*Journal of Organometallic Chemistry*
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

# ACETOXYSILOXANE OLIGOMERS
## I. THE INTERACTION OF ACETIC ANHYDRIDE WITH CYCLIC DIMETHYLSILOXANES

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(Received June 19th, 1967)

In the field of organosilicon chemistry much attention has lately been given to siloxane oligomers with functional end groups. This is due to the possibility of their use for preparing polysiloxanes of definite structure, having given properties.

In the series of siloxane oligomers $\alpha,\omega$-diacetoxypolydiorganosiloxanes containing highly reactive end groups are of special interest. In the literature there has been described a method of producing acetoxysiloxanes by treating acetic anhydride with siloxanes containing other functional end groups, *i.e.* halogen atom, alkoxyl or hydroxyl[1-3]. However this method requires the use of halogen-, alkoxyl- or hydroxyl-containing siloxane oligomers, the synthesis of which is rather difficult.

In 1958 Valade[4] reported the preparation of trimethylacetoxysilane in yields up to 90% by cleavage of hexamethyldisiloxane by acetic anhydride in the presence of anhydrous zinc chloride. Triacetoxyboron was also suggested as a catalyst.

The method of producing acetoxy derivatives by cleavage of organosiloxanes has been extended by Bailey and O'Konnors' to cyclic compounds[5]. However, boiling octamethylcyclotetrasiloxane with acetic anhydride in molar ratio 1 : 5 in the presence of concentrated $H_2SO_4$ for 40 hours gave only 60% conversion of the initial cyclic compound. By distillation of the reaction product after neutralization dimethyldiacetoxysilane, 1,3-diacetoxytetramethyldisiloxane, and 1,5-diacetoxyhexamethyltrisiloxane were obtained in ratio of 20 : 33 : 17 by weight.

Since the above results could not be considered wholly satisfactory we have undertaken a detailed investigation of the conditions under which cyclodiorganosiloxanes are cleaved by acetic acid derivatives. (Early results have been briefly reported[6])

Experiments demonstrated that cleavage of cyclodimethylsiloxanes by acetic anhydride did not occur in the absence of a catalyst at atmospheric pressure. Distillation of an equimolar mixture of $(Me_2SiO)_4$ and $Ac_2O$ after heating for 9 hours at 150° gave unchanged initial compounds. Anhydrous ferric chloride proved to be an active catalyst for cleavage; in the presence of approximately 1% by weight of $FeCl_3$ at 150°, cyclodimethylsiloxanes undergo complete conversion to $\alpha,\omega$-acetoxyoligodimethylsiloxanes in 1.5–4 hours, the time needed being independent of the molar ratio of cyclic compound to anhydride. (Acetic anhydride is consumed to about 80%.)

On the other hand, the reagent ratio affects the composition of acetoxysilanes, $AcO(Me_2SiO)_nAc$, obtained (Table 1).

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* Deceased August 6th, 1967.

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followed by heterolytic cleavage of a silicone bond (refs. 10, 11 etc). The reasons for this are:

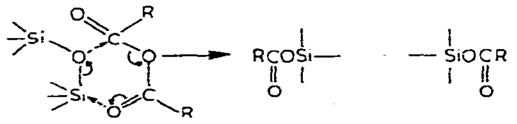
(1) Regeneration of $FeCl_3$ seems to be impossible under conditions of cleavage product interactions and limiting polymerization of cyclosiloxanes with ferric chloride in the presence of acetic anhydride. Ferric acetates are significantly less active than chlorides. Thus we found that there was no interaction between $D_4$ and $Ac_2O$ (1 : 2) in the presence of $Fe(OAc)_2$. When $Fe(OAc)_3$ is used the initial compounds remain essentially unchanged; about 6% of compounds with b.p. up to 320° (*i.e.* $n \simeq 7$) and about 2% of higher boiling compounds were formed in 4 hours, whereas in the presence of $FeCl_3$, $D_4$ is completely consumed in the reaction with AcOAc within the same time period.

(2) Acetyl chloride which may form in reaction of $Ac_2O$ with $FeCl_3$ or with compounds formed in the cleavage of cyclosiloxanes by ferric chlorides does not surpass acetic anhydride in activity (reaction of AcX with cyclodimethylsiloxanes is reported in a special paper)

(3) $ZnCl_2$ which is incapable of cleaving siloxane bonds, at least under such mild conditions, acts as an effective catalyst.

(4) Under more severe conditions, cleavage occurs either in the presence of traces of compounds such as Lewis acids (steel autoclave) or in the absence of such a catalyst (glass ampoule).

On the basis of the above considerations and experimental results one may assume that the cleavage involves formation of six-membered cyclic coordination intermediate products formed by interaction of cyclic (or linear) siloxanes with acetic anhydride or its complex with Lewis acid, as in eqns. (1) and (2) in which X is halogen,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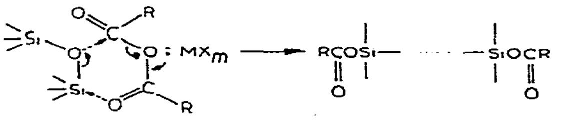
(2)

and $m$ is the valency of M (M = Fe, Zn; R = $CH_3$). Thus, metal halides act as catalysts due to the formation of complexes such as RCOY : $MX_m$ with Y = OCOR these complexes are mixed anhydrides of weak protonic acid, RCOOH, and the strong acid, RCOOH : $MX_m$. A constant concentration level of such complexes in the system is maintained because of incomplete conversion of acetic anhydride in the course of the reaction and the absence of side reaction products causing $MX_m$ consumption (such as are observed in catalytic cleavage of siloxanes by halosilanes[12]).

## EXPERIMENTAL

Cleavage runs with cyclosiloxanes and their mixtures in the presence of catalysts at atmosphere pressure or in the absence of catalysts under pressure were carried out under similar conditions. Given below are the most typical examples.

### 1. *Catalytic cleavage*

A 250 ml, two-necked flask equipped with a thermometer and a reflux condenser with a calcium chloride tube and a mechanical stirrer, was charged with 74.09 g of octamethylcyclotetrasiloxane (0.25 mole), 51.04 g of acetic anhydride (0.5 mole) and 1.2 g of anhydrous $FeCl_3$ (about 1 % by weight of initial mixture). The mixture was heated in an oil both to 150° and kept at a temperature of 150±2° for 4 h. After cooling, the reaction mixture was placed in the pot of glass-packed distillation column with an efficiency of about 10 theoretical plates and was fractionated in a vacuum. The distillation gave 12 g of acetic anhydride (23.5 % of the initial amount), 5.9 g of dimethyldiacetoxysilane (4.7 % by weight of the initial mixture); 25.0 g of 1,3-diacetoxytetramethyldisiloxane (20 %); 18.0 g of 1,5-diacetoxyhexamethyltrisiloxane (14.4 %); 12.1 g of 1,7-diacetoxyoctamethyltetrasiloxane (9.7 %); 10.0 g of 1,9-diacetoxydecamethylpentasiloxane (8.0 %); 17.52 g (14 %) of high boiling products. Properties of individual oligomers are given in Table 4.

TABLE 4

PROPERTIES OF ACETOXYSILOXANE OLIGOMERS, $AcO(Me_2SiO)_nAc$

| *n* | *B.p.* (°*C/mm*) | $n_D^{20}$ | $d_4^{20}$ | *Found (calcd.)* (%) | | |
|---|---|---|---|---|---|---|
| | | | | $MR_D$ | *AcO* | *Mol.wt.* |
| 1 | 56–7/12 | 1.4001 | 1.0528 | 40.60<br>(41.06) | 66.93<br>(67.10) | 188.4<br>(176.3) |
| 2 | 80–2/10 | 1.4002 | 1.0196 | 59.56<br>(59.76) | 47.87<br>(47.18) | 256.4<br>258.5<br>(250.4) |
| 3 | 102–3/10 | 1.4001 | 1.0057 | 78.26<br>(78.46) | 36.57<br>(36.41) | 317.0<br>331.7<br>(324.6) |
| 4 | 131/10 | 1.4002 | 1.0046 | 96.26<br>(97.15) | 29.04<br>30.37<br>(29.63) | 391.7<br>392.9<br>(398.7) |
| 5 | 142/9 | 1.4003 | 0.9985 | 114.89<br>(115.85) | 24.99<br>(24.99) | 477.5<br>470.9<br>(472.9) |

### 2. *Cleavage run carried out in an autoclave*

A 0.5-l, steel autoclave was charged with 74.09 g of $D_4$ and 51.04 g of $Ac_2O$. The autoclave was heated in an electrical oven at 250–265° for 2.5 h (12–15 atm). After cooling, the reaction mixture was placed in a distillation still and fractionated. The following products were obtained: 18.8 g of $Ac_2O$ (36 % of the initial amount); 8.7 g (7 %) of $Me_2Si(OAc)_2$ (b.p. 118–121°/43 mm, AcO 66.50 %, mol.wt. 187.3); 27.5 g (22 %) of oligomer $n=2$ (b.p. 87°/9 mm, AcO 46.40 %, mol.wt. 257.1); 13.76 g (11 %) of oligomer $n=3$ (b.p. 110°/9 mm, AcO 35.83 %; mol.wt. 330.7); 11.26 g (9 %) of oligomer $n=4$ (b.p. 134–136°/9 mm, AcO 29.91%, mol.wt. 400.1); 8.5 g (6.8%) of oligomer $n=5$ (b.p. 160°/9 mm, AcO 25.03, mol.wt. 463.4); 13.9 g (11.1%) of high-boiling products; 10.38 g (8.3%) of intermediate fractions.

### 3. *Cleavage run carried out in an ampoule*

A 150-ml glass ampoule was charged with the 18.6 g (0.062 mole) of octamethylcyclotetrasiloxane and 12.75 g (0.124 mole) of acetic anhydride. The ampoule was cooled in acetone/dry ice mixture, evacuated, sealed and placed in metallic cylinder containing several pieces of dry ice after which it was heated in a muffle furnace at 250–260° for 2.5 h. The reaction products of 3 ampoules were poured together and fractionated in a distillation column. The following products were obtained: 14.97 g of acetic anhydride (39% of the initial amount); 5.26 g of octamethylcyclotetrasiloxane (9.4% of the initial amount), b.p. 52–57°/8 mm; 1.5 g of dimethyldiacetoxysilane (1.6% by wt. of the initial mixture), b.p. 50–52°/8 mm; 13.2 g of 1,3-tetramethyldiacetoxydisiloxane (14.3%), b.p. 91–93°/11 mm, AcO 46.6%; 9.06 g of 1,5-diacetoxyhexamethyltrisiloxane (10%); b.p. 116°/11 mm, AcO 37.22%; 8.87 g of 1,7-diacetoxymethyltetrasiloxane (9.8%), b.p. 118–120°/3 mm, AcO 30.5%; 8.7 g of 1,9-diacetoxydecamethylpentasiloxane (9.6%), b.p. 135–146°/2.8 mm, AcO 25.36%; 14.95 g (16.4%) of high boiling products.

### 4. *Hydrolysate cleavage*

*a. Hydrolysis.* A round-bottomed flask containing 27.9 g (1.55 moles) of water was placed in a water bath and charged through a dropping funnel with 100 g (0.77 mole) of pure dimethyldichlorosilane for 40 min with stirring. The mixture was allowed to stand overnight, then an acid layer was separated and the mixture was washed with water to neutral point, dried by $CaCl_2$ and filtrated.

*b. Cleavage.* To 57.44 g of the above hydrolysate 39.54 g of acetic anhydride (0.5 mole $Ac_2O$ per $Me_2SiO$ unit) and 0.97 g of $FeCl_3$ (1%) were added. The mixture was refluxed in a flask at 130–145° for 2 h. After cooling, the mixture was filtered off through the Schott filter No 2.

*c. Distillation.* The filtrate (90.54 g) was used for distillation. The following products were obtained: 8.14 g of acetic anhydride (20.6% of initial amount); 6.71 g (6.9%) of $Me_2Si(OAc)_2$, b.p. 72°/15 mm; 17.6 g (18.1%) of oligomer $n=2$, b.p. 93–96°/15 mm; 15.2 g (15.7%) of oligomer $n=3$, b.p. 117–119°/13 mm; 12.67 g (12.7%) of oligomer $n=4$, b.p. 108–116°/3 mm; 5.0 g (5.1%) of oligomer $n=5$, b.p. 141–144°/4 mm; 9.25 g (9.5%) of high-boiling products; 3.6 g (3.7%) of intermediate fractions.

## SUMMARY

Cleavage of cyclodimethylsiloxanes by acetic anhydride in the presence of catalysts of Lewis acid-type ($FeCl_3$, $ZnCl_2$) or in the absence of catalysts under pressure (in an autoclave or in glass ampoule) has been investigated.

The possibility of formation of $\alpha,\omega$-diacetoxypolydimethylsiloxanes of the general formula $CH_3COO[(CH_3)_2SiO]_nCOCH_3$ has been established. For producing diacetoxysiloxane oligomers of $n=2$ to 5 the most favourable ratio of initial reagents was found to be 0.5 mole of acetic anhydride per $R_2SiO$ unit of cyclosiloxanes. A cleavage mechanism is proposed.

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