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Société suisse de chimie, Bâle – Società svizzera di chimica, Basilea
ISSN 0018-019X
Nachdruck verboten – Tous droits réservés
– Printed by Birkhäuser AG., Basel, Switzerland
Erscheint 9mal jährlich – Paraît 9 fois par an

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74. Note on the Preparation of Alkyl- and Oxaälkyl-dimethylsilanols

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(13. XI. 75)

Summary. The preparation of a series of alkyl- and (mono-, di- and poly-) oxaälkyl-dimethylsilanols is described. The stability of these compounds on storage is considerably increased by previous filtration through a silica gel column.

For a study of the reaction of silanols with surface hydroxyl groups of (hydrated) amorphous silicon dioxide, we prepared a series of R-dimethyl-silanols with the following R-substituents:

CH_3	C_2H_5	n-C_3H_7	n-C_6H_{13}	n-$C_{10}H_{21}$	n-$C_{14}H_{29}$	n-$C_{18}H_{37}$	n-$C_{22}H_{45}$
$\mathbf{A_1}$	$\mathbf{A_2}$	$\mathbf{A_3}$	$\mathbf{A_6}$	$\mathbf{A_{10}}$	$\mathbf{A_{14}}$	$\mathbf{A_{18}}$	$\mathbf{A_{22}}$

$CH_3{-}O{-}(CH_2)_n{-}$
$\mathbf{P_5}$ $n = 3$
$\mathbf{P_6}$ $n = 4$
$\mathbf{P_7}$ $n = 5$

$CH_3{-}O{-}CH_2{-}CH_2{-}O{-}(CH_2)_m{-}$
$\mathbf{P_8}$ $m = 3$
$\mathbf{P_9}$ $m = 4$
$\mathbf{P_{10}}$ $m = 5$

$CH_3{-}O{-}(CH_2{-}CH_2{-}O{-})_4{-}(CH_2)_4{-}$
$\mathbf{P_{18}}$

Of these, trimethylsilanol [1], ethyl-dimethylsilanol [2] and propyl-dimethylsilanol [3] have been described (see also [4] [5]).

The substituents R, to be introduced, were either 1-Bromo-(**1A** and **1P**) or the corresponding 1-vinyl-compounds (**2A** and **2P**). From these, alkyl-dimethyl-chlorosilanes $\mathbf{3A_3}$–$\mathbf{3A_{18}}$ could then be prepared in good yield by reaction of the *Grignard* derivative of the alkyl-bromides $\mathbf{1A_3}$–$\mathbf{1A_{18}}$ with dimethyl-dichloro-silane according to *reaction* (1) [4] [5]:

$$\left.\begin{array}{ccc} (CH_3)_2SiCl_2 + RMgBr & = & R(CH_3)_2\,SiCl + MgBrCl \\ \mathbf{1A_2} - \mathbf{1A_{18}} & & \mathbf{3A_2} - \mathbf{3A_{18}} \end{array}\right\} \quad (1)$$

This reaction was not efficacicus for introduction of oxaälkyl substituents. In our attempts to prepare $\mathbf{3P_9}$ in tetrahydrofuran (THF) by *reaction* (1), a complex mixture resulted, probably because the chlorosilane attacked the solvent, as it is known that dimethyl-dichloro-silane can attack the ether-C–O bond [6]. In replacing dichlorosilane by dimethyl-diethoxy-silane, the ethoxysilane $\mathbf{4P_9}$ could be isolated from the reaction mixture in good yield.

$$\left.\begin{array}{ccc} (CH_3)_2Si(OCH_2CH_3)_2 + RMgBr & = & R(CH_3)_2Si(OCH_2CH_3) + CH_3CH_2OMgBr \\ \mathbf{1P_9} & & \mathbf{4P_9} \end{array}\right\} \quad (2)$$

On the other hand the R-dimethyl-chloro-silanes **$3P_5$–$3P_8$**, **$3P_{10}$**, **$3P_{18}$** and **$3A_{22}$** were prepared in very good yield by catalytic hydrosilylation of the corresponding alkenes **2** [7] by *reaction* (3):

$$\left.\begin{array}{l} \mathbf{2} + (CH_3)_2SiHCl \xrightarrow{H_2PtCl_6 \cdot 6H_2O} \mathbf{3} \\ \text{for series } \mathbf{2}+\mathbf{3}\text{, compounds which include radicals } \mathbf{P_5}, \mathbf{P_6}, \mathbf{P_7}, \mathbf{P_8}, \mathbf{P_{10}}, \mathbf{P_{18}}, \mathbf{A_{22}} \end{array}\right\} \quad (3)$$

The hydrolysis of the dimethyl-chloro-silanes has been carried out by *reaction* (4):

$$\left.\begin{array}{l} R(CH_3)_2SiCl + H_2O + B = R(CH_3)_2SiOH + BH^+ + Cl^- \\ \text{method a: } \mathbf{3A_2}, \mathbf{3A_{22}}, \mathbf{3P_8}, \mathbf{3P_{10}}\text{; b: } \mathbf{3P_5}, \mathbf{3P_6}, \mathbf{3P_7} \text{ and c: } \mathbf{3A_3}, \mathbf{3A_6}, \mathbf{3A_{10}}, \mathbf{3A_{14}}, \mathbf{3A_{18}} \end{array}\right\} \quad (4)$$

using a) hydrogenocarbonate [4], b) naphthylamine or c) anilin [8] as the base B. Silanols with short-chain alkyl substituents dimerized partly during hydrolysis to give disiloxane as a by-product:

$$\left.\begin{array}{lcl} 2R(CH_3)_2SiOH & = & R(CH_3)_2Si{-}O{-}Si(CH_3)_2R + H_2O \\ \quad \mathbf{5} & & \quad \mathbf{6A_3}, \mathbf{6A_6} \end{array}\right\} \quad (5)$$

The ethoxysilane **$4P_9$** could be hydrolysed merely by agitating its etheric solution with water containing catalytic amounts of ammonium chloride:

$$\mathbf{4P_9} + H_2O \xrightarrow{NH_4Cl} \mathbf{5P_9} + CH_3CH_2OH \quad (6)$$

Finally, the trimethylsilanol, **$5A_1$**, was prepared according to *Birkofer et al.* [9] by hydrolysis of trimethylsilyl-acetamide.

The physical data and yields of the silanols prepared are summarized in Table 1. – It is interesting to mention that the silanols could be purified by chromatography on

Table 1. *Physical data of R-dimethylsilanols* **3**, *and preparative yields* (where yield of **1** (bromide) → **3** (chlorosilane) is given based on **1**; that of **2** (alkene) → **3** based on **2**; **3** → **5** (silanol) based on **3**; and total yield of **5** based on **1** or **2**)

R	m.p. °C	n_D^{20}	d^{20} $g \cdot cm^{-3}$	**1** → **3** %	**2** → **3** %	**3** → **5** %	total
A_1		1.3896	0.815	–	–	–	56 [a]
A_2		1.4004	0.828	61		29	18
A_3		1.4147	0.833	75		90	68
A_6		1.4296	0.838	73		88	64
A_{10}		1.4401	0.857	83		93	77
A_{14}	33–34			68		94	64
A_{18}	50–51			79		86	68
A_{22}	65–66				68	94	64
P_5		1.4290	0.884		69	76	52
P_6		1.4342	0.869		82	91	75
P_7		1.4374	0.875		87	90	78
P_8		1.4400	0.958		69	42	29
P_9		1.4405	0.946	50 [b]		95 [b]	48 [b]
P_{10}		1.4439	0.940		67	49	33
P_{18} [c]		1.4470	1.068		~90	~83	~75

[a] Overall yield for trimethyl-chloro-silane (**$3A_1$**) → trimethylsilyl-acetamide → trimethylsilanol (**$5A_1$**) based on **$3A_1$**.

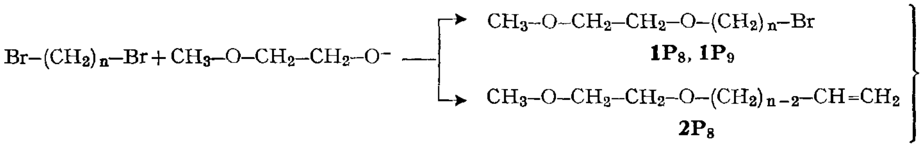
[b] Ethoxysilane was used instead of chlorosilane.

[c] Contained ~5% unidentified impurities.

silica gel and that they then showed a considerably increased stability on storage. We therefore recommend filtration, at least on a short column, even if purification is unnecessary.

Concerning preparative reactions: *Bromides* **1**, *and vinyl derivatives* **2**. The bromides $\mathbf{A_2}$–$\mathbf{A_{18}}$ are commercially available.

We intended to prepare the 1-bromo-dioxaälkanes $\mathbf{1P_8}$–$\mathbf{1P_{10}}$ by the *Williamson* synthesis following the *reaction scheme* (7):



$$Br{-}(CH_2)_n{-}Br + CH_3{-}O{-}CH_2{-}CH_2{-}O^- \longrightarrow \begin{cases} \to CH_3{-}O{-}CH_2{-}CH_2{-}O{-}(CH_2)_n{-}Br \quad \mathbf{1P_8}, \mathbf{1P_9} \\ \to CH_3{-}O{-}CH_2{-}CH_2{-}O{-}(CH_2)_{n-2}{-}CH{=}CH_2 \quad \mathbf{2P_8} \end{cases} \qquad (7)$$

Using 1,3-dibromopropane the dioxaälkene $\mathbf{2P_8}$ was isolated as the main product, together with a small quantity of the bromide $\mathbf{1P_8}$, even in the case when the alcoholate was added to the dibromide very slowly. Obviously the dehydrobromination of $\mathbf{1P_8}$ is a relatively fast competing reaction.

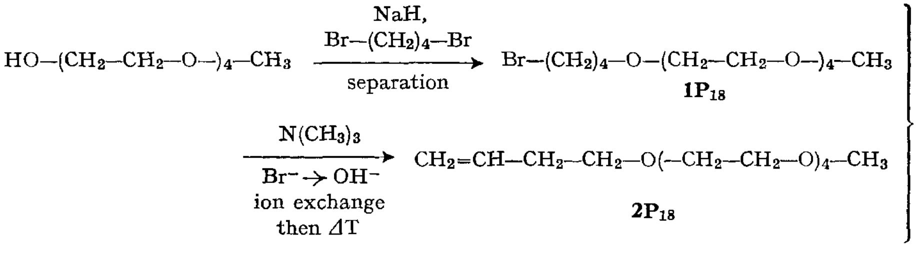
The alkene 1-docosene, $\mathbf{2A_{22}}$, is commercially available. The oxa- and dioxaalkenes $\mathbf{2P_5}$, $\mathbf{2P_7}$ and $\mathbf{2P_{10}}$ were prepared by the *Williamson* synthesis from the corresponding ω-bromo-1-alkene

$$CH_2{=}CH{-}(CH_2)_n{-}Br + CH_3{-}O^- = CH_2{=}CH{-}(CH_2)_n{-}OCH_3 \qquad \mathbf{2P_5}(n = 1),\ \mathbf{2P_7}(n = 3) \qquad (8)$$

$$CH_2{=}CH{-}(CH_2)_3{-}Br + CH_3{-}O{-}CH_2{-}CH_2{-}O^- = CH_2{=}CH{-}(CH_2)_3{-}O{-}CH_2{-}CH_2{-}O{-}CH_3 \qquad \mathbf{2P_{10}}$$

Obviously $\mathbf{2P_6}$ cannot be prepared from 4-bromobut-1-ene because the latter is quantitatively dehydrobrominated by the base, giving butadiene. Therefore, $\mathbf{1P_6}$ was first prepared following *reaclion scheme* (7) but using a methanolate, and then dehydrobrominated to $\mathbf{2P_6}$.

Finally the 5,8,11,14,17-pentaöxaöctadec-1-ene ($\mathbf{2P_{18}}$) was prepared according to (9):



$$HO{-}(CH_2{-}CH_2{-}O{-})_4{-}CH_3 \xrightarrow[\text{separation}]{NaH,\ Br{-}(CH_2)_4{-}Br} \underset{\mathbf{1P_{18}}}{Br{-}(CH_2)_4{-}O{-}(CH_2{-}CH_2{-}O{-})_4{-}CH_3} \xrightarrow[\substack{Br^- \to OH^- \\ \text{ion exchange} \\ \text{then } \Delta T}]{N(CH_3)_3} \underset{\mathbf{2P_{18}}}{CH_2{=}CH{-}CH_2{-}CH_2{-}O({-}CH_2{-}CH_2{-}O)_4{-}CH_3} \qquad (9)$$

This work is a report on a part of a project supported by the *Fonds National Suisse de la Recherche Scientifique*.

Experimental Part.– General. The elementary analyses were carried out at the Institute of Organic Chemistry ETH-Zurich by *W. Manser*. The m.p. are not corrected. Abbreviations used: DF.: dropping funnel; GC.: gas chromatography; MSt.: magnetic stirrer; RF.: refrigerator for reflux; RT.: room temperature.

The dimethyl-chloro-silane was a product of *Pierce Chem. Co.*, Rockford, Ill. USA; the silica gel used for preparative liquid chromatography was from *E. Merck*, Darmstadt: 'Kieselgel-60' with a particle diameter of 60–200 μ. Other commercial chemicals were products of *Fluka AG* Buchs, Switzerland. – The magnesium shavings were activated for *Grignard* reaction according to *Bryce-Smith & Cox* [10] by heating in the reaction vessel with RF. and DF. in N_2-atmosphere at about 200° for a few minutes.

Synthesis of the silanols (for properties see Table 2). – *1-Bromoalkanes* $\mathbf{1A_2}$, $\mathbf{1A_3}$, $\mathbf{1A_6}$, $\mathbf{1A_{10}}$, $\mathbf{1A_{14}}$ *and* $\mathbf{1A_{18}}$: were all *Fluka* commercial products.

1-Bromo-4,7-dioxaöctane ($\mathbf{1P_8}$). This substance will be described as by-product in the synthesis of 4,7-dioxaöct-1-ene ($\mathbf{2P_8}$).

1-Bromo-5,8-dioxanonane ($\mathbf{1P_9}$). To a vigorously stirred, ice-cooled suspension of 9.6 g sodium hydride (0.40 mol) in 100 ml anhydrous ether, 152.2 g 2-methoxyethanol (2.00 mol) were added dropwise at RT., and the mixture stirred for 1 h. 129.6 g (0.60 mmol) 1,4-dibromobutane contained in a flask (1 l, MSt., N_2-atm.) were heated to 80° and the prepared alcoholate solution was then added dropwise; a white precipitate of NaBr appeared after a few minutes. The mixture was stirred overnight (80°) then cooled and diluted with 250 ml ether. The etheric solution washed 3 × with water, dried over Na_2SO_4 and filtered, gave after evaporation of ether a residue (yellow oil) which was distilled under 13 Torr through a *Vigreux* column: Fr. 1 (20–60°): 1.5 g; Fr. 2 (60–85°): 42.0 g; Fr. 3 g (90–98°): 45.3; Fr. 2 consisted mainly of 1,4-dibromobutane. Redestillation of Fr. 3 at 98°/13 Torr gave 42.0 g (48% based on sodium 2-methoxyethanolate) of 1-bromo-5,8-dioxanonane ($\mathbf{1P_9}$).

$C_7H_{15}BrO_2$ (211.10) Calc. C 39.82 H 7.16 Br 37.86% Found C 39.85 H 7.06 Br 37.75%

1-Bromo-5,8,11,14,17-pentaöxaöctadecane ($\mathbf{1P_{18}}$). An alcoholate solution prepared from 60.0 g (0.288 mol) 3,6,9,12-tetraöxatridecan-1-ol and 6.9 g (0.288 mol) NaH in 300 ml anhydrous toluene was added dropwise at 80° under N_2 to 270.0 g (1.25 mol) 1,4-dibromobutane and the mixture stirred overnight at that temperature. After cooling it was washed with 200 ml water; the water phase contained unreacted 3,6,9,12-tetraöxatridecan-1-ol. The organic layer was distilled at ambient pressure to remove toluene and 1,4-dibromobutane. Distillation of the residue at 204°/0.5 Torr gave 28.6 g (28.9%) 1-bromo-5,8,11,14,17-pentaöxapentadecane ($\mathbf{1P_{18}}$).

$C_{13}H_{27}O_5Br$ (343.25) Calc. C 45.48 H 7.93 Br. 23.30% Found C 45.37 H 7.97 Br. 23.29%

Docosene-(1) ($\mathbf{2A_{22}}$) was a *Fluka* product.

4-Oxapent-1-ene ($\mathbf{2P_5}$). A solution of sodium methanolate (320 g methanol, 48.0 g (2.0 mol) NaH) was added dropwise at RT. to 242.0 g (2.0 mol) allyl bromide and refluxed for 8 h. The product was distilled directly from the reaction mixture and gave 103.0 g (71.5% based on allyl bromide) of 4-oxapent-1-ene at 39°/720 Torr.

C_4H_8O (72.11) Calc. C 66.63 H 11.18% Found C 66.34 H 11.01%

5-Oxahex-1-ene ($\mathbf{2P_6}$). A solution of sodium methanolate (128.0 g methanol, 18 g (0.75 mol) NaH) was added dropwise at 60° to 326.0 g (1.50 mol) 1,4-dibromobutane and stirred overnight at that temperature. After cooling, the mixture was taken up in ether, the ether phase was extracted with water, dried over Na_2SO_4 and filtered. After evaporation of the ether, the residue was distilled at 15 Torr. The main fraction (38–46°; 100.0 g) contained *ca.* 50% of 1-bromo-5-oxahexane and 50% of 1,4-dibromobutane. This mixture was added at 60° to a solution of 112.0 g (2.0 mol) KOH in 1 l tetraethylene glycol. By heating slowly to 170° water and reaction products were distilled off continuously. The two phases of the distillate were separated and the water phase extracted with ether. The combined organic layers were dried over Na_2SO_4, filtered and the ether evaporated. The residue consisted of pure 5-oxahex-1-ene which was distilled at 730 Torr: 67–68°: 11.4 g $\mathbf{2P_6}$ (18% based on sodium methylate).

$C_5H_{10}O$ (86.13) Calc. 69.72 H 11.70% Found C 69.60 H 11.60%

6-Oxahept-1-ene (**2P$_7$**). A solution of sodium methanolate (160 g methanol, 24.0 g (1.0 mol) NaH) was added dropwise at RT. to 149.0 g 5-bromopent-1-ene, and the mixture heated to reflux for 8 h. After cooling it was taken up in ether, the ether phase extracted twice with water, dried over Na_2SO_4 and filtered. After evaporation of ether, the residue was fractionated at 730 Torr: Fr. 1 (63–92°): 8.0 g; Fr. 2 (93–95°): 52.0 g; residue: 4.0 g. Fr, 2 was identified as **2P$_7$**, yield: 52%.

$C_6H_{12}O$ (100.16) Calc. C 71.95 H 12.05% Found C 71.91 H 12.18%

4,7-Dioxaöct-1-ene (**2P$_8$**). A solution of sodium 2-methoxyethanolate (152.2 g (2.00 mol) 2-methoxyethanol and 9.6 g (0.40 mol) NaH, *cf.* prepn. of **1P$_9$**) was added dropwise (30 min) to 40.0 g (0.20 mol) 1,3-dibromopropane. The mixture was stirred overnight at 60° (white precipitate of NaBr after 15 min). After cooling it was taken up in ether, the ether phase extracted 3 × with water, dried over Na_2SO_4 and filtered. After evaporation of ether the residue was fractionated through a *Vigreux* column (13 Torr): Fr. 1 (24°): 13.9 g; Fr. 2 (81°): 1.0 g; residue 0.1 g. Fr. 2 was identified as 1-bromo-4,7-dioxaöctane (**1P$_8$**). Yield: 1.5% based on 1,3-dibromopropane; purity: 99.8% (GC.).

$C_6H_{13}O_2Br$ (197.08) Calc. C 35.56 H 6.65 Br 40.55% Found C 35.56 H 6.59 Br 40.46%

Fr. 1 was identified as **2P$_8$**; yield: 60% based on 1,3-dibromopropane; purity: 99.0% (GC.). For a purified sample:

$C_6H_{12}O_2$ (116.16) Calc. C 62.04 H 10.41% Found C 61.85 H 10.42%

6,9-Dioxa-1-decene (**2P$_{10}$**) (*cf.* prepn. **2P$_8$**). To a solution of sodium 2-methoxyethanolate (20 ml ether, 0.15 g (84.5 mmol) NaH, 32.1 g (420 mmol) 2 methoxyethanol, *cf.* prepn. of **1P$_9$**) 12.6 g (84.5 mmol) of 5-bromopent-1-ene was added dropwise at RT. The mixture was heated to 60° and stirred for 18 h. After cooling it was taken up in 100 ml of ether, the ether solution was washed 3 × with water, dried over Na_2SO_4 and filtered. After evaporation of ether the residue was distilled through a *Vigreux* column (13 Torr): Fr. 1 (<56°): 0.7 g; Fr. 2 (56°): 8.5 g **2P$_{10}$**, as colorless oil; yield: 70% based on 5-bromopent-1-ene.

$C_8H_{16}O_2$ (144.21) Calc. C 66.63 H 11.18% Found C 66.42 H 11.26%

5,8,11,14,17-Pentaöxaöctadec-1-ene (**2P$_{18}$**). In a closed pressure flask 34.3 g 1-bromo-5,8,11,-14,17-pentaöxaöctadecene (**1P$_{18}$**; 0.100 mol) and 8.3 g trimethyl amine (0.14 mol) was allowed to stand for 72 h. A highly viscous oil of 5,8,11,14,17-pentaöxaöctadecyl-trimethylammonium bromide was formed. It was dissolved in 150 ml of water and filtered on an ion-exchange column (800 g Levatit) giving an aqueous solution of 5,8,11,14,17-pentaöxaöctadecyl-trimethylammonium hydroxide, from which water was evaporated at 0.1 Torr. The residue was pyrolysed dropwise at 190° whereby the pyrolysis-product distilled off into a cooled trap. The trap content was taken up in ether and purified by three-step counter current extraction between ether stationary-phase and water. The combined organic layers were dried over Na_2SO_4, filtered and ether distilled off. Distillation of the residue (138°/0.1 Torr) gave 12.7 g of a main fraction. (**2P$_{18}$**), as colorless oil, yield: 47.0% based on **1P$_{18}$**

$C_{13}H_{26}O_5$ (262.85) Calc. C 59.09 H 9.99% Found C 58.64 H 10.03%

Trimethylchlorosilane (**3A$_1$**) was a *Fluka* product.

Ethyl-dimethyl-chloro-silane (**3A$_2$**). A *Grignard* solution prepared from 24.0 g (1.0 mol) magnesium shavings and 109.0 g (1.00 mol) ethylbromide in 80 ml of anhydrous ether was added dropwise to a boiling solution of 100.0 g (0.782 mol) dimethyl-dichloro-silane in 150 ml anhydrous ether under N_2; a white precipitate of MgBrCl appeared after a few minutes. The mixture was refluxed with stirring for 24 h, then cooled and filtered under N_2. After removing ether, the residue was evaporated at RT. and 0.1 Torr into a cooled trap (liquid N_2). Distillation of the trap content gave 71.2 g of a main fraction (75–81°/730 Torr): colorless liquid, mixture of 90% **3A$_2$** and 10% unreacted dimethyl-dichloro-silane. Yield based on **3A$_2$** $\approx$ 44.1 g (47% based on dimethyl-dichloro-silane). Since separation of these components is very difficult, the crude product was used without further purification.

Propyl-dimethyl-chloro-silane (**3A$_3$**). 60.0 g magnesium shavings (2.50 mol) having been activated as described (see *general*), were covered with 150 ml anhydrous ether and a solution of 61.5 g (0.50 mol) 1-bromopropane (**1A$_3$**) in 150 ml anhydrous ether was added dropwise; the heat of reaction kept the mixture boiling. The solution of the *Grignard* reagent was then cooled and filtered from the excess Mg into a DF. in N_2-atmosphere. It was then added dropwise to a boiling solution of 193.5 g (1.50 mol) dimethyl-dichloro-silane in 200 ml anhydrous ether, the mixture stirred and refluxed for 24 h, cooled and filtered under N_2. Distillation (700 Torr; *Vigreux* column) gave a first fraction (mixture of ether and dimethyl-dichloro-silane) and a residue which contained in suspension further inorganic magnesium salts precipitated during distillation. This residue was evaporated at 0.1 Torr into a cooled trap (liquid N_2), and distillation of the trap content gave a main fraction (100–110°/720 Torr): 51.0 g (**3A$_3$**; yield, 75% based on **1A$_3$**). This **3A$_3$** was used without further purification; its physical and spectroscopical properties were determined on a small purified sample.

$C_5H_{13}ClSi$ (136.70) Calc. C 43.94 H 9.59 Cl 25.94% Found C 43.97 H 9.71 Cl 25.54%

Hexyl-dimethyl-chloro-silane (**3A$_6$**) (*cf.* **3A$_3$**). The *Grignard* solution, prepared with 60.0 g magnesium shavings (2.50 mol) and 82.5 g (0.50 mol) 1-bromohexane in 150 ml anhydrous ether, was added dropwise to a solution of 193.5 g (1.50 mol) dimethyl-dichloro-silane in 200 ml of anhydrous ether. After working-up, the distillation of the trap content through a *Vigreux* column at 16 Torr gave a main fraction (77–80°): 65.0 g crude **3A$_6$**; yield: 73% based on 1-bromohexane. This product was used without further purification; the physical and spectroscopical properties were determined on a small purified sample.

Decyl-dimethyl-chloro-silane (**3A$_{10}$**) (*cf.* prepn. **3A$_3$**). The *Grignard* solution, prepared with 11.0 g (0.45 mol) Mg shavings and 100.0 g (0.45 mol) 1-bromodecane in 150 ml anhydrous ether, was added dropwise to a solution of 260.0 g dimethyl-dichloro-silane (2.0 mol) in 200 ml anhydrous ether. After working-up, the distillation of the trap content through a *Vigreux* column at 1 Torr gave a main fraction (103–106°): 80.4 g crude **3A$_{10}$**; yield: 89% based on 1-bromodecane. This product was used without further purification; physical and spectroscopical properties were determined on a small purified sample.

Tetradecyl-dimethyl-chloro-silane (**3A$_{14}$**) (*cf.* prepn. **3A$_3$**). The *Grignard* solution, prepared with 8.7 g (0.36 mol) Mg shavings and 100.0 g (0.36 mol) 1-bromotetradecane in 150 ml anhydrous ether, was added dropwise to a solution of 193.5 g, (1.50 mol) dimethyl-dichloro-silane in 200 ml of anhydrous ether. After working-up, the distillation of the trap content through a *Vigreux* column at 0.5 Torr gave a main fraction (168–175°): 67.5 g crude **3A$_{14}$**; yield: 68% based on 1-bromotetradecane; this product was used without further purification, physical and spectroscopical properties were determined on a small purified sample.

Octadecyl-dimethyl-chloro-silane (**3A$_{18}$**) (*cf.* prepn. **3A$_3$**). The *Grignard* solution, prepared with 73.0 g (3.0 mol) magnesium shavings and 100.1 g (0.30 mol) 1-bromoöctadecane in 200 ml anhydrous ether was added dropwise to a solution of 129.0 g dimethyl-dichloro-silane (1.0 mol) in 200 ml anhydrous ether. After evaporation of ether and dimethyl-chloro-silane the residue was fractionated under reduced pressure (0.005 Torr): Fr. 1 (80–140°), 6.2 g: Fr. 2 (145–155°), 89.0 g. The latter was redistilled at the same pressure and gave 81.5 g **3A$_{18}$** as a crystalline mass (m.p. 28–30°); yield, 79% based on 1-bromoöctadecane. It was used without further purification; the physical and spectroscopical properties were determined on a small purified sample.

Docosyl-dimethyl-chloro-silane (**3A$_{22}$**). A solution of 16.7 g docos-1-ene (54.3 mmol) (**2A$_{22}$**), 5.14 g (54.3 mmol) dimethyl-chloro-silane and 0.9 mg H_2PtCl_6 in 150 ml anhydrous ether was refluxed for 10 h, and the low boiling parts were then removed at 13 Torr and RT. The residue was crystallized from ether/petroleum ether 1:1 and gave 14.9 g **3A$_{22}$** as a crystalline mass of m.p. 41–43°; yield, 68% based on docos-1-ene. This product was used without further purification; the physical and spectroscopical properties were determined on a small purified sample (see Table 2).

(4-Oxapentyl)-dimethyl-chloro-silane (**3P$_5$**). A mixture of 4.2 g (58.2 mmol), 4-oxapent-1-ene, 5.51 g (58.2 mmol) dimethyl-chloro-silane and 0.6 mg H_2PtCl_6 was stirred at 40° for 18 h., then filtered and distilled at 18 Torr. The distillation gave only one fraction (64–66°), yield of **3P$_5$**: 6.7 g, 69% based on dimethyl-chloro-silane. The raw product was used for hydrolysis immediately after preparation.

(5-Oxahexyl)-dimethyl-chloro-silane (**3P$_6$**). A mixture of 4.6 g (53.5 mmol) 5-oxahex-1-ene, 5.06 g (53.5 mmol) dimethyl-chloro-silane and 0.6 mg H_2PtCl_6 was stirred at 40° for 18 h, then filtered and distilled, which gave only one fraction (81–82°/18 Torr), 7.9 g of **3P$_6$** as colorless oil; yield 82%

based on dimethyl-chloro-silane. The crude product was used for hydrolysis immediately after preparation.

6-Oxaheptyl)-dimethyl-chloro-silane (**3P**$_7$). 8.3 g (83.0 mmol) 6-oxahept-1-ene, 7.85 g (83.0 mmol) dimethyl-chloro-silane and 1.0 mg H_2PtCl_6 were stirred at 40° for 18 h. After filtration the product was distilled and gave only one fraction (97–98°/18 Torr): 14.0 g of **3P**$_7$ as colorless oil; yield 87% based on dimethyl-chloro-silane. The crude product was used for hydrolysis immediately after preparation.

(4,7-Dioxaöctyl)-dimethyl-chloro-silane (**3P**$_8$). In a reaction flask (RF., DF., MSt., N_2-atmosphere) a mixture of 7.0 g (60 mmol) 4,7-dioxaoct-1-ene (**2P**$_8$) and 1.0 mg H_2PtCl_6 was heated to 100°, then 5.0 g dimethyl-chloro-silane were added dropwise (15 min). After 5 h low boiling products were removed under reduced pressure; further distillation at 0.05 Torr through a *Vigreux* column at 60° gave 7.5 g of **3P**$_8$; yield, 69% based on dimethyl-chloro-silane. The raw product was used for hydrolysis immediately after preparation.

(6,9-Dioxadecyl)-dimethyl-chloro-silane (**3P**$_{10}$) (*cf.* prepn. **3P**$_8$). The reaction was carried out with 5.9 g (40 mmol) 6,9-dioxadec-1-ene (**2P**$_{10}$), 3.8 g (40 mmol) dimethyl-chloro-silane and 0.7 mg H_2PtCl_6. Distillation at 0.05 Torr through a *Vigreux* column, at 100° gave 6.5 g **3P**$_{10}$; yield, 67% based on dimethyl-chloro-silane. The raw product was used for hydrolysis immediately after preparation.

(5,8,11,14,17-Pentaöxaöctadecyl)-dimethyl-chloro-silane (**3P**$_{18}$). A mixture of 8.3 g (31.6 mmol) 5,8,11,14,17-pentaöxaöctadec-1-ene (**2P**$_{18}$), 2.98 g (31.6 mmol) dimethyl-chloro-silane and 0.8 mg ($1.56 \cdot 10^{-6}$ mol) hexachloroplatinic acid was stirred unter N_2 for 6 h at 80°. After cooling, low boiling components were removed at 1.0 Torr. The residue, 11.0 g, containing mainly **3P**$_{18}$, was hydrolysed without further purification as it could be neither crystallized nor distilled.

(5,8-Dioxanonyl)-dimethyl-ethoxy-silane (**4P**$_9$). In a reaction flask (250 ml, RF., DF., MSt., N_2-atmosphere) 2.43 g (0.10 mol) Mg shavings were suspended in 30 ml anhydrous THF., and 21.1 g (0.10 mol) 1-bromo-5,8-dioxanonane then added dropwise, the temperature being kept at 40°. After complete dissolution of the magnesium, half of the solvent was evaporated at 720 Torr then 50.0 g dimethyl-diethoxy-silane (0.34 mol) added in one portion. The mixture was heated to 90° and stirred for 24 h. 200 ml anhydrous ether and 100 ml of a 10% solution of NH_4Cl were added after cooling, the etheric phase washed with water, dried over Na_2SO_4, filtered and the ether evaporated. Distillation of the residue through a *Vigreux* column at 0.08 Torr gave: Fr. 1 (<80°): 35.0 g dimethyl-diethoxy-silane in the cool trap; Fr. 2 (88°): 12.3 g **4P**$_9$; yield, 50.4% based on 1-bromo-5,8-dioxa-nonane.

$C_{11}H_{26}O_3Si$ (234.42) Calc. C 56.37 H 11.18% Found C 56.28 H 11.20%

Trimethylsilanol (**5A**$_1$), prepared according to *Birkofer et al.* [1]. In a reaction flask (DF., RF., MSt.) a solution of 40.0 g (0.35 mol) acetamid and 56.0 (0.55 mol) triethylamin in 200 ml benzene was heated to reflux, then 56.0 g (0.51 mol) trimethyl-chloro-silane (**3A**$_1$) added dropwise; a white precipitate appeared after the first drops. After addition (*ca.* 1 h) the mixture was refluxed with stirring for a further hour, then cooled and filtered. The solvent, the trimethylamine and the excess trimethyl-chloro-silane were distilled off (*Vigreux* column) at 720 Torr. Distillation of the residue at 13 Torr (83–85°) gave 56.0 g viscous oil which solidified on standing: *trimethylsilyl-acetamid*, m.p. 35–37°; yield 82% based on **3A**$_1$.

A solution of the amide in 150 ml ether was added dropwise to 400 g of a vigorously agitated water-ice mixture. The two phases were separated, the water phase washed twice with ether, and the combined ether extracts were cooled to −35° overnight, the water crystals filtered off, and the ether distilled. Distillation of the residue at 20 Torr gave 26.0 g of a colorless oil (29–33°), which was purified by chromatography on silica gel (260 g): Fr. 1: 0.5 g hexamethyl-disiloxane (**6A**$_1$) (eluent: petroleum ether); Fr. 2: 25.5 g **5A**$_1$ (eluent: ether), yield, 57% based on **3A**$_1$.

Ethyl-dimethyl-silanol (**5A**$_2$) (see [8]). In a reaction flask (VA., DF.) 350 ml ether, 10.6 g (0.586 mol) water and 54.6 g freshly distilled aniline were homogenized by addition of the necessary volume of acetone (*ca.* 150 ml), then cooled to 0° and, under vigorous agitation, a solution of the chlorosilane mixture (the whole of that prepared in the preceding step) in 150 ml anhydrous ether was added dropwise. After filtration of the white precipitate formed and evaporation of ether, the residue was distilled at 35 Torr: Fr. 1 (48°): 18.2 g (0.175 mol) **5A$_2$**, residue: 33.8 g; yield ≈ 28.5%.

$C_4H_{12}OSi$ (104.23) Calc. C 46.11 H 11.61% Found C 46.31 H 11.63%

Propyl-(1)-dimethyl-silanol (**5A$_3$**). (See [9]). In a reaction flask (VA., DF.) 600 ml ether 3.60 g, (0.20 mol) water and 18.6 g freshly distilled anilin were homogenized by addition of the necessary volume of acetone (~200 ml); then cooled to 0° and, under vigorous agitation, a solution of 27.2 g (0.20 mol) propyl-dimethyl-chloro-silane (**3A$_3$**) in 200 ml anhydrous ether was added dropwise, giving a white precipitate; the filtrate from which was washed 3× with 200 ml water in three separators. The combined ether extracts were dried over Na_2SO_4, the ether evaporated and the residue chromatographed on silica gel (240 g): Fr. 1 (eluent: 2000 ml petroleum ether): 0.4 g yellow oil; Fr. 2 (eluent: 750 ml ether): 22.2 g colorless oil. The second fraction was distilled through a *Vigreux* column at 13 Torr and gave (62–64°) 21.2 g **5A$_3$**, purity 99.5% (GC.); yield, 89.6%. $C_5H_{14}OSi$ (118.26) Calc. C 50.79 H 11.94% Found C 50.71 H 12.04%

Hexyl-dimethyl-silanol (**5A$_6$**) (*cf.* **5A$_3$**). After hydrolysis of 35.8 g hexyl-dimethyl-chloro-silane (**3A$_6$**) as in the mixture described above (same volume and composition) and working-up, chromatography on silica gel (320 g) gave: Fr. 1 (3200 ml petroleum ether), 0.80 g oil; Fr. 2 (750 ml ether), 28.2 g viscous oil, which on distillation, at 44–45°/0.1 Torr, gave 28.0 g **5A$_6$**; yield 88%.

$C_8H_{20}OSi$ (160.34) Calc. C 59.94 H 12.58% Found C 60.01 H 12.57%

Decyl-dimethyl-silanol (**5A$_{10}$**) (*cf.* prepn. **5A$_3$**). After hydrolysis of 47.0 g decyl-dimethyl-chloro-silane (**3A$_{10}$**) in the mixture described (same volume and composition) and working-up, chromatography on silica gel (450 g) gave: Fr. 1 (3600 ml petroleum ether): 1.6 g oil; Fr. 2 (800ml ether): 43.0 g viscous oil. The latter gave, 40.3 g **5A$_{10}$**, after recrystallisation from petroleum ether at −35°; yield, 93%.

$C_{12}H_{28}OSi$ (216.44) Calc. C 66.60 H 13.04% Found C 66.70 H 13.00%

Tetradecyl-dimethyl-silanol (**5A$_{14}$**) (*cf.* prepn. **5A$_3$**). After hydrolysis of 59.4 g (0.20 mol) tetradecyl-dimethyl-chloro-silane (**3A$_{14}$**) in the mixture described (same volume and composition) and working-up, chromatography on silica gel (500 g) gave: Fr. 1 (3500 ml petroleum ether), 2.7 g oil; Fr. 2 (800 ml ether), 53.5 g crystalline mass. Recrystallisation of the latter from petroleum ether gave 52.4 g **5A$_{14}$**, m.p. 33–34°; yield 94%.

$C_{16}H_{36}OSi$ (272.55) Calc. C 70.52 H 13.32% Found C 70.44 H 13.15%

Octadecyl-dimethyl-silanol (**5A$_{18}$**) (*cf.* prepn. **5A$_3$**). After hydrolysis of 52.3 g (0.15 mol) octadecyl-dimethyl-chloro-silane (**3A$_{18}$**) in the mixture described (same volume and same composition) and working-up, chromatography on silica gel (500 g) gave: Fr. 1 (4.0 l petroleum ether), 2.7 g yellow wax; Fr. 2 (1.0 l ether), 45.0 g crystalline mass. The latter gave, after three recrystallisations from petroleum ether, 42.3 g **5A$_{18}$** as white needles, m.p. 51°; yield 94%. Purity, 99.1 molar % (determined with a differential scanning calorimeter; *Perkin-Elmer*, model DSC-1).

$C_{20}H_{44}OSi$ (328.66) Calc. C 73.10 H 13.49% Found C 73.14 H 13.51%

Docosyl-dimethyl-silanol (**5A$_{22}$**). A solution of 14.9 g (37.0 mmol) docosyl-dimethyl-chloro-silane (**3A$_{22}$**) in 80 ml anhydrous ether was added dropwise (at 0°) to a vigorously agitated two-phase system composed of 80 ml ether and a solution of 3.04 g (37.0 mmol) $NaHCO_3$ in 80 ml of water. After 30 min the ether phase was separated, dried over Na_2SO_4, filtered and ether evaporated to give a crystalline mass. Recrystallisation of the latter in ether/petroleum ether 1:1 gave 13.4 g **5A$_{22}$**, white needles m.p. 65–66°; yield 94%.

$C_{24}H_{52}OSi$ (384.77) Calc. C 74.92 H 13.62% Found C 75.01 H 13.70%

(4-Oxapentyl)-dimethyl-silanol (**5P$_5$**). A solution of 6.7 g (40.2 mmol) (4-oxapentyl)-dimethyl-chloro-silane in 40 ml anhydrous ether was added dropwise at 0° to a homogenous mixture of 50 ml ether, 40 ml aceton, 0.724 g (40.2 mmol) H_2O and 5.76 g (40.2 mmol) naphthylamine. The mixture was stirred for 10 min, the precipitated naphthylaminehydrochloride filtered off and the filtrate purified on a chromatography column containing 30.0 g of silica gel. After evaporation of ether, distillation of the residue at 89–91°/18 Torr gave 4.5 g of **5P$_5$**; yield 76% based on **3P$_5$**.

$C_6H_6O_2Si$ (148.29) Calc. C 48.61 H 10.88% Found C 48.81 H 10.84%

(5-Oxahexyl)-dimethyl-silanol (**5P$_6$**) (*cf.* prepn. **5P$_5$**). After hydrolysis of 7.7 g (42.6 mmol) (5-oxahexyl)-dimethyl-chloro-silane as described, the distillation of the residue at 104–106°/18 Torr gave 6.3 g of **5P$_6$**; yield 91%, based on **3P$_6$**.

$C_7H_{18}O_2Si$ (162.31) Calc. C 51.81 H 11.18% Found C 51.74 H 11.21%

(6-Oxaheptyl)-dimethyl-silanol (**5P$_7$**) (*cf.* prepn. **5P$_5$**). After hydrolysis of 14.0 g (72.0 mmol) (6-oxaheptyl)-dimethyl-chloro-silane as described, distillation of the residue at 120–122°/18 Torr gave 11.4 g of **5P$_7$**; yield 90%, based on **3P$_7$**.

$C_8H_{20}O_2Si$ (176.33) Calc. C 54.50 H 11.44% Found C 54.58 H 11.49%

(4,7-Dioxaöctyl)-dimethyl-silanol (**5P$_8$**) (*cf.* prepn. **5A$_{22}$**). After hydrolysis of 7.5 g (35.2 mmol) of (4,7-dioxaöctyl)-dimethyl-chloro-silane (**3P$_8$**) in 5 ml ether in the two-phase system described (3.1 g $NaHCO_3$ (35 mmol) in 100 ml water/100 ml ether) and working-up, chromatography of the evaporation residue (5.9 g) on silica gel (35.0 g) gave: Fr. 1 (140 ml hexane), 2.8 g oil; Fr. 2 (80 ml benzene), 3.1 g **5P$_8$** as colorless oil, yield 42%.

$C_8H_{20}O_3Si$ (192.34) Calc. C 49.96 H 10.48% Found C 49.81 H 10.54%

(5,8-Dioxanonyl)-dimethyl-silanol (**5P$_9$**). A two phase system, consisting of 12.5 g (50.0 mmol) (5,8-dioxanonyl)-dimethyl-ethoxy-silane (**4P$_9$**), in 60 ml ether and 50 mg NH_4Cl in 70 ml water, was vigorously agitated for 20 h at RT.; the etheric phase was separated, dried over Na_2SO_4, filtered and ether evaporated. Chromatography of the residue (5.9 g) on silica gel (120 g) gave: Fr. 1 (220 ml hexane/benzene 95:5), 0.1 g oil; Fr. 2 (280 ml of ether), 12.2 g **5P$_9$** as colorless oil; yield 94.5%.

$C_9H_{22}O_3Si$ (206.36) Calc. C 52.39 H 10.75% Found C 52.49 H 10.70%

(6,9-Dioxadecyl)-dimethyl-silanol (**5P$_{10}$**) (*cf.* prepn. **5A$_{22}$**). After hydrolysis of 6.0 g (25.0 mmol) (6,9-dioxadecyl)-dimethyl-chloro-silane (**3P$_{10}$**) in 50 ml ether in the two-phase system described (2.11 g $NaHCO_3$ (25 mmol) in 100 ml water/50 ml ether) and working-up, chromatography of the evaporation residue (4.9 g colorless oil) on silica gel (40 g) gave: Fr. 1 (400 ml hexane), 2.2 g oil; Fr. 2 (250 ml hexane/ether 1:1), 2.70 g **5P$_{10}$** as colorless oil, yield 49%.

$C_{10}H_{24}O_3Si$ (220.38) Calc. C 54.50 H 10.98% Found C 54.33 H 11.06%

(5,8,11,14,17-Pentaöxaöctadecyl)-dimethyl-silanol (**5P$_{18}$**). A solution of 11.0 g non-purified (5,8,11,14,17-pentaöxaöctadecyl)-dimethyl-chloro-silane (**3P$_{18}$**) in 40 ml anhydrous ether was added dropwise at 0° to a vigorously agitated two phase system composed of 50 ml ether and 2.65 g $NaHCO_3$ in 50 ml of water. After 15 min the ether phase was separated, dried over Na_2SO_4, filtered and the ether evaporated. The residue (10 g) was taken up in cyclohexane and purified by chromatography on silica gel (80 g): Fr. 1 (360 ml cyclohexane), 1.5 g oil; Fr. 2 (150 ml ether), 8.4 g colorless oil. After evaporation of the solvent, Fr. 2 contained 95% of **5P$_{18}$** (purity determined by GC.). Further purification was not possible since the product could neither be crystallized nor distilled. The NMR.-spectrum gave evidence for the expected structure. Yield: ≃ 75% based on **2P$_{18}$**.

Physical properties of the substances synthesized. –

Spectra. The spectra of each substance synthesized conformed to the structure expected. The following spectrophotometers were used: IR.: *Perkin-Elmer* spectrograph 125 (optics: grating); ^{1}H-NMR.: *Varian* model T-60 (60 MHz); UV.: *Beckmann* registrating spectrophotometer type DK-24.

A detailed description of the spectra will be sent to anyone interested on request.

Other properties. The individual densities indicated, corrected for vacuum, are the resp. means of two measurements, each on a sample of about 100 mg (limits of error for mean ± 0.002). The refractive indices were determined with a thermostated (20.0 ± 0.2°) *Zeiss* refractometer (system *Abbé*), limit of error ± 0.0003). See summary, Table 2.

Table 2. *Physical properties*

Substance		Elementary formula	mol-wt	m.p. °C	d^{20} g cm^{-3}	n_D^{20}
$\mathbf{1P}_8$	1-bromo-4,7-dioxaöctane	$C_6H_{13}BrO_2$	197.08		1.206	1.4548
$\mathbf{1P}_9$	1-bromo-5,8-dioxanonane	$C_7H_{15}BrO_2$	211.10		1.206	1.4577
$\mathbf{1P}_{18}$	1-bromo-5,8,11,14,17-pentaoxaöctadecane	$C_{13}H_{27}BrO_5$	343.25		1.200	1.4650
$\mathbf{2P}_5$	4-oxapent-1-ene	C_4H_8O	72.11		0.776	1.3790
$\mathbf{2P}_6$	5-oxahex-1-ene	$C_5H_{10}O$	86.13		0.782	1.3878
$\mathbf{2P}_7$	6-oxahept-1-ene	$C_6H_{12}O$	100.16		0.784	1.3972
$\mathbf{2P}_8$	4,7-dioxaöct-1-ene	$C_6H_{12}O_2$	116.16		0.892	1.4131
$\mathbf{2P}_{10}$	6,9-dioxadec-1-ene	$C_8H_{16}O_2$	144.22		0.877	1.4187
$\mathbf{2P}_{18}$	5,8,11,14,17-pentaöxaöctadec-1-ene	$C_{13}H_{26}O_5$	262.35		0.981	1.4423
$\mathbf{3A}_3$	propyl-dimethyl-chloro-silane	$C_5H_{13}ClSi$	136.70		0.868	1.4145
$\mathbf{3A}_6$	hexyl-dimethyl-chloro-silane	$C_8H_{19}ClSi$	178.78		0.873	1.4307
$\mathbf{3A}_{10}$	decyl-dimethyl-chloro-silane	$C_{12}H_{27}ClSi$	234.89		0.912	1.4433
$\mathbf{3A}_{14}$	tetradecyl-dimethyl-chloro-silane	$C_{16}H_{35}ClSi$	291.00		0.890	1.4482
$\mathbf{3A}_{18}$	octadecyl-dimethyl-chloro-silane	$C_{20}H_{43}ClSi$	347.11	28–30		
$\mathbf{3A}_{22}$	docosyl-dimethyl-chloro-silane	$C_{24}H_{51}ClSi$	403.21	41–43		
$\mathbf{3P}_5$	(4-oxapentyl)-dimethyl-chloro-silane	$C_6H_{15}ClOSi$	166.73		0.945	1.4261
$\mathbf{3P}_6$	(5-oxahexyl)-dimethyl-chloro-silane	$C_7H_{17}ClOSi$	180.75		0.932	1.4331
$\mathbf{3P}_7$	(6-oxaheptyl)-dimethyl-chloro-silane	$C_8H_{19}ClOSi$	194.78		0.921	1.4357
$\mathbf{3P}_8$	(4,7-dioxaöctyl)-dimethyl-chloro-silane	$C_8H_{19}ClO_2Si$	210.78		0.969	1.4371
$\mathbf{3P}_{10}$	(6,9-dioxadecyl)-dimethyl-chloro-silane	$C_{10}H_{23}ClO_2Si$	238.83		0.966	1.4400
$\mathbf{4P}_9$	(5,8-dioxanonyl)-dimethyl-ethoxy-silane	$C_{11}H_{26}O_3Si$	234.42		0.902	1.4251
$\mathbf{5A}_1$	trimethylsilanol	$C_3H_{10}OSi$	90.20		0.815	1.3896
$\mathbf{5A}_2$	ethyl-dimethyl-silanol	$C_4H_{12}OSi$	104.23		0.828	1.4004
$\mathbf{5A}_3$	propyl-dimethyl-silanol	$C_5H_{14}OSi$	118.26		0.833	1.4147
$\mathbf{5A}_6$	hexyl-dimethyl-silanol	$C_8H_{20}OSi$	160.34		0.838	1.4296
$\mathbf{5A}_{10}$	decyl-dimethyl-silanol	$C_{12}H_{28}OSi$	216.44		0.857	1.4401
$\mathbf{5A}_{14}$	tetradecyl-dimethyl-silanol	$C_{16}H_{36}OSi$	272.55	33–34		
$\mathbf{5A}_{18}$	octadecyl-dimethyl-silanol	$C_{20}H_{44}OSi$	328.66	50–51		
$\mathbf{5A}_{22}$	docosyl-dimethyl-silanol	$C_{24}H_{52}OSi$	384.77	65–66		
$\mathbf{5P}_5$	(4-oxapentyl)-dimethyl-silanol	$C_6H_{16}O_2Si$	148.28		0.884	1.4290
$\mathbf{5P}_6$	(5-oxahexyl)-dimethyl-silanol	$C_7H_{18}O_2Si$	162.31		0.878	1.4342
$\mathbf{5P}_7$	(6-oxaheptyl)-dimethyl-silanol	$C_8H_{20}O_2Si$	176.33		0.875	1.4374
$\mathbf{5P}_8$	(4,7-dioxaöctyl)-dimethyl-silanol	$C_8H_{20}O_3Si$	192.34		0.958	1.4400
$\mathbf{5P}_9$	(5,8-dioxanonyl)-dimethyl-silanol	$C_9H_{22}O_3Si$	206.37		0.964	1.4405
$\mathbf{5P}_{10}$	(6,9-dioxadecyl)-dimethyl-silanol	$C_{10}H_{24}O_3Si$	220.39		0.940	1.4439
$\mathbf{5P}_{18}$	(5,8,11,14,17-pentaöxaöctadecyl)-dimethyl-silanol	$C_{15}H_{34}O_6Si$	338.52		1.068	1.4470

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75. Photochemische Reaktionen

88. Mitteilung [1]

Zur Photochemie des Iso-methyl-β,(*E*)-jonon-epoxids[1]

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(22. I. 76)

Photolysis of iso-methyl-β,(*E*)-ionone-epoxide. — Summary. On n,π^*-excitation ($\lambda \geqslant 347$ nm) the title compound **7** isomerizes to the (*Z*)-enone-epoxide **8**, which yields the bicyclic alcohol **9** in a second photochemical step. The photoisomerization **8** → **9** is a further example for the influence of a methyl substituent at C(α) of an enone-chromophore on the nature of the photochemical processes.

On UV. irradiation in the presence of traces of hydrochloric acid **7** gives quantitatively the furane **10**.

1. Einführung. – Wie wir kürzlich am Beispiel des Iso-methyl-α,(*E*)-jonons (**4**) zeigten [2], kann das photochemische Verhalten α,β-ungesättigter Ketone durch den Ersatz des C(α)-Wasserstoffatoms des Enon-chromophors durch eine Methylgruppe stark verändert werden (siehe *Schema 1*). Wird bei der Bestrahlung des α,(*E*)-Jonons (**1**) zunächst reversible (*E*/*Z*)-Isomerisierung (**1** $\rightleftarrows$ **2**) und dann irreversible Photoisomerisierung des α,(*Z*)-Jonons (**2**) unter Abstraktion des H–C(γ) zum Keton **3** beobachtet, so findet man für das Isomethyl-α,(*E*)-jonon (**4**) zwar in einem ersten Photoprozess ebenfalls reversible (*E*/*Z*)-Isomerisierung (**4** $\rightleftarrows$ **5**), bei fortgesetzter Bestrahlung jedoch die irreversible Photoisomerisierung des Iso-methyl-α,(*Z*)-jonons (**5**) zum Dihydrofuran **6**.

Im Rahmen von Versuchen zur Photochemie vinyloger Epoxyketone des Jonontypus [3–5] schien es von Interesse zu überprüfen, ob ein ähnlicher Methylgruppeneffekt bei der Bestrahlung des Iso-methyl-β,(*E*)-jonon-epoxids (**7**) [4] beobachtet

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[1] Für den systematischen Namen dieser Verbindung s. Tabelle 1, S. 734.