–10 mol% of **1a** generally are sufficient. The driving force of these reactions is the formation of the silicon-heteroatom bonds. More complex is the situation in reactions with nonsilylated nucleophiles H-Nu (Schemes 3,4). **1a** may interact with **EX** as well as with H-Nu and conse-

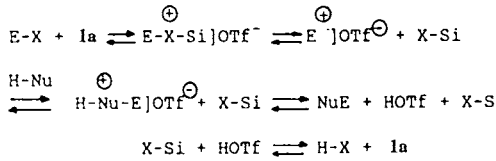


(Si = $SiMe_3$, OTf = CF_3SO_3)

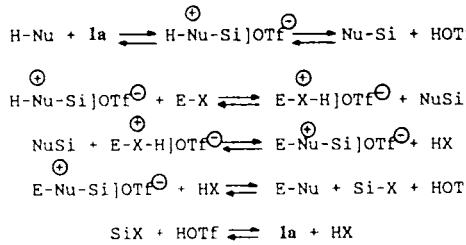
Scheme 1.



Scheme 2.



Scheme 3.



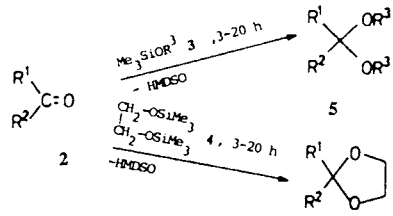
Scheme 4.

quently trifluoromethanesulfonic acid (HOTf) formed also can catalyze bond formations. The amount of **1a** required—frequently more than 10 mol%—depends on the equilibrium between X-Si and HOTf. The advantages of the catalytic processes, especially as seen in Schemes 1 and 2 are to be seen in the extraordinarily mild, aprotic, and nonbasic conditions and generally very high yields. Side reactions or polymerization processes are insignificant. All reactions can be accomplished in solvents such as ethers, dichloromethane, or 1,2-dichloroethane; acetonitrile is used only in special cases. If desired the products can be distilled directly from the reaction mixture. An aqueous workup, as is necessary in reactions catalyzed by molar amounts of $TiCl_4$ or $SnCl_4$, is not necessary. The scope of the reaction is limited by the concentration of the active species E-Si or E-X-Si formed in equilibrium and by their reactivity as well as by the nucleophilicity of NuSi or NuH. Bulky groups in E, EX, NuSi or NuH require higher amounts of catalyst **1a**.

2. CARBON–OXYGEN BOND FORMATIONS

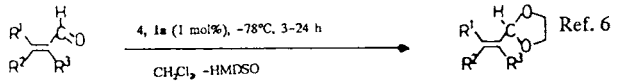
2.1. Acetalization of Aldehydes, Ketones and Lactones

In the presence of 1 mol% **1a** aldehydes and ketones **2** react with alkoxytrimethylsilanes **3** or **4** at low temperature in dichloromethane to afford acetals **5**, **6**. The yields are nearly quantitative. Owing to the great stability of hexamethyldisiloxane formed, the equilibria are shifted to the acetals.[1–4]



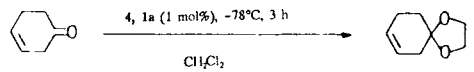
R^1–R^2 = cycloalkyl
R^1 = H, R^2 = aryl

This acetalization method is nicely suited for protection of carbonyl groups of unsaturated aldehydes and ketones[7,9] without isomerization of the double bond.[1–3,5,6] Even extensive conjugation does not prevent the acetalization. At the low temperatures possible acid labile groups (e.g., THP) are not cleaved. In the absence of steric hindrance saturated keto carbonyl groups react faster than enals.[6] Because of the "bulky proton catalyst"[5] **1a** selective acetalization of the sterically



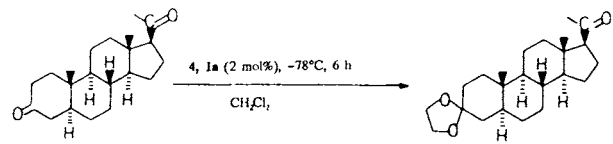
7 8 (50–100%)

7,8	R^1	R^2	R^3	7,8	R^1	R^2	R^3
a	H	H	*i*-Pr			$-CH_2-C(=CH_2)-(CH_2)_n-$	
trans-**b**	H	Ph	H	**g**	H		
trans-**c**	H	CH_2OCOCH_2Me	H				
trans-**d**	H	H_2CO		*trans*-**h**	Me	*n*-Bu	H
e	H		H	*trans*-**i**	Me		H
f	H	OEt	Me				

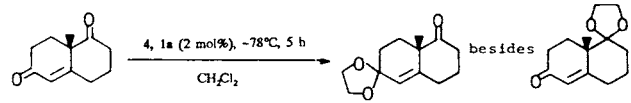


9a 10a (99%)

less hindered carbonyl groups in dicarbonyl compounds **11, 13** can be achieved,[5] e.g.,



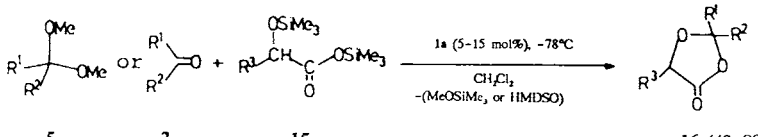
11 12 (100%)



13 14a (77%) 14b (2.9%)

Acetalization also can be carried out with TMS-Nafion (**1u**) in dichloromethane at 0°C.[2]

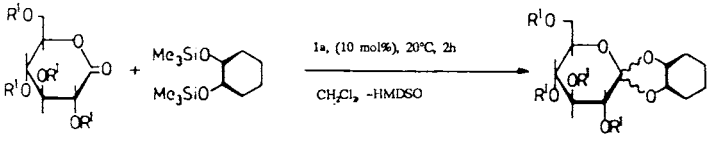
Under similar conditions 1,3-dioxolane-4-ones **16** are obtained in the reaction of acetals **5**[7,8] or carbonyl compounds[9–11] **2** with 2-(trimethylsiloxy)carboxylic acid silylesters **15.**



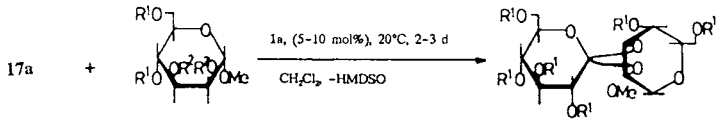
5 2 15 16 (43–99%)

R^1 = H, R^2 = *t*-Bu, *c*-C_6H_{11}, *n*-C_8H_{13}, Ph; R^1–R^2 = $(CH_2)_4$
R^3 = H,Me,$CH_2CO_2SiMe_3$,Ph

The ketalization of aldonolactones **17** by cis and trans bis-(trimethylsilyl)diols **18** requires higher reaction temperatures.[12–15] Under known methods the highest yields of spirocyclic orthoesters **19**, **20** are obtained in catalysis by **1a**, e.g.,



17a 18a 19a,b (73%)



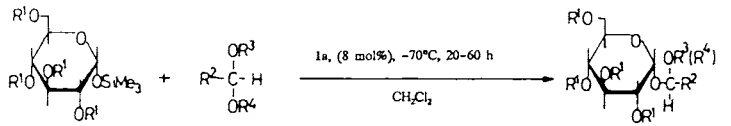
18b 20a,b (71%)

R^1 = CH_2Ph, R^2 = $SiMe_3$

2.2. Transacetalization

2.2.1 Acetal Glucosides from 1-O-Trimethylsilylglucosides and Acetals

In the reaction of 1-O-trimethylsilyl-α-glucosides **21**α with acetals **5** acetal-α-glucosides **22**α with retention of configuration are obtained at –70°C in dichloro-

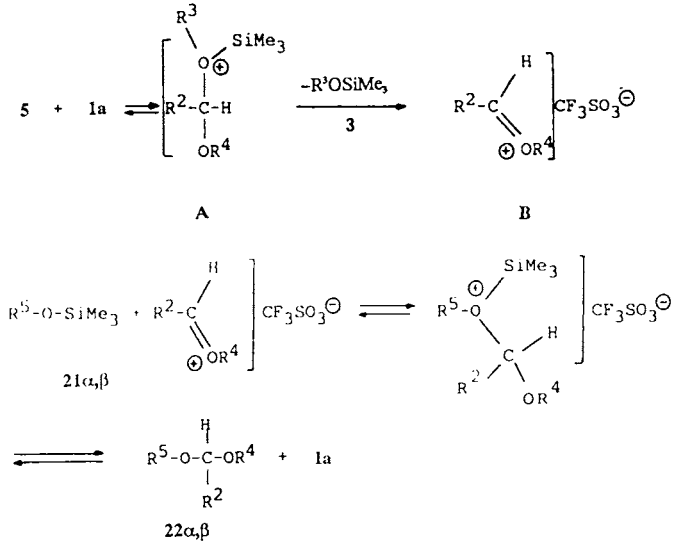


21α 5 22α

+ R^3OSiMe_3
or
R^4OSiMe_3
} 3

R^1 = CH_2Ph, MeCO
R^2 = H, Me, *n*-Pr, CH_2Ph, $CH_2CH(OMe)_2$, CH_2OCH_2Ph, CH_2OMe, CH_2Cl, CH_2Br
R^3, R^4 = Me, Et, Ph, $(CH_2)_2COOMe$

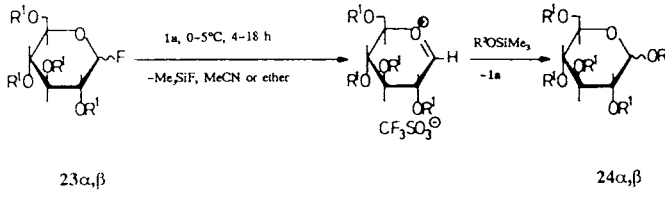
methane.[16–19] In the same manner acetal-β-glucosides **22β** result from the β-glucosides **21β**.[16,17,19–22] The reaction is also established with chloromethyl ethers. The rate of glucosidation is increased by removing the trimethylsilylethers **3** out of the equilibrium by adding acetone (see chapter II, 2.2.1). Also a mixture of aldehyde **2** and trimethylsilylether **3** can be employed instead of the acetals **5**.[18,20] In the first step of the reaction an oxonium ion **A** is formed, which decomposes to give a carboxonium ion **B**, which then attacks the trimethylsiloxy group in **21α,β** under regeneration of **1a** and retention of configuration to yield **22α,β**:



R^5 = α or β-glucosyl

2.2.2. *1-O-Alkylglycosides from Glucopyranosyl Fluorides*

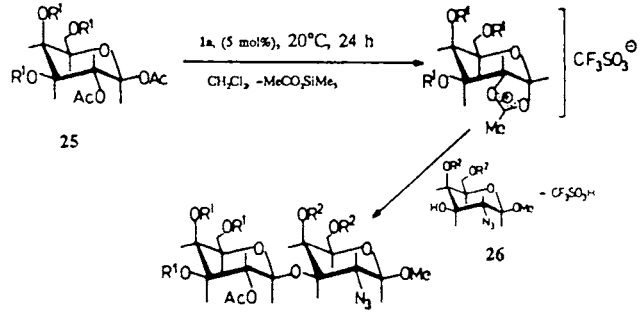
α and β-glucopyranosyl fluoride **23α,β** is converted to 1-O-alkylglucosides **24** by alkyltrimethylsilyl ethers **3** in the presence of 25–40 mol% **1a**. In acetonitrile the β-glucosides predominate, whereas in ether the α-anomers are the main products.[23]



R^1 = CH_2Ph
R^2 = Me, *t*-Bu, *c*-C_6H_{11}

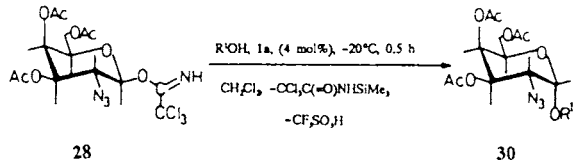
2.2.3. 1-O-Alkylglycosides and Disaccharides from1-O-Acylglycosides

1a is particularly suited for synthesis of oligosaccharides e.g., **27** via bond formation between low reactive hydroxyl groups as in **26** with the anomeric center in acyloxysubstituted glycosyl donors **25**. β-Selectivity is observed using 1,2-trans diacylates **25**.[24–28] The sensitive 4-methoxybenzyl group is retained in similar glycosidation reactions.[27,29]

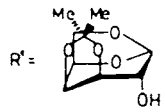


$$MeCO_2SiMe_3 + CF_3SO_3H \rightleftharpoons MeCO_2H + \mathbf{1a}$$

α-Disaccharides **30** result in high stereospecificy and reaction rate from the glycosidation of glycopyranosides **29** with β-glycosyltrichloracetimidates **28**[30], e.g.,



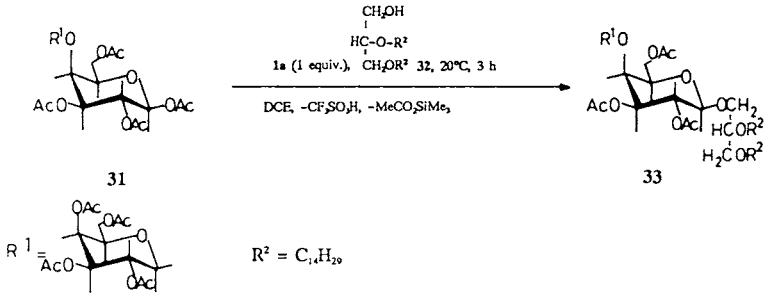
$$CCl_3CONHSiMe_3 + CF_3SO_3H \rightleftharpoons CCl_3CONH_2 + \mathbf{1a}$$



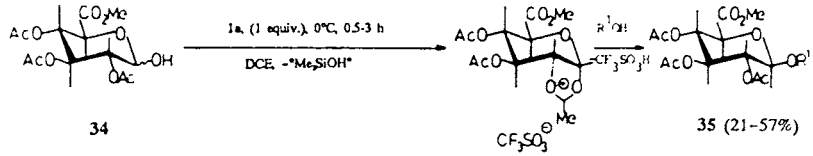
29

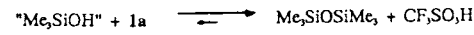
The glycosidation of anthracyclinones by means of 1-(4-nitrobenzoyl)-2-deoxyglycosides affords pure α-glycosides in the presence of two equivalents of

1a.[31,32] Molar amounts of **1a** are used in the synthesis of β-glycosides **33** starting with the 1,2-diacetate **31** and the glycerin derivative **32**.[24]



The β-glycosidation of alcohols with the free hydroxyglycosides **34** in presence of molar quantities **1a** offers some preparative advantages.[33]



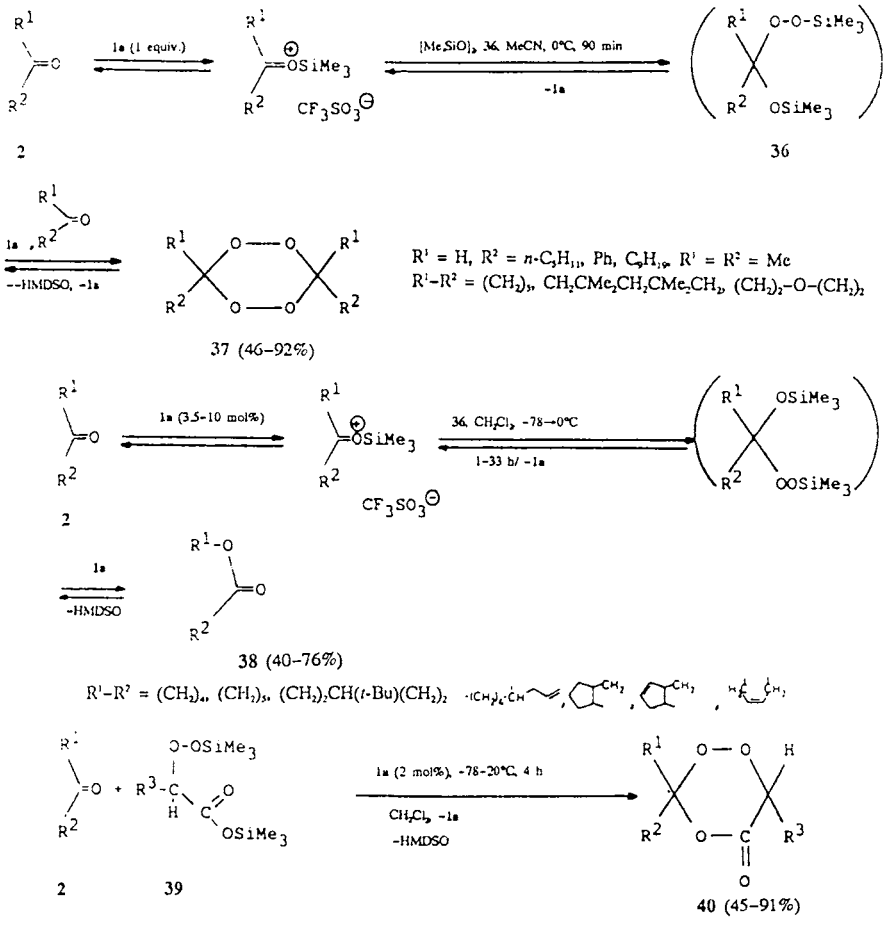


R^1 = CH_2Ph, CH_2CBr_3, CH_2CF_3, $CHMe_2$, Aryl, CR^3HCN

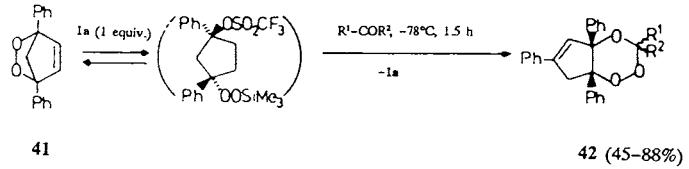
Whether equivalent or catalytic amounts of **1a** have to be used in glycosidation of alcoholic components depends on the equilibrium between trifluoromethane sulfonic acid and the silyl derivative ($MeCO_2SiMe_3$, $CCl_3CONHSiMe_3$, $HOSiMe_3$) formed. With trimethylsilylacetate and especially trimethylsilyltrichloracetimidate as leaving groups catalytic amounts of **1a** are sufficient because of its regeneration. However, in those reactions where trimethylsilanol is liberated two equivalents of **1a** should be used to accomodate the unfavorable equilibrium.

2.3. Peroxyacetalization of Aldehydes and Ketones

Tetroxanes **37** are obtained in the reaction of bis(trimethylsilyl)peroxide (**36**) with ketones and aldehydes **2** in the presence of molar amounts of **1a** in acetonitrile.[34] Under similar conditions, but with only catalytic quantities of **1a** in dichloromethane Baeyer-Villiger-oxidation occurs to yield lactones **38**.[35,36] Olefinic bonds are not affected. Trimethylsilyl α-trimethylsilylperoxy esters **39** react in a cycloacetalization with ketones **2** to yield 1,2,4-trioxan-5-ones **40**.[37] **1a**

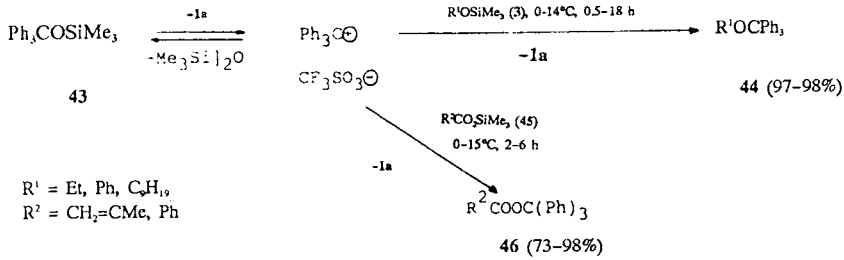


is also an efficient catalyst in the synthesis of 1,2,4-trioxanes **42** from 1,4-endoperoxides **41** or 1,2-dioxetanes and carbonyl compounds **2**.[38] The cycloannelation presumably begins with the cleavage of the allylic ether function in **41**, e.g.,

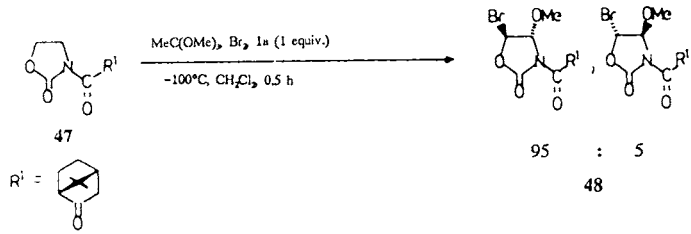


2.4. Other Carbon–Oxygen Bond Formations

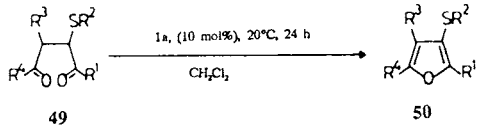
Cleavage of trityl-trimethylsilyl ether **43** by **1a** in the presence of alkyltrimethylsilyl ethers **3** or trimethylsilyl carboxylates **45** affords a convenient synthesis of trityl ethers **44** or esters **46**.[2,39]



Methoxybromination of the oxazolone **47** to give **48** proceeds with high diastereoselectivity in the presence of equivalent amounts of **1a** in trimethyl orthoacetate as solvent.[40]



1,4-Diketones **49** are cyclized under mild conditions to give furans **50**.[41] Trifluoromethane sulfonic acid may be the effective catalyst.



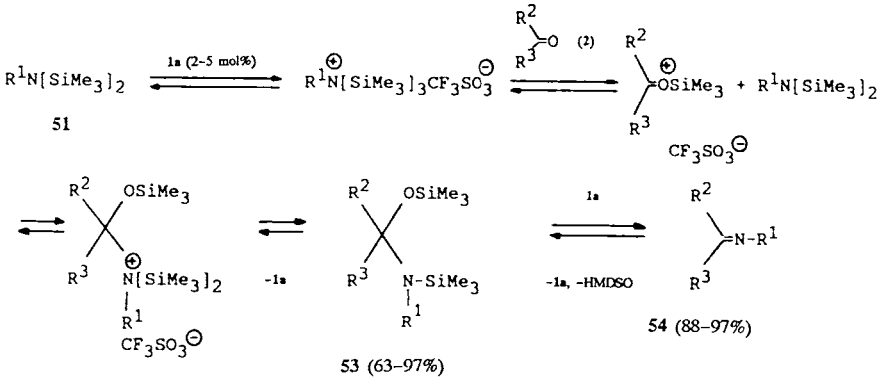
R^1, R^2 = Me, Ph; R^3-R^4 = $(CH_2)_4$, $(CH_2)_5$, R^3 = H, Me, R^4 = Me, Et

Polymerization of valerolactone and caprolactone is initiated by **1a** in DCE at 50°C. **1a** is a less effective catalyst than methyl triflate as a result of the smaller oxocarbenium ion concentration in the initiation step.[42] The initial rate of polymerization of octamethyltetrasiloxane is increased by **1a**.[43]

3. CARBON–NITROGEN BOND FORMATION

3.1. Reactions of Aldehydes, Ketones, and Lactones with N-Silylamines

The reaction of N,N-bis(trimethylsilyl)amines **51** with aldehydes and ketones **2** initiated by **1a** yields azomethines **54**.[44] The intermediate O,N-acetals **53** can be isolated with N,N-bis(trimethylsilyl)formamide **52** as amination reagent.[45] The synthesis of azomethines **54** is achieved even with ketones of low reactivity at room temperature in dichloromethane. O,N-acetals **53** are formed from aldehydes and

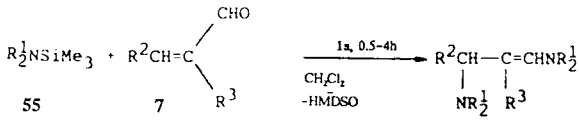


54: R^1 = Me, CH_2Ph,  ; $R^2 = R^3$ = Ph; R^2 = H, R^3 = Ph

52,53: R^1 = CHO; R^2 = H, R^3 = *n*-Pr, *i*-Pr, *t*-Bu, MeCH=CHCH$_2$, CH_2Ph

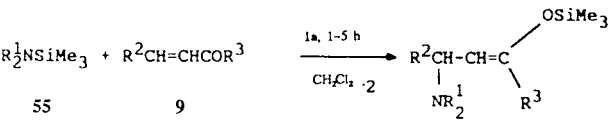
52 in chloroform by refluxing for some hours. Ketones give only very moderate yields of O,N-acetals **53**.

Under similar conditions (20°C, 2–5 mol% **1a**), α,β-unsaturated aldehydes **7** are transformed to vinylogous aminals **56** in a combined 1,2- + 1,4-addition of N,N-dialkyltrimethylsilyl amines **55**,[46] whereas ketones **9** are converted to vinylogous O,N-acetals **57** in a Michael-type reaction.[47]



R^1_2 = $(CH_2)_4$, $(CH_2)_5$, $(CH_2)_2O(CH_2)_2$

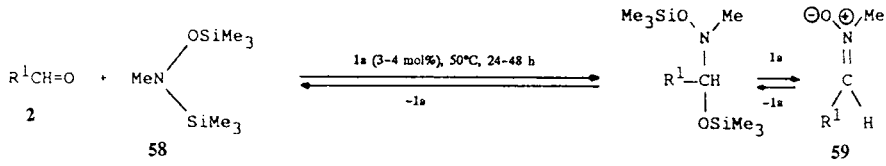
R^3 = H, R^2 = H, Me, Ph, *n*-Pr; R^3 = Me, R^2 = Et, Ph



R^1 = Me, R^1_2 = $(CH_2)_5$, $(CH_2)_2O(CH_2)_2$

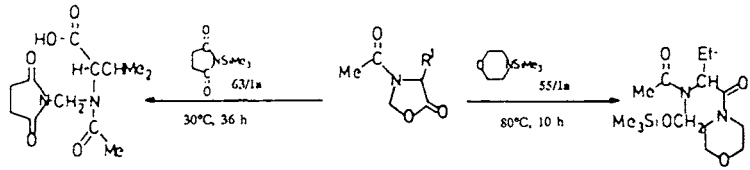
$R^2 = R^3$ = H, Me, Ph; R^2-R^3 = $(CH_2)_3$

N-Methylnitrones **59** can be synthesized in an efficient manner by addition of the hydroxylamine **58** to aromatic aldehydes **2** and subsequent **1a**-catalyzed elimination of HMDSO.[48]



R^1 = 4-Me_2N-C_6H_4, 4-O_2N-C_6H_4, 2-furyl

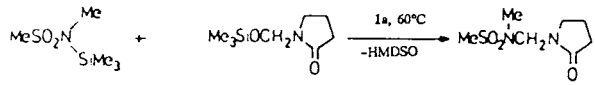
The reaction of amines with lactones has been scarcely investigated. Thus, the oxazolidinones **60** are converted into the carboxylic acid amide **61** by N-trimethylsilylmorpholine **55** [R^1_2=$(CH_2)_2O(CH_2)_2$], whereas the carboxylic acid **62** is obtained in reaction with N-trimethylsilylsuccinimide **63**.[49]



62 60 61

R^1 = $CHMe_2$, Et

Only little work has been done on the reactions of acetals or O,N-acetals with N-trimethylsilylamines. The O,N-acetal **63** in the presence of **1a** is transformed into the aminal **64** by reaction with the sulfonamide **65**.[50]

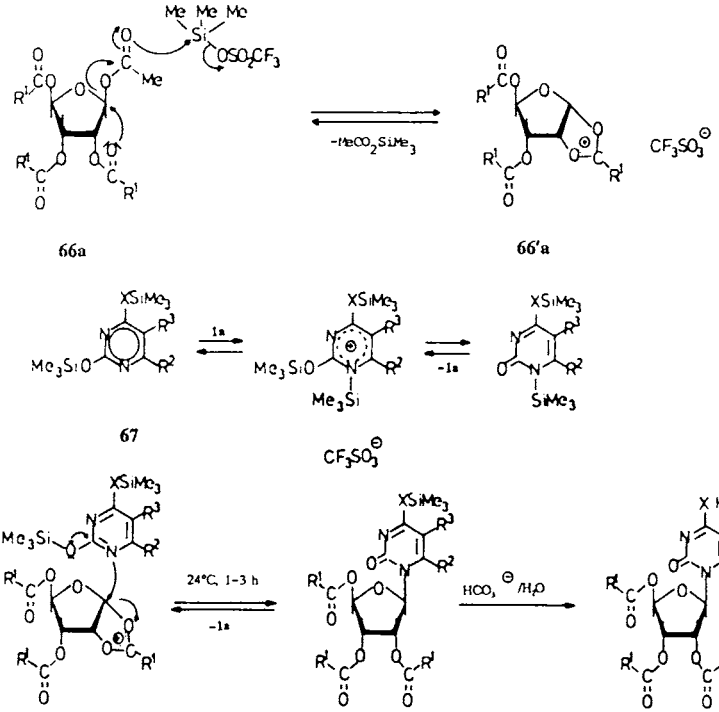


65 63 64 (92%)

3.2. Reaction of Silylated Hydroxy- and Amino Azaheterocycles with Glycosides (Nucleoside Synthesis)

The importance of **1a** and also trimethylsilylnonafluorobutane sulfonate **1r** as catalysts in generating oxocarbenium ions from acetals and glycosides was first discovered by Vorbrüggen et al.[1,51–56] The use of these catalysts found widest application in nucleoside synthesis. With sugars such as **66**, **1** forms cations **66'**. The major advantage of triflates **1** compared to tin(IV)chloride or other Lewis acids is the reversibility of their interaction with the silylated heterocyclic bases, e.g., **67** even at room temperature. Consequently, the heterocycles **67** are much less deactivated by **1** and C–N bond formation proceeds smoothly under mild conditions. In order to afford high reaction rates, it is useful to carry out nucleoside synthesis in the presence of 1.1–1.2 equivalents of **1** and in 1,2-dichloroethane or

better acetonitrile solution.[51,52] According to Vorbrüggen et al.,[53] C–N bond formation takes the following course as demonstrated for the synthesis of silylated pyrimidine ribonucleosides **68**. Simple workup with aqueous base gives rise to the desilylated nucleosides **69**.



R^1 = Ph

X = O, R^2 = H, R^3 = H, N-morpholinyl, NO_2

X = O, R^2 = Me, R^3 = H, Me

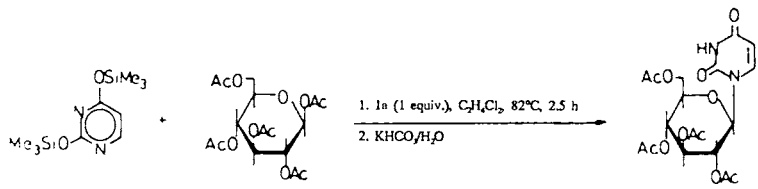
X = O, R^2 = OMe, R^3 = H

X = NH, R^2 = R^3 = H

Under these conditions the silylated base can only attack the sugar cation from the top to afford β-nucleosides **68** and **69**. Also because of thermodynamic control N-1-nucleosides are not observed. As a result of interaction between the basic moiety in **67** (R^3=N-morpholinyl) with **1a** the nucleoside formation requires a longer reaction period (24 h).[52]

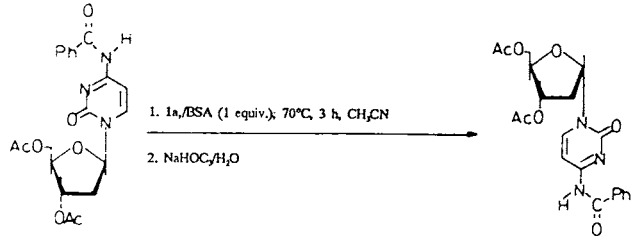
Predominantly the β-anomers are obtained in nucleoside synthesis with O-acyl protected deoxy-D-ribose[52] and 2,2-difluoro-2-deoxy-D-ribose.[57] The nucleoside synthesis also was successfully accomplished with 2(4)-trimethylsiloxy and 4-trimethylsilylamino pyridines.[52] As expected C–N bond formation also takes place with aldehyde acetals.[2]

In the same manner pyranosides **70** react with siloxypyrimidines **67** to give the β-nucleosides **71** although under more stringent conditions.[51,52]



67 β-70 β-71

The overall equilibrium character[52,53] of these C–N bond formations could be proved through partial anomerization of β-2'-deoxyfuranosyl pyrimidines **72** by **1a**/bis(trimethylsilyl) acetamide at 70°C.[58]

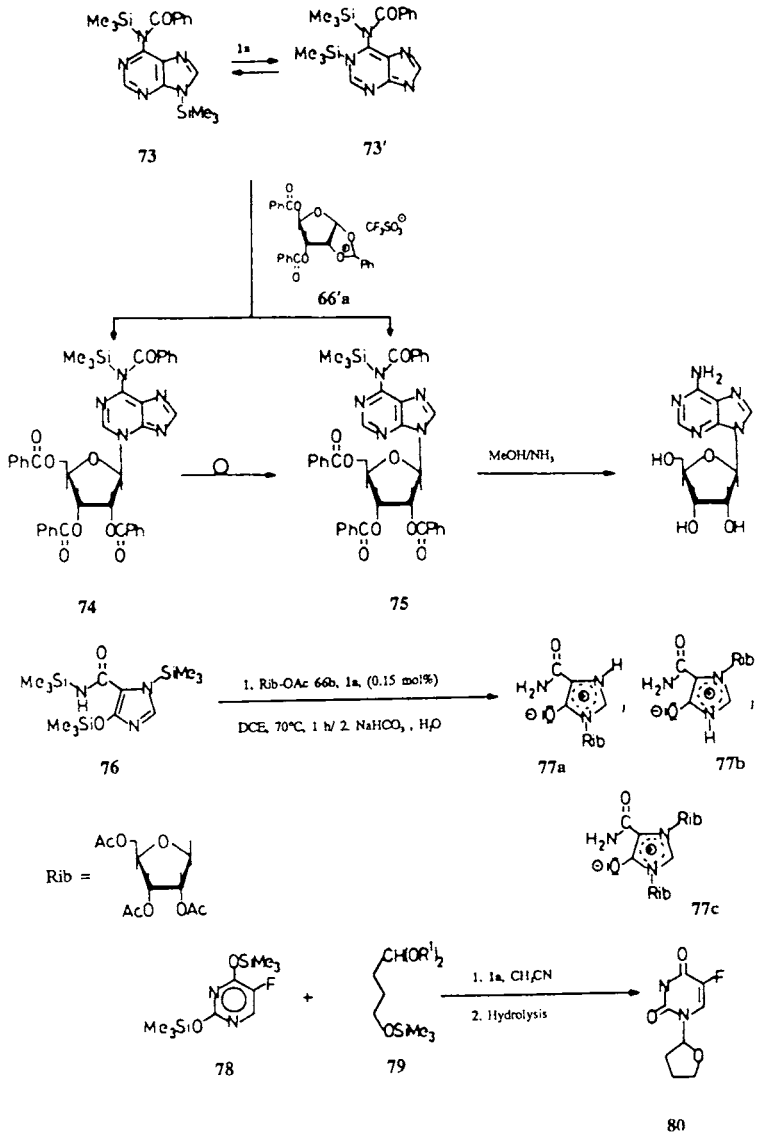


β-72 α-72

Purine and pteridine nucleosides are also readily accessible by the reaction of silylated purines and pteridines with the ribose or deoxyribose moieties in the presence of **1a** or **1r**.[51,52] The adenine derivative **73** first rearranges initiated by **1a** to give the isomer **73'** followed by glycosidation at N-9 to yield the nucleoside **75** possibly including formation of the N-3 nucleoside **74** as a kinetically controlled intermediate. The several steps of the Vorbrüggen-nucleoside-synthesis (i.e., silylation of heterocyclic bases, preparation of trimethylsilyl perfluoroalkane sulfonate, glycosidation) can be combined to a single step/one-pot procedure in acetonitrile as solvent.[55,56] Chlorotrimethylsilane and hexamethyldisilazane are used for silylation and producing **1r** from simultaneously added potassium nonafluorobutane sulfonate.

Glycosidation of the imidazole **76** with the ribose derivative **66b** in the presence of only catalytic amounts of **1a** leads to a mixture of β-nucleosides **77a,b,c**.[59] Silylated 1,2,4-triazoles upon reaction with **66a** afford the N-1-ribosides, whereas 3-substituted triazoles give the N-1- as well as the N-2 ribosides.[52] Starting from 4-trimethylsiloxy-1,2,3-triazole-5-carboxylic acid amide and **66a** ribosylation at N-1 in addition to N-2 is achieved.[60]

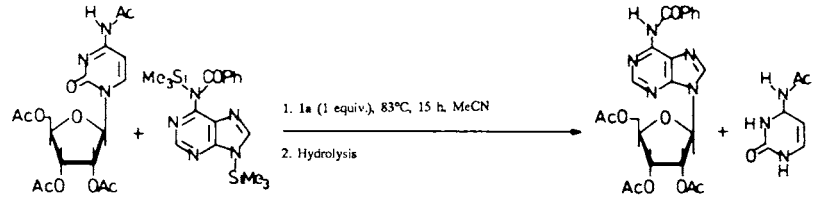
The 5-fluorouracil **78** is converted to the N-3 substituted derivative **80** in the reaction with 4-trimethylsiloxy butyraldehyde acetal **79**.[61]



3.3. Synthesis of Nucleosides by Transglycosylation

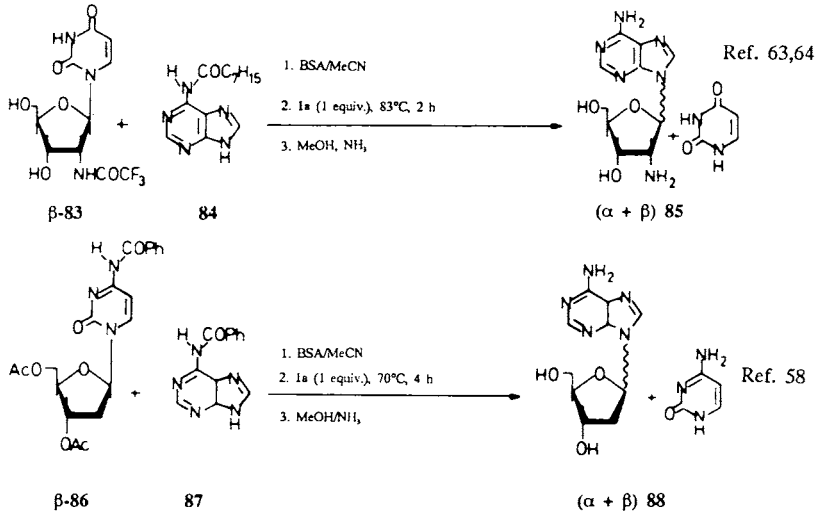
As a result of the equilibrium character in nucleoside synthesis **1a**[61–64] and **1r**[65] can be used to good advantage for transglycosylation of sugar moieties from pyrimidine nucleosides such as **81** to purines,[61–65] e.g., **73** or triazoles.[66] As has been shown transglycosylation is best achieved using **81** as the glycosyl donor. In

order to render the transsilylation of purine **73** sufficiently fast, the reaction must be run in acetonitrile as solvent. Yields are generally higher than those observed with tin(IV) chloride as catalyst.[62]



β-81 73 β-82 (81%)

Using **1a**/BSA and pyrimidine deoxyribofuranosides **83**, **86** as glycosyl donors a simplified one-pot synthesis of deoxyribofuranosyl purines such as **85**, **88** has been developed.[58,63,64]

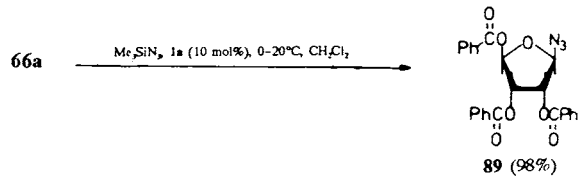


β-83 84 (α + β) 85

β-86 87 (α + β) 88

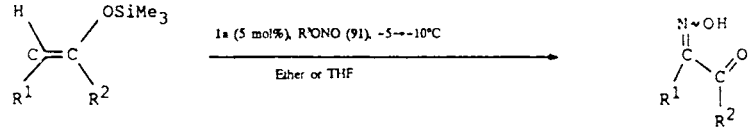
3.4. Other Carbon–Nitrogen Bond Formations

The **1a**-catalyzed reaction of the ribose derivative **66a** with trimethylsilyl azide readily affords the β-ribofuranosyl azide **89**[67]:



89 (98%)

Nitrosation of silyl enol ethers **90** by alkylnitrites **91** in the presence of **1a** are under investigation.[68]



90 **92**

R^1-R^2 = $(CH_2)_4$

R^1 = H, R^2 = Ph

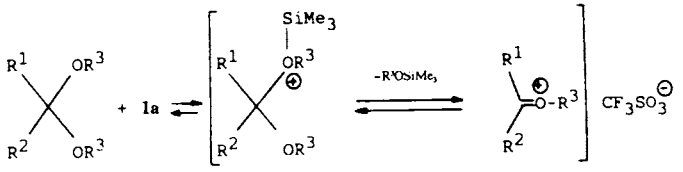
4. CARBON–CARBON BOND FORMATION

In aldol type reactions **1a** found by far the most extensive range of application.[1,2] Numerous electrophiles EX or E (Schemes 1,2) are available for these reactions. Silyl enol ethers, O-trialkylsilyl ketene acetals, allyl- and other carbosilanes are suitable as nucleophiles (Si-Nu).

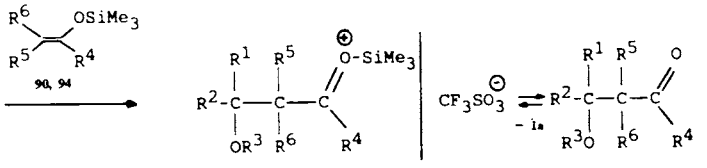
4.1. Carbon–Carbon Bond Formation of Silyl(di)enol Ethers and O-Trialkylsilyl Ketene Acetals

4.1.1. With Acetals and Carboxylic Acid Orthoesters

Acetals, ketals **5**, and carboxylic acid orthoesters **93** react with silyl enol ethers **90** and silyl ketene acetals **94** in the presence of 1–10 mol% **1a** to give β-alkoxy carbonyl compounds **95** or β-alkoxy carboxylic acid derivatives **96** in high yields (Table I). The driving force of the reaction is again the formation of the highly stable alkyltrimethylsilyl ethers **3**.[1,2] The first step of this process is the silylation

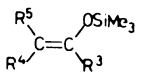
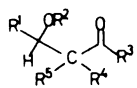
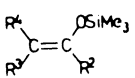
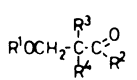


5, 93 **A** **B**



R^1-R^6 see Table I **C** **95, 96**

Table 1. Aldol-type Reactions of Acetals **5** and Orthoesters **93** with Silyl Enol Ethers **90** and Silyl Ketene Acetals **94** Catalyzed by **1a**.

Acetal, orthoester					*Silyl enol ether silyl ketene acetal*					*Product*					**1a** *[mol %]*	*Reaction conditions Temp. [°C], Time [h] Solvent*	*Yield [%]*	*Reference*
																		
R^1	R^2	R^3	R^4	R^5	R^1	R^2	R^3	R^4	R^5						5	–78→–90,4–12, CH_2Cl_2	75–98	1,2,70,79
n-Pr	Me	Ph	H	H	Ph	Me	Ph	H	Me									
n-Pr	Me	H	Me	Me	Ph	Me	*t*-Bu	H	Me									
n-Pr	Me	–$(CH_2)_4$–		H	Ph	Me	–$(CH_2)_4$–		H									
i-Pr	Me	–$(CH_2)_4$–		H	Ph	CH_2Ph	Ph	H	Me									
i-Pr	CH_2Ph	Ph	H	H	Ph	Me	OMe	H	Me									
i-Pr	CH_2Ph	*t*-Bu	H	H	Ph	Me	*t*-BuS	H	Me									
$H_2C(OR^1)_2$															10	12–18,12, CH_2Cl_2	48–92	2,72

R^1 = Me, R^2–R^3 = $(CH_2)_4$, R^4=H
R^1 = CH_2Ph, R^2–R^3 = $(CH_2)_3$,$(CH_2)_4$; R^2 = Ph, R^3 = R^4 = H;
R^2 = Ph, R^3 = Me, R^4 = H

Table I. (Continued)

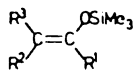
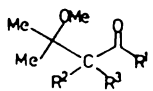
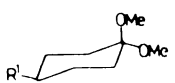
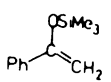
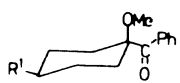
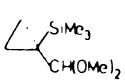
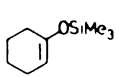
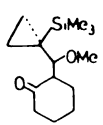
Acetal, orthoester	*Silyl enol ether silyl ketene acetal*	*Product*	1a *[mol %]*	*Reaction conditions Temp. [°C], Time [h] Solvent*	*Yield [%]*	*Reference*
$Me_2C(OMe)_2$			4–12	–78,4–12,CH_2Cl_2	87–96	1,2,70
R^1 = H, R^2 = R^3 = Me; R^1–R^2 = $(CH_2)_3$,$(CH_2)_4$, R^3 = H R^1 = Me, R^2 = R^3 = Me						
			1 equiv.	,—, CH_2Cl_2	~80	80
R^1 = Me,*t*-Bu						
			10	–78,8,CH_2Cl_2	90	81

Table I. (Continued)

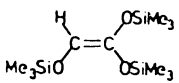
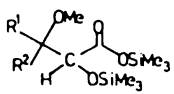
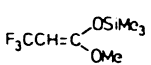
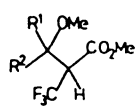
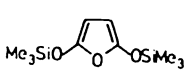
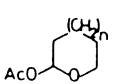
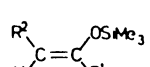
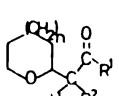
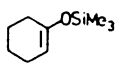
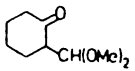
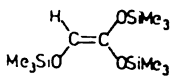
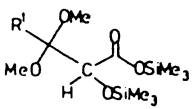
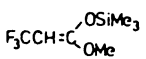
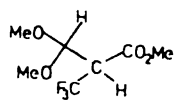
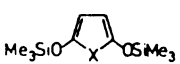
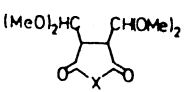
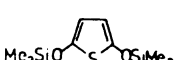
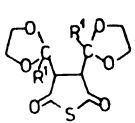
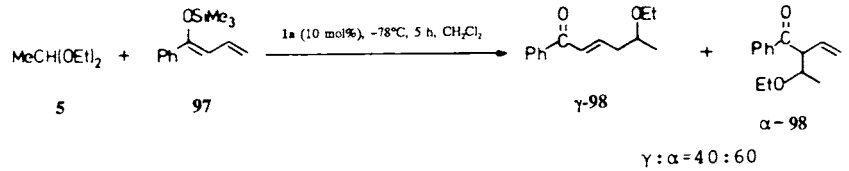
Acetal, orthoester	*Silyl enol ether silyl ketene acetal*	*Product*	**1a** *[mol %]*	*Reaction conditions Temp. [°C], Time [h] Solvent*	*Yield [%]*	*Reference*
			1–5	–78, 14–20; 0, 14 [$R^1 = R^2 = H$] CH_2Cl_2	73–81	71
R^1 = H, R^2 = Me, Ph, H $R^1 = R^2$ = Me						
			20	–78,4.5–9,CH_2Cl_2	74–92	82
R^1 = H, R^2 = Me,Ph,PhCH=CH $R^1 = R^2$ = Me, R^1–R^2 = $(CH_2)_2$-CH(*t*-Bu)$(CH_2)_2$						
$R^1CH(OMe)_2$ R^1 = H, Me, Ph			6	–60–0,12,DCE	60–97	83
			5–10	–78,4–16	78–96	84
n = 0, R^1 = Ph, R^2 = H n = 1, R^1 = Ph,*t*-Bu,*t*-BuS, R^2 = H R^1 = H, R^2 = Me; R^1 = Ph, R^2 = Me						

Table I. (Continued)

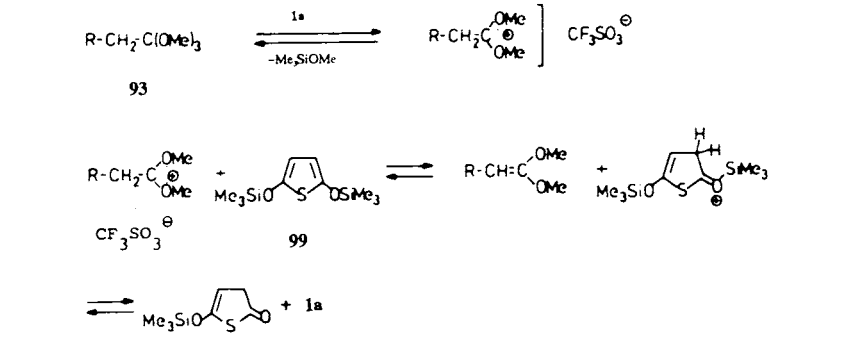
Acetal, orthoester	*Silyl enol ether silyl ketene acetal*	*Product*	**1a** *[mol %]*	*Reaction conditions Temp. [°C], Time [h] Solvent*	*Yield [%]*	*Reference*
$HC(OMe)_3$			5	–78,12	89	1,2,70
$R^1C(OMe)_3$ R^1 = H,Me			1	–78,16 [R^1 = Me] 0,0.5 [R^1 = H]	80–90	71
$HC(OMe)_3$			20	–78,–5,CH_2Cl_2	76	82
$HC(OMe)_3$ X = O,S			1	–60–0,12 [X = O] 20,4 [X = S], DCE	70–83	83,73
 R^1 = Me,*i*-Pr,Ph R^2 = Me,Et			10	20,4–24, DCE	70–80	73

of **5** or **93** by **1a** to afford oxonium ions **A**, which are in equilibrium with carbocations **B**. Siloxonium ions **C** result from nucleophilic substitution on **A** or addition to **B**. Attack of triflate anion on intermediate C regenerates **1a**. Whether **A** or **B** are the reactive intermediates will depend on the stabilization of the positive charge, the solvent, and the nucleophilicity of the carbon nucleophiles **90** and **94**. The dependence of the α/γ ratio in **98** from the Lewis acid employed—in analogous reactions with the dienol ether **97**—is an argument in favor of the intermediacy of **A**.[69]

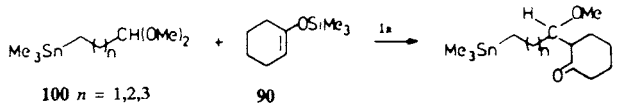


These aldol-type bond formations proceed already at –78°C under aprotic and nonbasic conditions with a high degree of erythro selectivity.[1,2,70] Side reactions[1,2,70] are not important, β-eliminations in **95** and **96** compete with increasing temperature and concentration of the catalyst **1a**.[71] The amount of catalyst employed is adjusted to the reactivity of the nucleophiles **90**, **94**. For bond formation with silyl enol ethers **90** 5–10 mol% of **1a** is enough (Table I). In the synthesis of alkoxymethylketones according to Noyori et al.,[72] addition of a sterically hindered base such as 2,6-di-*tert*-butyl-4-methylpyridine is necessary.

The reaction rates decrease with increasing bulkiness of the substituents in **5** or **93**.[71] In consequence, protodesilylation competes in their interaction with the more basic bis(trimethylsilyl)ketene acetals, e.g., **99**. By employing cyclic orthoesters **97** (Table I) this side reaction can be excluded.[73]

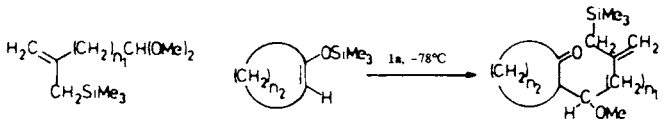


The cross-aldol reaction is also established between silyl enol ethers **90** and acid sensitive acetals such as **100**.[74]



100 n = 1,2,3 **90** **101**

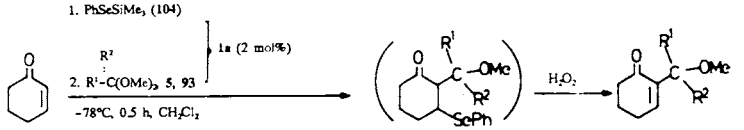
ω-Dialkoxymethylallylsilanes **102** selectively react at the acetal function with cyclic silyl enol ethers **90** to yield the aldol products **103**.[75] Interestingly, the resulting keto allylsilane **103** does not react further under these conditions.



102 **90** **103**

n_1 = 1,2, n_2 = 3,4,5

The **1a**-catalyzed addition of the selenide **104** to α,β-unsaturated ketones, e.g., **9b** and its subsequent aldol reaction with **5** or **93**/**1a** renders the α-functionalization of unsaturated ketones **9**.[2,76]

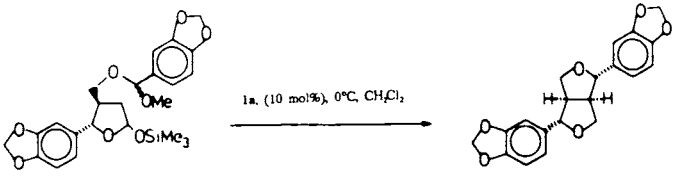


9b **105** (76–83%)

5: R^1 = H, R^2 = alkyl

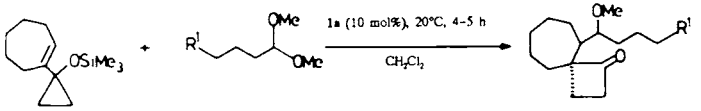
93: R^1 = H, R^2 = alkoxy

By intramolecular C–C bond formation in the dihydrofuran derivative **106**, a synthesis of the bicyclic ether **107** is achieved.[77]



106 **107** (47%)

1-Vinyl-1-trimethylsiloxy cyclopropanes **108** which can be viewed as extended silyl enol ethers, when reacted with acetals **5**, give stereoselectively the Z-alkylation products **109**.[78]

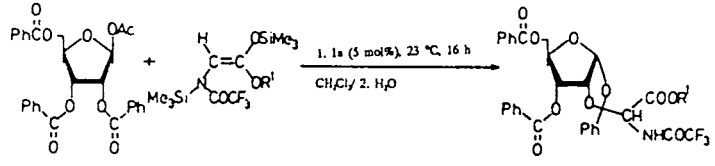


108 **5** **109** (77–95%)

R^1 = Et, EtOCO

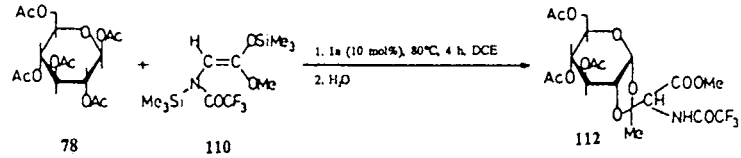
4.1.2. With Glycosides

Attempts to synthesize C-nucleosides by the reaction of 1,2-trans di-O-acyl-ribofuranoses **74** or glucopyranoses **78** with the ketene acetals **110** afford 1,3-dioxolanes **111, 112** under kinetic control.[85] Analogous results are obtained in reactions with silylenol ethers.[86,86a]



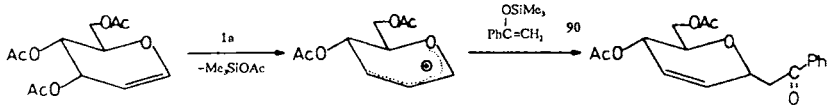
74 110 111 (85–98%)

R' = Me, CH_2Ph



78 110 112

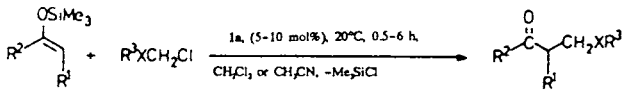
The glycosidic bond linkage, however, is achieved in reaction of glycals **113** with silyl enol ethers **90**. Under kinetic control the α-anomers **114** are formed predominantly.[87,88]



113 114 (α)

4.1.3. With α-Halo(thio)ethers

The activation of α-halo(thio)ethers **115, 116** in the reaction with silyl enol ethers **90** occurs exclusively at the chlorine atom to give selectively β-alkoxy(alkylthio) ketones **96,117**.[89] The stabilizing ability of the adjacent heteroatom toward an incipiently formed carbocation is responsible for this regioselectivity. No traces of β-chloroketones are observed.[89]



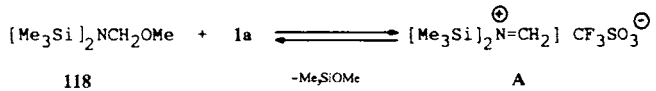
90 115, 116 96, 117 (56–83%)

115, 96: X = O, 116, 117: X = S

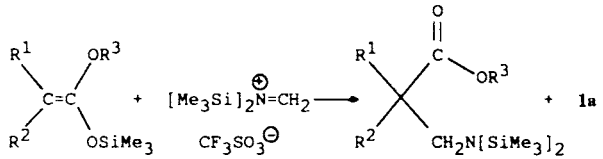
R^1 = Me, R^2 = Et, R^3 = Me, *i*-Pr, X = O
R^1-R^2 = $(CH_2)_4$, R^3 = Me, *n*-Bu, X = S

4.1.4. With O,N-, S,N-, N,N-Acetals and α-Halogen Amines

O,N-, S,N-, and N,N-acetals of formaldehyde, e.g., **118** react with silyl enol ethers **90** or silyl ketene acetals **94** essentially in the same manner as do the O,O-acetals to give β-aminoketones or β-amino carboxylic acid esters **119** (Table II). Iminium triflates **A** are to be considered as reasonable intermediates.[90]

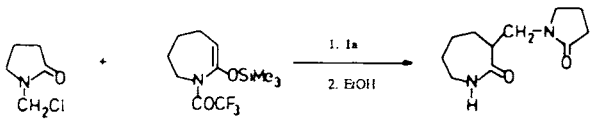


118 **A**



94 **119**

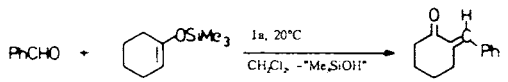
The aldol reaction also succeeds with 2-acetoxy-4-azetidinones without ring cleavage (Table II).[91] In an exothermic reaction the N-(acylaminomethyl)lactam **122** is obtained from N-(chloromethyl)pyrrolidon **120** and the ketene O,N-acetal[92] **121**.



120 **121** **122**

4.1.5. With Aldehydes, Ketones, Carboxylic Acid Derivatives, and Imino Carbonyl Compounds

Whereas silyl enol ethers react with acetals even at –78°C, bond linkage with aldehydes in the presence of **1a** proceeds only at room temperature accompanied by β-elimination of trimethylsilanol.



As can be pointed out, the β-elimination is avoidable by decreasing the amount of catalyst **1a**. Thus, bis(trimethylsiloxy)-1,3-dienes **123** are converted to mixtures of isomeric silyl enol ethers **124**, **125** in the aldol addition with aldehydes **2** in the presence of 0.1–1 mol% **1a**.[98]

Table II. Aldol-type Reactions of O,N-, S,N-, and N,N-Acetals with Silyl Enol Ethers and Silyl Ketene Acetals in the Presence of **1a**.

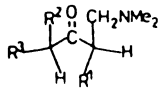
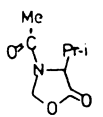
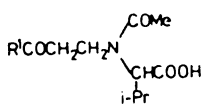
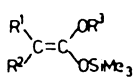
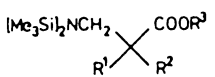
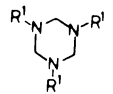
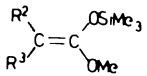
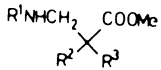
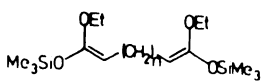
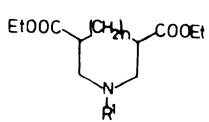
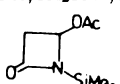
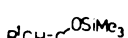
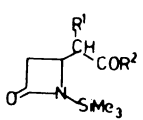
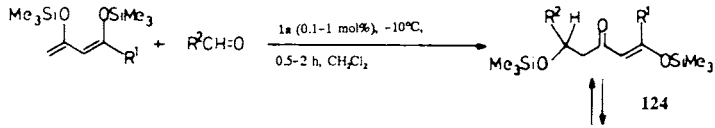
Acetal	*Silyl enol ether* *Silyl ketene acetal*	*Product*	**1a** *[mol %]*	*Reaction Conditions* *Temp. [°C], Time [h], Solvent*	*Yield [%]*	*Reference*
Me_2NCH_2OBu-*n*			5	20,1.5–4,CH_2Cl_2	63–68	93
R^1 = H, R^2 = Ph, R^3 = Me R^1–R^2 = $(CH_2)_4$, R^3 = H						
	1.  2. EtOH		~5	10,1 week, —	61–72	94
R^1 = 3,4-dichlorophenyl,1-naphthyl,4-iodophenyl						
$[Me_3Si]_2NCH_2OMe$			1	25–30,1, CH_2Cl_2	81–98	95,90
R^1 = Me, R^2 = H R^1 = R^2 = H R^1 = Me, R^2 = Me						
R^1 =  R^2 = H R^3 = Me,$SiMe_3$						

Table II. (Continued)

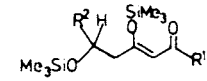
Acetal	*Silyl enol ether* *Silyl ketene acetal*	*Product*	**1a** *[mol %]*	*Reaction Conditions* *Temp. [°C], Time* *[h], Solvent*	*Yield* *[%]*	*Reference*
	1.  2. Hydrolysis		5	20,1.5–5, CH_2Cl_2	67–87	96
R^1 = Et,*i*-Pr,$CH_2CH{=}CH_2$,CH_2Ph, Ph; $R^2 = R^3$ = Me; R^2 = H, R^3 = Me						
R^1–$N[CH_2SMe)_2$			10	20,3–5, CH_2Cl_2	56–95	97
R^1 = Me,CH_2SMe,CH_2Ph; n=0,1,2						
			10	–78→20,—,CH_2Cl_2	71–95	91

R^1	H	Me	4-Methylphenyl	4-Chlorphenyl	Me	Me
R^2	Ph	Ph	H	H	OEt	SPh



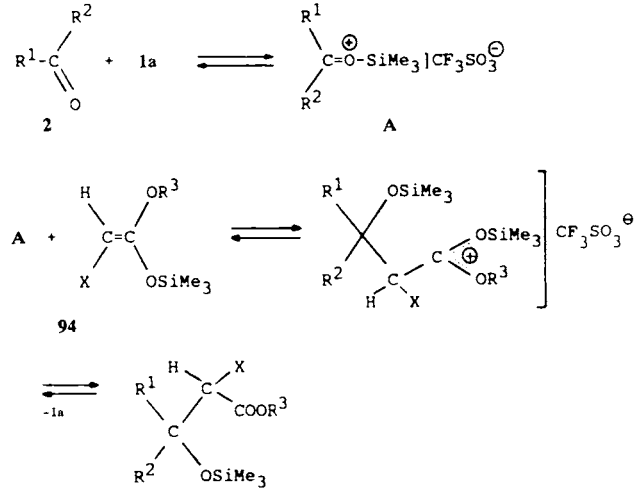
R^1 = H, Me

R^2 Et, *n*-C_5H_{11}, CCl_3, Ph, 4-nitrophenyl, 4-methoxyphenyl, 4-dimethylaminophenyl, 2-furyl, 2-thienyl, 1-methyl-2-pyrrolidinyl



125 (92–100%)

2,3-Bis(trimethylsiloxy)- and 2-acylamino-3-trimethylsiloxy carboxylic acid esters **126**, **127** (Table III) are obtained in high yield and erythro-selectivity by the reaction of aldehydes, ketones, or alkylformates **2** with the more nucleophilic silyl ketene acetals **94**.[71,73,99–106] Again the β-elimination, which is only of importance in reaction with aldehydes having carbocation-stabilizing groups, can be suppressed by decreasing the catalyst concentration and reaction temperature.[71] In the first step a siloxonium triflate **A** is formed from **2** and **1a** (see chapter II,1), followed by the addition of the silyl ketene acetal **94** and regeneration of the catalyst **1a**. The reaction rate is highly dependent on the equilibrium concentration of siloxonium ion **A**. Therefore, electron-releasing groups in the carbonyl components **2** increase the reaction rate, whereas the rate is decreased by electron-withdrawing substituents.[71]



126,127

X = $OSiMe_3$, R'NCOCF$_3$, R^3 = $SiMe_3$, Me

Table III. Aldol-type Reactions of Aldehydes, Ketones, and Carboxylic Acid Derivatives with Silyl ketene Acetals

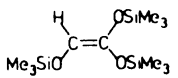
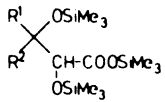
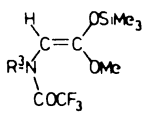
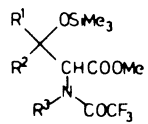
Carbonyl compound	*Silyl ketene acetal*	*Product*	**1a** *[mol %]*	*Reaction conditions Temp. [C], Time [h] Solvent*	*Yield [%]*	*Reference*
R^1COR^2			0.05–1	20, 3–18, CH_2Cl_2	76–93	71
$R^1 = H$, R^2 = Et,C_5H_{11},*t*-Bu,*c*-C_6H_{11},CCl_3,Ph 4-$Me_2NC_6H_4$,4-$MeOC_6H_4$,3-$MeOC_6H_4$,4-ClC_6H_4 3-ClC_6H_4,4-$O_2NC_6H_4$,3-$O_2NC_6H_4$,2-Furyl, 2-Thienyl,1-Methyl-2-pyrrolyl,1-Methyl-3-indolyl $R^1 = R^2$ = Me; R^1 = Me, R^2 = Ph; R^1–R^2 = $(CH_2)5$; R^1 = H, R^2 = OMe						
R^1COR^2			0.1–1	20, 1–20 CH_2Cl_2	75–94	99,100,102,104
R^1 = H, R^3 = SiMe3, R^2 = *t*-Bu, *c*-C_6H_{11}, CCl_3, Ph, 4-$O_2NC_6H_4$, + 3-$O_2NC_6H_4$,4-$Me_2NC_6H_4$,4-$MeOC_6H_4$, 3-ClC_6H_4,2-Furyl,2-Thienyl,1-Methyl-2 -pyrrolyl $R^1 = R^2$ = Me, R^1 = Me, R^2 = Ph, R^1–R^2 = $(CH_2)5$ $R^1 = H$, R^3 = Me, Et, *i*-Pr, CH_2Ph, R^2 = Et, *t*-Bu, *n*-C_5H_{11}, CCl_3, Ph 4-MeC_6H_4, 4-$MeOC_6H_4$, 3-ClC_6H_4 4-$O_2NC_6H_4$,2-Thienyl						

Table III. (Continued)

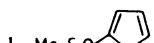
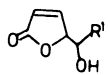
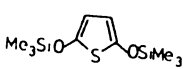
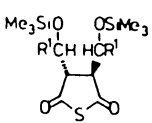
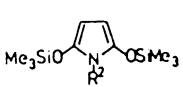
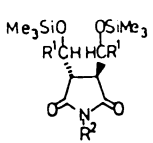
Carbonyl compound	*Silyl ketene acetal*	*Product*	**1a** *[mol %]*	*Reaction conditions Temp. [C], Time [h] Solvent*	*Yield [%]*	*Reference*
$R^1CH{=}O$	1. 		0.04-0.2	–78, 2, CH_2Cl_2	88–95	108
	2. Hydrolysis					
R^1 = *i*-Pr,*t*-Bu,CH_2Ph,*n*-C_5H_{11}						
$R^1CH{=}O$			0.1–1	20, 4–16 $C_2H_4Cl_2$	91–94	73,101,109
R^1 = Ph, 4-MeC_6H_4,4-$MeOC_6H_4$,3-$MeOC_6H_4$,3,4-$(MeO)_2C_6H_3$, 3,4-$(PhCH_2O)_2C_6H_3$,3,4-OCH_2-O-C_6H_3,3,4,5-$(MeO)_3C_6H_2$, 2-Furyl, 2-Thienyl						
$R^1CH{=}O$			0.1–1	20, 10 $C_2H_4Cl_2$	60–85	103
R^1 = Ph; R^2 = CH_2Ph,Ph,COPh,SiMe3						

Table III. (Continued)

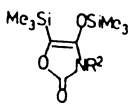
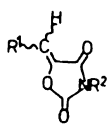
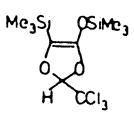
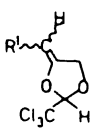
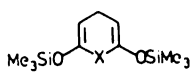
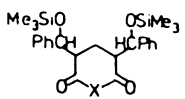
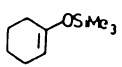
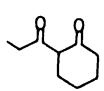
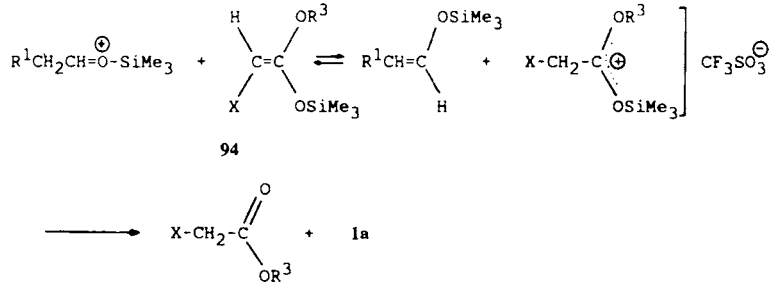
Carbonyl compound	*Silyl ketene acetal*	*Product*	**1a** *[mol %]*	*Reaction conditions Temp. [C], Time [h] Solvent*	*Yield [%]*	*Reference*
$R^1CH{=}O$			2.5–5	80, 2.5–15 $C_2H_4Cl_2$	50–87	105
R^1 = 4-MeC_6H_4, 4-$MeOC_6H_4$, 2-$MeOC_6H_4$, 4-$Me_2NC_6H_4$, 1-Methyl-2-pyrrolyl,2-Thienyl						
R^1CHO			2.5–5	80, 3–24 $C_2H_4Cl_2$	69–82	105
R^1 = C_6H_5,4-MeC_6H_4,4-$MeOC_6H_4$,4-$Me_2NC_6H_4$,2,3,4-$(MeO)_3C_6H_2$, 4-ClC_6H_4,4-$O_2NC_6H_4$,1-Methyl-2-pyrrolyl,2-Thienyl						

Table III. (Continued)

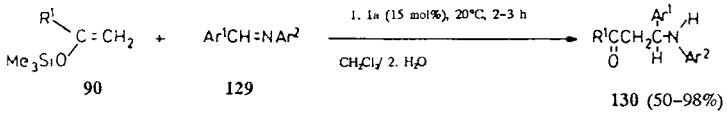
Carbonyl compound	*Silyl ketene acetal*	*Product*	**1a** *[mol %]*	*Reaction conditions Temp. [C], Time [h] Solvent*	*Yield [%]*	*Reference*
PhCH=O X = O,S			0.1–0.5	20, 12 $C_2H_4Cl_2$	60–80	106
$(EtCO)_2O$			10	17, 12, CH_2Cl_2	61	2

The aldol reactions with aliphatic aldehydes, containing α-methylene groups is accompanied by protodesilylation of the ketene acetals **94**. In these cases zinc bromide is a more suitable catalyst than **1a**.[104]



94

Ketene acetals **94** (X=N(Me)(SiMe3)) give by far lower yields of compounds **127**.[107] Optimum yields of β-(N-arylamino)ketones **130** are obtained in the reaction of azomethines **129** with silyl enol ethers **90** if **1a** is used as catalyst.[110]

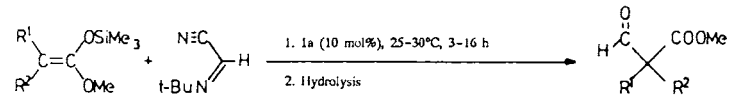


90 **129** **130** (50–98%)

R^1 = Ph, *t*-Bu; Ar^1 = Ph, 4-$O_2NC_6H_4$

Ar^2 = Ph, 4-BrC_6H_4

The synthesis of 2-formyl-2,2-disubstituted esters **132** is achieved by the reaction of the formimidoylcyanide **131** with disubstituted ketene acetals **95**.[111]



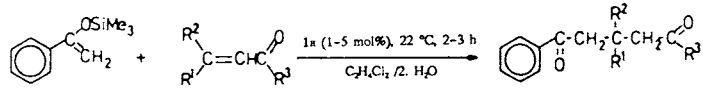
94 **131** **132** (35–98%)

The bond formations with iminocarbonyl compounds generally require higher amounts of catalyst **1a** because of complex formation between the catalyst and the products (see chapter I, 6.4).

In the synthesis of 2-arylthio-1,4-diketones from β-ketosulfoxides and silyl enol ethers promoted by stannic triflate only very low yields are obtained with **1a** as catalyst.[112]

4.1.6. *With α,β-Unsaturated Carbonyl Compounds*

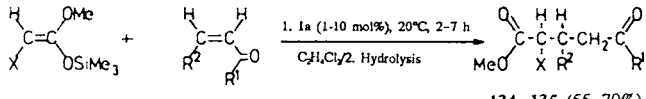
Triflate **1a** is especially suited as a catalyst in the "Silyl-Michael-addition". Ordinarily high yields are established under mild conditions. Apparently the regioselectivity of the addition depends mainly on the constitution of the Michael donors **90, 94.** Whereas tris(trimethylsiloxy)ethylene affords 1,4- as well as the 1,2-addition products,[71] simple silyl enol ethers **90** react exclusively in a 1,4-manner to yield 1,5-diketones **133** in those systems reported to date.[113]



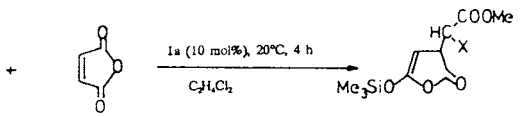
90 7 133 (60–85%)

R^1 = Me, H, R^2 = Me

The Michael reaction of 2-acylamino-substituted ketene acetals **94** with unsaturated carbonyl compounds **7** provides a synthesis of 2-amino-5-keto carboxylic and 2-amino tricarboxylic acid derivatives **134, 135.**[114]



94 7 134, 135 (55–70%)

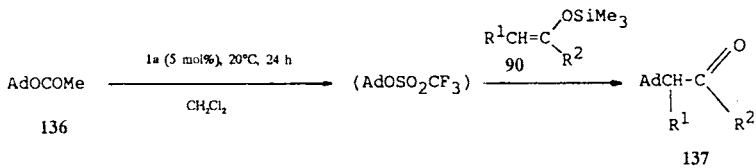


135 (54%)

X = $NCOCF_3$, $SiMe_3$ R^1-R^2 = $(CH_2)_2$, $(CH_2)_3$ R^1 = OMe, R^2 = Me

4.1.7. *With Other Carbon Electrophiles*

Silyl ketene acetals **94** are β-trimethylsiloxyalkylated upon treatment with oxiranes in the presence of **1a.**[115] The adamantyl ketone **137** is obtained in the reaction of 1-adamantyl acetate **136** with silyl enol ether **90** presumably via 1-adamantyl triflate.[116]

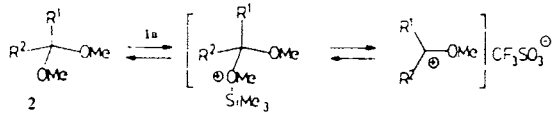


Ad = 1-adamantyl, R^1-R^2 = $(CH_2)_4$

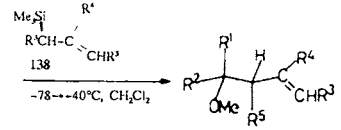
4.2. Carbon–Carbon Bond Formation of Allylsilanes

4.2.1. With Acetals and α-Halo Ethers

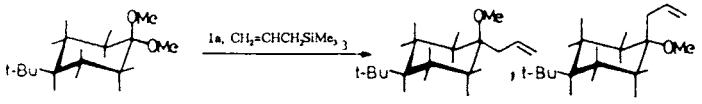
Homoallylethers **139** may be prepared in high yields from allyltrialkylsilanes **138** and acetals **2** in the presence of catalytic amounts of **1a** at low temperature (Table IV).[1,2,117] At higher temperatures **139** undergoes β-elimination of alkanol also catalyzed by **1a**.[118] The 4-*t*-butylcyclohexanone dimethyl ketal with allyltrimethylsilane yields a mixture of isomers **140** with the equatorial isomer predominating.[2,117]



2



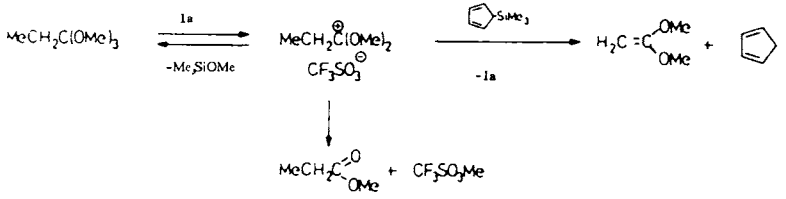
139



140 140′

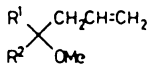
97 : 3 (89%)

The allylation of orthoformates (**2**, R^1=H,R^2=OMe) with allylsilanes **138** also proceeds smoothly under similar conditions (Table IV), whereas with homologous orthoesters products of the type **139** are not clearly formed due to side reactions.[119] Apparently with cyclic orthoesters these side reactions can be suppressed (see chapter II, 4.1.1).



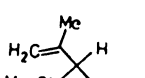
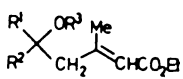
In reactions of allylsilanes with α-chloro ethers **115** the C–Cl bond is selectively activated by **1a** to yield homoallyl ethers **139**[122] (see chapter II, 4.1.3).

Table IV. Reactions of Acetals, Ketals, and Orthoformates with Allylsilanes in Presence of **1a**

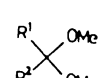
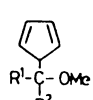
Acetal, ketal, orthoformate	*Allylsilane*	*Product*	**1a** *[mol %]*	*Reaction conditions Temp. [C], Time [h] solvent*	*Yield [%]*	*Reference*
	CH_2=$CHCH_2SiMe_3$		10	−78 →−40, 1–18 CH_2Cl_2	78–95	1,2,117,120

R^1	H	H	Et	Me	H	H
R^2	*n*-Pr	Ph	Et	Ph	PhCH=CH	CH_2CHMe | OCH_2Ph

R^1–R^2=$(CH_2)_5$,$(CH_2)_{11}$

			5–8	−78, 2–26 CH_2Cl_2	81–83	121

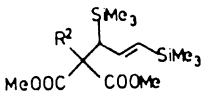
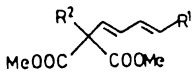
R^1 = R^2 = R^3 = Me
R^1 = 4-$MeOC_6H_4$, R^2 = H, R^3 = *n*-Bu

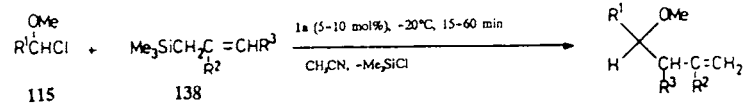
			10–12	−50→−40, 0.5 CH_2Cl_2	70–80	119

R^1 = R^2 = H
R^1 = H, R^2 = OMe

besides isomers

Table IV. (Continued)

Acetal, ketal, orthoformate	*Allylsilane*	*Product*	**1a** *[mol %]*	*Reaction conditions Temp. [C], Time [h] solvent*	*Yield [%]*	*Reference*
$R^1CH(OMe)_2$			10	20, — CH_2Cl_2	27–44	118
R^1 = Ph, 1-Naphthyl R^2 = Me, CH_2=CHEt		E,E				



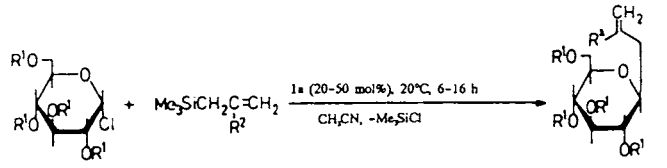
115 138 139

$R^1 = Me_2CHCH_2$, $R^2 = R^3 = H$; $R^2 = Me$, $R^3 = H$; $R^2 = H$, $R^3 = Me$

$R^3 = H$, $R^2 = CH{=}CH_2$

4.2.2. With Glycosides

Allylsilanes **138** are excellent reagents for the stereoselective introduction of functionalized allyl groups at the anomeric center of carbohydrates in the presence of **1a** in acetonitrile as solvent. Pyranosylchlorides such as **140** are more reactive than methylpyranosides and require less catalyst **1a** to give almost exclusively the α-anomers **141**.[123,124] Similar allylation in dichloromethane solution afford lower yields of products **141**.[125]



140 138 141 (71–81%)

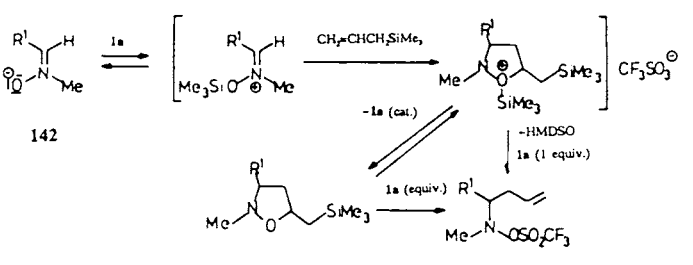
$R^1 = CH_2Ph$

R^2 = H, Me, Br

Unprotected α-1-allylglycosides are available in high yields by a one-pot synthesis starting from unprotected O-methylglycosides and bis(trimethylsilyl)trifluoroacetamide. Unusually high amounts of catalyst **1a** are employed in this procedure.[126]

4.2.3. With Carbonyl and Analogous Compounds

Aldehydes or ketones **2** do not react with allylsilanes **138** and **1a** under the usual conditions.[2] However, N-methylnitrones **142** add allylsilanes **138** in the presence of **1a** to give a diastereomeric mixture of cycloadducts **143** and homoallylhydroxylamine **144**. The use of one equivalent of **1a** is preferred since under these conditions **144** is formed clearly.[127]

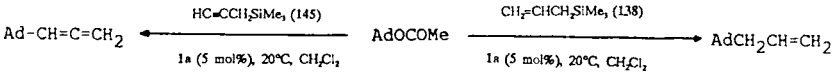


142 143 144

R^1 = Ph, CO_2Et, 3-pyridyl

4.2.4. With Other Carbon Electrophiles

Treatment of 1-adamantylacetate **137** with allylsilane **138** or propargylsilane **145** in the presence of **1a** affords the adamantane derivatives **146, 147.**[116]

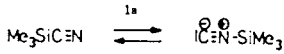


147 (46%) 137 146 (70%)

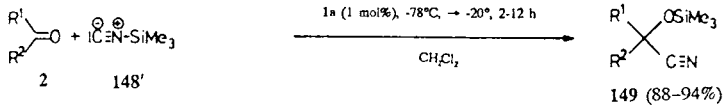
Ad = 1-adamantyl

4.3. Carbon–Carbon Bond Formation of Cyanotrimethylsilane with Ketones and Glycosides

Cyanation of ketones **2** with cyanotrimethylsilane **148** are catalyzed by **1a.** The nucleophilic additions proceed in dichloromethane at low temperature and in high yields. The actual nucleophilic species may be the trimethylsilyl isocyanide **148'.**[2]



148 148'

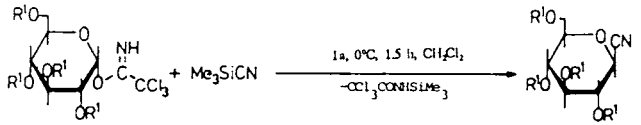


2 148' 149 (88–94%)

R^1 = Me, R^2 = Ph

R^1-R^2 = $(CH_2)_5$, $(CH_2)_7$,

1a is also an effective catalyst in the 1,2- and 1,4-addition of **148** to 1-aza-1,3-dienes.[127a] The α-trichloroacetimidate **150** is stereoselectively transformed to the β-D-glucopyranosylcyanide **151.**[128]



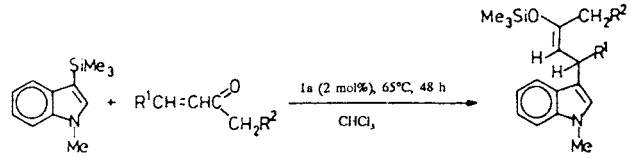
150 151 (87%)

R^1 = CH_2Ph

4.4. Carbon–Carbon Bond Formation of Heteroarylsilanes with α,β-Unsaturated Carbonyl Compounds

The scope and limitation of the employment of carbosilanes other than al-

lyltrimethylsilane or cyanotrimethylsilane as silyl donors in carbon–carbon bond linkages catalyzed by **1a** have only recently been established. As could be shown Michael addition of unsaturated ketones **7** to 3-trimethylsilylindole **152** proceeds readily in the presence of small amounts of **1a**.[129]



152 7 153 (70–80%)

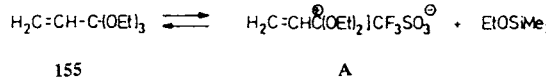
$R^1 = R^2 = H$

$R^1\text{-}R^2 = -(CH_2)_2-$

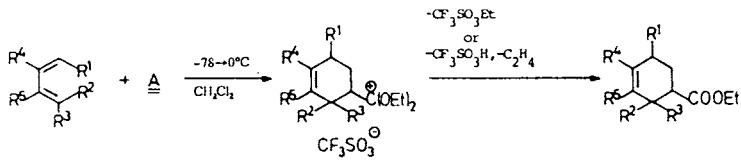
4.5. Carbon–Carbon Bond Formation with Nonsilylated Carbon Nucleophiles

The electrophilic substitution of electron rich aromatic hydrocarbons with acetals or glycosides generally affords equivalent amounts of **1a**.[1,52,130] Possibly trifluoromethane sulfonic acid, formed during the course of the reaction, activates the electrophile to some extent.

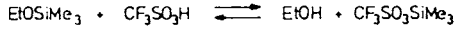
A low-temperature, ionic Diels-Alder addition is achieved by treatment of a 1,3-diene (**154**)/triethyl orthoacrylate (**155**) and **1a**. The 1,1-diethoxy allyl cation **A** is formed as an intermediate in the first reaction step. Subsequently, it adds to the 1,3-dienes to yield the cations **B**, which decompose to give the esters **156**. Whether **1a** is regenerated partially or trifluoromethane sulfonic acid also catalysis this reaction is not quite clear.[131]



155 A



154 B 156 (55–83%)



1a

$R^1\text{-}R^2 = CH_2, (CH_2)_2, R^3 = R^4 = R^5 = H$
$R^1 = R^2 = R^3 = R^5 = H, R^4 = Me$
$R^1 = R^2 = R^3 = H, R^4 = R^5 = Me$
$R^1 = R^5 = H, R^2 = R^3 = R^4 = Me$
$R^1 = R^2 = R^5 = H, R^3 = R^4 = Me$

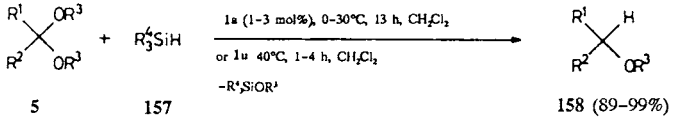
4.6. Polymerization of Vinylic Monomers

1a and TIPS-triflate (**1d**) initiate the polymerization of electron rich monomers such as N-vinylcarbazole, 4-methoxystyrene, α-methylstyrene, styrene, and vinyl ethers even at –78°C and provide polymers of high molecular weight. Because of steric hindrance the initiation with **1d** takes place more slowly.[132]

5. CARBON–HYDROGEN BOND FORMATION AND REDUCTION

5.1. Synthesis of Ethers from Acetals

Trialkylsilanes **157** act as hydride transfer agents toward acetals and ketals **5** in the presence of **1a**[1,2,133] or TMS-Nafion (**1u**)[2,134] to afford ethers **158**. The hydrogenation is also accomplished as a one-pot procedure starting from a mixture of the carbonyl compound, orthoformate, silane **157**, and Nafion-H.[134]



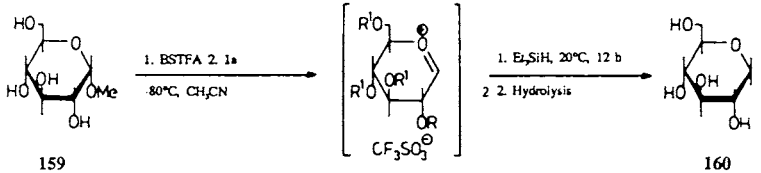
5 157 158 (89–99%)

R^1	H	H	H	Et	Me	Ph
R^2	*n*-Pr	Ph	C_9H_{19}	Et	Ph	Ph

$(CH_2)_5$

R^3 = Me, Et; R^4 = Me, Et

In the reductive cleavage of 1-O-methylpyranosides **159** 1,5-alditols **160** are obtained, accordingly 1-O-methyl furanosides afford 1,4-alditols.[126] In some cases ring contractions occur which can be prevented to some extent using bulkier silyl protective groups.[126] This method of reductive cleavage is applied to the determination of linkage positions and ring forms in polysaccharides.[135-137]



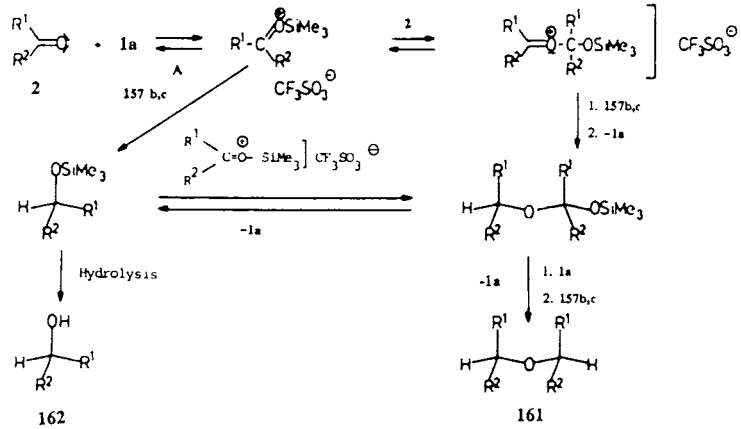
159 160

R^1 = $SiMe_3$

5.2. Synthesis of Ethers from Carbonyl Compounds and Reduction of Sulfoxides

The reaction of triethylsilane (**157b**) with aldehydes or ketones **2** in the presence of 10 mol% **1a** in dichloromethane at 0–20°C gives quantitative yields of symmetri-

cal ethers **161** within a few minutes.[2,138] Also tetramethyldisiloxane (**157c**) is employed as a hydride donor in boiling benzene.[139] In the reductive coupling of aromatic aldehydes benzyl alcohols **162** are formed as minor by products. Because the equilibrium **A** is shifted towards the educts, especially in the case of electron-withdrawing groups in the aromatic moiety (see chapter II,4.1.5), much 4-nitrobenzylalcohol results from the reaction with 4-nitrobenzaldehyde.[139] According to Olah et al.,[138] the reductive coupling of carbonyl compounds take the following course:



R^1 = H, R^2 = Et, Ph; R^1 = Me, R^2 Ph

R^1-R^2 = $(CH_2)_4$, $(CH_2)_5$, $(CH_2)_6$[138]

R^1 = H, R^2 = H, 2-ClC_6H_4, 4-ClC_6H_4,

4-$HOOCC_6H_4$, 4-$O_2NC_6H_4$, *n*-C_4H_9[139]

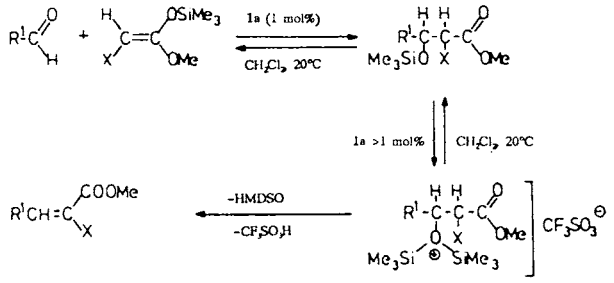
Benzylation of the aromatic solvent occurs in reaction of aromatic aldehydes with polymethylhydrosiloxane as hydride donor in benzene or toluene.[139] Methionine sulfoxide moieties in peptides are reduced by treatment with phenylthiotrimethylsilane in the presence of **1a**.[140]

6. ELIMINATION REACTIONS

6.1. 1,2-Elimination Reactions

β-Eliminations of trimethylsilanol, catalyzed by **1a**, are observed as subsequent reactions in aldol-type bond formations of silyl enol ethers, silyl ketene acetals,[71,104,115] or allylsilanes[118] with acetals or carbonyl compounds by increasing the amounts of catalyst or the temperature (see chapter II, 4.1.1; 4.1.5; 4.2.1; 4.2.3). A systematic survey of this reaction type has not been made until now. As expected

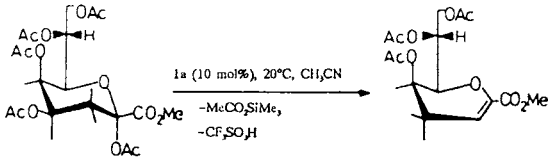
carbocation-stabilizing groups in the electrophilic component favor 1,2-elimination of the silanole.[71,104,115]



R^1 = 3,4-$(MeO)_2C_6H_3$, 2-furyl, 2-(1-methyl)pyrrolyl

X = $OSiMe_3$, $NSiMe_3$, $NCOCF_3$, $COCF_3$, R

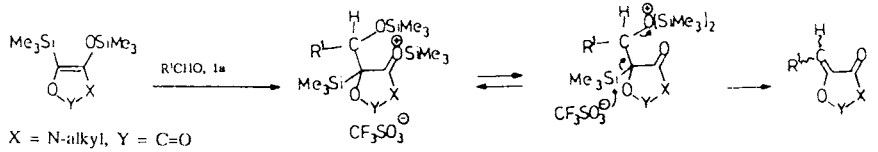
The anhydrosaccharide **164** is prepared from **163** by β-elimination of trimethylsilylacetate and/or acetic acid.[141]



163 164 (91%)

During the course of the elimination, the trifluoromethane sulfonic acid formed may also assume the catalytic function. β-Elimination of cyanotrimethylsilane from N-silylated α-aminonitriles is also observed[111] (see chapters I, 6.4.2; II, 4.1.5).

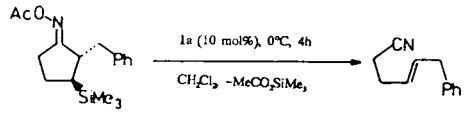
The Peterson olefination proceeds very readily in the presence of catalytic amounts of **1a** under mild conditions[105,118] (see chapter II, 4.1.5).



X = N-alkyl, Y = C=O

X = O, Y = $CHCCl_3$[105]

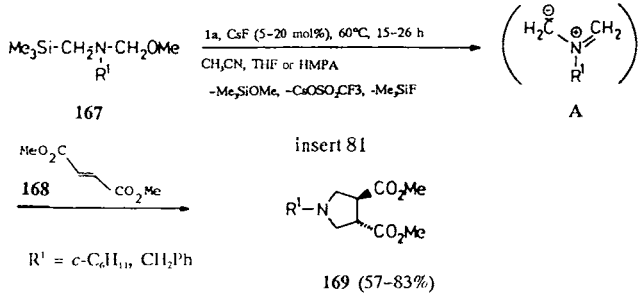
Cyclic(E)-β-(trimethylsilyl)ketoxime acetates **165** are cleaved in a Beckmann fragmentaton with **1a** to give unsaturated nitriles **166** with regiospecific and stereospecific formation of the double bond.[142]



165 166 (93%)

6.2. 1,3-Elimination Reactions

N-Alkyl-N-(trimethylsilyl)aminomethyl ethers **167** are converted to intermediate azomethine ylides **A** by treatment with **1a**. The reaction rate is enhanced by the addition of catalytic amounts of cesium fluoride (Me_3Si-C cleavage). The *in situ* produced ylides **A** are trapped with electron deficient alkenes **168** in a 1,3-dipolar-cycloaddition to yield pyrrolidines **169**.[143,144]



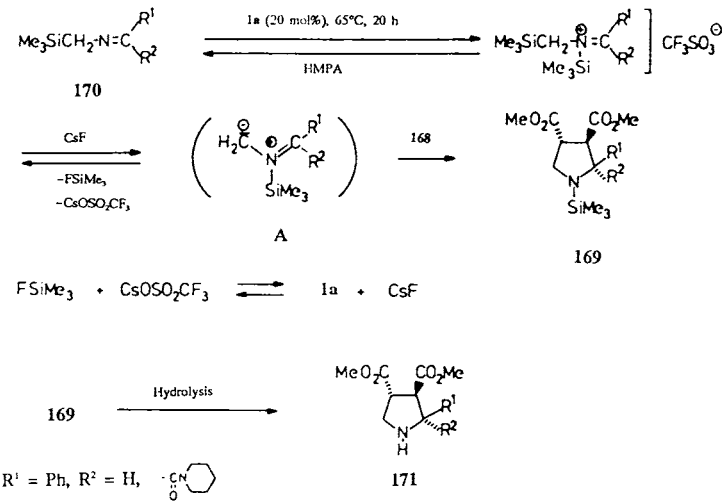
167 A

168

R^1 = *c*-C_6H_{11}, CH_2Ph

169 (57–83%)

Azomethine ylides of the type **A** are also generated from trimethylsilylazomethine **170** and **1a**/cesium fluoride. In presence of alkenes **168** the 1,3-dipolar cycloaddition affords pyrrolidines **169** (R^1=$SiMe_3$), which are hydrolysed to the N-unsubstituted heterocycles **171**. Dipolar aprotic solvents are most effective in this reaction.[145–147]



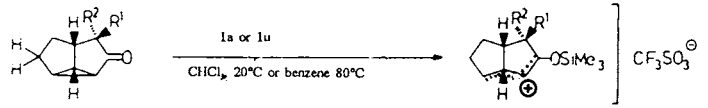
170 A 169

169 171

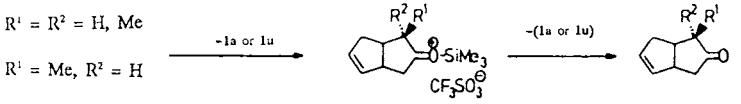
R^1 = Ph, R^2 = H,

7. REARRANGEMENT REACTIONS

1a isomerizes tricyclooctanones **172** to bicyclooctenones **173** in chloroform at room temperature. The isomerization is also catalyzed by TMS-Nafion (**1u**) in benzene at 80°C. Apparently, due to problems in working up the reaction mixture **1u** gives better results. Silyl enol ethers, formed as intermediates, serve as proton acceptors.[148–151] Aro-semibullvalenes are rearranged to arobarrelenes.[150]

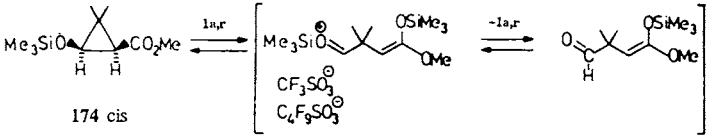


172



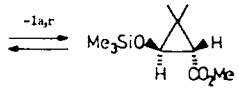
173

Trimethylsilyl perfluoroalkane sulfonates **1a,r** catalyze the cis/trans equilibration of vicinal donor–acceptor substituted cyclopropanes **174** at –78°C. O-Trimethylsilyl-O-alkyl ketene acetals are formed as intermediates.[152–154]

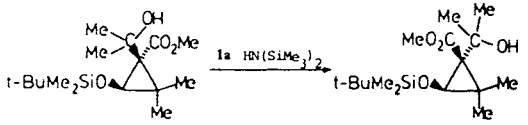


174 cis

84

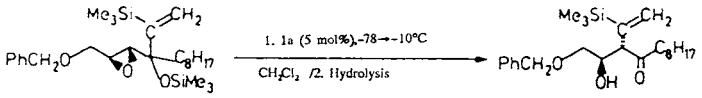


174 trans



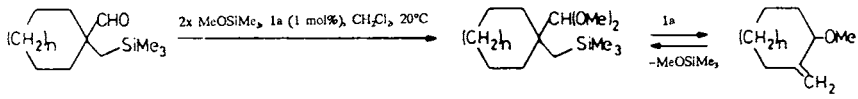
174 trans 174 cis

2-(1-Trimethylsiloxyalkyl)oxiranes **175** are rearranged to β-trimethylsiloxy ketones **176** with high stereospecifity.[155]



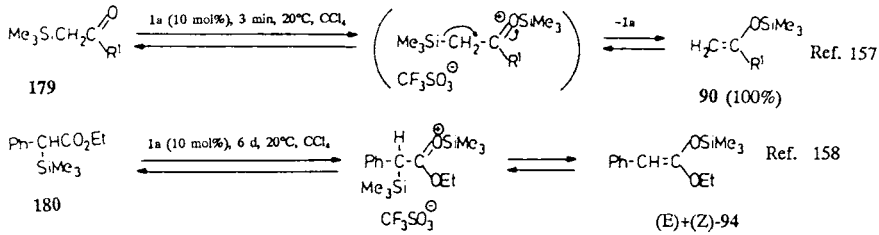
175 176 (92%)

Under very mild conditions one carbon ring expansions of 2-(trimethylsilylmethyl)carbaldehyde acetals **177** to 1-methoxy-2-methylencycloalkanes **178** is promoted by **1a**. The rearrangement proceeds with retention of configuration which may support a concerted mechanism.[156] Ketals do not undergo such rearrangements.



177 **178**

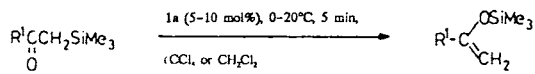
α-Trimethylsilyl ketones **179** rearrange spontaneously to the thermodynamically far more stable trimethylsilyl enol ethers **90** after addition of **1a**.[1,157] In a slow equilibrium reaction 2-trimethylsilyl carboxylic acid esters **180** are transformed to O-trimethylsilyl-O-alkylketene acetals **94**[1,158,159] (see chapter I, 6.2.6.5).



179 **90** (100%) Ref. 157

180 (E)+(Z)-94 Ref. 158

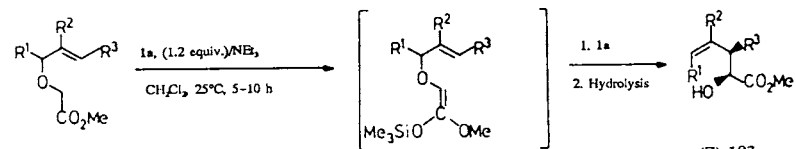
The isomerization of α-trimethylsilylketones **179** with **1a** was used for a regioselective synthesis of silyl enol ethers **90**[160,161].



179 (Z)-90

R^1 = *n*-Pr, *i*-Bu, *n*-C_7H_{15}, CH_2Ph, $EtO_2C(CH_2)_2$

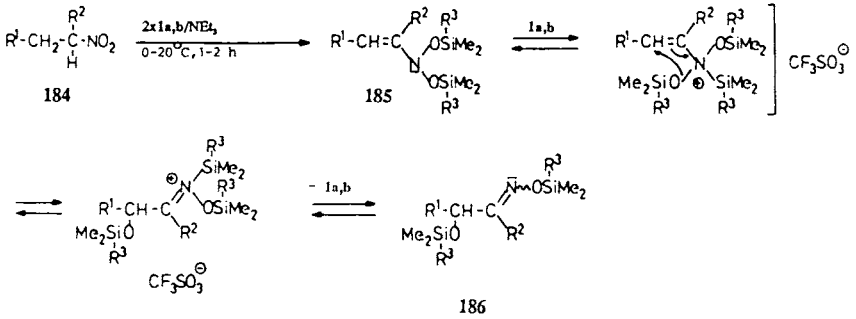
β-Allyloxy ketene acetals **181** formed *in situ* by silylation of β-allyloxyacetates **182** (see also chapter I, 6.2.6.5) with **1a**/NEt_3 are converted in a [2,3]-Wittig rearrangement to the (Z)-γ,δ-unsaturated esters **183** with high erythro selectivity.[162]



182 **181** (Z)-183 (86–93%)

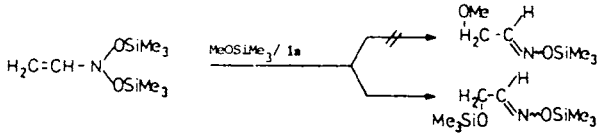
R^1 = Me, R^2 = R^3 = H (Z)
R^1 = R^2 = Me, R^3 = H (Z)
R^1 = R^2 = H, R^3 = Me (erythro)

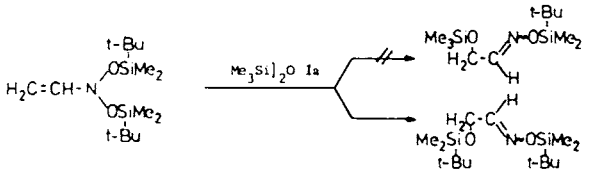
The silylation of nitroalkanes **184** yields the nitrosoacetals **185**, which are rearranged to α-trialkylsiloxyoxim-O-trialkyl silyl ethers **186**[163,164] (see chapter I, 6.2.6.12). The 1,3-trialkylsiloxy shift is initiated by silylation of the enamine nitrogen in **185**. A synchronous reaction course is supported since no signs for an incorporation of foreign nucleophiles are found if rearrangements of **185** are carried out in methyl trimethylsilyl ether or hexamethyldisiloxane as solvents,[164] e.g.,



184 185 186

R^3=Me, tBu





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