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VINYL ORTHOFORMATES AND VINYL ACETALS. PART I

Synthesis of divinyloxymethyl and diaryloxymethyl halides and carboxylates

BY

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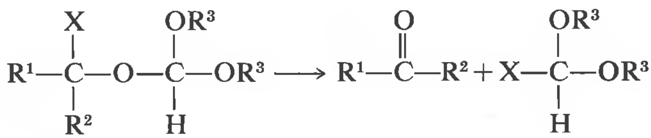
Diaryloxymethyl halides and divinyloxymethyl halides, formates, trichloroacetates, monochloroacetates, and acetates have been synthesized from corresponding vinyl orthoformates.

In a previous paper[1] the mechanism of the acid-catalyzed decomposition of compounds $R^1R^2CXOCH(OR^3)_2$ (I) according to

 (1)

I II III

has been discussed for X = OR or CN. The decomposition proceeds *via* $R^1R^2C(OH)X$ (IV) as an intermediate and is faster as the intermediate has lower stability.

This decomposition might be used for the synthesis of reactive compounds III with X = halogen or acyloxy, provided a suitable preparative method for the appropriate derivative (I) be available. For this purpose we decided to investigate reactions of orthoformates, containing one or more vinyl residues* $HC(OR)_2OCH{=}CH_2$ (V), with hydrogen chloride, hydrogen bromide, or carboxylic acids.

Dimethoxy-vinyloxymethane $HC(OCH_3)_2OCH{=}CH_2$ could be obtained by exchange of an alkoxy group[2,3] from methyl orthoformate and β-chloroethanol,

* Trivinyl orthoformate and triisopropenyl orthoformate have recently also been prepared by *H. Stetter* and *E. Reske*, Chem. Ber. **103**, 639 (1970).

1 *J. W. Scheeren, J. E. W. van Melick*, and *R. J. F. Nivard*, Chem. Comm. 1175 (1969).

2 *H. W. Post* and *E. R. Erickson*, J. Am. Chem. Soc. **55**, 3851 (1933).

3 *R. M. Roberts, T. D. Higgens Jr.*, and *P. R. Noyes*, J. Am. Chem. Soc. **77**, 3801 (1955).

$$HC(OCH_3)_3 + HOCH_2CH_2Cl \overset{H^+}{\rightleftharpoons} HC(OCH_3)_2OCH_2CH_2Cl + CH_3OH \quad (2)$$

followed by dehydrohalogenation with *tert*-butoxide,

$$HC(OCH_3)_2OCH_2CH_2Cl + t \cdot BuO^- \rightarrow HC(OCH_3)_2OCH{=}CH_2 + tert\text{-}BuOH + Cl^- \quad (3)$$

The latter reaction was performed by dropping the β-chloroethyl orthoformate into a suspension of sodium hydride in 1,2-dimethoxyethane to which some *tert*-butyl alcohol had been added. During the reaction the eliminating agent, *tert*-butoxide, is continuously re-formed. Dimethyl sulfoxide could be used as the solvent instead of 1,2 dimethoxyethane, but in that case the product was contaminated with an unpleasantly smelling impurity.

The synthesis of the corresponding ethyl compound, $HC(OC_2H_5)_2$-OCH_2CH_2Cl, *via* reaction (2) failed because of serious disproportionation. The compound could be obtained, however, from diethoxymethyl acetate[4], $HC(OC_2H_5)_2OCOCH_3$, and β-chloroethanol in the presence of an excess of triethylamine.

The reactivity of vinyl orthoformates (V) towards acids was followed by NMR measurements on reaction mixtures of $HC(OCH_3)_2OCH{=}CH_2$ or $HC(OC_2H_5)_2OCH{=}CH_2$ and formic acid. They revealed that dialkoxymethyl formates (III, X = HCOO) and acetaldehyde (II, R^2 = H) were formed.

It is not yet clear whether the products arise *via* an intermediate addition product I, $R^1 = CH_3$, R^2 = H (reaction 4), which decomposes in an acid medium (reaction 1), or by simple acid-catalysed substitution.

$$HC(OR)_2OCH{=}CH_2 + HX \rightarrow HC(OR)_2OCHXCH_3 \quad (4)$$

The fact that even a weak electrophile like bromine converts $HC(OCH_3)_2OCH{=}CH_2$ nearly quantitatively into bromoacetaldehyde and the decomposition products of $HC(OCH_3)_2Br$, methyl formate, and methyl bromide, in this case seems to be more consistent with the former possibility. The exact mechanism is under further investigation, together with that of analogous reactions with vinyl acetals.

The preparation of dialkoxymethyl carboxylates or halides by the reactions mentioned is complicated by disproportionation[4] of the vinyl orthoformate (V) in the presence of acids according to:

$$HC(OR)_2OCH{=}CH_2 \overset{H^+}{\rightleftharpoons} HC(OR)_3 + HCOR(OCH{=}CH_2)_2 \quad (5)$$

[4] *J. W. Scheeren* and *W. Stevens*, Rec. Trav. Chim. **88**, 897 (1969).

and by a reaction between the products:

$$HC(OR)_2X + CH_3CHO \rightarrow CH_3CH(OR)X + HCOOR \qquad (6)$$

Compounds $HC(OR)_2X$ (R = alkyl, X = acetate or formate), therefore, can be synthesized more effectively by a procedure previously described[5].

Because aryl orthoformates disproportionate much more slowly than alkyl orthoformates, and diaryloxymethyl halides are more stable than their alkoxy analogues[6], several diaryloxymethyl halides could be obtained from the corresponding diaryloxy-vinyloxymethanes, $HC(OAr)_2OCH{=}CH_2$ (VI), and hydrogen chloride or hydrogen bromide.

The method appeared to be especially useful for the synthesis of compounds such as $HC(OCH{=}CH_2)_2X$ (VII) and $HC(OCCH_3{=}CH_2)_2X$, (VIII), which have not been described before. Because reaction (6) is very slow with acetone instead of acetaldehyde[7], the yields of the latter compounds (VIII) are generally higher (Table III).

Divinyloxymethyl halides are interesting compounds for the synthesis of tetravinyloxyethenes. Diaryloxymethyl halides give high, dialkoxymethyl halides low yields of "ethenes" on treatment with a strong base. The reactivity of divinyloxymethyl halides towards bases lies between those of the corresponding aryloxy and alkoxy compounds. These results will be discussed more fully in a subsequent paper, together with the possible occurrence of carbenes as intermediates.

Experimental (with the technical assistance of Mrs. *F. Janssen*).

1.1 *β-chloroethyl orthoformates and 2-chloro-1-methylethyl orthoformates (Table I).*

Ethyl or methyl orthoformate was mixed with a proper alcohol* in the ratio required for the exchange of one, two, or three alkoxy groups. Some drops of trifluoro-acetic acid were added, and ethanol or methanol was removed at 15 mm or 5 cm pressure, depending on the boiling points of the components used. After enough alcohol had been collected (4–8 h), the β-chloroethyl orthoformates were distilled at reduced pressure after neutralization of the mixture with sodium methoxide.

1.2 *β-chloroethyl diethyl orthoformate (Table I).*

20 g (0.25 mole) of β-chloroethanol dissolved in 75 ml of pentane was added to a mixture of 40.5 g (0.25 mole) of diethoxymethyl acetate[5] and 34 g (0.35 mole) of triethylamine. After standing for 30 minutes, the solution was washed with water four times, dried on sodium sulfate, and distilled.

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* Pure 1-chloro-2-propanol was obtained from a sample containing 25% of 2-chloro-1-propanol (Fluka AG., Chemische Fabrik, Buchs SG) by distillation with a Nester Faust spinning band column.

[5] *J. W. Scheeren* and *W. Stevens*, Rec. Trav. Chim. **88**, 195 (1969).

[6] *J. W. Scheeren*, Tetrahedron Letters, **54**. 5613 (1968).

[7] *J. W. Scheeren* and *R. J. F. Nivard*, Rec. Trav. Chim. **90**, 000 (1971).

Table I

β-chloroethyl orthoformates, $HC(OR)_2OCHR'CH_2Cl$

R	R′	Bp	n_D^{20}	Yield	Method
methyl	H	69°/14 mm	1.4230	45%	1.1
ethyl	H	85°/13 mm	1.4204	80%	1.2
phenyl	H	185°/1.3 mm	1.5525	60%	1.3
p-chlorophenyl	H	not isolated			1.3
p-tolyl	H	190°/1.3 mm	1.5425	50%	1.3
β-chloroethyl*	H	125–127°/0.9 mm	1.4685	80%	1.1
2-chloro-1-methylethyl**	CH_3	107°/0.6 mm	1.4622	86%	1.1

* Lit. Bp 163–165°/11 mm.[9]
** Lit. Bp 105–107°/0.5 mm.[9]

1.3 *Aryl β-chloroethyl orthoformates (Table I).*

Tri-β-chloroethyl orthoformate was mixed with 2 equivalents of a phenol. The mixture was boiled at reduced pressure (15 mm) and β-chloroethanol was distilled off (Vigreux column 100 × 15 mm) until about $\frac{3}{2}$ equivalent had been removed (24–48 h). From the relative residues, diphenyl and di-*p*-tolyl β-chloroethyl orthoformate were isolated by distillation. Because of the high boiling point of the corresponding *p*-chlorophenyl compound the *p*-chlorophenyl orthoformates $HC(OCH_2CH_2Cl)_2OC_6H_4Cl$ and $HC(OCH_2CH_2Cl)(OC_6H_4Cl)_2$ were not separated and used as a mixture in the reaction with NaH. The resultant vinyl orthoformates boil at a much lower temperature and can easily be separated.

2.1 *Vinyl orthoformates (Table II).*

To a suspension of NaH in 1,2-dimethoxyethane (100 ml per mole of NaH) 20 g of *tert*-butyl alcohol per 100 ml of solvent was added. The β-chloroethyl orthoformate was added dropwise and the reaction system was then refluxed for about 2 h until the evolution of hydrogen had stopped. In all the experiments NaH was used in about 10% excess. After reaction, the 1,2-dimethoxy-ethane was removed at 15 mm pressure; then water and ether were added carefully, and the ether solution was washed several times with water, dried, and distilled.

Di-*p*-chlorophenyl vinyl orthoformate was prepared from the mixture of *p*-chlorophenyl orthoformates described under 1.3. This procedure can also be used with the other aryl β-chloroethyl orthoformates. In these cases also aryldivinyl orthoformates were isolated.

$HC(OC_6H_5)(OCH{=}CH_2)_2$ Bp 112°/13 mm, n_D^{20} 1.5043

$HC(OC_6H_4{-}CH_3{-}p)(OCH{=}CH_2)_2$ Bp 82°/0.7 mm, n_D^{20} 1.5028

$HC(OC_6H_4{-}Cl{-}p)(OCH{=}CH_2)_2$ Bp 94°/0.7 mm, n_D^{20} 1.5165

The NMR spectra in $CCl_4\delta[HC(OR)_3]$ showed 6.00, 5.90, and 6.35 ppm, respectively.

3.1 *Divinyloxy- and diaryloxymethyl halides.*

The chlorides were prepared by adding a 4 *N* HCl solution in ether (in 10% excess) to the proper vinyl orthoformates at room temperature. After standing for 15 minutes, the ether was removed at reduced pressure and the compounds were distilled.

Table II

Vinyl orthoformates, $HC(OR)_2OCR'{=}CH_2$

R	R′	n_D^{20}	Bp	$\delta HC(OR)_3$	Yield
methyl	H	1.4011	119°	5.55	65%
ethyl	H	1.4027	42°/14 mm	5.50	65%
phenyl	H	1.5430	135°/1.4 mm	6.45	75%
p-chlorophenyl	H	1.5642	162°/0.7 mm		45%
p-tolyl	H	1.5429	136°/0.2 mm	6.20	70%
vinyl*	H	1.4313	38°/13 mm	5.85	70%
1-methylvinyl**	CH_3	1.4381	72°/14 mm	6.20	85%

* Lit. Bp 141.5–143°[9]
** Lit. Bp 70–73°/10 mm[9]

Table III

Dialkoxymethyl compounds, $HC(OR)_2X$

R	X	B.p.	$\delta HC(OR)_2X$	Yield
vinyl	CH_3COO	84°/48 mm	6.80	40%
vinyl	CH_2ClCOO	98–100°/15 mm	6.90	55%
vinyl	CCl_3COO	66°/2.5 mm	6.95	60%
vinyl	HCOO	50–51°/44 mm	6.90	55%
vinyl	Cl	37–38°/17 mm	6.90	50%
phenyl	Cl	134°/0.8 mm*	7.25	60%
phenyl	Br	150–155°/1 mm	7.85	50%
p-chlorophenyl	Cl	152°/0.4 mm	**	50%
p-tolyl	Cl	155°/1 mm	7.40	65%
1-methylvinyl	Cl	59°/15 mm	7.15	90%
1-methylvinyl	HCOO	72°/15 mm	7.20	85%
1-methylvinyl	CH_3COO	78°/15 mm	7.10	70%
1-methylvinyl	$ClCH_2COO$	82°/3.3 mm	7.20	80%
1-methylvinyl	Cl_3CCOO	85°/1.7 mm	7.10	85%

* Bp lit.[8] 128°/0.15 mm.
** Absorption is hidden under the aromatic proton absorptions. The structure of the compound appeared from its mass spectrum; peaks at $m/e = 302$, $HC(OC_6H_4Cl)_2Cl^+$; $m/e = 267$ $(HC(OC_6H_4Cl)_2{}^+$; $m/e = 175$ $(HC(OC_6H_4\text{-}Cl)Cl)^+$.

[8] *H. Böhme* and *V. Neidlein*, Chem. Ber. **95**, 1859 (1962).
[9] *H. Stetter* and *E. Reske*, Chem. Ber. 103, 639 (1970).

The monochloro- and trichloro-acetates were prepared in a similar way. These reaction mixtures were kept in a water bath at about 50°C for half an hour, and worked up as the halides.

Formic acid and acetic acid were added pure (in 10% excess), and the reaction mixtures were kept at 50° for one hour at a pressure of 10 cm and then distilled at reduced pressure. In those cases where acetaldehyde was formed, it had to be removed as quickly as possible at reduced pressure.

Purification and analyses

Analytical samples of all the compounds were obtained by distillation with Vigreux columns of 50 cm × 12 mm. They were identified by NMR spectroscopy (Varian HA 100) in CCl_4 (± 10% solutions), using hexamethyldisiloxane as external standard (see the table). In all the cases measured the differences with TMS as internal standard were 20 Hz to lower field.

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