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THE OXYMERCURATION—DEMERCURATION OF ALKENYLSILANES IN AQUEOUS TETRAHYDROFURAN *

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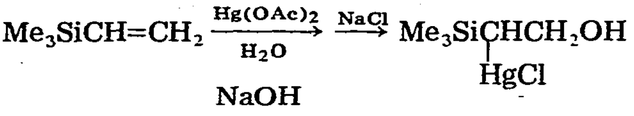
Summary

The oxymercuration—demercuration (OM—DM) of representative trimethylsilylalkenes in aqueous tetrahydrofuran was investigated. Vinyltrimethylsilane gives only the *anti*-Markovnikov alcohol, 2-trimethylsilylethanol in 90% yield. Allyltrimethylsilane gives mainly allylmercuric acetate which reacts further to give a 1,3-dimercurated-2-propanol. This species reacts slowly with allyltrimethylsilane to give allylmercuric acetate. 3-Buten-1-yltrimethylsilane gives only the Markovnikov product, 1-trimethylsilyl-3-butanol in 99% yield. *cis*-1-Propenyltrimethylsilane gives 1-trimethylsilyl-2-propanol in 44% yield along with cleavage products. The formation of one of these products, 2-propanol, was found by PMR to arise from the OM—DM of *cis*-1-propenylmercuric acetate which gives the 1,1-dimercurated-2-propanol. While the oxymercuration of *cis*-1-propenylmercuric acetate is regiospecific giving exclusive placement of the mercury α to the silicon, it is completely nonstereospecific giving equal amounts of diastereomeric adducts. The OM—DM of 2-propenyl trimethylsilane (XIX) leads only to desilylation and oxidation products. Possible reasons for the diverse behavior of these silylated alkenes are discussed.

Introduction

The first reported study on the oxymercuration of a silylated alkene was by Seyferth and Kahlen [1]. Vinyltrimethylsilane was oxymercurated with mercuric acetate in water using the Hofmann—Sand procedure (eq. 1).



$$Me_3SiCH{=}CH_2 \xrightarrow[H_2O \quad NaOH]{Hg(OAc)_2} \xrightarrow{NaCl} Me_3Si\underset{HgCl}{\underset{|}{C}}HCH_2OH \qquad (1)$$

(88% crude isolated)

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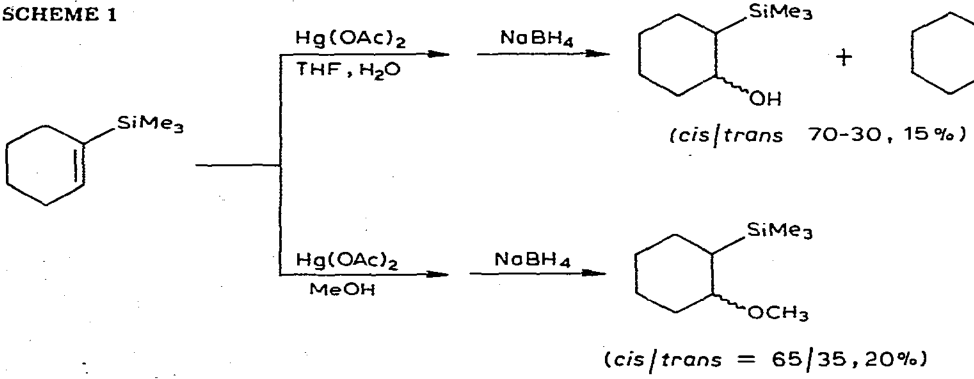
* Dedicated to Professor Herbert C. Brown on the occasion of his 66th birthday for his contributions to chemistry.

The regiochemistry was determined by sodium—amalgam reduction of this adduct to 2-trimethylsilylethanol in 26% yield. Roberts has examined the reaction of mercuric salts with allyltrimethylsilane in acetonitrile and observed only cleavage products [2]. During the course of this work, Voronkov and coworkers [3] reported the oxymercuration of several vinylsilanes, 1-propenyl, β-styryl and allyltrimethylsilane in methanol and acetic acid employing PMR analysis of the adducts.

The oxymercuration—demercuration (OM—DM) procedure developed by Brown and Geoghegan is a mild, extremely effective method for effecting the Markovnikov hydration of olefins [4]. Musker and Larson have applied this procedure for the conversion of 1-trimethylsilylcyclohexene to a mixture of *cis*- and *trans*-2-trimethylsilylcyclohexanols and the corresponding ethers [5] (Scheme 1).

SCHEME 1



Because of the widespread interest in organosilicon chemistry and the synthetic utility of the OM—DM procedure, we undertook to examine several representative trimethylsilylalkenes using this procedure.

Results and discussion

Vinyl-, allyl-, 3-buten-1-yl-, *cis*-1-propenyl- and 2-propenyl-trimethylsilane were oxymercurated in aqueous tetrahydrofuran (50/50) with mercuric acetate. The resulting mercurials were reduced in situ with aqueous alkaline sodium borohydride. After workup, the reaction mixtures were analyzed by GLC [4]. In several cases the oxymercuration reaction was carried out in deuterium oxide-perdeuteriotetrahydrofuran and analyzed by NMR.

Vinyltrimethylsilane (I) underwent oxymercuration rapidly (T_1 36 sec) *.

$$\underset{(\mathrm{I})}{\mathrm{CH_2{=}CHSiMe_3}} \xrightarrow[2.\,\mathrm{DM}]{1.\,\mathrm{OM}} \underset{(\mathrm{II},\ 90\%)}{\mathrm{HOCH_2CH_2SiMe_3}} + \underset{(\mathrm{III},\ 1\%)}{\mathrm{AcOCH_2CH_2SiMe_3}} + \underset{(6\%)}{\mathrm{Me_3SiOH}} + \underset{(3\%)}{\mathrm{CH_3CH_2OH}} \qquad (2)$$

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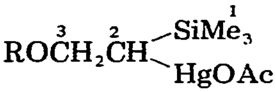
* T_1 refers to the time required for the yellow color to disappear (Experimental). It corresponds to ca. 40—60% reaction [4].

After 5 minutes, reduction resulted in a 90% yield of 2-trimethylsilylethanol (II), 1% of the corresponding acetate (III), 6% trimethylsilanol and 3% ethanol. Unreacted I (7%) was observed although all of the mercuric salt was consumed (eq. 2).

No 1-trimethylsilylethanol was detected in the reaction mixture. Furthermore, when the OM of I was carried out in deuterated solvents, PMR analysis revealed a single adduct (IV).

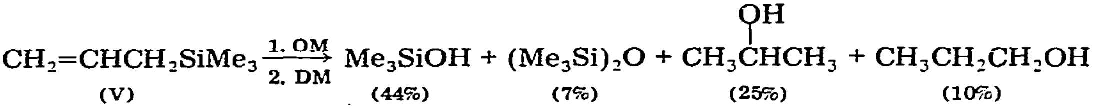


$$RO\overset{3}{C}H_2\overset{2}{C}H\begin{matrix}\diagup \overset{1}{Si}Me_3\\ \diagdown HgOAc\end{matrix}$$

(IV)

Using $D_2O/THF\text{-}d_8$, IV (R = D) showed singlet absorbances at δ 0.13 and 2.00 ppm as well as multiplets centered at 2.1 and 3.9 ppm (1/2 ratio) which were in good agreement with reported values for such systems [3]. In perdeuterated acetic acid, the OM of I gave the corresponding acetate (IV; R = $COCD_3(H_3)$). In this derivative the downfield multiplet was centered at 4.35 ppm. All other chemical shifts were unchanged from the alcohol (IV; R = D). Removal of solvent gave an oil in which only a small amount of residual protic acetate remains. The ^{13}C NMR of this deuterated derivative exhibits signals at 0.04, 34.69 and 65.38 ppm (see 1, 2, and 3 in IV) with $^{199}Hg—^{13}C$ coupling constants of 61, 1331 and 138 Hz, respectively *.

In contrast to the smooth *anti*-Markovnikov hydration of I to give II, the OM—DM of allyltrimethylsilane (V) gave no silylated alcohols. This compound underwent reaction with mercuric acetate extremely rapidly (T_1 too fast to measure). After 5 minutes, reduction yielded 44% trimethylsilanol, 7% hexamethyldisiloxane, 25% 2-propanol, 10% 1-propanol. Unreacted V (38%) was detected although all of the mercuric salt was consumed (eq. 3).



$$\underset{(V)}{CH_2{=}CHCH_2SiMe_3} \xrightarrow[2.\ DM]{1.\ OM} \underset{(44\%)}{Me_3SiOH} + \underset{(7\%)}{(Me_3Si)_2O} + \underset{(25\%)}{CH_3\overset{OH}{\overset{|}{C}}HCH_3} + \underset{(10\%)}{CH_3CH_2CH_2OH} \qquad (3)$$

To corroborate the analysis, the reaction mixture was treated with *p*-toluenesulfonic acid. This process resulted in the clean disappearance of trimethylsilanol with a corresponding increase in the yield of hexamethyldisiloxane. No change in the yields of 1- and 2-propanols were observed. However, the appearance of propene (6%) suggested some decomposition of V had occurred during this operation [6].

Surprisingly, elemental mercury was also observed in this acid-treated mixture. This could indicate the presence of bis-mercurials. These compounds are well known to be inert to sodium borohydride. Mercury formation is often observed in the acid cleavage of bis-mercurials [7].

These interesting observations led us to investigate this reaction under a variety of conditions (Table 1). With one equivalent of mercuric acetate, the

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* Two different deuterated acetoxy groups in IV (R = $COCD_3$) were indicated by carbonyl absorbances at 176.8 (HgOAc) and 171.1 (R'OAc) ppm. Some splitting of these signals by the adjacent CD_3 group (δ ~22 ppm) was observed.

TABLE 1

OM—DM OF ALLYLTRIMETHYLSILANE (V) IN AQUEOUS TETRAHYDROFURAN

X[a]	Time (min)		V	Yield of products (%)				
				$(Me_3Si)_2O$	Me_3SiOH	$CH_3\overset{OH}{C}HCH_3$	$CH_3CH_2CH_2OH$	$CH_2{=}CHCH_3$
1	1.5		37	6	37	34	5	5
		(*p*-TsOH)[b]	0	48	0	34	5	37
1	5		38	7	44	25	10	0
		(*p*-TsOH)	33	29	0	25	10	6
1	20°C		32	2	62	12	6	27[d]
1	720[c]		9	20	46	0	4	18[d]
2	1.5		0	10	65	84	3	0
		(*p*-TsOH)	0	51	0	82	2	22
2	5		0	11	57	86	5	0
		(*p*-TsOH)	0	47	0	86	5	10

[a] Equivalents of $Hg(OAc)_2$ per equivalent of V. [b] Results after treatment with *p*-toluenesulfonic acid. [c] Not treated with *p*-TsOH. [d] Vigorous gas evolution upon workup.

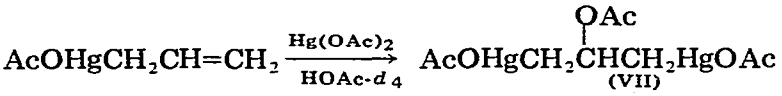
product yields varied markedly with time. While over 60% of V is consumed in 90 sec, it requires 12 h to attain 90% consumption. The amount of 2-propanol diminishes with longer reaction time. Correspondingly, propene increases. However, the yield of 1-propanol shows no significant dependence on reaction time. With two equivalents of mercuric acetate, all of V is consumed rapidly and the yields of all products remain constant with time.

These results suggested that allylmercuric acetate (VI) is formed in these oxymercurations (eq. 4).

$$\underset{\text{(V)}}{CH_2{=}CHCH_2SiMe_3} \xrightarrow[-AcOSiMe_3]{Hg(OAc)_2} \underset{\text{(VI)}}{AcOHgCH_2CH{=}CH_2} \qquad (4)$$

Such reactivity of V with mercuric salts is well precedented in the literature [2,3]. Accordingly, we undertook to prepare VI and investigate its chemistry. Voronkov and coworkers have recently reported that the OM of V with mercuric acetate in acetic acid led to the quantitative formation of VI. This appeared to be an attractive route to VI considering the ready availability of V (see Experimental).

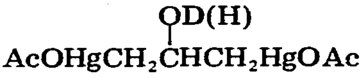
However, we found that the conversion of V to VI is not clean. After 1 h, we isolated VI in only 40% yield. In addition, unreacted V, as well as another mercury compound, was observed in the reaction mixture. This led us to suspect that VI may be undergoing further reaction with mercuric acetate. Consequently, VI was treated with mercuric acetate in perdeuterated acetic acid solvent. Complete consumption of VI was observed with formation of a single adduct whose PMR spectrum is consistent with structure VII (eq. 5). Compound VII exhibited a quintet at 5.58 ppm and a doublet at 2.28 ppm in a 1/4 ratio, with the coupling constants ^3J(H—H) 5.6 Hz, $^2J(^{199}Hg—H)$ 230 Hz and $^3J(^{199}Hg—H)$ 130 Hz.



$$AcOHgCH_2CH{=}CH_2 \xrightarrow[HOAc\text{-}d_4]{Hg(OAc)_2} \underset{\text{(VII)}}{AcOHgCH_2\overset{OAc}{\overset{|}{C}}HCH_2HgOAc} \qquad (5)$$

The oxymercuration of V in perdeuterated acetic acid was examined by PMR analysis. After 15 min (33°C), 36% of V remained unreacted, VI was formed in 21% yield and also VII was observed in 36% yield. After 1 h the yields of these compounds had changed to 23, 45 and 27% respectively. After 9 h, values of 10, 85 and 5% respectively were observed. These results are remarkably similar to those obtained from the OM—DM of V in aqueous tetrahydrofuran.

Consequently, we examined the OM of V and VI in D_2O/THF-d_8 using PMR. VI gives one product, VIII, which exhibits a quintet at 4.60 ppm and a doublet at 2.28 ppm in a ratio of 1/4, with coupling constants ^3J(H=H) 5.2 Hz, $^2J(^{199}Hg—H)$ 232 Hz and $^3J(^{199}Hg—H)$ 145 Hz.

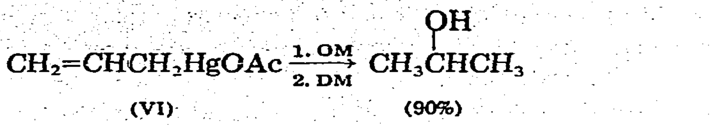


$$AcOHgCH_2\overset{OD(H)}{\overset{|}{C}}HCH_2HgOAc$$

(VIII)

The OM of V under these conditions gave a mixture of VI (15%) and VIII (40%) as well as unreacted V (34%) after 10 min (33°C). After 12 h, VI and VIII diminished to less than 5% and the yield of VI increased to ca. 80%.

To corroborate the results of the OM of VI in $D_2O/THF\text{-}d_8$, we examined the OM—DM of VI in aqueous THF. The only observed product was 2-propanol in 90% yield (eq. 6).

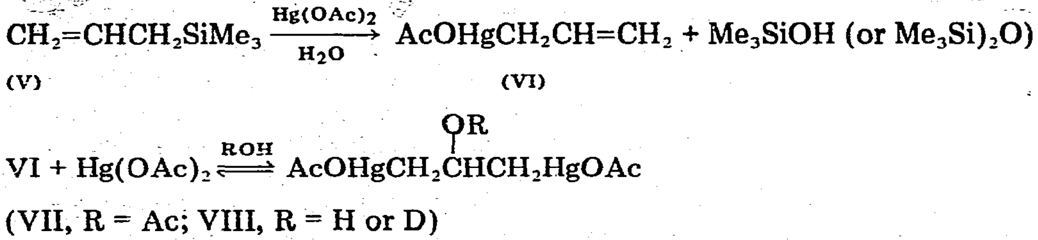


$$\underset{\text{(VI)}}{CH_2{=}CHCH_2HgOAc} \xrightarrow[\text{2. DM}]{\text{1. OM}} \underset{(90\%)}{CH_3\overset{OH}{C}HCH_3} \qquad (6)$$

Consequently, VI and VIII appear to be likely precursors to propene and 2-propanol, respectively, in the OM—DM of V.

The results can be explained by Scheme 2. While this scheme readily explains the formation of propene, 2-propanol, trimethylsilanol and hexamethyldisiloxane, it does not explain the formation of 1-propanol. A possible precursor to this alcohol, propion aldehyde, was not detected in any of the PMR experiments. In addition, the absence of elemental mercury and mercurous acetate in the reaction mixtures indicited that oxidation of V by mercuric acetate was not occurring.

SCHEME 2



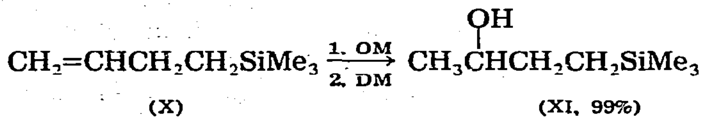
$$\underset{\text{(V)}}{CH_2{=}CHCH_2SiMe_3} \xrightarrow[H_2O]{Hg(OAc)_2} \underset{\text{(VI)}}{AcOHgCH_2CH{=}CH_2} + Me_3SiOH \text{ (or } (Me_3Si)_2O)$$

$$VI + Hg(OAc)_2 \overset{ROH}{\rightleftharpoons} AcOHgCH_2\overset{OR}{C}HCH_2HgOAc$$

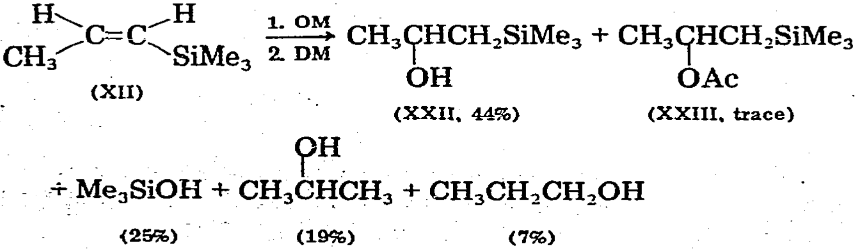
(VII, R = Ac; VIII, R = H or D)

Regrettably, the exact precursor(s) of 1-propanol was present in amounts too small to be detected by PMR. Consequently, its formation in the OM—DM of V as well as other propenyl derivatives (vide infra) is not understood at present.

By contrast to vinyl- and allyl-trimethylsilane, the OM—DM of 3-buten-1-yltrimethylsilane (X) proceeds cleanly (T_1 24 sec) in 5 min to give only the Markovnikov alcohol (XI) in 99% yield (eq. 7). This behavior is the same as that exhibited by a representative mono-substituted olefin such as 1-hexene [4]. The complete spectrum of reactivities shown by the vinyl-, allyl- and butenyl-silicon derivatives led us to examine the behavior of two additional propenylsilanes in the OM—DM reaction.



$$\underset{\text{(X)}}{CH_2{=}CHCH_2CH_2SiMe_3} \xrightarrow[\text{2. DM}]{\text{1. OM}} \underset{\text{(XI, 99\%)}}{CH_3\overset{OH}{C}HCH_2CH_2SiMe_3} \qquad (7)$$

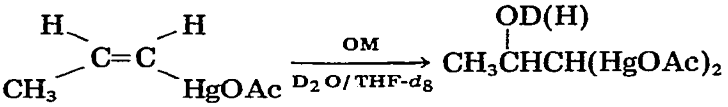


$$\underset{\text{(XII)}}{\overset{H}{\underset{CH_3}{\;}}\!\!>C{=}C<\!\!\overset{H}{\underset{SiMe_3}{\;}}} \xrightarrow[\text{2. DM}]{\text{1. OM}} \underset{\text{(XXII, 44\%)}}{CH_3\underset{OH}{C}HCH_2SiMe_3} + \underset{\text{(XXIII, trace)}}{CH_3\underset{OAc}{C}HCH_2SiMe_3}$$

$$+ \underset{(25\%)}{Me_3SiOH} + \underset{(19\%)}{CH_3\overset{OH}{C}HCH_3} + \underset{(7\%)}{CH_3CH_2CH_2OH} \qquad (8)$$

cis-1-Propenyltrimethylsilane (XII) reacted very rapidly (T_1 18 sec). After 5 minutes, reduction yielded 44% β-alcohol (XXII), trace amounts of the β-acetate (XXIII), 25% trimethylsilanol, 19% 2-propanol, and 7% 1-propanol. Unreacted XII (28%) was detected while all of the mercuric salt was consumed (eq. 8). Treatment of this reaction mixture with *p*-toluenesulfonic acid destroys trimethylsilanol and XXII * completely, forming hexamethyldisiloxane and propene as products. Both 1- and 2-propanol were found to be inert under these conditions. These results are intermediate to those of vinyl- and allyl-trimethylsilane as major amounts of both silylated and desilylated products are observed. As was the case in V, we felt that 1- and 2-propanols might arise from intermediate mercury compounds resulting from the desilylation of XII. Accordingly, we examined this possibility by PMR in $D_2O/THF\text{-}d_8$.

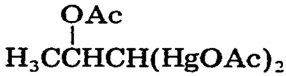
It appeared that a likely intermediate was *cis*-1-propenylmercuric acetate (XIII). The OM of XIII in $D_2O/THF\text{-}d_8$ resulted in only one adduct (XIV, eq. 9)



(9)

(XIII) (XIV)

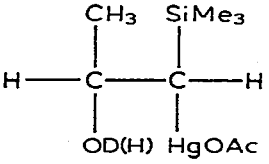
by PMR. This compound exhibited resonances at 4.52 ppm as a quintet, 3.18 ppm as a doublet and 1.42 ppm as a doublet in the ratio 1/1/3. The coupling constants were $^3J(H{-}H)$ 5.8 Hz, $^2J(^{199}Hg{-}H)$ 218 and 223 Hz. When the OM of XIII was examined by PMR in perdeuterated acetic acid, a single adduct XV was formed. This adduct exhibited a pattern similar to XIV, showing absorbances at 5.43, 3.12 and 1.42 ppm, respectively ($^3J(H{-}H)$ 5.6 Hz, $^2J(^{199}Hg{-}H)$ 200 and 205 Hz). The OM—DM of XIII led after 5 min of reaction to 2-propanol in ca. 30% yield with propene (6%) being the only other product detected by GLC.



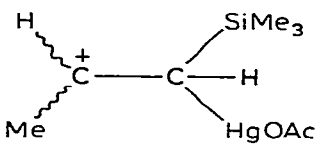
$$H_3C\overset{\overset{OAc}{|}}{C}HCH(HgOAc)_2$$

(XV)

We examined the OM of XII in $D_2O/THF\text{-}d_8$ by PMR. The spectrum was quite complex revealing unreacted XII, trimethylsilanol, as well as XIV and a



(XVI)



(XVII)

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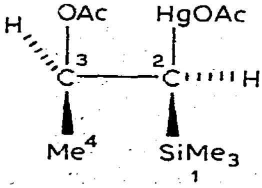
* Separation of XXII from the isomeric 1-trimethylsilyl-1-propanol by GLC is quite difficult [8]. This latter alcohol is inert to *p*-TsOH under these conditions. Consequently, the clean disappearance of the peak attributable to XXII on treatment of the reaction mixture with *p*-TsOH confirms the lack of this isomeric product in the OM—DM of XII.

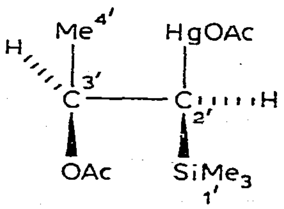
new adduct XVI in a ca. 1/2 ratio. This compound exhibited resonances at 4.25 (quintet; ^3J 5.8 Hz), 2.23 (doublet; ^3J 5.8 Hz), 1.37 (doublet; ^3J 5.8 Hz) ppm in a 1/1/3 ratio as well as two peaks of approximately equal intensities at 0.1 ppm. By analogy with IV, the geminal arrangement of the trimethylsilyl and acetoxymercuri groups in XVI was suggested.

Furthermore, the presence of two different trimethylsilyl groups attributable to XVI indicated a diastereomeric mixture. Since pure *cis*-olefin (XII) was used, equal amounts of diastereomeric adducts would suggest that all of the stereochemistry is lost in the intermediate cation XVII.

In perdeuterated acetic acid, the addition was cleaner and no significant amount of desilylation occurs. Once again, two diastereomeric adducts were formed in ca. 50/50 ratio. However, in this solvent we were able to obtain even more definitive evidence by PMR for the formation of two diastereomeric adducts (XVIII) in roughly equal amounts (84% total yield). The mixture was concentrated to an oil to remove acetate signals. In $CDCl_3$ these adducts exhibited resonances at 5.37 (quintet; ^3J(H—H) 6 Hz), 2.42 (d, ^3J(H—H) 6 Hz), 2.15 (d, ^3J(H—H) 6 Hz), 1.35 (d, ^3J(H—H) 6 Hz), 0.15 (s) and 0.12 (s) (^2J(^{199}Hg—H) 264 and 284 Hz) ppm.



(XVIII-E)



(XVIII-T)

These structures were corroborated further by ^{13}C NMR analysis. The four indicated carbons in these structures exhibited two sets of resonances; one at 0.53, 44.62, 72.08 and 26.63 ppm and the other at 0.80, 44.80, 72.44 and 25.31 ppm. Signals centered at 176.96 and 170.15 ppm as well as 22.1 ppm indicated the presence of deuterated acetoxy groups.

These data are clearly inconsistent with the formation of regioisomers of XVI and XVIII which have been reported in methanol solvent [3]. Furthermore, since all previously studied additions of mercuric salts to acyclic olefins are stereospecific, occurring in a *trans* fashion, or in one case a *cis* fashion [9], the behavior of XXI is clearly anomalous in this reaction.

2-Propenyltrimethylsilane (XIX) exhibited characteristics which were not observed in the oxymercuration of the other silylated alkenes. The yellow color did diminish during the course of the reaction but did not completely disappear. Also, elemental mercury and a white precipitate * was formed. After 5 min, reduction yielded 38% trimethylsilanol, 39% 2-propanol, 5% acetone and 9% 1-propanol. Unreacted III (ca. 45—50%) was observed but we could not accurately determine it since small amounts of hexamethyldisiloxane were present which could not be conveniently separated by GLC (eq. 10).

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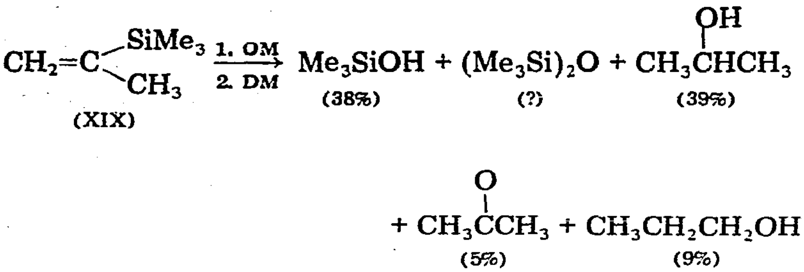
* This material has been previously identified as mercury(I) acetate [10].

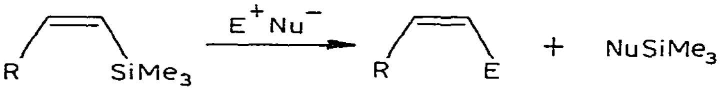


$$\underset{\text{(XIX)}}{CH_2{=}C\begin{smallmatrix}SiMe_3\\CH_3\end{smallmatrix}} \xrightarrow[\text{2. DM}]{\text{1. OM}} \underset{(38\%)}{Me_3SiOH} + \underset{(?)}{(Me_3Si)_2O} + \underset{(39\%)}{CH_3\overset{OH}{C}HCH_3} + \underset{(5\%)}{CH_3\overset{O}{C}CH_3} + \underset{(9\%)}{CH_3CH_2CH_2OH} \qquad (10)$$

XIX is a 1,1-disubstituted olefin. Some, but not all olefins of this type, when oxymercurated with mercuric acetate in aqueous tetrahydrofuran, give β-mercurated alcohols which undergo decomposition with time [4]. This might in part explain the absence of any silylated alcohols. It is not possible to say what effect a trimethylsilyl group would have on such a side reaction. Due to the extraordinary complexity of the reaction, we chose not to pursue it further.

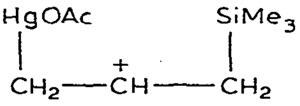
The behavior of these silylalkenes in the OM reaction illustrates a remarkable dependence on the exact relationship of the trimethylsilyl group to the double bond. Comparison of the amounts of desilylated products in the OM—DM of I, V, and XII reveal the order: allyl > 1-propenyl > vinyl.

Reaction of silylated alkenes with electrophilic reagents often leads directly to desilylation with retention of configuration (eq. 11) [11,12]. This would



(11)

appear to require that the carbon—silicon bond overlap with the vacant ρ-orbital in the β-silyl cationic intermediate [11]. However, mercury has been shown to impart even greater stabilization of β cations than silicon [13]. This is consistent with our results which show that VI undergoes oxymercuration faster than V. Therefore, the ideal arrangement for stabilization by both mercury and silicon would appear to be found in an intermediate cation such as XX derived from V.



$$\overset{HgOAc}{CH_2}-\overset{+}{C}H-\overset{SiMe_3}{CH_2}$$

(XX)

Considerable involvement of the Si—C bond with charge stabilization is possible in XX and complete desilylation occurs.

In the 1-propenyl case (XII), the isomeric ion has the mercury and silicon in a 1,1-relationship, therefore limiting participation by both groups simultaneously. Only partial desilylation occurs in this case. This arrangement is also found in the OM of the vinyl derivative, I. However, in this case, the primary cation is evidently too reactive to allow the silicon—carbon bond to completely align itself with the positive charge and only minor amounts of desilylation occur.

Experimental

Chlorotrimethylsilane, allyl bromide, 2-bromopropene, and 4-bromo-1-butene (Aldrich) were distilled from calcium hydride prior to use. Tetrahydrofuran (technical grade) was predried over calcium hydride and distilled from lithium aluminum hydride ($LiAlH_4$). This pretreatment was unnecessary in the OM—DM reaction. Cyclohexene was distilled from $LiAlH_4$. Excepting the high purity magnesium chips (Alfa), all other reagents were of reagent quality and were used without prior purification.

The NMR data were obtained on Varian T-60 and FT-80A spectrometers. Infrared spectra were recorded using a Perkin—Elmer 137 spectrophotometer. Melting points were determined using a Hoover—Thomas apparatus and are uncorrected.

Excepting the OM—DM procedures, all reactions were carried out under a nitrogen atmosphere using oven-dried equipment. A Nester—Faust spinning band (platinum) distillation apparatus was used routinely in the following preparations to obtain products of 99 ± 1% purity. 2-Trimethylsilylethanol, 1-trimethylsilyl-2-propanol and trimethylsilanol were prepared as described [24—26]. Vinyltrimethylsilane (I) and 2-propenyltrimethylsilane (XIX) were prepared from chlorotrimethylsilane and the appropriate vinylmagnesium bromide in THF [17,18,30].

Allyltrimethylsilane (V)

To a stirred mixture of magnesium chips (4.00 g, 165 mg-atoms), THF (120 ml) and chlorotrimethylsilane (16.3 g, 150 mmol) was added allyl bromide (20.0 g, 165 mmol) at a rate sufficient to maintain reflux temperature. After the addition was complete, the mixture was held at reflux for 15 min more and poured onto 100 g of ice. Saturated NH_4Cl solution (50 ml) was added and the layers were separated. The organic layer was washed with H_2O (3 × 100 ml). After drying over anhydrous $MgSO_4$, the mixture was distilled to give 13.8 g (81%) V, b.p. 84°C (740 Torr) (lit. [6] b.p. 84.9°C, 737 Torr).

3-Buten-1-yltrimethylsilane (X)

The procedure illustrated for V was used to prepare X, b.p. 106°C (740 Torr) (lit. [15] 110.5°C, 752 Torr), in 55% yield.

1-Propynyltrimethylsilane (XXI)

To a stirred mixture of n-BuLi in hexane (400 ml 2.50 *M*; 1.00 mol) and THF (200 ml) at —78°C, a solution of propyne (44 g, 1.1 mol) in THF (200 ml) was added over ca. 1 hour. The resulting slurry was treated with chlorotrimethylsilane (108.5 g, 1.00 mol) over ca. 1 h maintaining a reaction temperature of below 25°C using an ice bath to cool the mixture. The contents were poured onto ice (ca. 500 g) and the organic layer was washed with saturated NH_4Cl, dried over anhydrous $MgSO_4$ and distilled to give 70.2 g (63%) of product, b.p. 99°C (740 Torr) (lit. [16] 99—100°C 760 torr).

cis-1-Propenyltrimethylsilane (XII)

A dicyclohexylborane [21] slurry (0.160 mol) in THF (100 ml) was treated with 1-propynyltrimethylsilane (17.9 g, 0.160 mol) over 5 min. After 1 h at 0°C, dissolution had occurred and no active hydride remained. This mixture was concentrated at 25°C (0.20 Torr) to constant weight (46.5 g, 100%) to give an oil which ignites in air. The PMR (CCl_4) shows at δ 0.10 (s, 9 H); 1.02—2.0 (m, 22 H); 1.96 (d, 3 H); ^3J 6.6 Hz; 5.63 ppm (q, 1 H); ^3J 6.6 Hz. The IR (CCl_4) reveals a C=C stretch at 1680 cm^{-1}. To this α-silylvinylborane in ethanol (50 ml) solution at 0°C was added acetic acid (9.6 g, 0.16 mol) dropwise. After 1 h, 3.0 *N* NaOH (100 ml, 0.30 mol) was added to the mixture followed by the dropwise addition of 30% H_2O_2 (35 ml) (reaction temperature 30—50°C). The organic layer was washed with H_2O (2 × 50 ml), dried over anhydrous K_2CO_3 and distilled to give 10.0 g (55%) of XII, b.p. 87—88°C (740 Torr). The spectral properties of XII were identical to those previously reported [17].

cis-1-Iodopropene

This compound was prepared using the procedure of Zweifel and Arzoumanian [31]. The preparation of dicyclohexylborane (0.25 mol) was carried out from boranedimethyl sulfide and cyclohexene using ether solvent following the reported procedure [22]. 1-Iodopropyne (41.5 g, 0.25 mol) was added over 15 min while maintaining a temperature of 0°C using an ice bath. After 1 h, the borane had dissolved and the hydride activity was zero. Acetic acid (15 g, 0.25 mol) was added dropwise and the volatiles were pumped off and trapped at —78°C. Distillation of this material gives 12.6 g (30%) of product, b.p. 92—93.5°C. PMR ($CDCl_3$): δ 6.2 (m, 2 H), 1.75 ppm (m, 3 H) [28,29]; IR (neat) 1608 cm^{-1} (C=C).

cis-1-Propenylmercuric acetate (XIII)

cis-1-Iodopropene (9.4 g, 56 mmol) was dissolved in ether (20 ml) and to this cold (—78°C) mixture, t-butyllithium (59 ml 1.9 *M*; 112 mmol) was added dropwise over 1 h. After the addition was complete, this solution was added to mercuric iodide (25.4 g, 56 mmol) in ether (10 ml) at —78°C. This mixture was thoroughly stirred and allowed to warm to 25°C over 30 minutes. Water (20 ml) was added carefully and after separation of the aqueous layer the organic material was dried over anhydrous magnesium sulfate, filtered and concentrated in vacuo. The residue (12.4 g) was stirred with silver acetate (5.6 g, 33 mmol) in ether (150 ml) for 12 h in the absence of light. After filtration and concentration, the crude XIII was recrystallized from ether/hexane to give 4.5 g (27%) of XIII, m.p. 84°C; lit. [19] 75—78°C. PMR ($CDCl_3$): δ 6.5 (m, 1 H), 5.7 (m, 1 H), 2.0 (m, 6 H) ppm. $J(H(Me)—^{199}Hg)$ 41 Hz, $^2J(^1H—^{199}Hg)$ 263 Hz. IR ($CDCl_3$): 3012, 1639, 1612, 1379, 1299, 1219, 1058, 1020, 934, 694 cm^{-1}. The ^{13}C NMR of XIII showed absorbances for the propenyl group at 128.24, 142.57 and 23.71 ppm with ^{199}Hg coupling constants of 2196, 18 and 230 Hz, respectively. The acetoxy carbons absorbed at 177.60 and 23.38 ppm.

Allylmercuric acetate (VI)

To a stirred suspension of mercuric acetate (31.87 g, 100 mmol) in glacial acetic acid (84 ml) was added V (11.4 g; 100 mmol). After 1 h at room temperature, the acetic acid was removed in vacuo to yield a solid which was stirred for 12 h in ether. After filtration of undissolved solid material, the ether solution was cooled to 0°C to give 12.0 g (40%) of VI, m.p. 77—78°C; lit. [20] m.p.

77.5—78°C. The PMR data was identical to that previously reported [20]. The ^{13}C NMR ($CDCl_3$) of VI showed absorbances at 28.56, 135.12 and 115.07 ppm for the carbons of the allyl group with ^{199}Hg—^{13}C coupling constants of 1461, 192 and 222 Hz, respectively. The acetoxy carbons absorbed at 177.43 and 23.38 ppm.

2-Trimethylsilylethyl acetate (III)

To a stirred mixture (at 0°C) of 2-trimethylsilylethanol (2.37 g; 20 mmol) and pyridine (1.58 g; 20 mmol) was added acetyl chloride (1.57 g; 20 mmol) dropwise. When the addition was complete, the mixture was stirred at room temperature for 1 h. Water (4 ml) was added followed by ether (10 ml). The layers were separated and the organic phase was washed with chilled 1 *M* HCl (1 × 10 ml). After drying over anhydrous K_2CO_3, distillation gave 1.88 g (65%) of the desired compound, b.p. 57—58°C (30 Torr). PMR (CCl_4): δ 4.10 (ct, 2 H), 1.93 (s, 3 H), 0.93 (ct, 2 H), 0.07 ppm (s, 9 H). IR (neat): ν (C=O), 1730 cm^{-1}. Found: C, 52.27; H, 9.96. $C_7H_{16}O_2Si$ calcd.: C, 52.45; H, 10.06%.

1-Trimethylsilylprop-2-yl acetate (XXIII)

This compound, b.p. 64°C (33 Torr), was prepared on a 20-mmol scale in 70% isolated yield using the above described procedure. PMR (CCl_4): δ 4.80 (m, 1 H), 1.22 (d, *J* 6 Hz, 3 H), 0.95 (d, *J* 7 Hz), 0.88 (d, *J* 7.8 Hz) (2 H total), 0.07 ppm (s, 9 H). IR (neat) ν(C=O) 1754 cm^{-1}. Found: C, 54.82; H, 10.42. $C_8H_{18}O_2Si$ calcd.: C, 55.12; H, 10.41%.

1-Trimethylsilyl-3-butanol (XI)

This compound was prepared on a 50-mmol scale in 60% isolated yield using the OM—DM procedure subsequently described with the exception that the reduction was carried out at 0°C, b.p. 81—82°C (25 Torr) (lit. [27] 78°C, 25 Torr). PMR ($CDCl_3$): δ 3.6 (m, 1 H), 2.9 (d, *J* 4 Hz, 1 H), 1.0—1.6 (m, 2 H), 1.13 (d, *J* 6 Hz, 3 H), 0.50 (m, 2 H), 0.00 ppm (s, 9 H). With D_2O, signal at 2.9 ppm disappears and signal at 3.6 ppm becomes a sextet (*J* 6 Hz).

General OM—DM procedure for the alkenylsilanes

Mercuric acetate (5.00 mmol, 1.59 g) was dissolved in water (5 ml). THF (5 ml) was added producing a yellow color [4]. The appropriate olefin (5.00 mmol) was added by syringe to the stirred mixture. The time required for the yellow color to disappear was recorded as T_1. At the appropriate time, the mixture was reduced by adding 3 *M* NaOH (5 ml) followed by 0.5 *M* $NaBH_4$/3 *M* NaOH (5 ml). After 15 minutes, a known amount of n-$C_{14}H_{30}$ (standard) was added and the aqueous phase was saturated with K_2CO_3. An aliquot of the organic phase was further dried over K_2CO_3. When 2 equivalents of mercuric acetate were used as in the case of V as well as when a vinylmercurial was oxymercurated, the reduction was effected by adding 7 ml each of 3 *M* NaOH and 0.5 *M* $NaBH_4$/3 *M* NaOH solutions.

GLC analysis was carried out on an HP 5750 gas chromatograph, using a 12′ (or 6′) × 1/4″ 20% Carbowax 20 M on 60/80 Chromosorb W (AW—DCMS). Product identification was made by spiking the reaction mixtures with authentic samples whose preparation and properties are described above. 1-Propanol was identified by PMR analysis of a sample obtained by preparative GLC.

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