The following full text is a publisher's version.

For additional information about this publication click this link.
http://hdl.handle.net/2066/142261

Please be advised that this information was generated on 2017-08-19 and may be subject to change.
VINYL ORTHOFORMATES AND VINYL ACETALS II
The reactions of alkenyl orthoesters and dialkenyloxyalkyl carboxylates with carboxylic acids

BY
J.E.W. VAN MELICK, J.W. SCHEEREN and R.J.F. NIVARD
(Department of Organic Chemistry, Catholic University, Nijmegen, The Netherlands)

Several new alkenyl orthoesters have been synthesized by dehydrohalogenation of the corresponding β-chloroalkyl orthoesters with various bases. With one equivalent of a carboxylic acid these compounds are converted into dialkenyloxyalkyl carboxylates in good yields. Dependent upon their composition, the latter products give with another equivalent of a carboxylic acid either predominantly alkenyl esters and acylals, or alkenyl esters, carboxylic anhydrides and carbonyl derivatives. The synthetic applications have been investigated and a possible mechanism for these reactions is given.

In part I we described\(^1\) a synthetic procedure for the preparation of dialkenyloxymethyl carboxylates (II) from alkenyl orthoformates (I) as formulated in equation 1.

\[
\begin{align*}
\text{I} & \quad \text{II} \\
\text{H–C(OCR}^1\text{=CH}_2\text{)}_2\text{+ RCOOH}&\rightarrow\text{H–C(OCR}^1\text{=CH}_2\text{)OCOR} + \text{R}^1\text{–CO–CH}_3
\end{align*}
\]

Subsequently we found\(^2\) that renewed treatment of the product (II) with a carboxylic acid did not result in the substitution of a second alkenyloxy group by an acyloxy residue, but in the formation of an alkenyl formate (III) and an acylal (IV).

\[
\begin{align*}
\text{II} & \quad \text{III} \quad \text{IV} \\
\text{H–C(OCR}^1\text{=CH}_2\text{)OCOR} + \text{RCOOH} & \rightarrow \text{H–CO–OCR}^1\text{=CH}_2 + \text{H}_3\text{C–CR}^1\text{(OCOR)}_2
\end{align*}
\]

Comparison of equations [1] and [2] shows that the reaction of compounds H–C(OCR\(^1\)=CH\(_2\))\(_2\)A with carboxylic acids strongly depends


on the nature of A. When A is an alkenyloxy residue an apparent sub-
stitution reaction takes place, whereas a further fragmentation is in-
volved when A is an acyloxy group. This difference justifies a closer
examination of these reactions with various types of orthoester.

In this paper we present the results of reactions of carboxylic acids
(RCOOH) with a large series of compounds R^3—C(OCR^1=CHR^2)_2A,
in which besides A, also R^1, R^2 and R^3 were varied. The results give an
insight into the scope of the synthetic applicability and have been used
to propose a tentative reaction scheme.

The reaction R^3—C(OCR^1=CHR^2)_3 + RCOOH

The reaction of an alkenyl orthoester with one equivalent of a car-
boxylic acid leads always to the formation of a substitution product
in accordance with equation 1. From a comparison of the reaction
conditions (Table IV, Experimental part), which appeared to be neces-
sary for a conversion of at least 90%, determined by following the pro-
gress of the reaction by NMR, an estimate could be made of the in-
fluences of variations in R^1, R^2, R^3 and R on the reaction rate. It
appears that the rate of the conversion depends on R^1, R^2, R^3 and R
as follows:

R^1: CH₃ > H > CH₂OCH₃ > CH₂Cl
R^2: probably no significant influence
R^3: CH₃, H > C₆H₅
R : CHCl₂ > CH₂Cl > H > CH₃

The results are in agreement with a reaction pathway via a carbonium
ion V (Equation [3]), as is also found in acid-catalysed substitutions of
saturated orthoesters. However, protonation is probably on the
double bond instead of on oxygen, because the alkenyl residue lowers
the basicity of ether oxygen considerably, and alkene protonation
should lead to a carboxonium ion.

3 J. W. Scheeren, A. P. M. van der Veek and W. Stevens, Rec. Trav. Chim. 88, 195
Alkene protonation as well as cleavage of a C—O bond (formation of V) will proceed better when the donating properties of R¹ are enhanced; the influence of the nature of R² in this respect should be smaller, as is observed experimentally.

The influence of variations of R³ on the reaction rate of the alkenyl orthoesters does not correspond with their influence on the stability of the resultant carboxonium ion: V will be more stable when R³ is phenyl than with hydrogen or methyl. Apparently the lower reactivity of the orthobenzoates has to be ascribed to their lower basicity; protonation is dependent on the inductive, not on the mesomeric effect of R³. This phenomenon indicates that protonation is in any case involved in the rate determining step. An analogous phenomenon, more pronounced, has been found in the acid-catalyzed hydrolysis of orthoesters⁷,⁸.

Finally, the influence of variations in the carboxylic acid used corresponds qualitatively with the influence on dissociation or catalytic constants, as may be expected when protonation is involved in the rate determining step. Also the influence of the solvent appeared to be in accordance with this supposition; the reactivity of H—C(OCR¹=CHR²)₃ with R¹ is CH₂OCH₃ or CH₂Cl towards monochloroacetic acid varies with the solvent as follows: neat ≥ carbon tetrachloride > acetonitrile > 1,2-dimethoxyethane ≥ hexamethylphosphonamide.

The reaction: \( \text{R}^3\text{C} (\text{OCR}^1=\text{CHR}^2)_2\text{OCOR} + \text{RCOOH} \)

The acid used in these reactions was always that corresponding to the acid residue in the starting compound; if not the reaction mixture becomes very complex as a consequence of exchange reactions⁹. Variations in R¹, R², R³ and R in this type of compounds not only influences the reaction rate, but also the nature of the products (Table I).

---

⁸ For a discussion of these points, see E. H. Cordes, Progr. Phys. Org. Chem. 4, 1 (1967), and ref. 4, p. 137.
Table I

Reaction products* from $R^3$—C(OCR$^1$=CH$_2$)$_2$OCOR + RCOOH

<table>
<thead>
<tr>
<th>$R^3$</th>
<th>$R^1$</th>
<th>$R$</th>
<th>main*** products</th>
<th>minor products</th>
</tr>
</thead>
<tbody>
<tr>
<td>H, CH$_3$, C$_6$H$_5$</td>
<td>H, CH$_3$</td>
<td>CHCl$_2$, CH$_2$Cl, H, CH$_3$</td>
<td>X, XI</td>
<td>XII, XIII (0–20%)</td>
</tr>
<tr>
<td>H</td>
<td>CH$_3$OCH$_3$**</td>
<td>CH$_3$</td>
<td>X, XII, XIII</td>
<td>XI (~30%)</td>
</tr>
<tr>
<td>H</td>
<td>CH$_3$OCH$_3$**</td>
<td>H</td>
<td>X, XII, XIII</td>
<td>XI (~30%)</td>
</tr>
<tr>
<td>H</td>
<td>CH$_3$OCH$_3$**</td>
<td>CH$_2$Cl</td>
<td>X, XI</td>
<td>XII, XIII (~12%) XIV (~6%)</td>
</tr>
<tr>
<td>H</td>
<td>CH$_2$Cl</td>
<td>CHCl$_2$</td>
<td>X, XI</td>
<td>XII, XIII (~5%) XIV (~2%)</td>
</tr>
<tr>
<td>H</td>
<td>CH$_2$Cl</td>
<td>CH$_2$Cl</td>
<td>X, XI</td>
<td>XII, XIII (~35%) XIV (~12%)</td>
</tr>
<tr>
<td>H</td>
<td>CH$_2$Cl</td>
<td>CHCl$_2$</td>
<td>X, XI</td>
<td>XII, XIII (~15%) XIV (~6%)</td>
</tr>
</tbody>
</table>

* The numbering refers to the reaction scheme.

** For $R^1$=CH$_2$OC$_2$H$_5$ or CH$_2$OCH(CH$_3$)$_2$ the results were similar.

*** Percentage main products is 100% minus percentage minor products.
Tentative reaction scheme for reactions between $R^3\text{-C(OCR}_1^1\text{=}\text{CHR}_2^2\text{)}_2\text{OCOR}$ and $\text{RCOOH}$

Because an acyloxy residue is more electron-withdrawing than an alkenyloxy group, the reaction of the dialkenyloxyalkyl carboxylates with carboxylic acids is slower than that of the corresponding alkenyl orthoesters. The influence of variations in $R$, $R^1$, $R^2$ and $R^3$ is, however, similar to that on the reaction of alkenyl orthoesters. According to
these results, in this case also the attack of the acid should be involved in the rate-determining step. Subsequent or synchronous cleavage of a C—O bond is, however, less probable because a carboxonium ion such as VIII should be less stable than V. On the contrary, the oxonium ion VIIa may rearrange into a more stable trioxenium ion VIIb or via that into carboxonium ion VIIc. The formation of alkenyl esters (X) and acylals (XI) as the main products in several cases, and of alkenyl esters (X), anhydrides (XIII) and ketones or acetaldehyde (XII) in others, may be explained by the supposition of such a cyclic trioxenium cation (VIIb) as an intermediate (see reaction scheme).

Contrary to the case of dioxenium ions which have been suggested before as reaction intermediates\textsuperscript{10,11}, trioxenium ions have never been mentioned in the literature. In our case they seem especially apt to explain the simultaneous formation of the products X, XII and XIII, namely by an attack of the acid on C\textsubscript{2} in VIIb, because these products are found just in those cases where VIIb should be relatively stable (R=H or CH\textsubscript{3}). When the acid used is a very strong acid (R=CHCl\textsubscript{2} or CH\textsubscript{2}Cl\textsubscript{2}), or when R\textsuperscript{1} has no electron withdrawing properties, the trioxenium ion VIIb will function more as a transition state in the rearrangement of VIIa into the more stable carboxonium ion VIIc. This decomposes\textsuperscript{12} under the influence of acids into alkenyl esters (X) and acylals (XI).

In several of our experiments small amounts of the "normal" substitution product XIV were found. This side-product might arise by an attack of the acid on C\textsubscript{x} in VIIa or via carboxonium ion VIII.

It is of interest that a simple addition product XV, which may arise

\[
\text{OCR}^1=\text{CHR}^2 \\
\text{R}^3-\text{C}-\text{OCR}^1-\text{CH}^2\text{R}^2 \\
\text{RCOO} \quad \text{OCOR}
\]

via attack of the acid on C\textsubscript{x} (in VIIb or c) or C\textsubscript{y} (in VIIa or b) has never been found in our reaction mixtures, whereas an analogous product is surely obtained from dioxenium and dioxolenium ions\textsuperscript{10,11} in acid

\textsuperscript{11} H. Paulsen in Advances in Carbohydrate Chemistry and Biochemistry 26, 127 (1971).
media*. The reason may be that all decompositions of VII leading to X + XI, X + XII + XIII, or XII + XIV, are accompanied by the formation of at least two new carbonyl functions. The rather high bonding energy of C=O might be the driving force in these decompositions. In reactions with dioxenium ions never more than one carbonyl function can arise.

Inspection of our tentative reaction scheme shows that the formation of X, XII and XIII as reaction products might also be explained along two other pathways. Acid-catalysed fragmentation of XI should give rise to XII + XIII in accordance with equation 4.

\[
\begin{align*}
\text{R}_1\text{CH}_2\text{R}_2 & \xrightarrow{(H)} \text{R}_1\text{CH}_2\text{R}_2 + \text{R}-\text{C}-\text{O}-\text{C}-\text{R} \\
\text{XI} & \quad \text{XII} \quad \text{XIII}
\end{align*}
\]

Such a reaction is known\textsuperscript{13}, but could be excluded because compounds XI appeared to be stable under the reaction conditions used in most of our experiments.

A second alternative is the formation of X + XIII by fragmentation of XIV in an acidic reaction medium (equation 5).

\[
\begin{align*}
\text{R}_3\text{OCR}_1=\text{CHR}_2 & \xrightarrow{(H)} \text{R}_3\text{OCR}_1=\text{CHR}_2 + \text{R}-\text{C}-\text{O}-\text{C}-\text{R} \\
\text{XIV} & \quad \text{X} \quad \text{XIII}
\end{align*}
\]

Such a fragmentation seems quite general\textsuperscript{14}; also we found that H–C(OCR\textsubscript{1}=CH\textsubscript{2})(OCOR)\textsubscript{2} (R\textsubscript{1}=CH\textsubscript{2}OC\textsubscript{3}H\textsubscript{3} or CH\textsubscript{2}Cl, and

\* The reactions of R\textsubscript{2}–C–OCR\textsubscript{1}=CH\textsubscript{2} with RCOOH give rise to addition products which may be good starting compounds for investigations on the occurrence and behaviour of trioxenium ions.

\textsuperscript{13} C. Coffin, J. Dacey and N. Parlee, Can. J. Research 15\textsuperscript{B}, 247 (1937).

R=CHCl₂ or CH₂Cl) and a saturated analogue H—C(OCH₃)—(OCOCH₃)₂ decompose slowly under the influence of acid into a carboxylic anhydride and a formate. Acceleration by acid probably occurs by protonation of the carbonyl oxygen. Following the progress of the reaction of H—C(OCR¹=CH₂)₂OCOCH₂Cl (R¹=CH₃OCH₃ or CH₂Cl) with monochloroacetic acid at 65°C by NMR, it appeared, however, that the decomposition of XIV was too slow to explain the formation of X and XIII entirely, so that we conclude that in these cases X, XII and XIII were formed via VIIb at least partly.

**Synthesis of starting compounds**

Vinyl orthoesters, R³—C(OCR¹=CH₂)₃ with R³=H, CH₃ or C₆H₅ and R¹=H can be synthesized from β-chloroethyl orthoesters with a mixture of sodium hydride and sodium tert-butoxide. A weaker base like sodium methoxide in methanol yields mainly substitution products. The rate of elimination and the subsequent formation of polymeric products during treatment with a base appear sensitive to small structural variations in the parent compound. Thus when R³ was CH₂Br, CHBr₂ and OCH₂CH₂Cl we found only polymeric products; when R³ or R¹ was CH₃ or C₆H₅ the elimination was slower than for H, and more polymeric products occurred; neither H₃C—C(O—CCH₃=CH₂)₃ nor H—C(0—CC₆H₅=CH₂)₃ could be prepared by the procedure used.

In the elimination of H—C(OCHCH₃—CHCl—CH₃)₃ only sodium hydride was used, in order to get a higher yield of the required Saytzeff-product. The elimination of the orthoformate H—C[OCH(CH₂Cl)₂]₃ is possible with weaker bases. When an alcoholate dissolved in the corresponding alcohol was used, the elimination was accompanied by substitution of the second chlorine atom, yielding H—C[OC(CH₂OR)=CH₂]₃, R=CH₃, C₂H₅ or CH(CH₃)₂. With potassium hydroxide in water/1,2-dimethoxyethane (1:1), however, only elimination takes place, leading to H—C[OC(CH₂Cl)=CH₂]₃. We did not succeed in substituting the chlorine atom by other substituents, such as CN, OH, OCOCH₃.

**2-Alkenyl formates**

The acid-stability of 2-alkenyl formates, H—CO—OCR¹=CH₂, increases with increasing electron withdrawing properties of R¹. At the same time their reactivity towards nucleophilic reagents increases.

---

Under the conditions described previously\textsuperscript{16}, \textit{N}-formylation of the methyl ester of tyrosine could be completed with 3-methoxy-2-propenyl formate, H—CO—OC(CH\textsubscript{2}OCH\textsubscript{3})=CH\textsubscript{2}, within 5 min., with 2-propenyl formate in about 15 min.; with sec-butene-2-yl formate (\textit{cis-trans} mixture) as much as 90 min. appeared to be necessary. With all three reagents the phenolic hydroxy group was left unchanged. 3-Methoxy-2-propenyl formate has also the advantage over 2-propenyl formate in that its synthesis is more facile.

\textbf{Experimental}

Isolation and purification of reaction products were performed by distillation with Vigreux columns of 70 × 1.2 cm, 20 × 1.0 cm, 20 × 0.8 cm or with a spinning band column (Normag) of 25 plates.

Products were identified by NMR spectroscopy (Varian HA100 or Varian T60) in CCl\textsubscript{4} (±10\% solutions) with TMS as internal standard. Occasionally an additional identification was performed by mass spectroscopy (Varian-Mat-SM1-B) or by elemental analysis.

1. \textit{β-Chloroalcohols}

a. \textit{3-Chloro-2-butanol}; 0.75 Mole of thionyl chloride was added drop by drop into 1 mole of 2,3-butanediol (a mixture of the \textit{meso} and racemic form) to which 2 ml of DMF had been added, and the mixture was refluxed for 6 hours. The fraction boiling at 35–50°/15 mm was collected by distillation at reduced pressure. Redistillation of this fraction yielded a pure product with b.p. 42–45°/20 mm, \textit{n}\textsubscript{D} 1.4410 (lit. \textsuperscript{17} b.p. 52–54°/30 mm, \textit{n}\textsubscript{D} 1.4432); yield 55\%.

b. \textit{1-Chloro-2-propanol} was separated from a sample (Fluka AG.) containing 25\% of 2-chloro-1-propanol by distillation with a Nester Faust spinning band column.

c. \textit{Styrene chlorohydrin} was synthesized from styrene and tert-butyl hypochlorite\textsuperscript{18}.

2. \textit{β-Chloroalkyl orthoesters} (Table II)

The appropriate \textit{β}-chloroalcohol in 50–100\% excess was mixed with ethyl ortho-formate, -acetate, -benzoate or -carbonate, and a trace of \textit{p}-toluene sulfonic acid was added\textsuperscript{19}. The alcohol liberated was evaporated, in the case of the orthobenzoate and ortho-carbonate at reduced pressure to prevent the temperature in the distillation vessel rising above 100°. The orthoesters were isolated by distillation at low pressure after neutralization of the mixture with sodium methoxide; only H—C—[O—C(C\textsubscript{6}H\textsubscript{5})H—CH\textsubscript{2}Cl], was

used without distillation. β-Chloroethyl orthomono- and di-bromoacetate were synthesized from β-chloroethyl orthoacetate and bromine in pyridine20.

### Table II

**β-Chloroalkyl orthoesters, **\( R^3-(OCHR^1\text{-CHCIR}^2)_3 \)**

<table>
<thead>
<tr>
<th>( R^2 )</th>
<th>( R^3 )</th>
<th>( R^1 )</th>
<th>B.p. °C/mm</th>
<th>( n_D^{20} )</th>
<th>Yield</th>
<th>( δ-H(R^3) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>H</td>
<td>CH₃</td>
<td>119–121°/0.5</td>
<td>1.4638</td>
<td>70%</td>
<td>5.42</td>
</tr>
<tr>
<td>H</td>
<td>CH₃</td>
<td>H</td>
<td>122°/1.4*</td>
<td>1.4720</td>
<td>75%</td>
<td>1.51</td>
</tr>
<tr>
<td>H</td>
<td>CH₃</td>
<td>CH₃</td>
<td>110°/0.4</td>
<td>1.4608</td>
<td>65%</td>
<td>1.52</td>
</tr>
<tr>
<td>H</td>
<td>C₂H₅</td>
<td>H</td>
<td>165–168°/0.7</td>
<td>1.5212</td>
<td>70%</td>
<td>—</td>
</tr>
<tr>
<td>H</td>
<td>CH₂Br</td>
<td>H</td>
<td>138°/0.6</td>
<td>1.5060</td>
<td>40%</td>
<td>3.72</td>
</tr>
<tr>
<td>H</td>
<td>CHBr₂</td>
<td>H</td>
<td>150–152°/0.6</td>
<td>1.5280</td>
<td>15%</td>
<td>5.69</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>CH₂Cl</td>
<td>163–165°/0.2</td>
<td>1.5020</td>
<td>80%</td>
<td>5.50</td>
</tr>
<tr>
<td>H</td>
<td>OCH₂CH₂Cl</td>
<td>H</td>
<td>136°/0.1**</td>
<td>—</td>
<td>20%</td>
<td>—</td>
</tr>
</tbody>
</table>

* Lit. 21 b.p. 151–159°/9 mm, yield 74%.

** M.p. 60–61°.

3. Alkenyl orthoesters (Table III)

**Method a.** The procedure as described in part I1 was followed for all β-chloroalkyl orthoesters except for 1,3-dichloroisopropyl orthoformate (see 3b, c). Refluxing of the reaction mixture was continued until evolution of hydrogen ceased (2–24 hours). In the elimination of 3-chloro-sec-butyl orthoformate tert-butanol was omitted from the reaction mixture and reflux was continued for 48 hours. Products were isolated by distillation at reduced pressure. sec-but-en-2-yl orthoformate as a mixture of the cis and trans isomers.

### Table III

**Alkenyl orthoesters, **\( R^3-(OCR^1=CHR^2)_3 \)**

<table>
<thead>
<tr>
<th>( R^3 )</th>
<th>( R^1 )</th>
<th>( R^2 )</th>
<th>B.p. °C/mm</th>
<th>( n_D^{20} )</th>
<th>Yield</th>
<th>( δ-H(R^3) )</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>CH₃</td>
<td>CH₃</td>
<td>75–77°/0.8</td>
<td>1.4610</td>
<td>50%</td>
<td>5.94*</td>
<td>a</td>
</tr>
<tr>
<td>CH₃</td>
<td>H</td>
<td>H</td>
<td>43°/18**</td>
<td>1.4355</td>
<td>70%</td>
<td>1.64</td>
<td>a</td>
</tr>
<tr>
<td>C₂H₅</td>
<td>H</td>
<td>H</td>
<td>68°/0.2</td>
<td>1.5085</td>
<td>70%</td>
<td>—</td>
<td>a</td>
</tr>
<tr>
<td>H</td>
<td>CH₂OCH₃</td>
<td>H</td>
<td>115°/0.1</td>
<td>1.4595</td>
<td>90%</td>
<td>6.06</td>
<td>b</td>
</tr>
<tr>
<td>H</td>
<td>CH₂OCH₂H₃</td>
<td>H</td>
<td>123°/0.2</td>
<td>1.4527</td>
<td>90%</td>
<td>6.05</td>
<td>b</td>
</tr>
<tr>
<td>H</td>
<td>CH₂OCH(CH₃)₂</td>
<td>H</td>
<td>125°/0.1</td>
<td>1.4520</td>
<td>80%</td>
<td>6.05</td>
<td>b</td>
</tr>
<tr>
<td>H</td>
<td>CH₂Cl</td>
<td>H</td>
<td>120°/0.2</td>
<td>45%</td>
<td>6.15</td>
<td>—</td>
<td>c</td>
</tr>
</tbody>
</table>

* The main peak is accompanied by small peaks at δ 5.99 and δ 5.87 ppm.

** Lit. 21 b.p. 145–147°, \( n_D^{20} \) 1.4355, yield 42%.

Method b. Over a period of about half an hour 0.1 mole of 1,3-dichloro-2-propyl orthoformate was added to a refluxing solution of 0.75 mole of sodium alcoholate in 200 ml of methanol, 300 ml of ethanol or 600 ml of 2-propanol. Refluxing was continued for 2 hours after completion of the addition. The mixture was concentrated at reduced pressure, the resulting suspension dissolved in water and extracted three times with ether. The ethereal solution was washed with water, dried over magnesium sulphate and distilled at reduced pressure.

Method c. 0.1 Mole of 1,3-dichloro-2-propyl orthoformate was added to a solution of 0.6 moles of potassium hydroxide in 50 ml of water/1,2-dimethoxyethane (1:1). The mixture was kept at about 80° under vigorous stirring. Every 24 hours 0.2 mole of KOH was added to the mixture and, after 80 hours, the reaction mixture was worked up as described under method b. The product was crystallized from cyclohexane, m.p. 64–65°.

4. Reactions of alkenyl orthoesters with carboxylic acids; Syntheses of dialkenyloxyalkyl carboxylates (Table VI)22

a. With aliphatic carboxylic acids

0.055 Mole of pure formic, acetic or dichloroacetic acid, or the same amount of mono-chloroacetic acid dissolved in 10 ml of dry ether, was added drop by drop to 0.05 mole of an alkenyl orthoester during 15 minutes [with H—C(OCR1=CHR2)3 a double amount of carboxylic acid was used]. Ether if used, and acetaldehyde if liberated, were immediately evaporated at reduced pressure, and the mixture was heated until at least 90%

Table IV

<table>
<thead>
<tr>
<th>R3</th>
<th>R1</th>
<th>R2</th>
<th>R=CHCl2</th>
<th>R=CH2Cl</th>
<th>R=H</th>
<th>R=CH3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>°C h.rs.</td>
<td>°C h.rs.</td>
<td>°C h.rs.</td>
<td>°C h.rs.</td>
</tr>
<tr>
<td>H</td>
<td>CH3</td>
<td>CH3</td>
<td>40 0.5</td>
<td>50 0.75</td>
<td>50 0.75</td>
<td>80 2</td>
</tr>
<tr>
<td>H</td>
<td>CH3</td>
<td>H</td>
<td>40 0.5</td>
<td>50 0.75</td>
<td>50 1</td>
<td>80 2.5</td>
</tr>
<tr>
<td>CH3</td>
<td>H</td>
<td>H</td>
<td>— —</td>
<td>50 1</td>
<td>50 3</td>
<td>80 3.5</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td>50 0.5</td>
<td>50 1</td>
<td>50 3</td>
<td>80 4</td>
</tr>
<tr>
<td>C6H5</td>
<td>H</td>
<td>H</td>
<td>50 1</td>
<td>— —</td>
<td>60 3.5</td>
<td>120 2.5</td>
</tr>
<tr>
<td>H</td>
<td>CH3OCH3*</td>
<td>H</td>
<td>50 1.5</td>
<td>80 2</td>
<td>80 3</td>
<td>100 10</td>
</tr>
<tr>
<td>H**</td>
<td>CH3Cl</td>
<td>H</td>
<td>70 2</td>
<td>70 4.5</td>
<td>70 6</td>
<td>— —</td>
</tr>
</tbody>
</table>

* For R1=CH2OC2H3 or CH2OCH(CH3)2 the conversions were slightly faster.
** Two equivalents of acid were used.

22 Physical constants of compounds, which have not been given in this paper, are available at the editorial office (Table VI, VII, VIII and IX).
of the starting compound had been converted. Reaction temperatures and times are given in Table IV; the reactions can be accelerated by the addition of catalytic amounts of trifluoroacetic acid or hydrochloric acid. The products were isolated by distillation. Physical constants of some representative compounds are

| H—C(0—C(CH_{3})=CHCH_{3})_{2}OCOCH_{3} | b.p. 65°/0.6 mm n_{D}^{20} 1.4435 |
| H—C[O—C(CH_{2}OCH_{3})=CH_{2}]_{2}OCOH | b.p. 93°/0.1 mm n_{D}^{20} 1.4494 |
| H—C[O—C(CH_{2}OC_{2}H_{5})=CH_{2}]_{2}OCOCH_{2}Cl | b.p. 112°/0.1 mm n_{D}^{20} 1.4582 |
| H—C[O—C(CH_{2}Cl)=CH_{2}]_{2}OCOCHCl_{2} | b.p. 127°/0.6 mm n_{D}^{20} 1.4961 |

(δ H—C(O—) are between 6.75 and 7.09 ppm).

b. With aromatic carboxylic acids

In these experiments the orthoester was used in excess (0.08 mole of the acid, dissolved in 20 ml of dry ether, and 0.1 mole of the orthoester) because the high melting point of the acids hindered their removal from the reaction mixture by distillation. The procedure was similar to that in 4a; the reaction temperature was 120° and the reaction time from 2 hours (with p-chloro-) to 4 hours (with p-methoxybenzoic acid).

5. Reactions of dialkenyloxyalkyl carboxylates with carboxylic acids; Syntheses of acylals (Tables VII and VIII) \textsuperscript{22} and alkenyl esters (Table IX) \textsuperscript{22}

a. With aliphatic carboxylic acids

The procedure is quite similar to that described in 4a, the alkenyl orthoester being replaced by a dialkenyloxyalkyl carboxylate. The reaction conditions for a conversion of at least 90% are given in Table V, as well as those leading to the highest yields of acylals. To get a maximal amount of an alkenylformate \textsuperscript{16}, 1.5 equivalents of dichloroacetic acid are added to a dialkenyloxymethyl carboxylate or 2.5 equivalents of the same acid to an alkenyl orthoformate, and the carbonyl compound and alkenyl formate are removed

<table>
<thead>
<tr>
<th>Table V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction conditions for: R^{3}—C(OCR^{1}=CHR^{2})_{2}OCOR + RCOOH \rightarrow products</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>R^{3}</th>
<th>R^{1}</th>
<th>R^{2}</th>
<th>R=CHCl_{2}</th>
<th>R=CH_{2}Cl</th>
<th>R=H</th>
<th>R=CH_{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>CH_{3}</td>
<td>CH_{3}</td>
<td>40 0.75 50 1</td>
<td>50 1.25 80 3</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>CH_{3}</td>
<td>H</td>
<td>40 0.75 50 1</td>
<td>50 1.5 90 3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>CH_{3}</td>
<td>H</td>
<td>H</td>
<td>50 0.75 50 1.5</td>
<td>65 3 100 4</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td>50 1.25 60 4</td>
<td>60 1.5 90 6</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>C_{6}H_{5}</td>
<td>H</td>
<td>H</td>
<td>50 1.25 60 4</td>
<td>60 1.5 90 6</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>CH_{3}OCH_{3}</td>
<td>H</td>
<td>50 2.5 80 4</td>
<td>20 240 60 50**</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>H**</td>
<td>CH_{2}Cl</td>
<td>H</td>
<td>70 4 70 8</td>
<td>60 15 60 15</td>
<td>40</td>
<td></td>
</tr>
</tbody>
</table>

* For R^{1}=CH_{2}OC_{2}H_{5} or CH_{2}OCH(CH_{3})_{2} the conversions were slightly faster.
** Two equivalents of acid were used.
from the reaction mixture by distillation at reduced pressure. The cis-trans mixture of sec-buten-2-yl formate obtained by this procedure could be separated by repeated distillation with a spinning band column. The assignment of the physical constants to the isomers (Table IX) is tentative. Physical constants of some representative compounds:

<table>
<thead>
<tr>
<th>Compound</th>
<th>b.p. (°C)</th>
<th>nD^20</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_3C-C(CH_2H_2)(OCONH)_2</td>
<td>53/6.5</td>
<td>1.4242</td>
</tr>
<tr>
<td>H_3C-C(CH_2OCH)_2(OCONCl)_2</td>
<td>102/0.25</td>
<td>1.4619</td>
</tr>
<tr>
<td>H_3C-C(CH_2Cl)(OCONCl)_2</td>
<td>109/0.15</td>
<td>1.4863</td>
</tr>
<tr>
<td>H-C-OCH(CH_2OCH_2)=CH_2</td>
<td>48/17</td>
<td>1.4230</td>
</tr>
</tbody>
</table>

b. With aromatic carboxylic acids

The procedure is similar to that in 4b (dialkenyloxymethyl carboxylate used in excess). The reaction temperature was 150° and the reaction time from 4 hours (with p-chloro-) to 8 hours (with p-methoxy-benzoic acid).

6. Isolation of alkenyl 1,1-diacyloxyethyl ethers

In two experiments according to 4a, the treatment of H-C(OCR=CH_2)=CH_2OCOCH_2Cl (R=CH_2OCH_3 or CH_2Cl) with monochloroacetic acid, alkenyl 1,1-diacyloxyethyl ethers (XIV) could be isolated as side products in yields of 3% and 5%, respectively. Because their separation from the starting compound is difficult, the latter must be converted completely before isolation by distillation is attempted. For this reason a larger excess of the acid used (threefold) is useful to isolate these products. Other reaction conditions (temperature and time) are those given in Table V.

<table>
<thead>
<tr>
<th>Compound</th>
<th>b.p. (°C)</th>
<th>nD^20</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-C-[OC(CH_2OCH_2)=CH_2] (OCOCH_2Cl)_2</td>
<td>125/0.2</td>
<td>1.4710</td>
</tr>
<tr>
<td>H-C-[OC(CH_2Cl)=CH_2] (OCOCH_2Cl)_2</td>
<td>130/0.1</td>
<td>1.4830</td>
</tr>
</tbody>
</table>

The mass spectrum showed peaks at m/e = 213 probably for H-O-[OC(CH_2Cl)=CH_2] (OCOCH_2Cl) and m/e = 197 probably for H-C-[OC(CH_2Cl)=CH_2] (OCOCH_2Cl).

Acknowledgement

We thank Drs. F. Gerhartl and Mr. H. Mous for recording the mass spectra, Mr. J. Diersmann for performing the elemental analyses and Mrs. L. van Herpen for assistance in recording the NMR spectra.

(Received November 1st, 1972)