[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF BUFFALO]

# STUDIES IN SILICO-ORGANIC COMPOUNDS. XXIII. ACYLOXY DERIVATIVES OF THE β-CHLOROETHYLTRIALKOXYSILANES

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*Received April 18, 1952*

## INTRODUCTION

As far back as 1868, Friedel and Ladenburg (1) prepared a "new type" of orthoester, silicon tetraacetate, by the reaction of acetic acid with silicon tetrachloride. When the anhydride was used, acetyl chloride was a by-product. Acetate esters were later obtained by interchange of acetoxyl for alkoxyl using acetic anhydride (2), by replacement of bromine attached to silicon by acetate through the use of silver acetate (3), by slow prolonged boiling of acetate esters of the normal type with silicon tetrachloride (4), and by reaction of silicon tetrachloride with sodium acetate (5). Montana (6) found that the tetraacetate decomposed into silicon dioxide and acetic anhydride. Excess silicon tetrachloride plus acetic anhydride gave acetyl chloride as a by-product. Tetraethoxysilane was found to react with propionic anhydride (7) yielding triethoxypropionoxysilane and diethoxydipropionoxysilane. Whitmore (8) arrived at the acetate through the reaction of triethylsilanol with acetic anhydride.

## DISCUSSION

Replacement of alkoxyl in β-chloroethyltrialkoxysilanes has been realized through the medium of acetic anhydride. Both mono- and di-substitution were observed by using appropriate molar proportions. When the proportions favored the mono-substituted product over the di-, none of the latter was isolated. When proportions favored the di-substituted product, none of the mono- could be separated in a state sufficiently pure for identification. The conservative yields obtained are attributed to the difficulty of separation and to possible decomposition, as well as to the possibility that these may be equilibrium reactions.

## EXPERIMENTAL

*β-Chloroethyldimethoxyacetoxysilane.* β-Chloroethyltrimethoxysilane (29 g., 0.157 mole) was allowed to react with 17 g. (0.166 mole) of acetic anhydride by keeping the mixture at slow reflux for five hours before fractionation. The product was β-chloroethyldimethoxyacetoxysilane, b.p. 96.0–97.5° (9 mm.), $n_D^{25}$ 1.4211, $d^{25}$ 1.161, 7 g., yield 21%.

*Anal.* Calc'd for $C_6H_{13}ClO_4Si$: Si, 13.19; Cl, 16.67; M.R., 46.66.

Found: Si, 13.12, 13.04; Cl, 16.44, 16.19; M.R., 46.46.

Acetic anhydride was allowed to react with other selected β-chloroethyltrialkoxysilanes in a similar manner using suitable proportions of reagents and the optimum reaction time. Data covering preparations, yields, and analyses are found in Table IV. Table IV also contains similar data covering the propionoxy-substituted derivatives.

*β-Chloroethyltrialkoxysilanes* were prepared in accordance with methods already in the

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[1] Presented by the first author as part of a thesis submitted as partial requirement for the degree of Doctor of Philosophy at the University of Buffalo.

# TABLE I

## PHYSICAL PROPERTIES OF THE $\beta$-CHLOROETHYLACETOXYDIALKOXYSILANES

| NO. | ALKOXYL | B.P., °C. | MM. | $n_D^{25}$ | $d_4^{25}$ |
|---|---|---|---|---|---|
| 1 | $CH_3O$ | 96.0–97.5 | 9 | 1.4211 | 1.161 |
| 2 | $C_2H_5O$ | 117.5 | 20 | 1.4184 | 1.079 |
| 3 | $n$-$C_3H_7O$ | 122.5 | 6.5 | 1.4228 | 1.052 |
| 4 | $n$-$C_4H_9O$ | 144.0 | 8 | 1.4265 | 1.018 |
| 5 | $n$-$C_5H_{11}O$ | 155.5 | 5 | 1.4311 | 1.000 |

# TABLE II

## PHYSICAL PROPERTIES OF THE $\beta$-CHLOROETHYLDIACETOXYALKOXYSILANES

| No. | ALKOXYL | B.P., °C. | MM. | $n_D^{25}$ | $d_4^{25}$ |
|---|---|---|---|---|---|
| 6 | $CH_3O$ | 114–115 | 8 | 1.4216 | 1.190 |
| 7 | $C_2H_5O$ | 119.5–120.5 | 8 | 1.4243 | 1.157 |
| 8 | $n$-$C_3H_7O$ | 115.3 | 3 | 1.4241 | 1.129 |

# TABLE III

## PHYSICAL PROPERTIES OF THE $\beta$-CHLOROETHYLPROPIONOXYDIALKOXYSILANES

| No. | ALKOXYL | B.P., °C. | MM. | $n_D^{25}$ | $d_4^{25}$ |
|---|---|---|---|---|---|
| 9 | $CH_3O$ | 98–99 | 7 | 1.4206 | 1.124 |
| 10 | $C_2H_5O$ | 118–119 | 11 | 1.4206 | 1.068 |
| 11 | $n$-$C_3H_7O$ | 139.0–139.5 | 10 | 1.4252 | 1.035 |

# TABLE IV

## EXPERIMENTAL DATA—ACYLOXY DERIVATIVES

| NUMBER OF COMPOUND[a] | MOLAR QUANTITIES | | TIME, HOURS | YIELD, % | Si CALC'D | FOUND | Cl CALC'D | FOUND | M.R. CAL'CD | FOUND |
|---|---|---|---|---|---|---|---|---|---|---|
| | SILANE | ANHYDRIDE | | | | | | | | |
| 1 | 0.157 | 0.166 | 5 | 21 | 13.19 | 13.20,<br>13.04 | 16.67 | 16.44,<br>16.38 | 46.66 | 46.46 |
| 2 | .110 | .110 | 14 | 30 | 11.66 | 11.65,<br>11.71 | 14.73 | 14.37,<br>14.34 | 55.92 | 56.28 |
| 3 | .092 | .093 | 18 | 24 | 10.44 | 10.47,<br>10.62 | 13.20 | 13.19,<br>13.03 | 65.18 | 65.03 |
| 4 | .088 | .088 | 37 | 14 | 9.45 | 9.35,<br>9.55 | 11.95 | 11.87,<br>11.87 | 74.44 | 74.81 |
| 5 | .091 | .098 | 24 | 31 | 8.64 | 8.63,<br>8.80 | 10.91 | 10.88,<br>11.04 | 83.70 | 83.90 |
| 6 | .373 | .705 | 42 | 15 | 11.66 | 11.48,<br>11.51 | 14.73 | 14.73,<br>14.62 | 51.39 | 51.36 |
| 7 | .142 | .470 | 4.5 | 22 | 11.02 | 10.99,<br>11.05 | 13.92 | 13.98,<br>13.78 | 55.92 | 56.22 |
| 8 | .126 | .490 | 53 | 34 | 10.44 | 10.38,<br>10.35 | 13.20 | 13.20,<br>13.20 | 60.55 | 60.86 |
| 9 | .243 | .245 | 13 | 14 | 12.37 | 12.29,<br>12.27 | 15.64 | 15.77 | 51.29 | 51.10 |
| 10 | .110 | .111 | 20 | 31 | 11.02 | 11.04,<br>11.12 | 13.92 | 13.99,<br>14.09 | 60.55 | 60.44 |
| 11 | .085 | .085 | 24 | 24 | 9.92 | 9.91,<br>9.97 | 12.54 | 12.60,<br>12.43 | 69.81 | 69.88 |

[a] From Tables I, II, and III.

literature (9). Physical properties were found in agreement with those recorded (9). *Acetic* and *propionic anhydrides* were purchased from reliable sources and also found to have satisfactory physical properties.

*Silicon* and *chlorine* were determined in accordance with methods already in the literature (9). In certain instances it was found that the silica was not perfectly white after repeated treatment with fuming nitric acid. A procedure was adopted according to which the fuming nitric acid (about 1 cc.) was added carefully to the substance. Fuming sulfuric acid (5 to 10 drops) was added after the reaction had subsided. Final treatment and ignition were then carried out as before.

*Molar refractions* were calculated by the method of Warrick (10).

## SUMMARY

1. Acetic anhydride has been found to react with β-chloroethyltrimethoxysilane and its triethoxy-, tri-*n*-propoxy, tri-*n*-butoxy, and tri-*n*-amoxy homologs. Compounds of the type $CH_3COOSi(OR)_2CH_2CH_2Cl$ have been isolated from all five trialkoxysilanes. The methoxy, ethoxy, and *n*-propoxy homologs gave, in addition, diacetates.

2. Propionic anhydride reacts with the first three of the above mentioned compounds to form compounds of the type $C_2H_5COOSi(OR)_2CH_2CH_2Cl$.

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