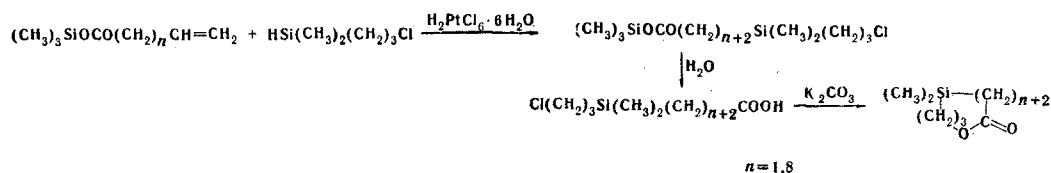
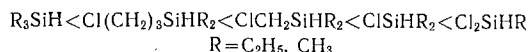


The synthesis of 4-silalactones was accomplished by the addition of γ -chloropropyldimethylsilane to trimethylsilyl esters of unsaturated acids. It was shown that γ -chloropropyldimethylsilane adds to these esters considerably more slowly than does α -chloromethyldimethylsilane.

We recently described routes to the synthesis of 1- and 2-silalactones [1-3].* In the present study we have for the first time obtained several 4-silalactones (see Table 1) via the scheme previously used for the synthesis of 2-silalactones.



γ -Chloropropyldimethylsilane adds considerably more slowly than α -chloromethyldimethylsilane to the trimethylsilyl esters of any unsaturated acids, and the yields are poorer. Incidentally, we estimated the relative reactivities of other hydrosilanes in this reaction, and they are arranged in the following order with respect to their activities:



In contrast to the analogous α -(chloromethyldimethylsilyl)-substituted compounds, the cyclization of ω -(γ -chloropropyldimethylsilyl)-substituted carboxylic acids proceeds under more severe conditions and gives comparatively low yields (30-50%).

The nine-membered silalactone (X) obtained in this manner is monomeric and stable on long storage. On the other hand, the 14-membered lactone (XI) readily polymerizes on brief storage to give an oligomer with a molecular weight of ~ 2000 .

EXPERIMENTAL

Trimethylsilyl ω -(γ -Chloropropyldimethylsilyl)butyrate (I). A 28-g (0.2 mole) sample of γ -chloropropyldimethylsilane was added dropwise in the course of 2 h to 32 g (0.2 mole) of trimethylsilyl vinylacetate in the presence of 0.1 ml of 0.1 M $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution in isopropyl alcohol. The reaction mixture was refluxed for 4 h (the temperature at the end of the heating was 211°) and then vacuum-distilled to give 31 g of I. Compounds II-V (see Table 1) were similarly synthesized.

ω -(γ -Chloropropyldimethylsilyl)butyric Acid (VI). Water (50 ml) was added with stirring in the course of 1 h to 28 g (0.2 mole) of I, and the reaction mixture was stirred and refluxed for 1 h. The aqueous layer was separated from the organic layer and extracted with 50 ml of ether. The organic layer and the ether ex-

*The position of the silicon atom in the silalactone ring was reckoned from the ester oxygen atom in the direction counter to the carbonyl group.

State Scientific-Research Institute of the Chemistry and Technology of Heteroorganic Compounds, Moscow. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 6, pp. 748-750, June, 1972. Original article submitted April 13, 1971.

© 1974 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00.

TABLE 1. Physical Constants and Yields of the Compounds Obtained

| No. | Compound | Bp, °C (mm) | d_4^{20} | n_D^{20} | MR_D | Empirical formula | Found, % | | | | Calc., % | | | | Yield, % |
|------|------------------------------------------------------------------------------------------------------------------|------------------|------------|------------|--------|----------------------|----------|------|------|------|----------|------|------|------|----------|
| | | | | | | | C | H | Cl | Si | C | H | Cl | Si | |
| I | $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2(\text{CH}_2)_3\text{COOSi}(\text{CH}_3)_3$ | 120—121 (2.5) | 0.9581 | 1.4498 | 82.10 | 82.60 | 48.9 | 8.9 | 11.8 | 18.7 | 48.8 | 9.2 | 12.0 | 19.0 | 53 |
| II | $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2(\text{CH}_2)_2\text{COOSi}(\text{CH}_3)_3$ | 88—90 (1) | 0.9543 | 1.4471 | 77.80 | 77.89 | 47.1 | 8.9 | — | 19.9 | 47.0 | 9.0 | 12.6 | 20.0 | 40 |
| III | $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{COOSi}(\text{CH}_3)_3$ | 113—114 (3) | 0.9612 | 1.4477 | 82.11 | 82.60 | 48.5 | 9.2 | 12.2 | 18.9 | 48.8 | 9.2 | 12.0 | 19.0 | 47 |
| IV | $\text{ClCH}_2\text{Si}(\text{CH}_3)_2(\text{CH}_2)_2\text{COOSi}(\text{CH}_3)_3$ | 180—185 (3) | 0.9380 | 1.4533 | 105.27 | 105.78 | — | — | 9.8 | — | — | — | 9.7 | — | 64 |
| V | $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2(\text{CH}_2)_{10}\text{COOSi}(\text{CH}_3)_3$ | 192—193 (1) | 0.9344 | 1.4555 | 114.28 | 115.00 | — | — | 9.0 | 14.7 | — | — | 9.0 | 14.3 | 54 |
| VI | $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2(\text{CH}_2)_3\text{COOH}$ | 144—145 (2.5) | 1.0361 | 1.4677 | 59.75 | 59.89 | — | — | 15.6 | 12.5 | — | — | 15.9 | 12.6 | 81 |
| VII | $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{COOH}$ | 142—143 (1) | 1.0378 | 1.4668 | 59.55 | 59.79 | 48.3 | 8.3 | 15.8 | 12.2 | 48.5 | 8.6 | 15.9 | 12.6 | 69 |
| VIII | $\text{ClCH}_2\text{Si}(\text{CH}_3)_2(\text{CH}_2)_{10}\text{COOH}$ | 197—200 (3.5) | 0.9823 | 1.4638 | 82.73 | 83.13 | — | — | 11.6 | 9.8 | 57.4 | 10.0 | 12.1 | 9.6 | 93 |
| IX | $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2(\text{CH}_2)_{10}\text{COOH}$ | 205—206 (1) | 0.9676 | 1.4672 | 92.10 | 92.45 | — | — | 10.5 | — | — | — | 11.1 | — | 72 |
| X | $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2(\text{CH}_2)_2\text{CH}_2$ $\text{O} \text{---} \text{C=O}$ | 108—110 (18) | 0.9928 | 1.4691 | 52.30 | 52.13 | 58.1 | 9.7 | — | 14.3 | 58.0 | 9.7 | — | 15.1 | 33 |
| XI | $\text{CH}_2\text{Si}(\text{CH}_3)_2(\text{CH}_2)_3\text{CH}_2$ $\text{O} \text{---} \text{C=O}$ | 108—112 (1) | 0.9493 | 1.4707 | 75.45 | 76.55 | 65.5 | 10.8 | — | 10.8 | 65.6 | 11.0 | — | 10.9 | 70 |
| XII | $(\text{CH}_3)_3\text{Si}(\text{CH}_3)_2(\text{CH}_2)_3\text{CH}_2$ $\text{O} \text{---} \text{C=O}$ | 145—147 (3) | 0.9300 | 1.4687 | 85.13 | 85.66 | 67.1 | 11.5 | — | 10.4 | 67.5 | 11.3 | — | 11.2 | 53 |
| XIII | $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2(\text{CH}_2)_3\text{COCl}$ | 148—149 (12) | 1.0547 | 1.4700 | 63.80 | 63.07 | 44.7 | 7.5 | 29.3 | 11.4 | 44.8 | 7.5 | 29.4 | 11.6 | 77 |

tracts were combined and dried with MgSO_4 . The ether was removed by distillation, and the residue was vacuum-fractionated to give 17.2 g of VI. Compounds VII-IX (see Table 1) were similarly obtained.

4,4-Dimethyl-4-silapelargonolactone (X). A mixture of 17.7 g (0.08 mole) of IV and 8 g of calcined potassium carbonate was heated at 60-80° for 4 h until carbon dioxide evolution ceased, and 150 ml of dry acetone was added to the residue. The insoluble material was removed by filtration, the acetone was removed by distillation, and the residue was vacuum-distilled to give 5 g of X. Compounds XI and XII (see Table 1) were similarly obtained using sodium ethoxide in place of K_2CO_3 .

γ -Chloropropyldimethylsilylbutyryl Chloride (XIII). A 12.7-g (0.107 mole) sample of thionyl chloride was added to 25.4 g (0.086 mole) of I in the course of 30 min, and the reaction mixture was heated at 60° for 30 min and then vacuum-distilled to give 15.6 g of XIII.

LITERATURE CITED

1. V. F. Mironov and N. S. Fedotov, *Khim. Geterotsikl. Soedin.*, 453 (1966).
2. V. F. Mironov and N. S. Fedotov, *Khim. Geterotsikl. Soedin.*, 179 (1967).
3. V. F. Mironov, N. S. Fedotov, and I. G. Rybalka, *Khim. Geterotsikl. Soedin.*, 440 (1969).