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Preparation of 2-Chlorovinyl Esters

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The 2-chlorovinyl esters of the three chloroacetic acids have been prepared and their *E* and *Z* isomers separated with preparative GLC. 2-Chlorovinyl acetate was prepared from 2,2-dichlorovinyl acetate by reduction with tributyltin hydride, whereas the other acetates were prepared by ester exchange from 2-chlorovinyl acetate using tributyltin methoxide as a transfer agent.

The only known method for synthesis of 2-halovinyl esters is that of Mylo,[1] who prepared 2-bromovinyl acetate from acetyl bromide and dibromoacetaldehyde by dehalogenation with copper. Later, after modifications of the method, it proved usable for preparation of 2-bromovinyl chloroacetate as well as 2-chlorovinyl acetate.[2] However, this is not a general method and attempts to prepare other esters have failed. Yet, it was possible to develop a more general method by using selective reduction with organotin hydride[3] followed by ester exchange,[4] *i.e.* first 2,2-dichlorovinyl acetate is reduced with tributyltin hydride to 2-chlorovinyl acetate which is then treated with tributyltin methoxide, reactions (1) and (2). The resulting tributyl-2-chlorovinyloxytin yields the desired ester after reaction with acyl halide, (3). Using mild reaction conditions the hydrostannolysis of the alkyl–oxygen bond or addition of tributyltin hydride to the vinyl double bond can be avoided.

$$RCO_2CH{=}CCl_2 + Bu_3SnH \rightarrow RCO_2CH{=}CHCl + Bu_3SnCl \quad (1)$$

$$RCO_2CH{=}CHCl + Bu_3SnOCH_3 \rightarrow RCO_2CH_3 + Bu_3SnOCH{=}CHCl \quad (2)$$

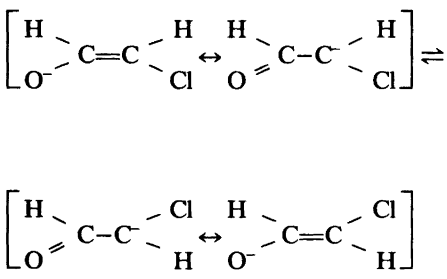
$$Bu_3SnOCH{=}CHCl + R'COCl \rightarrow Bu_3SnCl + R'CO_2CH{=}CHCl \quad (3)$$

2-Chlorovinyl esters consist of a pair of *E* and *Z* isomers. The *E*:*Z* ratio of isomers was found to vary from 1:2.4 to 1:3.9 in different experiments. The configuration of the ester was not retained, when the ester exchange reactions (1) and (2) were carried out using pure *E* or *Z* isomer as starting material. The resulting mixture contained *E* and *Z* isomers in the same ratio as mentioned above. Hence, the separation of isomers must be performed after reaction (3) if an isomerically pure ester is required.

In the cases of enolic acetates, some investigators have proposed that a metallotropic tautomerism between species *1* and *2* in (4) may result in a change of configuration, but no detailed mechanistic study concerning this kind of tautomerism has been carried out.[5] On the other hand, French authors[6] suggest that the existence of an enolate-type intermediate in the transfer of the alkoxy group can explain the change of the configuration, eqn. (5). In the case of tributyl-2-chlorovinyloxytin species *2* was not detected, thus the existence of the enolate-type intermediate seems to be a more likely explanation for the change of configuration.

$$\underset{1}{Bu_3Sn{-}OCR{=}CR'_2} \rightleftharpoons \underset{2}{Bu_3Sn{-}CR'_2{-}C(R){=}O} \quad (4)$$

0302-4369/83 $2.50



(5)

The isomeric purity of 2-chlorovinyl acetate was not retained during storage. Initially pure *E* and *Z* isomers changed slowly to a mixture of both isomers. This was probably caused by the presence of a trace of moisture which hydrolyzes the ester partly to acetic acid. Acetic acid is further capable of promoting an exchange of alkoxy groups,[9] which then leads to a mixture of isomers through the intermediate presented above.

EXPERIMENTAL

Apparatus. Infrared spectra were recorded on a Perkin-Elmer 180 IR spectrophotometer, and nuclear magnetic resonance spectra on a Jeol JNM–PMX 60 and a Jeol FX-60 spectrometer at 60 MHz (^{1}H NMR spectra) and at 15.03 MHz (^{13}C NMR spectra), respectively. Separation of *E* and *Z* isomers was carried out with a Perkin-Elmer F 21 preparative gas chromatograph using 0.5 cm^2×600 cm columns filled with 8 % Antarox CO-990 (for 2-chlorovinyl acetate) or with 10 % Silicone XE-60 (for other 2-chlorovinyl esters) on Chromosorb W. A Philips 125 W mercury lamp was used to provide UV light in reductions.

Reagents. Zinc powder (G.R., Merck AG) and zinc chloride (G. R., Merck AG) were used as received. The quality and dryness of these reagents seem to be crucial in regard to the yield in the synthesis of 2,2-dichlorovinyl acetate. Tributyltin hydride[7] and tributyltin methoxide[8] were prepared according to procedures described in the literature. 2,2-Dichlorovinyl acetate was prepared according to the method of Euranto *et al.*[4] with a slight modification to increase the original low yield (see below). Acyl halides were commercial products (*purum*, Fluka AG) and they were purified by distillation before use. All reactions involving tributyltin hydride were carried out under dry nitrogen.

2,2-Dichlorovinyl acetate. Chloral (195 g, 1.32 mol), acetyl chloride (133 g, 1.69 mol) and some zinc chloride were refluxed for 25 h. The resulting 1,2,2,2-tetrachloroethyl acetate was distilled at 80 °C/1.9 kPa. Yield 171 g (57 %).

1,2,2,2-Tetrachloroethyl acetate (171 g, 0.76 mol), zinc powder (149 g, 2.28 mol) and diethyl ether (140 ml) were refluxed for 19 h and the ether was evaporated. 2,2-Dichlorovinyl acetate was then collected from the reaction mixture at 0.1–0.2 kPa (low pressure and temperature are necessary to prevent polymerization) and redistilled, b.p. 61 °C/3.2 kPa. Yield 82 g (70 %).

2-Chlorovinyl acetate. Tributyltin hydride (33.25 g, 0.114 mol) was added under stirring during 1 h to 2,2-dichlorovinyl acetate (17.5 g, 0.113 mol) at 0 °C under influence of UV light. Stirring was continued for 0.5 h in room temperature after the addition. A fraction of 12.6 g, which contained (by GLC) 2-chlorovinyl acetate (80 %), 2,2-dichlorovinyl acetate (18 %), and vinyl acetate (2 %), was evaporated from the reaction mixture at 0.1–0.2 kPa. Distillation through a fractionating column gave pure 2-chlorovinyl acetate, b.p. 71–72 °C/13 kPa, 130–132 °C/101 kPa. IR (film), *E* isomer: 1770 cm^{-1} (C=O), *Z* isomer: 1767 cm^{-1} (C=O), 1651 cm^{-1} (C=C). ^{1}H NMR (CCl_4), *E* isomer: δ 2.10 (3H, s), 6.06 (1H, d, *J* 11.6 Hz), 7.42 (1H, d, *J* 11.6 Hz), *Z* isomer: δ 2.21 (3H, s), 5.52 (1H, d, *J* 4.8 Hz), 7.39 (1H, d, *J* 4.8 Hz). ^{13}C NMR ($CDCl_3$), *E* isomer: δ 20.5 (CH_3), 167.1 (C=O), 138.5 (CH), 108.4 (CHCl), *Z* isomer: δ 20.5 (CH_3), 167.1 (C=O), 135.3 (CH), 103.2 (CHCl).

When AIBN (2,2'-azobis(2-methylpropionitrile)) was used in one of the experiments as a reaction promoter instead of UV light, an uncontrolled, vigorous reaction took place. This was probably caused by the fast polymerization of the starting ester.

2-Chlorovinyl dichloroacetate. Tributyltin methoxide (27.8 g, 86.5 mmol) and 2-chlorovinyl acetate (10.0 g, 83.0 mmol) were mixed and heated at 60 °C for 20 min. Methyl acetate was then evaporated off at 3.0 kPa. Dichloroacetyl chloride (12.75 g, 86.5 mmol) was added slowly to the resulting tributyl-2-chlorovinyloxytin. Distillation of the reaction mixture gave 7.2 g (44 %) pure 2-chlorovinyl dichloroacetate, b.p. 83–86 °C/2.1 kPa. IR (film), *E* isomer: 1767 cm^{-1} (C=O), *Z* isomer: 1783 cm^{-1} (C=O), 1652 cm^{-1} (C=C).

^{1}H NMR, *E* isomer ($CDCl_3$): δ 5.96 (1H, s), 6.33 (1H, d, *J* 11.4 Hz), 7.41 (1H, d, *J* 11.4 Hz), *Z* isomer (CCl_4): δ 6.10 (1H, s), 5.82 (1H, d, *J* 4.2 Hz), 7.41 (1H, d, *J* 4.2 Hz).

^{13}C NMR ($CDCl_3$), *E* isomer: δ 63.3 ($CHCl_2$), 160.8 (C=O), 137.9 (CH), 111.6 (CHCl), *Z* isomer: δ 63.4 ($CHCl_2$), 161.0 (C=O), 135.1

(CH), 107.1 (CHCl).

2-Chlorovinyl chloroacetate. Prepared as in the case of dichloroacetate. Yield 42 %, b.p. 80 °C/ 2.0 kPa. Melting point of the *E* isomer was found to be 31 °C. IR (film), *E* isomer: 1777 cm^{-1} (C=O), *Z* isomer: 1782 cm^{-1} (C=O), 1651 cm^{-1} (C=C). ^1H NMR ($CDCl_3$), *E* isomer: δ 4.13 (2H, s), 6.23 (1H, d, *J* 11.2 Hz), 7.44 (1H, d, *J* 11.2 Hz), *Z* isomer: δ 4.24 (2H, s), 5.72, d, *J* 4.4 Hz), 7.43 (1H, d, *J* 4.4 Hz). ^{13}C NMR ($CDCl_3$), *E* isomer: δ 40.1 (CH_2Cl), 163.6 (C=O), 138.0 (CH), 110.2 (CHCl), *Z* isomer: δ 40.3 (CH_2Cl), 163.9 (C=O), 135.1 (CH), 105.3 (CHCl).

2-Chlorovinyl trichloroacetate. Prepared as in the case of dichloroacetate. Yield 41 %, b.p. 63–65 °C/0.55 kPa. IR (film), *Z* isomer: 1783 cm^{-1} (C=O), 1651 cm^{-1} (C=C). ^1H NMR (CCl_4), *E* isomer: δ 6.46 (1H, d, *J* 11.8 Hz), 7.47 (1H, d, *J* 11.8 Hz), *Z* isomer: δ 5.88 (1H, d, *J* 4.4 Hz), 7.42 (1H, d, *J* 4.4 Hz). ^{13}C NMR ($CDCl_3$), *E* isomer: δ 88.6 (CCl_3), 158.4 (C=O), 138.3 (CH), 112.4 (CHCl), *Z* isomer: δ 88.6 (CCl_3), 158.5 (C=O), 135.7 (CH), 108.1 (CHCl).

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REFERENCES

1. Mylo, B. *Ber. Dtsch. Chem. Ges. 45* (1912) 645.
2. Euranto, E. K., Hamunen, A. and Rohunen, M. *Unpublished results.*
3. Kuivila, H. G. *Synthesis 10* (1970) 499.
4. Euranto, E. K., Rossi, K., Nuutila, H., Vihanto, J., Laitinen, I. and Lappalainen, K. *Finn. Chem. Lett.* (1976) 125.
5. Lutsenko, I. F., Baukov, Yu. I. and Belavin, I. Yu. *J. Organomet. Chem. 24* (1970) 359.
6. Pereyre, M., Bellegarde, B., Mendelsohn, J. and Valade, J. *J. Organomet. Chem. 11* (1968) 97.
7. Hayashi, K., Iyoda, J. and Shiihara, I. *J. Organomet. Chem. 10* (1967) 81.
8. Davies, A. G., Kleinschmidt, D. C., Palan, P. R. and Vasishtha, S. C. *J. Chem. Soc. C* (1971) 3972.
9. Vihanto, J. *Unpublished results.*

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