

A NEW PRACTICAL SYNTHESIS OF SILYL ENOL ETHERS.

II. FROM α,β -UNSATURATED ALDEHYDES AND KETONES

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Abstract

In acetonitrile as the solvent and in the presence of a tertiary amine the trimethylchlorosilane/sodium iodide (trimethyliodosilane "in situ") reagent provides the corresponding siloxy dienes when reacted with α,β -unsaturated series. These reactions occurs via the formation of 1,2 or -1,4 onium salt intermediates.

INTRODUCTION





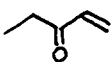
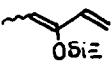
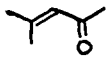
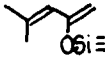
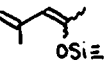
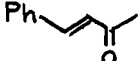
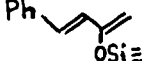
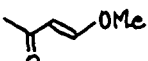
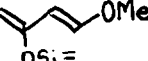
In a previous paper¹ we have reported a new and general route to silyl enol ethers from simple enolizable aldehydes or ketones using the trimethylchlorosilane-sodium-iodide-tertiary amine reagent in acetonitrile as the solvent. Regarding the potentialities of siloxy dienes as versatile synthons for pure organic purposes², we have focused our interest in the preparation of these species since we thought that the route we proposed previously could offer similar advantages in the α,β -unsaturated series: the most convenient ways to dienoxysilanes consisted in the silylation of dienolates generated from α,β -unsaturated carbonyl derivatives and a strong base such as iPr_2NLi ^{3,4} or in the direct silylation of the same substrates by $Me_3SiCl-Et_3N$ ($ZnCl_2$ cat.)⁵, $R_3SiCl-Et_3N-DMF$ ⁶, $R_3SiCl-DBU$ ⁷, $F_3C-SO_3SiMe_3-Et_3N$ ⁸, $Me_3SiI-(Me_3Si)_2NH$ ⁹. Because of the advantages of the $Me_3SiCl-NaI-Et_3N$ reagent in acetonitrile (fast reaction under very mild conditions, satisfactory yields, and, especially, commercially available and not expensive reagents), we have investigated the synthesis of dienoxysilanes and here we report our results.

RESULTS AND DISCUSSION

In acetonitrile, $Me_3SiCl-NaI-Et_3N$ reacts with α,β -unsaturated enolizable aldehydes or ketones to afford dienoxysilanes at room temperature.

Results are summarized in Table 1.

Table 1. Synthesis of Dioxysilanes from α,β -Unsaturated Aldehydes and Ketones and the $\text{Me}_3\text{SiCl-NaI-Et}_3\text{N}$ Reagent in Acetonitrile

Starting Carbonyl Deriv. <u>1</u>	Dioxysilanes <u>2</u>	% Yield	Configu-ration	Observations
 <u>1a</u>	 <u>2a</u>	55	E	
 <u>1b</u>	 <u>2b</u>	80		
 <u>1c</u>	 <u>2c</u>	40	Z : 35 E : 65	
 <u>1d</u>	 <u>2d</u> ¹	91		Only one isomer Z or E *after distillation quant. yield for crude product. ** id.
	 <u>2d</u> ²	74 9	Z or E**	
 <u>1e</u>	 <u>2e</u>	40*		
 <u>1f</u>	 <u>2f</u>	60*		

These results require following comments :

°moderate yields are due to the very easy polymerization of dioxysilanes which also are very hydrolyzable compounds. When the dioxysilanes products were not stable under our conditions, the reaction was carried out in the biphasic medium (acetonitrile-pentane) : in contrast with the reagents, the formed dioxysilane is more soluble in pentane than in acetonitrile and so was isolated from the reaction mixture.

°from crotonaldehyde 1a only the E isomer was isolated, whereas a mixture E/Z c.a. 80/20 was formed using the $\text{Me}_3\text{SiCl-Et}_3\text{N}$ (ZnCl_2 cat.) reagent⁵.

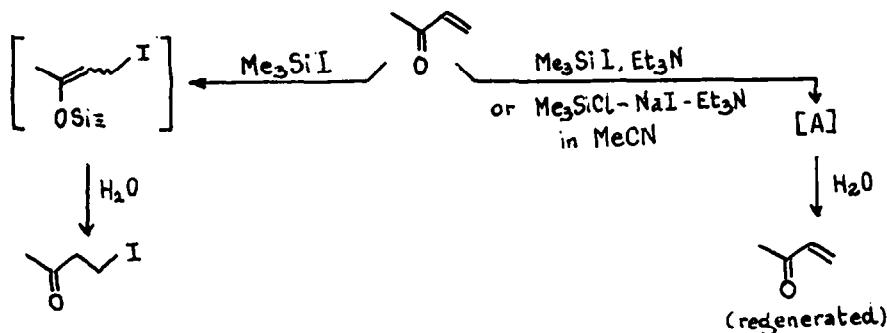
However the Z isomer can be favoured by replacement of triethylamine by a more sterically hindered amine (for example a ratio Z/E = 54/46 was observed with lutidine).

°from the ketone 1d, hydrogen in α -position with respect to the carbonyl group was essentially concerned and from 1e and 1f the E configuration of the double bond was preserved.

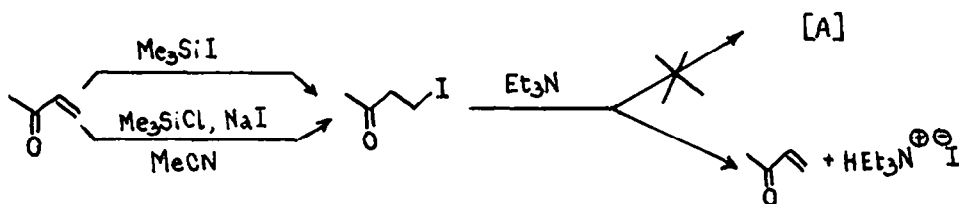
°with reference to our preliminary report¹⁰ some other dioxysilanes were synthesized in satisfactory yields¹¹.

From some saturated aldehydes we have observed¹ the formation of stable complexes such as :

$$\begin{array}{c} \text{R} \quad \text{OSi}\equiv \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{NEt}_3^{\oplus}, \text{I}^{\ominus} \end{array}$$
 from RCH_2CHO and this suggested the formation of similar intermediates in the α,β -unsaturated series. First we observed the formation of an intermediate from 1a-c and we have verified with methyl vinyl ketone that the complex was different from that obtained by McKean et al.¹² with Me_3SiI alone :



Similarly the [A] complex did not result from the action of Et_3N on β -iodoethyl methyl ketone formed as follows :



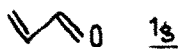
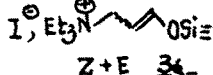
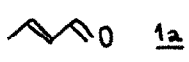

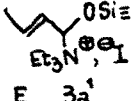
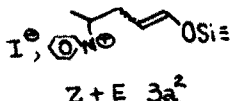


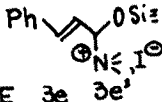
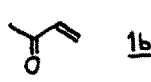

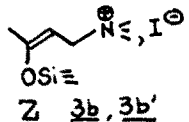
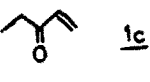

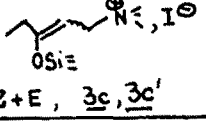
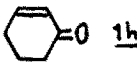

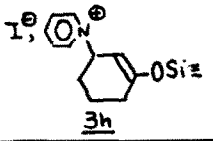
By comparison with the adduct sometimes isolated in the saturated series and with respect to the physico-chemical data (IR ^1H and ^{13}C NMR) we assume the formation of -1,2 or -1,4 adduct similar to those observed with RCH_2CHO . The results are summarized in Table 2.

In general -1,4 adducts exhibit a higher thermal stability than the corresponding -1,2 ones. Thus, the -1,4 adducts isolated with the mentioned ketones, in the case of Et_3N , are decomposed only after warming to 80°C for 12 h. In contrast adducts from saturated ketones (obviously 1,2) could not be detected under our reaction conditions¹.

With acrolein 1g (run 1), the 1,4 adduct was observed, $E/Z = 83/17$. Similarly¹³ it was shown that acrolein 1g gave with trimethylchlorosilane and triethylamine a similar onium salt the constitution of which depended on the nature of the solvent $Z/E = 97/3$ (ligroin), 20/80 (carbon tetrachloride), 50/50 (CDCl_3). When the solution of NaI in acetonitrile was completely added, the configuration changed to reach $E/Z = 25/75$ after 48 h. In contrast, crotonaldehyde 1a provided the 1,2 adduct which rapidly decomposed at room temperature into the E dienoxysilane, whereas (run 2) the replacement of triethylamine by pyridine yielded the stable 1,4-adduct. The structure of this adduct was assigned by comparison with previous studies in our laboratory¹⁴ : $Z/E = 15/85$ after the end of the addition, to reach 50/50 after

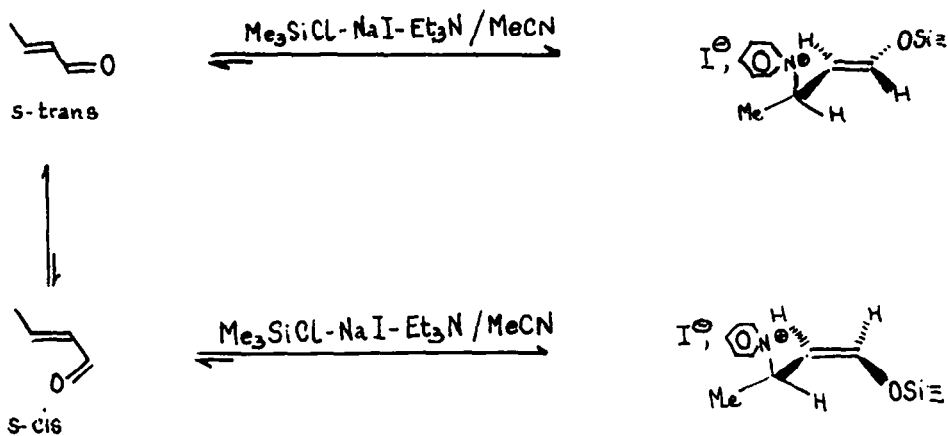
48 h.

Table 2. Adducts Obtained from α,β -Unsaturated Aldehydes or Ketones and the $\text{Me}_3\text{SiCl-NaI-Et}_3\text{N}$ reagent in Acetonitrile

Run	Carbonyl derivative	Base (t° of the reaction)	Adduct	
			1,2	1,4
1	 <u>1g</u>	Et_3N (-20°C)		$\text{I}^\ominus, \text{Et}_3\text{N}^\oplus$  Z+E <u>3g</u>
2 3	 <u>1a</u>	Et_3N (-20°C)  (room temp.)	 $\text{Et}_3\text{N}^\oplus, \text{I}^\ominus$ E <u>3a'</u>	$\text{I}^\ominus, \text{Pyridinium}^\oplus$  Z+E <u>3a''</u>
4 5	 <u>1e</u>	Et_3N (room temp.)  (0°C)	 $\text{Et}_3\text{N}^\oplus, \text{I}^\ominus$ E <u>3e, 3e'</u>	
6 7	 <u>1b</u>	Et_3N (room temp.)  (0°C)		 Z <u>3b, 3b'</u>
8 9	 <u>1c</u>	Et_3N (room temp.)  (0°C)		 Z+E, <u>3c, 3c'</u>
10	 <u>1h</u>	 (0°C)		$\text{I}^\ominus, \text{Pyridinium}^\oplus$  <u>3h</u>

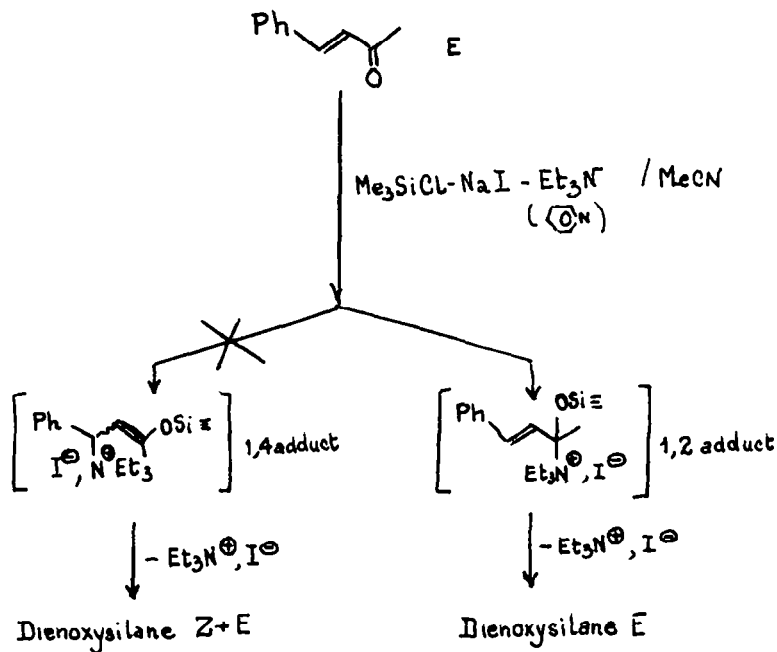
The initial major E configuration of these 1,4 adducts from 1a and 1g indicate a kinetic control of the reaction: telereactions (1,4-additions to conjugated sequences) are syn additions¹⁵, so the preferential formation of the E-isomer should result from the attack of the major conformer¹⁶ of 1a (cf. Scheme 1).

In the case of ketones, only the non-substituted in position -4 or 2-cyclohexenones form 1,4-adducts. All these results exhibit the important role of steric considerations, especially the steric hindrance in position 2 and 4 of the carbonyl derivative and the nature of the involved amine. Moreover the stability of the adduct also has to be considered: the formation of the -1,4 adduct in the case of acrolein (run 1) can be rationalized regarding the repulsive effect of the electronegative groups in the -1,2 adduct, and the more substituted character of the double bond stabilized by the OSi[≡] group, in the -1,4 adduct.



Scheme 1

In the case of ketones 1d-f adducts were not detected but the formation of the *E* isomer uniquely suggests an 1,2-adduct since the 1,4 one would afford a *Z/E* mixture as shown in Scheme 2 with benzalacetone :

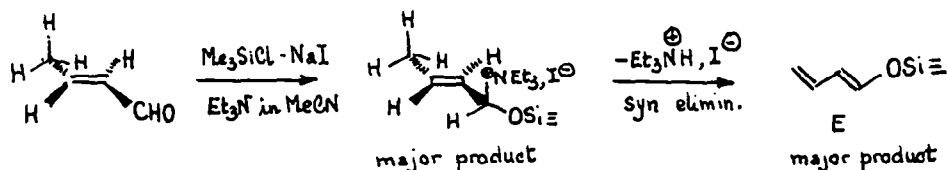


Scheme 2

As we have previously argued in the saturated series¹ onium salts should be responsible for the formation of enoxysilanes. The obtention of dienoxysilanes results from 1,2 or 1,4-elimination according to the nature of the onium salt intermediate.

For 1,2-elimination from 1,2-adducts one can propose the same process as in the saturated series¹.

Concerning 1,4-elimination either from 1,2- (corresponding to 1a) or 1,4-adducts (corresponding to 1b and 1c), this reaction occurs according to a syn process^{16,17} and governs the stereochemistry of the formed dienoxysilane. Our result with crotonaldehyde is in good agreement with the predicted stereochemistry :



EXPERIMENTAL SECTION

Proton nmr spectra were recorded at 60 MHz on Varian A 60 or Perkin-Elmer R 12 or R 24 B spectrometers (in CCl_4 as the solvent and with tetramethylsilane as the internal standard) or in the case of 2a and 2b, at 100 locked on the trimethylsiloxy signal. ¹³C nmr spectra were recorded at 15.08 MHz on a Bruker WP 60 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 Serie 204 with capillary columns. Analytical gas chromatography analyses were effected on F & M 810 R 12, Hewlett-Packard 5720 or Intersmat IGC 15 instruments with a catharometer detector using helium as the carrier gas and columns (1/8 inch 6 feet) packed with silicones SE 30, DC 410, carbowax 20 M or QF₁ on chromosorb P or W. Infrared spectra in the wavenumber range 4000-600 cm^{-1} were obtained with a Perkin-Elmer Model 427 spectrometer and sodium chloride pellets. All the trimethylsilyl derivatives exhibit absorption at about 1250, 840 and 755 cm^{-1} . All the dienoxysilanes gave satisfactory elemental analyses available on request (C calc $\pm 1,1\%$, H calc $\pm 1,3\%$, Si Calc $\pm 1,5\%$).

Aldehydes and ketones were purchased from Fluka, Aldrich Chemicals or Merck and distilled just before use. Triethylamine or pyridine, from Aldrich or Prolabo were refluxed over calcium hydroxyde pellets, distilled, then distilled a second time from calcium hydride.

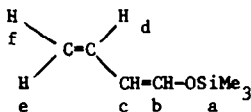
Acetonitrile (Aldrich) was refluxed over P_2O_5 , distilled and stored under argon over molecular sieves 3 Å. Pentane was stored over sodium wires. Trimethylchlorosilane generously provided by Rhône-Poulenc Spécialités Chimiques (Dr. Brison) was distilled. NaI purchased from Aldrich or Prolabo was dried 24 h under atmospheric pressure at 140°C and stored under argon. Trimethyliodosilane was prepared as described by Kumada *et al.*¹⁸.

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.

SYNTHESIS OF DIENOXYLSILANES

1 - From Crotonaldehyde. Synthesis of 2a

Sodium iodide (9.3 g, 62 mmol) in acetonitrile (62 ml) was added dropwise with stirring to a solution of dry pentane (60 ml) crotonaldehyde 1a (3.5 g, 50 mmol), trimethylchlorosilane (6.73 g, 62 mmol) and triethylamine (6.26 g, 62 mmol) or eventually pyridine (4.9 g, 62 mmol) or lutidine (6.63 g, 62 mmol), successively introduced in the reaction flask at room temperature. The reaction medium was left overnight and then warmed at 40°C for 4 h. Then the mixture was poured on 100 ml of ice-water and extracted with pentane (3 x 50 ml). The combined organic layers were washed with an aqueous solution of ammonium chloride until neutrality, dried over sodium sulfate and distilled under dry inert atmosphere to remove pentane (760 mmHg). Then the dienoxysilane was distilled under vacuum 2a (3.5 g, 55 %, b.p./60 mmHg : 56°C). The nmr spectrum of 2a was analyzed with a Laocoon program modified for using with a 360-44 IBM computer. After obtaining good agreement between the experimental and calculated shifts (difference lower than 0.1 Hz) the coupling constant $J_{bc} = 12$ Hz led us to assign to 2a the structure E by comparison with data given :



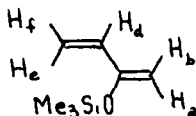
by the Z/E mixture prepared according to ref. 5, ($J_{bc} = 6$ Hz for the Z isomer).

2b : ir (cm^{-1}) : $\nu_{(\text{C}=\text{C OSi})}$: 1650 ; $\nu_{(\text{C}=\text{C})}$: 1605 cm^{-1} ; ^1H nmr (100 MHz, δ ppm ; J Hz) : 6.25, m, H_b ; 5.93 m, H_d ; 5.44, m, H_c ; 4.72, m, H_e ; 4.56 m, H_f ; 0, s, 9H_a ; $J_{bc} = 11.9$; $J_{cd} = 10.9$; $J_{bd} = 0.7$; $J_{be} = 0.6$; $J_{ce} = -0.8$; $J_{cf} = -0.7$; $J_{df} = 10.3$; $J_{ef} = 2.0$.

2 - From Methyl Vinyl Ketone. Synthesis of 2b

2b was synthesized according to a similar procedure without addition of pentane during the reaction. However in order to achieve the decomposition of the onium intermediate, the reaction mixture was warmed at 100°C for 12 h (instead of 40°C for 4 h). 2b also was separated by distillation (5.3 g, 80 %, b.p./25 mmHg : 38°C).

2b : ir (cm^{-1}) $\nu_{\text{C}=\text{C}}$ 1630 (enoxysilane), 1580 ; ^1H nmr (100 MHz, δ ppm, JHz) : 5.87, m, H_d ; 5.17, m, H_e ; 4.79, m, H_f ; 4.03, m, H_a ; 4.02, m, H_b ; 0, s, 9H_c ; $J_{ab} = 0.6$; $J_{ad} = 0.01$; $J_{bd} = 0.01$; $J_{ae} = 0.6$; $J_{be} = 0.6$; $J_{de} = 17.0$; $J_{af} = 1.4$; $J_{bf} = 0.7$; $J_{df} = 10.4$; $J_{ce} = 1.9$.



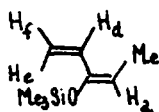
2b

3 - From Ethyl Vinyl Ketone. Synthesis of 2c

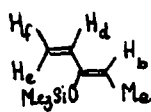
The onium salt 3c was synthesized, at 0°C, from NaI (4.65 g, 31 mmol) in acetonitrile (31 ml) added dropwise, with stirring to a solution of ethyl vinyl ketone (2.1 g, 25 mmol) triethylamine (3.13 g, 31 mmol) and trimethylchlorosilane (3.36 g, 31 mmol) successively introduced in the reaction flask. As soon as the addition was achieved, the 1,4-onium salt was quantitatively formed (Z/E c.a. 40/60). After warming at 80°C for 5 h a study by ¹H nmr (60 MHz) showed the formation of dienoxysilanes (Z and E) while the E adduct disappeared and the Z adduct remained present (molar ratio : Z and E dienoxysilanes/Z adduct = 50/50).

This was due to the competition between the decomposition of both adducts into the corresponding dienoxysilanes and the isomerisation of the E adduct into the corresponding Z adduct. After 10 h at 80°C the decomposition of the onium salt was complete. A final treatment (cf the synthesis of 2a) led to 2c separated by distillation (1.6 g, 40 %, low yield, due to the facile polymerization of the product, b.p./25 mmHg : 52°C, E/Z = 65/35).

2c (E + Z) : ir (cm⁻¹) $\nu_{(C=C)}$: 1645 (enoxysilane), 1600, 1590 ; ¹H nmr E isomer : 6.1, m, H_d (part X of an ABX system 4 lines J_{de} + J_{dh} = 27 ; 5.1, m, H_e ; 4.8, m, H_f ; 4.7, q, H_a ; 1.60, d, 3H_b ; 0.18, s, 9H_c ; J_{ab} = 7 ; J_{de} = 17 ; J_{df} = 10. Z isomer : 6.46, m, H_d (part X of an ABX system 4 lines, J_{de} + J_{dh} = 27 ; 5.3, m, H_e ; 4.8, m, H_f ; 4.7, q, H_b ; 1.6, d, 3H_a ; 0.16, s, 9H_c .



2c E

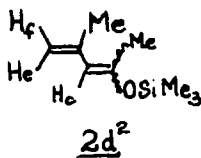
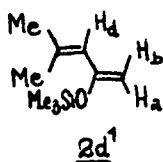


2c Z

4 - From Mesityl Oxide - Synthesis of 2d¹ and 2d²

2d¹ and 2d² were directly obtained at 0°C, from NaI (3.75 g, 25 mmol) in acetonitrile (25 ml) added dropwise to a solution of dry pentane (15 ml), mesityl oxide (1.96 g, 20 mmol), triethylamine (2.52 g, 25 mmol) and trimethylchlorosilane (2.71 g, 25 mmol). The mixture remained white during the reaction and, as soon as the addition was achieved, the complete disappearance of mesityl oxide was observed by nmr spectroscopy in both pentane and acetonitrile phases, as well as the quantitative formation of 4-methyl 2-trimethylsiloxy 1,3-pentadiene 2d¹ and 4-methyl 2-trimethylsiloxy 2,4-pentadiene 2d² (2d¹/2d² = 91/9). The mixture 2d¹ + 2d² was separated by distillation (2.5 g, 74 %, b.p./30 mmHg = 65°C). In the absence of pentane the ratio 2d¹/2d² was changed 80/20. This was probably due to the possible isomerisation of 2d¹ in acetonitrile.

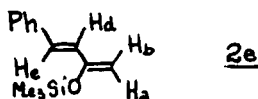
2d¹ + 2d² : ir (cm⁻¹) : $\nu_{(C=C)}$ 1655 (enoxysilane), 1620, 1585, 2d¹ ¹H nmr : 5.51, m, H_d ; 4.16, broad s, H_a ; 4.08 broad s, H_b ; 1.90 and 1.76, 2m, 2CH₃ coupling constant with H_d J = 0.4 ; 0.20, s, Me₃Si. 2d² ¹H nmr : 4.92, m, H_c ; 4.80, m, H_e ; 4.62, m, H_f ; 1.90, m and 1.80 m, 2 CH₃ ; 0.20, s, Me₃Si.



5 - From Benzalacetone - Synthesis of 2e

Using the same proportions of reagents as for 2b an exothermic reaction occurred when sodium iodide in acetonitrile was added. As soon as the addition was achieved, the quantitative conversion of benzalacetone into the corresponding dienoxysilane 2e was observed by ^1H nmr spectroscopy. Separation of 2e was effected as described for 2a and 2b (4.3 g, 40 % (low yield due to a polymerization reaction), b.p./25 mmHg : 140°C). By distillation between $140\text{--}200^\circ\text{C}/25$ mmHg an oligomeric fraction was isolated (5g).

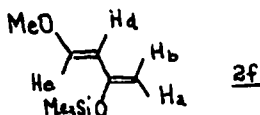
2e : ir (cm^{-1}) : $\nu(\text{C}=\text{C})$ 1640 (enoxysilane) 1610 ; ^1H nmr 7.07–7.57, m, 5 H_{Ar} ; 6.97, m and 6.25, m, H_{d} and H_{e} (non assigned), $J_{\text{de}} = 16$ Hz (E isomer) ; 4.47, broad, s, H_{a} and H_{b} ; 0.27, s, Me_3Si .



6 - From Trans 4-methoxy 2-butenone. Synthesis of 2f

Using the same proportions of reagents as for mesityl oxide the reaction was carried out at -15°C . During the addition of sodium iodide the pentane phase became yellow while the acetonitrile one became orange. As soon as the addition was achieved the quantitative conversion of the starting ketone into 2f was observed by ^1H nmr spectroscopy. Separation of 2f was effected as described for 2a and 2b (2.1 g, 60 %, b.p./5 mmHg : 74°C).

2f : ir (cm^{-1}) : $\nu(\text{C}=\text{C})$ 1690, 1660 ; ^1H nmr ; 6.83, m, H_{e} ; 5.26, m, H_{d} , $J_{\text{de}} = 12$; 4.03 broad s, H_{a} and H_{b} ; 3.56, s, OMe ; 0.22, s, Me_3Si .



7 - Synthesis of 4-Iodo 2-butanone

This compound was synthesized from methyl vinyl ketone and trimethyliodosilane⁹ or trimethylchlorosilane and sodium iodide in acetonitrile according to the conditions given for the synthesis of 2b, but without triethylamine. Subsequent treatment of 4-iodo 2-butanone by 1 molar equiv. of triethylamine as the solvent, at room temperature, regenerated the star-

ting methyl vinyl ketone accompanied by triethylamine hydroiodide.

SYNTHESIS OF ONIUM SALTS

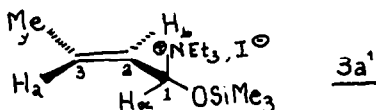
Onium salts from 1a-c, e, g, h were quantitatively formed under the conditions of temperature given in Table 2 whereas no adducts were isolated from 1d and 1f under our reaction conditions.

In order to optimize the formation of the adducts, the experimental procedure was sometimes changed. For instance in the case of cinnamaldehyde, this compound was added dropwise to the mixture of acetonitrile, sodium iodide, trimethylchlorosilane and pyridine, while in the case of acrolein or crotonaldehyde, trimethylchlorosilane was added at -20°C or room temperature respectively (procedures X and Y). In the case of acrolein or 2-cyclohexenone, the reaction can be carried out in mono or biphasic (pentane) medium. In the case of 1,4-adducts the ratio Z/E changed with the temperature of the reaction. Thus, from ethyl vinyl ketone the percentage Z/E was found 40/60 when the reaction was performed at 0°C or 60/40 at room temperature respectively.

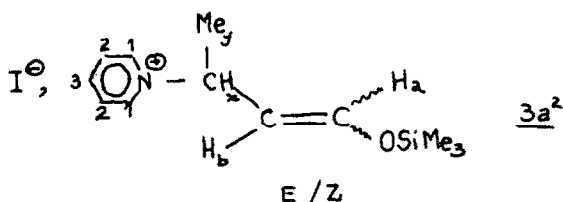
Moreover this ratio changed when the reaction mixture was left at room temperature. Thus, from acrolein, (using Et_3N), the reaction mixture 3g obtained by procedure X was constituted by both isomer Z and E, Z/E = 17/83 just after reaction 50/50 after 12 h or 75/25 after 48 h at room temperature. Similarly, procedure Y from crotonaldehyde (using pyridine) afforded 3a² Z/E = 15/85 just after reaction and 50/50 after 48 h.

¹H nmr data permitted to assign unambiguous structures to the adducts (solvent MeCN)
 $(\text{CH}_3)_2\text{CH}_2\text{N}^{\oplus} : J_{12} = 7-8 \text{ Hz}$.

3a¹ : 6.42, m, H_a ; 5.73, m H_b ($J_{ab} = 14.3$), ($J_{by} = 1.3$) ; 5.32, broad d, H_x ($J_{bx} = 8$) ; 3.33, q, 3CH₂(N) ; 1.37, t, 3CH₃(CH₂N), 1.90, broad d, MeC=Cⁱ ($J_{ay} = 6.6$) ; 0.20, s, Me₃Si. The very small value of J_{ax} (≈ 0) supports a preferential conformation for 3a¹ in which the dihedral angle C₃H_a, C₁H_x, is near 0° , by comparison with data from the literature in other series²⁰.

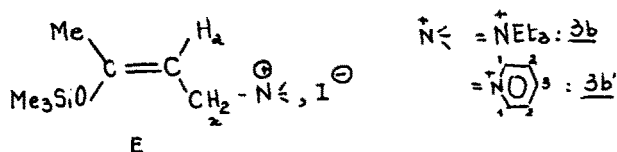


3a² : E isomer ; 9.33, broad d, 2H₁ ; 8.86, broad t, H₃ ; 8.10 broad t, 2H₂ ; 7.1, d, H_a ($J_{ab} = 12$) ; 5.9, m, H_x ; 5.4, 4 lines, H_b, $J_{bx} = 10$; 1.80, broad d, MeC=Cⁱ ($J_{xy} = 6$) ; 0.20, s, Me₃Si. Z isomer ; 9.33, broad d, 2H₁ ; 8.86, broad t, H₃ ; 8.10, broad t, 2H₂ ; 6.53, 4 lines, H_a ($J_{ab} = 6$, $J_{ax} = 2$) ; 5.90, m, H_x ; 5.00, 4 lines, H_b ($J_{bx} = 8$) ; 1.80, broad d, MeC=Cⁱ ($J_{xy} = 6$) ; 0.20, s, Me₃Si.



3b : 4.66, t, Ha (Jax = 8) ; 3.70, d, 2 Hx ; 3.23, q, 3CH₂(N) ; 2.00, s, Me₃C- ; 1.37, t, 3CH₃(CH₂N <) ; 0.27, s, Me₃Si.

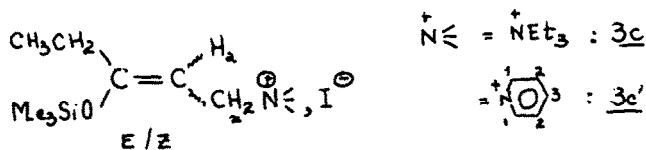
3b' : 9.16, broad d, 2H₁ ; 8.63, broad t, H₃ ; 8.13, broad t, 2H₂ ; 5.60-4.83, m, Ha + 2Hx ; 1.90, s, Me-C=C- ; 0.17, s, Me₃Si.



3c : 4.65 (Z), 4.59 (E), t, Ha ; 3.73 (Z), 3.86 (E), d, 2 Hx (Jax = 8) ; 3.30, q, 3CH₂ (N) ; 2.20, q, CH₂-C=C- ; 1.30, t, 3CH₃(CH₂N <) ; 1.00, s, CH₃(CH₂-C=C-) ; 0.24, s, Me₃Si.

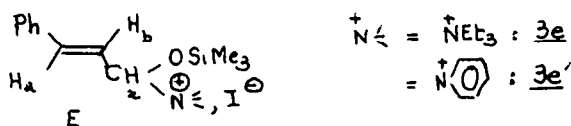
¹³C nmr (CDCl₃, Me₄Si as the internal standard) : 163.8 (E) 163.2 (Z), =C-OSi< ; 90.5 (E), 90.0 (Z), C-Ha ; 55.6 (E), 51.5 (Z), CH₂(x), 23.9 (E), 28.1 (Z), CH₂(-C=C-) ; 10.3 (E), 7.3 (Z) CH₃ (CH₂-C=C-) ; -0.9 (E), -0.3 (Z), SiMe₃ ; 51.6 (E, Z), CH₂(Et₃N⁺), 7.8 (E,Z), CH₃ (Et₃N⁺).

3c' : 9.23, broad d, 2H₁ ; 8.73, broad t, H₃ ; 8.13, broad d, 2H₂ ; 5.7-4.9, m, Ha + 2Hx ; 2.33, q, CH₂-C=C- (J = 8) ; 1.00, t, CH₃-(CH₂C=C-) ; 0.20, s, Me₃Si. Isomers Z and E were differentiated in ¹³C nmr : (E was largely the major isomer) 163.1 (E), 161.8 (Z), C-OSi ; 95.8 (E), 96.2 (Z), C-Ha ; 58.5 (E), 56.2 (Z), CH_x 24.2 (E), 27.7 (Z), CH₂-(C=C-) ; 10.6 (E), 10.0 (Z) CH₃-(CH₂-C=C-) ; -0.7 (E), -0.15 (Z), SiMe₃ ; pyridinium ion : 144 (Z,E) CH₁ ; 142 (Z,E), CH₂ ; 127 (Z,E) CH₃.



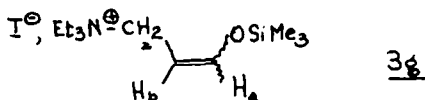
3e : 8.72, m, Har + Ha ; 6.10, 4 lines, Hb (Jab = 16 : E isomer) ; 5.70, 2 lines, H_x (Jbx=8) ; 3.43, q, 3CH₂ (N) ; 1.34, t, 3 CH₃ (CH₂N) ; 0.24, s, Me₃Si.

3e' : 9.50, broad d, 2H₁ ; 8.70, broad t, H₃ ; 8.20, broad t, 2H₂ ; 7.70-7.10, m, Har + Ha + Hx ; 6.56, 4 lines Hb (Jab = 16 E isomer Jbx = 5.8) ; 0.30, s, Me₃Si.

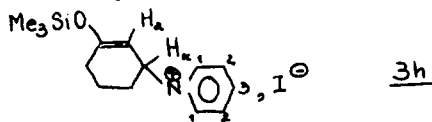


3g : Z isomer : 6.87, broad d, Ha (Jab = 6) ; 4.6, m, Hb ; 3.8, d, 2 Hx (Jbx = 8) ; 3.20, q, 3CH₂ (N) ; 1.30, t, 3CH₃(CH₂N) ; 0.20, s, Me₃Si.

E isomer : 7.00, broad d, Ha (Jab = 12) ; 5.00, m Hb ; 3.80, d, 2Hx (Jbx = 8) ; 3.20, q, 3CH₂(N) ; 1.30, t, 3CH₃ (CH₂N) ; 0.20, s, Me₃Si .



3h : 9.1⁰, broad d, 2 H₁ ; 8.70, m, H₃ ; 8.16, m, 2H₂ ; 5.80, m, Hx ; 5.00, d, Ha (Jax = 4) ; 2.5-1.5, m, 3CH₂ ; 0.27, s, SiMe₃.



BIBLIOGRAPHY AND NOTES

- 1 - P. Cazeau, F. Duboudin, F. Moulines, O. Babot and J. Dunoguès, *Tetrahedron*, submitted for publication.
- 2 - P. Brownbridge, *Synthesis*, 85(1983).
- 3 - G. Stork and P.F. Hudrlik, *J. Am. Chem. Soc.*, **90**, 4462 and 4464 (1968).
- 4 - a) I. Fleming and I. Paterson, *Synthesis*, 736(1979) ; b) M.J. Carter, I. Fleming and A. Percival, *J. Chem. Soc. Perkin I*, 2415(1981).
- 5 - A. Bazouin, J. Dunoguès and M. Lefort (Rhône-Poulenc Co.) French Pat. 1,436,568 (1966) ; French Addn, 88, 358 (1967).
- 6 - a) C. Girard, P. Amice, J.-P. Barnier and J.-M. Conia, *Tetrahedron Lett.*, 3329(1974) ; b) M.E. Jung and C.A. McCombs, *Tetrahedron Lett.*, 2935(1976) ; c) M.E. Jung and C.A. McCombs, *Org. Synth.*, **58**, 163(1976).
- 7 - Y. Yaniguchi, J. Inanaga and M. Yamaguchi, *Bull. Chem. Soc. Japan*, **54**, 3229(1981).
- 8 - H. Emde, A. Goetz, K. Hofmann and G. Simchen, *Liebigs Ann. Chem.*, 1643(1981).
- 9 - R.D. Miller and D.R. McKean, *Synthesis*, 730(1979).
- 10 - P. Cazeau, F. Moulines, O. Laporte and F. Duboudin, *J. Organometal. Chem.*, **201**, C9 (1980).
- 11 - I. Fleming and J. Iqbal, *Tetrahedron Lett.*, 2913(1983).
- 12 - R.D. Miller and D.R. McKean, *Tetrahedron Lett.*, 2305 (1979).
- 13 - I. Crossland and S.I. Hommeltoft, *Acta, Chim. Scand.*, **B37**, 21(1983).
- 14 - R. Bourhis, Thèse d'Etat, Bordeaux (1973).
- 15 - J.F. Arens, *Bull. Soc. Chim. France*, 3043(1968).
- 16 - a) W.F. Forbes and R. Shilton, *J. Am. Chem. Soc.*, **81**, 786(1959) ; b) A.J. Bowles, W.D. George and W.F. Maddams, *J. Chem. Soc. B*, 810(1969).
- 17 - W.N. Saunders Jr. and A.F. Cockerill "Mechanisms of Elimination Reactions", John Wiley and Sons, New-York (1973).
- 18 - M. Kumada and M. Yamaguchi, *Bull. Soc. Chim. Japan*, **57**, 175(1954).
- 19 - a) L.M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry (2nd Ed.)", Pergamon Press, N.-Y., 316(1969) ; b) S. Sternhell, *Quat. Rev.*, 264(1969).