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A NEW PRACTICAL SYNTHESIS OF SILYL ENOL ETHERS. PART.I. FROM SIMPLE ALDEHYDES AND KETONES.

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Abstract

A new, practical route to enoxysilanes is described from simple enolizable aldehydes or ketones, using the trimethylchlorosilane-sodium iodide-tertiary amine reagent in acetonitrile. From certain aldehydes, an onium intermediate has been isolated. A conformational study of this onium intermediate and a thermal unimolecular syn-elimination process may explain the stereoselectivity of the reaction. Such an interpretation can be extended to all the aldehydes and ketones considered. Steric factors related to the nature both of the carbonyl derivative and of the amine play a capital role for the regio- as well as for the stereo-control of the reaction.

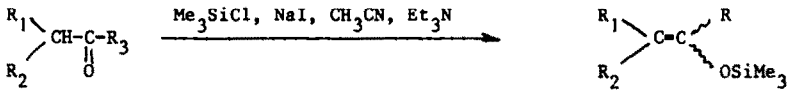
INTRODUCTION

Since the first practical syntheses of silyl enol ethers, (the 1,4-hydrosilylation of α,β-unsaturated carbonyl derivatives[1]) other syntheses from enolizable aldehydes and ketones with hydrogenosilanes[2,3] or chlorosilanes[4-6], have been developed and reviewed[7], such that enoxysilanes are now well recognized as versatile and powerful synthons used as the key intermediates in many important syntheses. Because of the potential of these reagents, we thought that a more general way of preparation of these species from readily available starting materials, under very mild conditions, would be desirable. Among the silylation reagents proposed for that purpose, trimethyliodosilane had been used[8] and Hundeck[9] had reported the facile silylation of acetonitrile despite its low acidity (pKa (DMSO) = 31)[10], by the couple Me_3SiI/Et_3N. In this context an because of the similar reactivity of Me_3SiI and the Me_3SiCl-NaI-Et_3N reagent in acetonitrile (i.e. Me_3Si I prepared *in situ*)[11], we assumed it might be possible to use Me_3SiI prepared *in situ*, in the presence of a tertiary amine, under very mild conditions, to perform an improved synthesis of silyl enol ethers. Enolizable aldehydes and ketones generally have a pKa lower than that of acetonitrile (e.g. pKa (DMSO) = 24-27 for $RCOCH_2R'$)[10] so we might expect a rapid and complete reaction at room temperature. Following the publication of our preliminary results[12], we now report our more extensive results in this field and demonstrate the advantage of our process over other general and practical routes to silyl enol ethers from simple aldehydes and ketones. These results only concern non-conjugated olefinic aldehydes and ketones.

The behavior of α,β-unsaturated aldehydes and ketones will be described in a forthcoming paper.

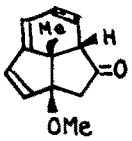
RESULTS

Reaction of the Me_3SiCl-NaI-Et_3N reagent in acetonitrile as the solvent was investigated with enolizable ketones and aldehydes successively according to :



Reaction with Enolizable Ketones. Sodium iodide dissolved in acetonitrile was slowly added to the mixture of ketone, triethylamine and trimethylchlorosilane at room temperature (Procedure A). In some cases, because of the regeneration of the starting ketone from its enoxysilane, the reaction was carried out in the biphasic acetronitrile-pentane medium: in contrast with the reagents, the formed enoxysilane is more soluble in pentane than in acetonitrile and so was isolated from the reaction mixture (Procedure B). Results are summarized in Tables 1 and 2 according to the structure of the starting ketone in which either one or both sides may allow enolization.

The observed results require the following comments : i) the route we propose is a very general one and readily affords enoxysilanes under very mild conditions. So enoxysilanes could be obtained using our route[13,14] even in the case of 1[15] and with sterically hindered chlorosilanes such as 2[16].



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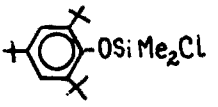


2

ii) Our method resulted in the formation of the enoxysilane from camphor (IX) although only a few routes for this compound are known[17-19] and the House methods[6] are not convenient for that purpose.

iii) It is noteworthy that our route generally affords enoxysilanes in high yield by a simple and rapid (15 mn) procedure. The reaction proceeds without warming since the exothermicity assures a complete conversion of the starting carbonyl derivative. Furthermore, in the case of unsymmetrical ketones, our method sometimes offers a high regioselectivity (cf Table 2). For instance, with methylalkylketones (XII-XVI), the major product has a carbon-carbon double bond on the less substituted side except for the butanone XII. Even in the particular case of the methylbenzylketone XVIII, the enoxysilane in which the carbon-carbon double bond is not conjugated with the aromatic ring is formed in 40 % yield whereas the House methods[6] do not provide this regio isomer. Concerning the different behavior of XVII and XIX despite their similar structure, we have to specify that the high ratio of the more substituted enoxysilane was not due to the isomerisation of the derivative since the use of pentane as a cosolvent did not change this ratio.

Table 1 - Silylation of Ketones Having One Possibility for Enolization

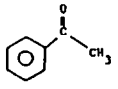
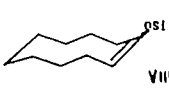
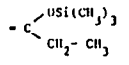
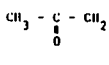
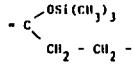
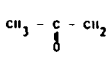
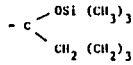
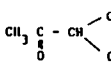
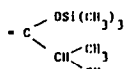
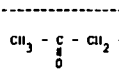
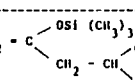
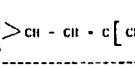
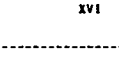
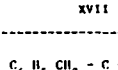
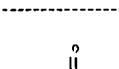
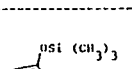
Ketone	Enoxysilane	% Isomer	Yield %	Reaction Time	Experimental Procedure
$CH_3-C(=O)-CH_3$ I	$CH_2=C(CH_3)OSi(CH_3)_3$ Ia		95	15 mn	A
$CH_3CH_2-C(=O)-CH_2-CH_3$ II	$CH_3CH=C(CH_2CH_3)OSi(CH_3)_3$ IIa	100	74	15 mn	A
$(CH_3)_2CH-C(=O)-CH(CH_3)_2$ III	$(CH_3)_2C=C[CH(CH_3)_2]OSi(CH_3)_3$ IIIa		60	12 h	A
$CH_3-C(=O)-C(CH_3)_3$ IV	$CH_2=C[C(CH_3)_3]OSi(CH_3)_3$ IVa		70	15 mn	A
 V	$CH_2=C(C_6H_5)OSi(CH_3)_3$ Va		98	15 mn	A
 VI	 VIa		78	15 mn	A
 VII	 VIIa		78	15 mn	A
 VIII	 VIIIa	23	83	15 mn	A
 IX	 IXa		46	12 h	A
			59	96 h*	B
 X	 Xa		53	12 h	A
			67	12 h	B
 XI	 XIa		60	5 h	A
			90	3 h	B

Table 2 Silylation of Ketones Having Two Possibilities for Enolization

Ketone	Enoxysilan	Regio isomer %	Z %	Yield %	Reaction Time	Experimental Procedure
 XII	 XIIa	36		92	15 mn	A
	$CH_3-CH=C(CH_3)-OSi(CH_3)_3$ XIIb	64	100			
 XIII	 XIIIa	60		80	15 mn	A
	$CH_3-CH_2-CH=C(CH_3)-OSi(CH_3)_3$ XIIIb	40	100			
 XIV	 XIVa	56		80	15 mn	A
	$C_4H_9-CH=C\left[CH_3\right]-OSi(CH_3)_3$ XIVb	44	100			
 XV	 XVa	80		80	15 mn	A
	$(CH_3)_2C=C\left[CH_3\right]-OSi(CH_3)_3$ XVb	20				
 XVI	 XVIa	95		70	15 mn	A
	 XVIb	5	100			
 XVII	$CH_3-CH=C\left[CH(CH_3)_2\right]-OSi(CH_3)_3$ XVIIa	46	71	70	60 mn	A
	$(CH_3)_2C=C\left[CH_2CH_3\right]-OSi(CH_3)_3$ XVIIb	54				
 XVIII	$CH_2=C\left[CH_2-C_6H_5\right]-OSi(CH_3)_3$ XVIIIa	40			15 mn	B
	$C_6H_5-CH=C\left[CH_3\right]-OSi(CH_3)_3$ XVIIIb	60	85	56		
 XIX	 XIXa	10		92	15 mn	A
	XIXb	90				

iv) Finally we wish to underline the high stereoselectivity in favor of the Z isomer which is formed uniquely in the case of II, XII, XIII, XIV and XVI. This stereoselectivity differs from that observed by House[6a] with Me_3SiCl-DMF-Et_3N, Olah[20] with Me_3SiCl-Li_2S-Et_3N, Gerval and Frainnet[21] with Me_6Si_2-εNa-HMPA, Frainnet *et al.*[2] with Et_3SiH-$Ni(Et_2S)$ or Simchen[18] with $F_3CSO_3SiMe_3$-Et_3N, who observed the almost exclusive formation of the E isomer. In contrast our results are in good agreement with these of Kuwajima[22] using Me_3SiCH_2COOEt-$Bu_4N^+F^-$ (cat.) as the silylation agent or these of Dédier[17] with bis(trimethylsilyl)acetamide (BSA) in the presence of sodium and HMPA. However our method does not need the use of a silylating reagent prepared in advance from trimethylchlorosilane. After the publication of our preliminary results[12], Corey et al.[23] proposed a quite different approach of silyl enol ethers (use of lithium amides) offering possibilities in the regio- and stereo- control of such a synthesis.

When triethylamine was replaced by N,N-diisopropyl-3 pentylamine, pyridine or 2,6-dimethylpyridine (lutidine) the isomer proportions of the product changed as summarized in Table 3.

Table 3 Ratio of Enoxysilane Regio and Stereo Isomers According to the Nature of the Tertiary Amine

Starting ketone	Enoxysilane	% of Formed Enoxysilane Regio and Stereo Isomers in the Presence of				
		Et_3N	Pr_3N	iPr_2NCHEt_2	Pyridine	Lutidine
XII	XIIa	35	40	11	17	21
	XIIb	65 (100 Z, 0 E)	60 (100 Z, 0 E)	89 (85 Z, 15 Z)	83 (85 Z, 15 E)	79 (85 Z, 15 E)
XV	XVa	80			35	
	XVb	20			65	
XVI	XVIa	95		26	33	
	XVIb	5 (100 Z, 0 E)		74 (80 Z, 20 E)	67 (79 Z, 21 E)	
XIX	XIXb	90			95	
	XIXa	10			5	

Table 4. Silylation of Aldehydes

Aldehyde	Enoxysilane	Z Isomer %	Yield %	Reaction Conditions	Experimental Procedure
CH_3-CHO (XX)	$CH_2 = CH\ OSi\ (CH_3)_3$ XXa		20	15 mn RT	C
CH_3-CH_2-CHO (XXI)	$CH_3 - CH = CH\ OSi(CH_3)_3$ XXIa	70	60	15 mn RT 12 h 40° C	D
$CH_3 - CH_2 - CH_2 - CHO$ (XXII)	$CH_3\ CH_2 - CH = CH\ OSi(CH_3)_3$ XXIIa	76	51	15 mn RT 4 h 40° C	D
$CH_3 - (CH_2)_4-CH_2-CHO$ (XXIII)	$CH_3(CH_2)_4\ CH = CH\ OSi(CH_3)_3$ XXIIIa	63	94	15 mn RT 2 h 70° C	C
$CH_3 > CH - CHO$ CH_3 (XXIV)	$CH_3 > C = CH\ OSi(CH_3)_3$ CH_3 XXIVa		52	15 mn RT	D
$CH_3 > CH - CH_2 - CHO$ CH_3 (XXV)	$(CH_3)_2\ CH - CH = CH\ O\ Si\ (CH_3)_3$ XXVa	75	93	15 mn RT 2 h 70° C	C
$(C_6\ H_5)_2\ CH - CHO$ (XXVI)	$(C_6\ H_5)_2\ C = CH\ OSi(CH_3)_3$ XXVIa		67	15 mn RT	C

In the Discussion Section (see below) we propose a complete rationalization of all the results.

Reaction with Enolizable Aldehydes. The more facile aldolization of aldehydes compared to that of ketones led us to settle two experimental procedures C and D different from A and B. Procedure C consists in the addition at room temperature of a mixture of aldehyde, triethylamine, sodium iodide in acetonitrile to the trimethylchlorosilane, followed by warming at moderate temperature (40–70°C) to complete the reaction. Procedure D differs from C by the addition of pentane to the acetonitrile as an extractive solvent for separating the enoxysilane which, in contrast with the reagents, is more soluble in pentane than in acetonitrile, from the reaction medium as soon as it was formed. Results are summarized in Table 4.

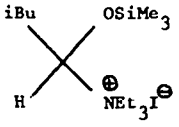
As mentioned in this Table our route easily provides enoxysilanes from aldehydes in satisfactory yields (except for acetaldehyde) and with a stereoselectivity oriented towards the formation of the Z stereoisomer. Here again this method is more simple and/or general than the other common routes to enoxysilanes derived from aldehydes[1-7]. For instance the Kuwajima process[22] is not convenient for aldehydes while the route proposed by Simchen[24] requires the use of trimethylsilyl triflate, a very expensive silylation reagent.

As discussed below we observed the formation of a stable adduct with some aldehydes the decomposition of which requires moderate warming (40–70°C). Moreover in the case of acetaldehyde it was necessary to change the solvent to observe the complete formation of the expected vinyloxytrimethylsilane (cf Experimental Section). Here again all the results are rationalized in the Discussion Section.

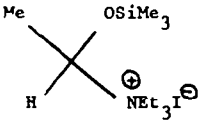
DISCUSSION

It is now admitted that the formation of organometallic enolates can proceed from another way different from the reaction of the tautomeric enol form [23,24]. Concerning our own results stable intermediates from some aldehydes were isolated and identified unambiguously by NMR spectroscopy.

So with isolvaleraldehyde an onium salt has been isolated which decomposes either alone slowly since 0°C or rapidly under the reaction conditions to give the same percentage Z/E c.a. 3/1 of enoxysilanes. This salt XXV c was identified by NMR spectroscopy (cf Table 5 and from the complete NMR identification of the onium salt XXc given by acetaldehyde.



XXV c

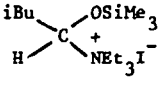


XXc

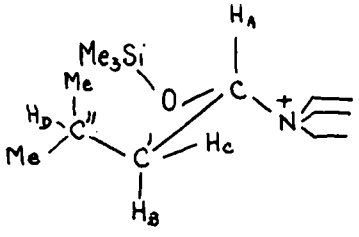
Indeed XXc presents a doublet of three equal intensity lines for the Me signal (^2J = 6 Hz and $^3J\ ^{14}_{N-C-C-H}$ = 1,3 Hz).

Similar onium salts were observed with RCH_2CHO but, from R_2CHCHO (R = Me, Ph) or ketones, it was not possible to put in evidence such type of intermediates. Moreover we noted that the replacement of triethylamine by pyridine allowed us to characterize the onium salt in the case of Me_2CH-CHO and the replacement of triethylamine by pyridine produced and appreciable stabilization of the onium salt from isovaleraldehyde. Finally we observed that pyridine displaces triethylamine in the formed onium products. All these results exhibit the capital importance of sterical considerations in the formation and thermal stabilyty of the onium salts.

These results led us to consider that the formation of the onium salt could constitute a necessary step in the reaction and an unimolecular thermal elimination from these onium intermediates would explain the formation enoxysilanes. Such an interpretation is proposed for the first time. Since this type of elimination involves a syn elimination process[26] the conformation 3 of XXV c deduced from NMR data (table 5) would undergo elimination.

Table 5. ^1H NMR Assignments for  XXVc

	ppm	Coupling Constants	Diedral Angles
H_A	4.70	$^3J_{AB} = 9$; $^3J_{AC} \simeq 0$; $^4J_{AD} \simeq 0$	H_A-C, C'H_B ≃ 0 or 180°
H_B	1.73	$^2J_{BC} = 13.5$; $^3J_{BD} = 2.5$	H_A-C, C'-H_C ≃ 90°
H_C	1.97	$^3J_{CD} = 11.5$	H_B-C', C''-H_D ≃ 90°
H_D	1.73		H_C-C', C''-H_D ≃ 0 or 180°

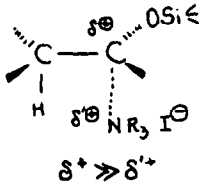


3

In the case of ketones both regio and stereoselectivity have been examinated. With acyclic ketones, replacement of triethylamine by some more or less sterically hindered amines modifies the regio and the stereoselectivity of the reaction (cf Table 3). These results suggest a transition state somewhat polarized depending on the steric hindrance of the amine and the carbonyl skeleton, with eventual assistance of the lone pair of either the nitrogen or I^- for the abstraction of the proton. This transition state could be stabilized by the mesomeric effect (+M) of the trimethylsiloxy group.

The regiochemistry would be governed by the length and the strength of the nitrogen functional carbon bond which depends on the steric hindrance of the ketone and the amine in the transition state.

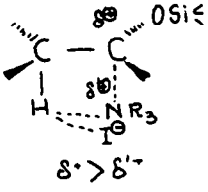
Strong steric hindrance



$\delta^+ \gg \delta'^+$

(formation of the more substituted enoxysilane)

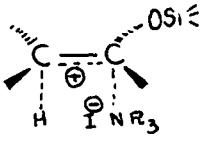
middle



$\delta^+ > \delta'^+$

(formation of the less substituted enoxysilane)

weak



(formation of the more substituted enoxysilane)

With acyclic ketones the stereoselectivity also would be explained by steric factors involving the decomposition of onium salt conformers similar to these of aldehydes.

EXPERIMENTAL SECTION

Proton nuclear magnetic resonance spectra were recorded at 60 MHz on Varian A60 or Perkin-Elmer R12 or R24 B spectrometers or in FT mode at 90 MHz or 270 MHz on Bruker WH 90 or WH 270 spectrometers with tetramethylsilane as the internal standard. ^{13}C nuclear magnetic resonance spectra were recorded at 15,08 MHz on a Bruker WP 60 and at 22,63 MHz on a Bruker WH 90 spectrometer CD_3CN, $DCCl_3$ and C_6D_6 were used as the solvent and tetramethylsilane was used as the internal standard. ^{29}Si nuclear magnetique resonance were recorded at 17,87 MHz on a Bruker WH 90 spectrometer. Mass spectra were checked on a VG Micromass 16 F at 70 eV and using a direct inlet system or a gas chromatography inlet. In this case gas chromatography was performed with a Pye Unicam Series 204 with capillary columns. Analytical gas chromatography analyses were effected on F8M 810 R 12, Hewlett-Packard 5720 or Intersmat IGC 15 instruments fitted with a catharometer detector using helium as the carrier gas. The column used were 1/8 in. 6 ft packed with silicone SE 30, DC 410, carbowax 20 M or QF_1 on chromosorb P or W. Infrared spectra in the wavenumber range 4000-600 cm^{-1} were obtained

with a Perkin-Elmer Model 427 spectrometer using sodium chloride pellets.

Aldehydes and ketones were purchased from Fluka, Aldrich, Merck or Prolabo, distilled and stored over molecular sieves 3 Å, under argon. Triethylamine, pyridine, lutidine, tripropylamine from Aldrich or Prolabo, were refluxed over potassium hydroxide pellets, simply distilled and then distilled once more from calcium hydride.

Acetonitrile (Aldrich) was refluxed over P_2O_5, distilled and stored under argon over molecular sieves 3 Å. Pentane was stored over sodium wires. Trimethylchlorosilane generously provided by Rhône-Poulenc Specialités Chimiques (Dr. Brison) was distilled. NaI purchased from Aldrich or Prolabo was dried 24 h under atmospheric pressure at 140°C and stored under argon. Trimethyliodosilane was prepared as described by Kumada[34].

All the reactions were carried out under argon atmosphere in a standard apparatus composed with a 250 ml three-necked round-bottomed flask equipped with a reflux condenser fitted with a drying tube containing calcium chloride, a pressure-equalizing dropping funnel and a magnetic stirring bar.

Enoxysilanes from Ketones. Procedure A. Sodium iodide (9.3 g, 62 mmol) in acetonitrile (62 ml) was added dropwise (15 mn), at room temperature, to a solution of the ketone (50 mmol), triethylamine (6.26 g, 62 mmol) excess)) and trimethylchlorosilane (6.72 g, 62 mmol (excess)) successively introduced in the reaction flask.

An exothermic reaction generally occured with concomitant formation of an abundant white precipitate ($Et_3^+NHI^-$), while the acetonitrile solution became brownish. The stirring was maintained a few minutes to complete the reaction. The progress of the reaction was monitored by ^1H NMR spectroscopy (particularly the signal corresponding to trimethylchlorosilane (δ = 0.47 ppm) disappeared and a more shifted signal corresponding to $>C=\overset{|}{C}-OSiMe_3$ appeared). Cold pentane (50 ml) and then ice-water (50 ml) were successively added. After decantation, the aqueous layer was extract with pentane (2 x 50 ml) and the gathered organic layers were washed with icewater (2 x 50 ml, or with aqueous solution of NH_4Cl until neutrality (pH = 7), dried over sodium sulfate and distilled under inert atmosphere. This procedure is convenient for most of the ketones. However enoxysilanes corresponding to IX, X and XI were not available using this procedure and were obtained via Procedure B, because of their easy hydrolysis.

Procedure B. This procedure differs from A by the initial introduction of pentane (50 ml) in the reaction vessel. Characteristics of the synthesized enoxysilanes are given in Table 6. On stopping the stirring three layers appeared (pentane, acetonitrile and triethylamine hydroiodide. The progress of the reaction was controlled in the two upper ones. The formed enoxysilanes are collected from the pentane phase, as well as the unreacted trimethylchlorosilane and triethylamine. The starting ketone and a part of the ammonium salt are dissolved in the acetonitrile layer. Enoxysilanes can be separated as previously described in Procedure A or by extraction of the two lower phases with dry pentane (3 x 50 ml) in order to avoid the possible hydrolysis of enoxysilanes especially in the case of ketone XI.

Enoxysilanes from Aldehydes. Procedure C. A mixture of aldehyde (50 mmol), triethylamine (5.05 g, 50 mmol), sodium iodide (7.5 g, 5 mmol) in acetonitrile (50 ml) was added dropwise (15 mn) at room temperature, to trimethylchlorosilane (97.7 g, 90 mmol (excess)). An exothermic reaction (more than with ketones) occurred with concomitant formation of an abundant white precipitate in the brownish solution. When the stirring was stopped the precipitate settled sometimes with difficulty. The progress of the reaction was controlled as previously mentioned for the ketones by ^{1}H NMR spectroscopy. However the absence of signals corresponding to the aldehydic proton and to the trimethylchlorosilane is not sufficient to assume the completion of the reaction, but the presence of a broad singlet near δ = 9 ppm ($Et_3\overset{+}{N}H\overset{-}{I}$) and especially signals near δ = 6 ppm (>C=CHOSi<) allowed the monitoring of the course of the reaction. In the case of aldehydes XX, XXI, XXII, XXIII and XXV, signals corresponding to the stable ammonium salt also appeared (Table 8) between 4.7 and 5 ppm. Then it was necessary to warm (2 h at 70°C) to decompose the formed ammonium (In the special case of acetaldehyde XX, acetonitrile was replaced after reaction by benzonitrile allowing to warm the medium at 140°C (12 h) to decompose the onium salt giving the vinyloxytrimethylsilane in 85 % yield). The separation of the formed enoxysilanes was performed according to the procedure A given for ketones.

Procedure D This procedure differs from C by the initial introduction of dry pentane (50 ml) with trimethylchlorosilane in the reaction vessel. Procedure D was similar to B since three layers appeared when the stirring was stopped, but when the ammonium salt was stable at room temperature, it was decomposed by warming the reaction medium (like in Procedure C). The course of the reaction was monitored in the middle layer by ^{1}H NMR spectroscopy. Characteristics of the synthesized enoxysilanes are given in Tables 6 and 7.

Enoxysilanes Using an Amine Different from Triethylamine When triethylamine was replaced by tripropylamine, diisopropyl 3-pentylamine, pyridine or lutidine the experimental procedure was identical to Procedure B using the same molar equiv. (50 mmol) of these amines.

Table 6 . Physicochemical Data of Enoxysilanes from Ketones

Number of enoxysilanes ; bp °C$_{mn}$ Hg ; IR νcm^{-1}; NMR (CCl_4); δppm, multiplicity, JHz, assignment (s: singulet, d: doublet, t: triplet, q: quadruplet, Ph: phenyl).
Ia : 100/760 ; 1651, 1638, 1620 ; 4,0,s,H_2C=; 1,74, s,CH_3; 0,2,s,Me_3Si.
IIa;139/760 ; 1680 ; 4.37 , m, ^3J = 6.5, ^4J = 0.8, CH= ; 2.00, q, ^3J = 7.2, CH_2; 1.60, d, ^3J = 6,5 CH_3; 1.00, t, ^3J = 7.2, CH_3; 0,15, s, Me_3Si.
IIIa: 83/35 ; 1680 ; 2.76, sept, ^3J = 7, =CHMe$_2$; 1.53, s and 1.60, s, $(CH_3)_2C$= ; 0.93, d, ^3J = 7, $(CH_3)_2CH$; 0.2, s, Me_3Si.
IVa: 68/80 ; 1620 ; 4.08, d, ^2J = 2 and 3.93, d, ^2J = 2 , H_2C=; 1.05, s, CH_3; 0.2, s, Me_3Si ...
Va: 82/5 ; 1605, 1560 ; 7.7-7.4, m, Ph (2H); 7.4-7.1, Ph, (3H); 4.86, d , ^2J = 1.5 and 4.30, d, ^2J = 1.5, H_2C= ; 0.20, s, Me_3Si.
VIa: 106/08 ; 1645 ; 7.4-6.7, m, Ph(4H); 5.0, t, ^3J = 4.3, H-C= ; 2.9-2, m, CH_2CH_2-; 0.2, s, Me_3Si.
VIIa: 76/30 ; 1670 ; 4.75, m, H-C=; 2.2-1.3, m, $(CH_2)_4$-; 0.15, s, Me_3Si.
VIIIa: 127/1 ; 1670 ; Z: 4.49, t, ^3J = 7.6, HC= ; E: 4.56, t, ^3J = 7, CH=; 2.26-1.7, m, CH_2CH= and -$CH_2\overset{14}{C}$-OSiMe_3; 1.30, s, $(CH_2)_3$-; 0.26, s, Me_3Si. In C_6H_6: Z: 0.10, s, Me_3Si ; E: 0. 17, s, Me_3Si.

IXa: 102-105/30 ; 1624 ; 4.71, d, ^3J = 3.3 H-C=; 2.28, t, ^3J = 3.3, allylic H's 2.12-0.92, m, $-(CH_2)_2$ 0.91, s, CH_3; 0.77, s, $2CH_3$, 0.21, s, Me_3Si.

Xa: 86/25 ; 1620 ; 4.63, d, ^3J = 3, H-C=; 2.66, s (broad), 1H, 2.46, s broad, 1H, 2 - 0.83 m, 4H, $-CH_2-$ and $-(CH_2)_2-$; 0.15, s, Me_3Si.

XIa: decomposes ; 3061 ; 6.87, m, H-C=C-H; 5.17, d, ^3J = 3, H-C=; 3.47, s broad, 1H, 3.07 s broad 1H, 2.37, m, $-CH_2-$; 0.21, s, Me_3Si.

XIIa: 120/760 ; 1626 ; 3.92, s, $H_2C=$; 1.96, q, ^3J = 7.3, $-CH_2-$; 0.96, t, ^3J = 7.3, CH_3, 0.1, s, Me_3Si.

XIIb: 120/760 ; 1685 ; 4.41, q, ^3J = 6.6, H-C=, 1.66, s (broad), $CH_3-\overset{\overset{O}{\|}}{C}-OSi$; 1.42, s broad $\underline{CH}_3-C=$; 0.2, s, Me_3Si.

XIIIa: 135/60 ; 1660, 1635, 1620 ; 4.03, s, $H_2C=$; 2.07, t, ^3J = 6.5, $CH_2-C=$; 1.67, m, $-CH_2-$; 1.00, t, ^3J = 7.5, CH_3-; 0.14, s, Me_3Si.

XIIIb: 135/60 ; 1680 ; 4.41, t, ^3J = 6.5, H-C=; 2.07, m, $-CH_2-$; 1.80, m, $CH_3-C=$; 1.00, t, ^3J = 7.5, $\underline{CH}_3-CH_2$; 0.14, s, Me_3Si.

XIVa : 80/30 ; 1660, 1640, 1630 ; 4.00, s, $H_2C=$; 2.00, m, $-CH_2-C=$; 1.34, m, $-(CH_2)_3-$; 0.90, m, CH_3; 0.20, s, Me_3Si.

XVa : 44/25 ; 1690, 1660 ; 3.96, s, and 3.88, s, $H_2C=$; 2.15, m, $\underline{CH}Me_2$; 1.32, d, ^3J = 7, $(CH_3)_2C<$; 0.22, s, Me_3Si.

XVb : 44/25 ; 1690 ; 1.73, s broad, $CH_3-\overset{\overset{O}{\|}}{C}-OSi$; 1.57, s, $(CH_3)_2C=$; 0.22, s, Me_3Si.

XVIa : 86/105 ; 1660, 1640, 1620 ; 3.90, s, $H_2C=$; 1.75, m, $-CH_2-$; 1.0, m, $\underline{H}CMe_2$; 0.9, d, ^3J = 6, $(CH_3)_2C<$; 0.2, s, Me_3Si.

XVIb : 86/105 ; 1680 ; 4.13, d, ^3J = 8.5, H-C=; 1.83, m, $\underline{H}\ CMe_2$; 1.80, s, $CH_3-C=$; 0.90, d, ^3J = 6, $(\underline{CH}_3)_2CH$; 0.2, s, Me_3Si.

XVIIa: 85/80 ; 1675 (Z), 1665 (E) ; Z: 4.46, q, ^3J = 6.8, H-C=; 2.08, m, $\underline{H}-CMe_2$, 1.47, d, ^3J = 6.8, $CH_3C=$; 1.01, d, ^3J = 7.1, $(CH_3)_2C<$; 0.15, s, Me_3Si; E: 4.37, q, ^3J = 6.8, $HC=$; 2.6, m, $\underline{HC}Me_2$; 1.52, d, ^3J = 6.8, $CH_3-C=$; 0.93, d, ^3J = 6.8, $(\underline{CH}_3)_2CH$; 0.15, s, Me_3Si.

XVIIb: 85/80 ; 1678 ; 2.08, q ^3J = 7.2, $-CH_2-C<$; 1.58 and 1.52, s, $(CH_3)_2C=$; 0.98, t, J = 7.2, CH_3; 0.15, s, Me_3Si.

XVIIIa: 72-78/0.5 ; 1640 ; 7.03, m, Ph (5H); 3.97, m, $H_2C=$; 3.14, s, $-CH_2-$; 0.06, s, Me_3Si.

XVIIIb: 72-78/05 ; 1654 (Z), 1651 (E) ; Z: 7.03, m, Ph(5H); 5.31, s (broad), $HC=$; 1.80, d, ^4J = 0.8, CH_3; 0.08, s, Me_3Si. E: 7.03 m, Ph(5H); 5.73, s (broad), $HC=$; 1.80, d, ^4J = 0.8, $CH_3C=$; 0.08, s, Me_3Si.

XIXa: 90/20 ; 1665 ; 4.65, t, ^3J = 3.3, $HC=$; 2.2-1.3, m, $-(CH_2)_3-$; 0.98, d, ^3J = 6.5, CH_3-; 0.15, s, Me_3Si.

XIX: b 90/20 ; 1686 ; 2.2-1.3, m, $-(CH_2)_4-$; 1.55, s (broad), $CH_3-C=$; 0.16, s, Me_3Si.

Table 7 Physiochemical Data of Enoxysilanes from Aldehydes $RCH_b=CH_aOSiMe_3$; bp. °C mmHg IR(ν C=C) cm^{-1} ; NMR (CCl_4) δppm, assignment, JHz : ab, aR, bR.

XXa : 74/760 ; 1620 ; 6.27, d of d, ^3J = 5.8, ^2J = 0.6, Ha ; 4.01, d of d, ^3J = 13.4, Hb ; 4.30, d of d, HR ; 0.16, s, $SiMe_3$; 13.4, 0.60, 5.8.

XXIa : 46/120 ; 1660 ; Z : 6.06, d of q, ^3J = 5.8, ^4J = 1.8, Ha ; 4.43, m, ^3J = 6.6, Hb ; 1.51, d of d, ^3J = 6.6, ^4J = 1.8 ; 0.14, s, $SiMe_3$; 5.8, 6.6, 1.8, E : 6.07, d of q, ^3J = 11.8, ^4J = 1.5, Ha ; 4.87, m, ^3J = 6.8, Hb ; 1.50, d of d, ^3J = 6.8, ^4J = 1.5 ; 0.14, s, $SiMe_3$; 11.8, 6.8, 1.5.

XXIIa : 48/50 ; 1655 ; Z : 5.97, t of d, ^3J = 6.1, ^4J = 1.3 ; Ha 4.35, m, ^3J = 7.3, Hb ;

2.03, m, CH_2 ; 0.90, t, ^3J = 6.5 ; 0.13, s, $SiMe_3$; 6.1, 7.3, 1.3. E : 6.12, t, d, ^3J = 12.1, ^4J = 1.3, H_A ; 4.90, m, J, 7.1, Hb, 2.83, m, CH_2 ; 0.95, t, ^3J = 6.5 ; 0.13, s, $SiMe_3$; 12.1, 7.1, 1.13.

XXIIIa : 83/25 ; 1665 ; Z : 5.95, d of q, ^3J = 6, ^4J = 1.3, Ha ; 4.32, q, ^3J = 6.5 Hb ; 1.95, m, CH_2 ; 1,15, m, $(CH_2)_3$; 0.75, t, CH_3 ; 0.14, s, $SiMe_3$; 6.0, 7.0, 1.3, E : 5.98, d of q, ^3J = 12. ^4J = 1.3, Ha ; 4.78, q, ^3J, 6.5, Hb ; 1.95, m, CH_2 ; 1.15, m, $(CH_2)_3$; 0.75, t, CH_3 ; 0.14, s, $SiMe_3$; 12.0, 7.0, 1.3.

XXIVa : 69/120 ; 1680 ; 5.93, m, Ha, 1.55, s (broad), CH_3 ; 0.17,s, $SiMe_3$.

XXVa : 115/120 ; 1665 , Z : 5.94, d of d, ^3J = 5.5, ^4J : 2, H_A ; 4.27, d, d, ^3J = 8.5, Hb ; 2.5, m, $HCMe_2$; 0.94, d, ^3J = 6.5, CH_3 ; 0.13, s, $SiMe_3$, 5.5, 8.5, 2.0, E : 6.09, d of d, ^3J = 12, ^4J = 2, H_A ; 4.85, d of d, ^3J = 7.5 ; H_b ; 2.5, m, $HCMe_2$; 0.94, d, ^3J = 6.5, CH_3 ; 0.13, s, $SiMe_3$; 12.0, 7.5, 2s.

XXVIa : 132/05 ; 1635 ; 6.58, s, H_A ; 0.20, s, $SiMe_3$.

Table 8 ^1H NMR Data of Onium Complexes in Acetonitrile Solution

δ : multiplicity ; J Hz ; assignment

XXc : 5.07, q, ^2J = 5.3, Ha; 1.57, t of d, $^3J_{H}{}^{14}N$ = 1.4, ^3J = 5.3, $CH_3-\overset{+}{C}-OSi\equiv$; 3.33, q, CH_2CH_3 ; 1.30, t, CH_3CH_2; 0.27, s, $SiMe_3$.

XXc' : 6.08 , q, ^3J = 6, Ha ; 0.17, s, $SiMe_3$.

XXIc : 4.8 d (broad) ^3J = 8, Ha; 3.32, q, CH_2-N< , 1.27, t, CH_3-CH_2N ; 0.27, s, $SiMe_3$

XXIIc : 4.83 d (broad) ^3J = 8, Ha ; 3.37, q, CH_2-N< , 1.37, t, CH_3CH_2N , 0.27, s, $SiMe_3$

XXIIIc : 4.76 d (broad) ^3J = 8, Ha ; 3.30, q, CH_2-N< , 1.30, t, CH_3CH_2N , 0.27, s, $SiMe_3$

XXVc : 4.70, d, ^3J = 9, Ha ; 3.30, q, CH_2-N< ; 1.24, t, CH_3CH_2N , 0.20, s, $SiMe_3$

XXVc' : 6.60 , m , Ha; 0.20 , s, $SiMe_3$.

XXIVc' : 6.50 , d, ^3J = 5.3 , Ha; 0.27, s, $SiMe_3$.

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