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VINYL ORTHOFORMATES AND VINYL ACETALS. PART III
The reactions of alkenyl acetals and 1-alkenyloxyalkyl carboxylates
with carboxylic acids

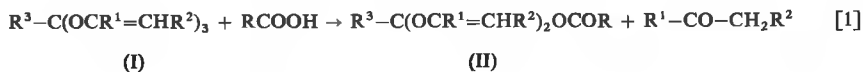
BY

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Treatment of alkenyl acetals IV with one equivalent of a carboxylic acid leads to the formation of either addition products, 1-acyloxyalkyl alkenyl acetals VI, or substitution products, 1-alkenyloxyalkyl carboxylates V, dependent upon the structure of the starting compounds. In a similar way the 1-alkenyloxyalkyl carboxylates V give 1,1'-diacyloxy ethers X, or acylals XI, with a second equivalent of a carboxylic acid. Synthetic applications and tentative reaction schemes of these conversions are given.

In previous papers of this series^{1,2} we described the reactions of alkenyl orthoesters I with carboxylic acids. It was shown that treatment of orthoesters with one equivalent of an acid leads to the formation of substitution products II *via* an intermediate carboxonium ion according to the overall equation [1].



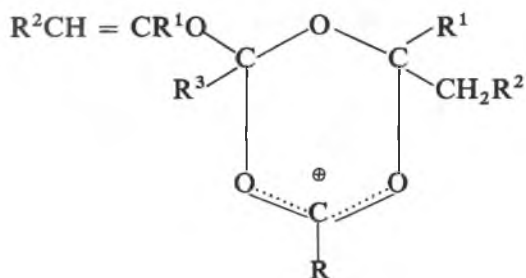
Addition of a second equivalent of the acid did not lead to further substitution. Instead, the 1,1-dialkenyloxyalkyl carboxylates II decomposed^{2,3}. Dependent on the nature of the substituents R, R¹, R², R³, either alkenyl carboxylates (R³-CO-OCR¹=CHR²) and acylals

¹ J. W. Scheeren, J. E. W. van Melick and R. J. F. Nivard, *Rec. Trav. Chim.* **90**, 1123 (1971).

² J. E. W. van Melick, J. W. Scheeren and R. J. F. Nivard, *Rec. Trav. Chim.* **92**, 775 (1973).

³ *Idem*, *Tetrahedron Letters* **1971**, 2083.

[$R^1-C(OCOR)_2CH_2R^2$] or alkenyl carboxylates, acid anhydrides [$(RCO)_2O$] and carbonyl compounds ($R^1-CO-CH_2R^2$) were obtained as the main products. It was suggested that a trioxenium cation III participates in the fragmentations.



(III)

In this paper our investigation of the reactions between the corresponding alkenyl acetals IV and carboxylic acids are presented.

The reaction: $R^2-CH(OCR^1=CH_2)_2 + RCOOH$

The addition of one equivalent of an acid to alkenyl acetals did not lead always to the expected substitution products. In general, these hitherto unknown 1-alkenyloxyalkyl carboxylates V^4 were only obtained if R^2 was a phenyl residue (preferably with an electron-donating substituent), or if R^1 contained an electron-withdrawing group (*e.g.* $R^1=CH_2OCH_3$). In other cases addition products, 1-acyloxyalkyl alkenyl acetals VI, always accompanied by small amounts of di-addition products VII, arose. Table I summarises the reaction products obtained from several alkenyl acetals. The results can best be explained by the reaction scheme [2].

⁴ Some products V of the type $R^1-CH(OCOR)OCH=CHR^2$ (R^1 and R^2 are aliphatic) are described by *L. W. McTeer* in a U.S. Patent, 3,383,374 (1968). See also C.A. 69, 26768 (1968).

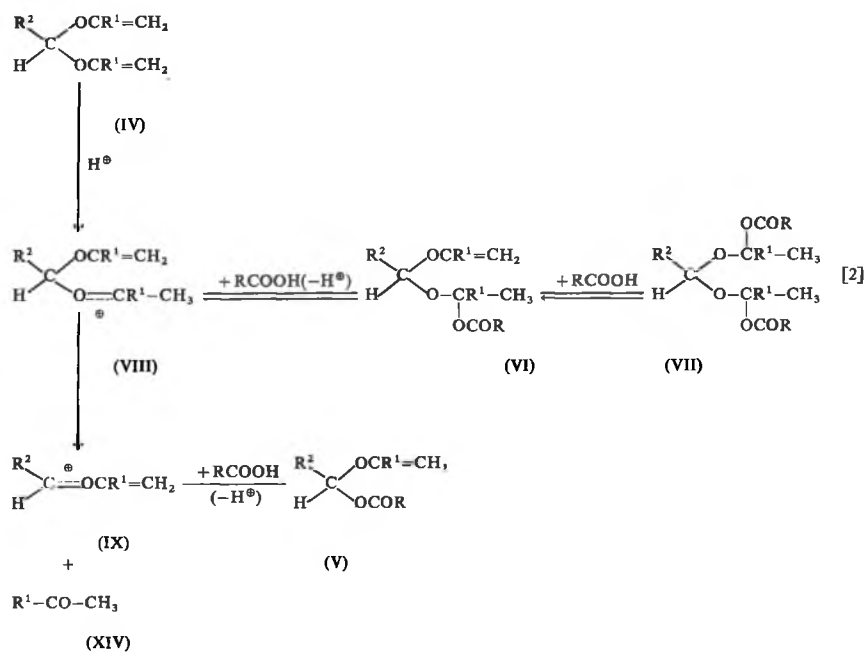
Table I

Reaction products from $R^2-CH(OCR^1=CH_2)_2 + RCOOH$

R ¹	R ²	main product	minor products
H	H	VI	VII
H	CH ₃ , <i>n</i> -C ₃ H ₇ , 2,6-Cl ₂ -C ₆ H ₃	VI	VII, V
H	<i>p</i> -X-C ₆ H ₄ *	V	—
CH ₃	CH ₂ Cl, CH ₃ **	VI	VII, V
CH ₃	<i>p</i> -X-C ₆ H ₄ *	V	—
CH ₂ OCH ₃	CH ₂ Cl	V	VI, VII
CH ₂ OCH ₃	CH ₃ , <i>n</i> -C ₃ H ₇ , <i>p</i> -X-C ₆ H ₄ *	V	—

* X = H, Cl, CH₃ or OCH₃.

** After prolonged reaction time V becomes the main product (see text).



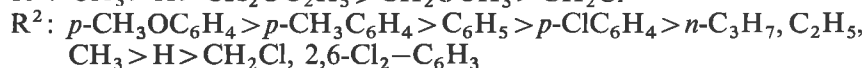
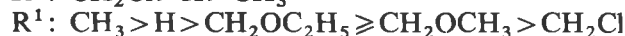
The scheme suggests that the carboxonium ion VIII, formed in an initial protonating step, does not always produce a carboxonium

ion IX. This ion IX is less stable than the corresponding cation ($\text{H}_2\text{C} = \text{CR}^1 - \text{O} = \overset{\oplus}{\text{C}}\text{R}^2 = \text{O} - \text{CR}^1 = \text{CH}_2$), formed in the analogous reactions of alkenyl orthoesters with acids. IX arises only if strongly stabilizing, donating groups R^2 are present, or if electron-withdrawing substituents in R^1 make its precursor VIII less stable.

The addition of a carboxylic acid to VI proceeds at a rate comparable to the formation of VI, because VII was always found as a second product in reactions where VI was the main product. This can be understood because substituent influences on the reactivity of the double bond in IV and VI will be about the same. A similar addition of acid to the substitution product V was generally not observed under the applied reaction conditions, using only one equivalent of the acid (see, however, the following section).

The formation of VI from VIII is probably a reversible process. In one case [$\text{CH}_3 - \text{CH}(\text{OCCH}_3 = \text{CH}_2)_2$] the amount of the initial addition product decreased gradually after prolonged reaction times, and the substitution product (V, $\text{R}^1 = \text{R}^2 = \text{CH}_3$) became the main product. The conversion of VI into V could have occurred directly *via* a cyclic transition state, but in the presence of acid a pathway *via* the cations VIII and IX seems more probable.

The reactions between alkenyl acetals and carboxylic acids have been followed by NMR to get an idea of the influence of R, R^1 and R^2 on the rate of product formation. It appeared that the rate decreased in the following sequences:

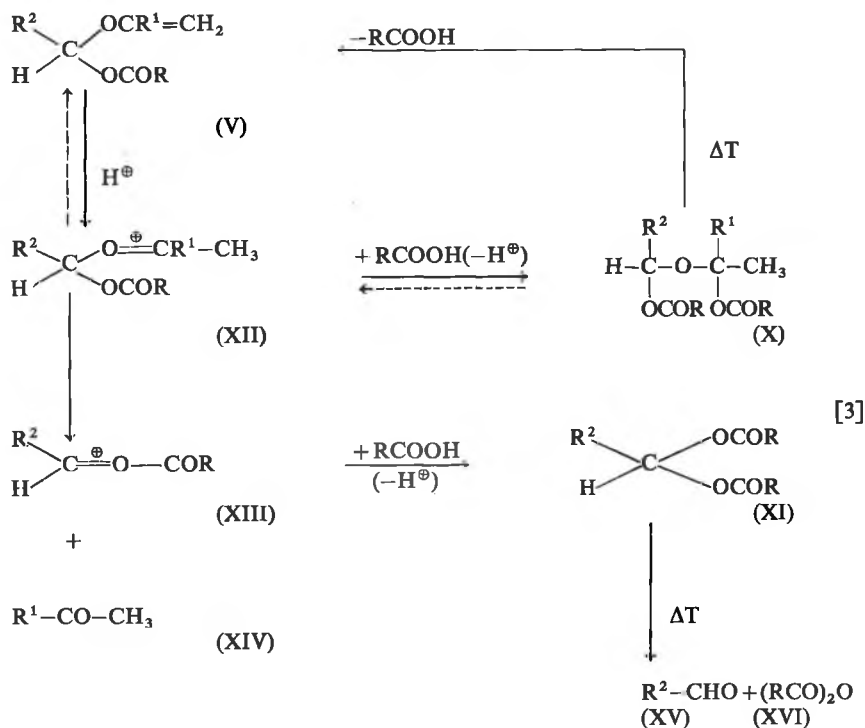


These data are in accordance with the proposed reaction scheme, in so far as both supposed intermediate cations are better stabilized by stronger electron-donating groups in R^1 or R^2 , and protonation, probably involved in the rate-determining step, becomes faster with stronger acids.

The reaction: $\text{R}^2 - \text{CH}(\text{OCR}^1 = \text{CH}_2)\text{OCOR} + \text{RCOOH}$

The 1-alkenyloxyalkyl carboxylates V behave similarly towards carboxylic acids as the alkenyl acetals, although their reactivity is lower.

Dependent upon the nature of the substituents (R , R^1 , R^2) and also upon temperature, either addition products, viz. 1,1'-diacyloxy-ethers X, or substitution products, viz. acylals XI, were obtained. These results suggest that the reactions proceed according to scheme [3], in outline similar to the scheme [2] given above. Slight modifications will be explained in the subsequent discussion.



At temperatures not exceeding 50° , addition, leading to compounds X, appeared to be the usual route in this reaction. Acylals XI were only formed in substantial amounts under these conditions if R^2 was an aryl group, strongly stabilizing a carboxonium ion such as XIII, and at the same time R^1 was an electron-withdrawing group (CH_2OCH_3 , CH_2Cl). However, in every case the amount of XI increased at higher temperatures ($80\text{--}100^\circ$) at the cost of previously formed X.

It was shown by means of NMR studies that pure 1,1'-diacyloxy ethers X decompose at higher temperatures into the acid (RCOOH) and the parent compound V, especially when $R^1 \neq \text{H}$. Subsequently acylals XI and ketones XIV appear in the reaction mixtures. On prolonged

heating the acylals themselves gradually decompose⁵, giving rise to aldehydes XV and acid anhydrides XVI.

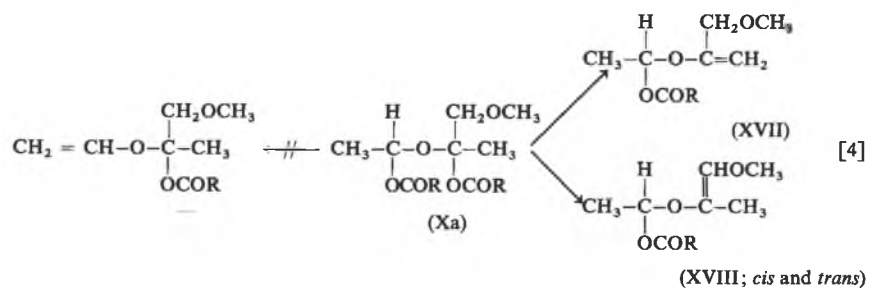
The influence of substituents R, R¹ and R² on the rate of thermal decomposition of X differs from that on its formation-rate. In both cases R² has no significant influence, and both reactions slow down in the series R = CH₂Cl > H > CH₃. For the influence of R¹, however, we found

CH₃ > CH₂OCH₃, CH₂OC₂H₅, CH₂Cl ≫ H in the decomposition of X, but

CH₃ > H > CH₂OC₂H₅ ≧ CH₂OCH₃ > CH₂Cl in the formation of X from V.

A possible explanation of these data is that, at higher temperatures and at the low acid concentrations in the initial stage of the reaction, the decomposition of X to V proceeds *via* a pathway comparable with that in ester pyrolyses⁶ rather than *via* a reversal of its synthetic route. The rate of this way of elimination will decrease as the olefins formed become less stable (R¹ = CH₃ > CH₂OCH₃ ≧ H). Similar eliminations in compounds VI (Scheme 2) have not been observed, but cannot be excluded under appropriate conditions.

The relatively slow decomposition of 1,1'-diacyloxy ethers X, with R¹ = H, explains why the elimination of acid in the example Xa represented in scheme [4] is restricted to that side of the molecule bearing the CH₂OCH₃ group (the scheme represents only overall reactions). Two products XVII and XVIII appeared to be formed, the latter in *cis* and *trans* configuration. The presumably less stable product XVII

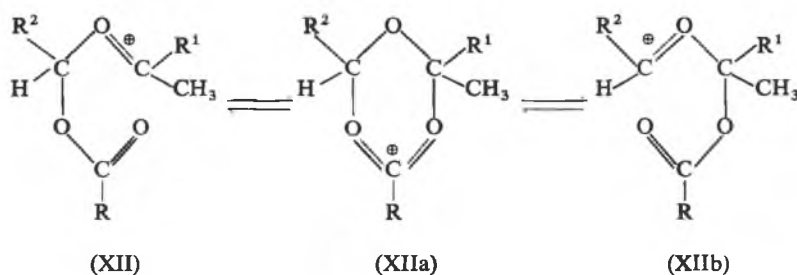


⁵ C. Coffin, J. Dacey and N. Parlee, *Can. J. Research* 15^B, 247 (1937).

⁶ Houben-Weyl, *Methoden der Organische Chemie*. Georg Thieme Verlag, Stuttgart, 1972. Band V/1b, p. 105.

arose faster, but was also converted more rapidly into an acylal or back into Xa. On careful decomposition more XVIII than XVII was eventually obtained, due to the "reversibility" of the reaction. However, XVIII also undergoes substitution by the acid present, giving mainly the ketone, $\text{CH}_3\text{-CO-CH}_2\text{OCH}_3$, and an acylal, $\text{CH}_3\text{-CH(OCOR)}_2$.

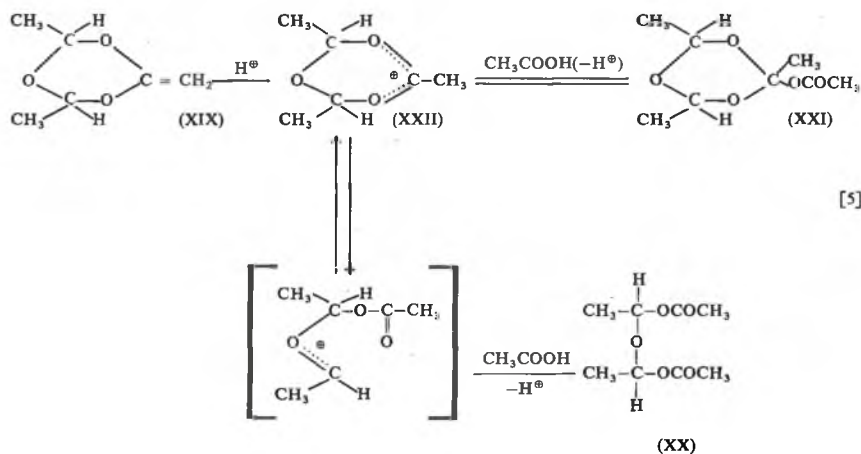
As to the intermediate carboxonium ions in scheme [3], it might be expected that XII and XIII will be less stable than the corresponding cations VIII and IX in scheme [2], respectively. The lower reactivity of the 1-alkenyloxyalkyl carboxylates V in comparison with alkenyl acetals IV seems in accordance with this expectation. The ion XII might be stabilized by isomerisation, giving a trioxenium ion XIIa, comparable to that (III) suggested in reactions of alkenyl orthoesters with two equivalents of an acid².



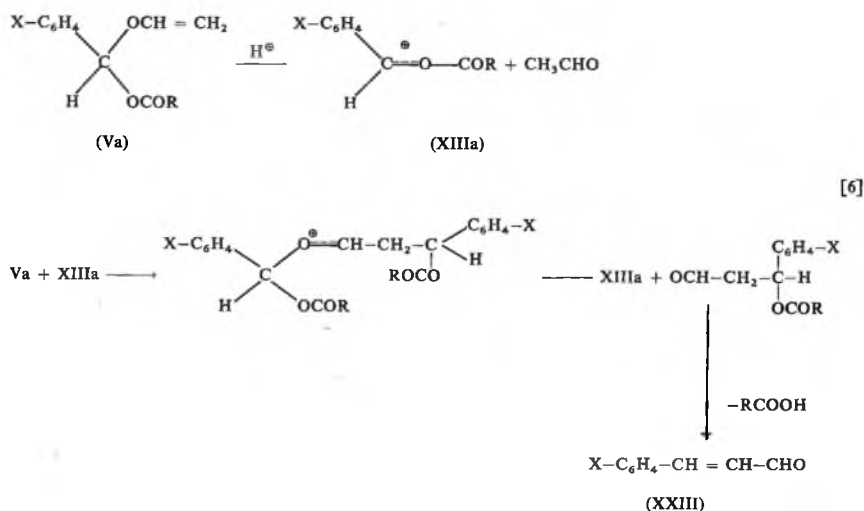
However, the ion XIIa might also equilibrate with the carboxonium ion XIIb. This should lead to the same addition product X as obtained *via* XII, but by substitution other products, $\text{R}^1\text{-C(OCOR)}_2\text{CH}_3$ and R^2CHO , should arise. These have never been found in our reaction mixtures. Hence, the occurrence of a trioxenium ion as an intermediate in this reaction remains uncertain.

A trioxenium ion⁷ such as XIIa can surely be expected as an intermediate in the reaction of methylenetrioxanes with acids. We found that treatment of 2,4-dimethyl-6-methylenetrioxane (XIX) with acetic acid at room temperature gives quantitatively di(1-acetoxyethyl) ether (XX) in a strongly exothermic reaction. NMR studies using 20% solutions in CDCl_3 showed that at low temperature (below -60°) the addition product XXI, which is only stable below -40° (Scheme 5), was formed quantitatively.

⁷ S. Hünig, *Angew. Chem.* 76, 400 (1964); *Angew. Chemie, Intern. Ed. English* 3, 548 (1964).



Finally, a brief remark may be made concerning the incidental occurrence of other side-products in reactions of 1-alkenyloxyalkyl carboxylates with acids. If $R^1 = H$ and $R^2 = p\text{-X-C}_6\text{H}_4$ ($X = H, \text{CH}_3, \text{OCH}_3$) in the parent compound, a cinnamic aldehyde XXIII also appeared in the reaction mixture. The amount of this side-product was higher when a stronger acid was used ($R = \text{CH}_2\text{Cl}$) and when X was more electron donating ($\text{CH}_3\text{O} > \text{CH}_3 > \text{H}$). A possible explanation is given in scheme [6]. It was shown that condensation of an aliphatic and aromatic aldehyde, which might also explain formation of XXIII did not occur under the reaction conditions used.



Experimental

In general, isolation and purification of reaction products was performed by distillation with 70×1.2 , 20×1.0 or 20×0.8 cm. Vigreux columns or with a spinning band column (Normag) of 25 plates. The use of other techniques is explicitly mentioned where appropriate.

Products were identified by NMR (Varian HA-100 or Varian T-60) from 10% solutions in carbon tetrachloride with TMS as internal standard. A mass spectrum (Varian-Mat-SM1-B) was sometimes also recorded.

In view of the large number of new compounds prepared, only a small number of each type are listed in Table II and III. Boiling points, refractive indices, NMR-data, and yields of preparations for many other examples from the various classes are available.

1) Synthesis of β -chloroalkyl acetals (Table II)

a. β -Chloroalkyl acetals of acetaldehyde, propionaldehyde and butyraldehyde were synthesized from the appropriate aldehydes and a β -chloroalcohol in the presence of granulated calcium chloride⁸.

b. β -Chloroalkyl acetals of benzaldehydes and chloroacetaldehyde were obtained via an acid catalyzed alcohol exchange from appropriate ethyl acetals⁹. The products were isolated after neutralization of the reaction mixture with sodium methoxide.

c. The β -chloroethyl acetal of formaldehyde was obtained by refluxing a mixture of equimolar amounts of paraformaldehyde, β -chloroethanol and β -chloroethyl orthoformate in the presence of a catalytic amount of *p*-toluenesulfonic acid¹⁰ for 8 hours.

d. 6-Bromomethyl-2,4-dimethyltrioxane was prepared by slow addition of 0.6 moles of bromine to 1 mole of paraldehyde¹¹, in the presence of enough potassium carbonate to neutralize the hydrogen bromide formed, and at a temperature below -10° . The mixture was left until it was discoloured and the p_H had increased to about 5. It was then filtered, and the filtrate distilled at reduced pressure, b.p. $78^\circ/14$ mm, yield 75%, n_D^{20} 1.4626.

2) Synthesis of alkenyl acetals IV (Table II)

a. Elimination of hydrogen chloride from β -chloroalkyl acetals was performed as described previously for β -chloroalkyl orthoesters^{1,2}. With acetals of formaldehyde and acetaldehyde sodium hydride in diglyme was used and the alkenyl acetals were directly distilled from the reaction mixtures. With those of propionaldehyde, butyraldehyde, benzaldehydes and chloroacetaldehyde sodium hydride in 1,2-dimethoxyethane, to which some *tert*-butyl alcohol had been added, was used.

⁸ Houben-Weyl, Methoden der Organische Chemie. Georg Thieme Verlag, Stuttgart, 1965. Band VI/3, p. 204.

⁹ Ref. 8, p. 250.

¹⁰ Ref. 8, p. 222.

¹¹ A. Stepanow, N. Preobraschensky and M. Schtschukina, Ber. 59, 2533 (1926).

Table II

R ²	R ¹	B.p. °C/mm	n _D ²⁰	yield	δ H _α
β-Chloroalkyl acetals, R ² -CH ₂ (OCHR ¹ -CH ₂ Cl) ₂					
H	H	73°/1.7	1.4550	65 %	4.71
CH ₃	CH ₃	76°/0.8	1.4492	45 %	4.85
<i>n</i> -C ₃ H ₇	CH ₂ Cl	130°/0.1	1.4799	35 %	4.74
CH ₂ Cl	CH ₃	92°/0.5	1.4706	70 %	4.77
C ₆ H ₅	CH ₂ Cl	158°/0.2	1.5322	80 %	5.76
<i>p</i> -Cl-C ₆ H ₄	CH ₃	162°/0.8	1.5188	80 %	5.75*
2,6-Cl ₂ -C ₆ H ₃	H	151°/0.1	1.5450	80 %	6.05
Alkenyl acetals, R ² -CH ₂ (OCR ¹ =CH ₂) ₂					
CH ₃	CH ₃	48°/26	1.4261	70 %	5.46
CH ₃	CH ₂ OCH ₃	75°/0.6	1.4476	90 %	5.56
CH ₃	CH ₂ Cl	76°/0.2	1.4801	40 %	5.50
CH ₂ Cl	CH ₃	70°/16	1.4480	70 %	5.40
C ₆ H ₅	CH ₂ OCH ₃	115°/0.3	1.5069	55 %	6.25
<i>p</i> -Cl-C ₆ H ₄	CH ₃	95°/0.9	1.5175	75 %	6.12
2,6-Cl ₂ -C ₆ H ₃	H	93°/0.1	1.5463	80 %	6.62

* At both sides of the main peak a small peak from diastereoisomers is present.

1,3-Dichloroisopropyl acetals were converted into the corresponding 3-alkoxyisopropenyl acetals with sodium alkoxide in alcohol. With potassium hydroxide in water/1,2-dimethoxyethane (1/1) the same starting compounds gave 3-chloroisopropenyl acetals. In the reaction between 1,3-dichloroisopropyl acetals of a benzaldehyde and sodium methoxide in methanol the dimethyl acetal of the benzaldehyde used was a substantial side-product.

b. 2,4-Dimethyl-6-methylenetrioxane (XIX) was obtained by the addition of 0.1 mole of 6-bromomethyl-2,4-dimethyltrioxane to a suspension of 0.13 moles of sodium hydride in 35 ml hexamethylphosphonamide. The mixture was heated at 80° for four hours and then distilled at reduced pressure. The fraction collected from 45–55° (40 mm) was redistilled; b.p. 52° (48 mm), yield 40%, n_D²⁰ 1.4265. The *cis-trans* mixture was not separated.

3) Reactions of alkenyl acetals with carboxylic acid

Syntheses of 1-alkenyloxyalkyl carboxylates V (Table III) and 1-acyloxyalkyl alkenyl acetals VI.

Anhydrous formic or acetic acid (0.055 moles), or a solution of 0.055 moles of chloroacetic acid in 10 ml of dry ether, was added dropwise to 0.05 moles of an alkenyl acetal over half an hour. Volatile compounds (ether, acetaldehyde), if present, were evaporated at reduced pressure. In most cases the reaction mixture was then heated at about 50° until the starting compound had for the most part (>90%) disappeared. The reaction times varied from 1 to 36 hours; slow reactions ($R = CH_3$, $R^1 = CH_2OCH_3$ or CH_2Cl , Scheme 2) could be catalyzed by addition of a small amount of trifluoroacetic acid. Reactions of compounds with $R^1 = CH_3$ were performed at 20°. In cases where 1-acyloxyalkyl alkenyl acetals VI were isolated as the main product, small amounts of 1-acyloxyalkyl acetals (VII) were obtained as side products. Physical constants of some isolated mono-addition products VI are given below.

$ClH_2C-CH(OCH=CH_2)OCH(OCOCH_3)CH_3$ b.p. 81°/14 mm; $n_D^{20} = 1.4376$; yield 50%;
 $n-C_3H_7-CH(OCH=CH_2)-OCH(OCOH)CH_3$ b.p. 78°/14 mm; $n_D^{20} = 1.4228$; yield 50%.

4) Synthesis of 1-acyloxyethyl acetals of aliphatic aldehydes (VII)

1-Acyloxyethyl acetals can be isolated in good yields from reaction mixtures similar to those used in the foregoing procedure, but containing a vinyl acetal of an aliphatic aldehyde and 2.5 instead of 1.1 equivalent of an acid, e.g.

$H_2-C[O-CH(OCOH)CH_3]_2$ b.p. 107°/16 mm; $n_D^{20} 1.4161$; yield 80%;
 $ClH_2C-CH[O-CH(OCOH)CH_3]_2$ b.p. 131°/16 mm; $n_D^{20} 1.4386$; yield 90%.

5) Synthesis of 1,1'-diacyloxy ethers¹² (X) (Table III)

a. Reaction mixtures similar to those used in the reactions between alkenyl acetals and acids were employed, using an alkenyloxyalkyl carboxylate instead of an alkenyl acetal. Generally, best results were obtained at low reaction temperatures (0° for $R^1 = CH_3$, 50° for $R^1 = H$, room temperature in other cases). Reaction times needed for at least 90% conversion varied considerably; 2–36 hours with mono-chloroacetic acid, 2–72 hours with formic acid, 6 hours – two weeks with acetic acid. In general the fastest conversions were found for $R^1 = CH_3$ and the slowest for $R^1 = CH_2OCH_3$ or CH_2Cl . Higher temperatures or catalysis with trifluoroacetic acid have to be avoided, however, in order to prevent formation of acylals. Because the products can decompose during distillation at too high temperature, isolation and purification were performed at low pressure and in some cases by molecular distillation.

b. 1-Acyloxyethyl acetals (VII, $R^1 = H$) can be converted into 1,1'-diacyloxy ethers (X) by heating them with 0.5 equivalent of the acid corresponding with the acyloxy residue at 100–120° for 2–6 hours.

6) Synthesis of acylals of benzaldehydes (XI)

1.1 Equivalents of a carboxylic acid were added to an 1-alkenyloxybenzyl carboxylate (V, $R^2 = p-XC_6H_4$, $R^1 \neq H$) or 2.5 equivalents to an alkenyl acetal of benzaldehyde

¹² For a simple synthesis of symmetrical 1,1'-diacyloxy ethers of the type $R^1-CH(OCOR)OCH(OCOR)R^1$ (R^1 is aliphatic) see ref. 4.

Table III

R ²	R ¹	R	B.p. °C/mm	n _D ²⁰	yield	δ H _α
1-alkenyloxyalkyl carboxylates, R ² -CH ₂ (OCR ¹ =CH ₂)OCOR						
CH ₃	H	CH ₂ Cl	43°/0.7	1.4415	10 %	6.18
CH ₃	CH ₂ OCH ₃	H	53°/1.0	1.4273	80 %	6.40
CH ₃	CH ₂ Cl	CH ₂ Cl	74°/0.2	1.4682	70 %	6.38
CH ₂ Cl	CH ₂ OCH ₃	H	91°/3.5	1.4533	70 %	6.42
C ₆ H ₅	H	H	76°/1.0	1.5091	80 %	6.90
C ₆ H ₅	CH ₃	CH ₂ Cl	113°/0.4	1.5154	75 %	7.04
C ₆ H ₅	CH ₂ OCH ₃	CH ₃	102°/0.3	1.5010	80 %	7.07
<i>p</i> -Cl-C ₆ H ₄	CH ₃	H	101°/0.2	1.5183	85 %	7.14
2,6-Cl ₂ -C ₆ H ₃	H	CH ₃	93°/0.1	1.5392	5 %	7.52
1,1'-diacyloxy ethers, R ² -CH ₂ (OCOR)-O-CCH ₃ (OCOR)R ¹						
H	H	H	80°/15	1.4142	75 %	5.40
CH ₃	H	CH ₂ Cl	106°/0.6	1.4540	75 %	6.13
CH ₃	CH ₃	H	56°/1.5	1.4190	65 %	6.41
CH ₃	CH ₂ OCH ₃	CH ₃	81°/1.3	1.4246	80 %	6.28
<i>n</i> -C ₃ H ₇	CH ₂ OCH ₃	CH ₂ Cl	**	1.4590	50 %	6.31
CH ₂ Cl	H	CH ₂ Cl	136°/1.3	1.4698	70 %	6.13
CH ₂ Cl	CH ₃	CH ₃	69°/0.1	1.4365	80 %	6.28
C ₆ H ₅	H	CH ₃	117°/1.1	1.4823	60 %	6.83*
C ₆ H ₅	CH ₃	CH ₃	108°/0.1	1.4842	65 %	7.09
<i>p</i> -Cl-C ₆ H ₄	CH ₃	H	**	1.5155	50 %	7.23
2,6-Cl ₂ -C ₆ H ₃	H	H	120°/0.1	1.5238	80 %	7.52*

* The main peak is accompanied by a small peak due to diastereoisomers.

** Isolated by molecular distillation at ~40°/10⁻³ mm.

(IV, R² = *p*-XC₆H₄, R¹ ≠ H), and the mixture was heated to 50° for about 2 hours for R¹ = CH₃, or about 12 hours for R¹ = CH₂OCH₃; in this way we isolated, e.g.

C₆H₅-CH(OCOH)₂ b.p. 80°/0.1 mm; n_D²⁰ 1.5065; yield 70 %;

p-ClC₆H₄-CH(OCOH)₂ b.p. 121°/1.5 mm; n_D²⁰ 1.5261; yield 60 %.

7) Decomposition of 1,1'-diacyloxy ethers (X)

Pure 1,1'-diacyloxy ethers were heated at such a pressure that the acid eliminated evaporated from the reaction mixture at a suitable rate. Temperatures were 100–120° for

$R^1 = CH_3$ and about 200° for $R^1 = H$. Elimination products $R^2CH(OCR^1=CH_2)OCOR$ could be isolated by distillation and redistillation, *e.g.*

$CH_2Cl-CH(OCCH_3=CH_2)OCOH$ b.p. $68^\circ/15$ mm; n_D^{20} 1.4416; yield 80%;
 $CH_3-CH(OCCH_3=CH_2)OCOCH_3$ b.p. $96^\circ/18$ mm; n_D^{20} 1.4149; yield 70%;
 $H-CH(OCH=CH_2)OCOCH_3$ b.p. $75^\circ/100$ mm; n_D^{20} a.4105; yield 60%.

To obtain elimination product of general structure $R^2-CH(OCCH_3=CHOCH_3)OCOR$ (XVIII) appropriate 1,1'-diacyloxy ethers were heated at slightly lower temperatures (90° for $R = H$ or CH_2Cl , 100° for $R = CH_3$) until the starting compound had disappeared (3–9 hours). By distillation of the residue acylals XI, as well as the alkenyloxy-alkyl carboxylates $R^2CH(OCCH_3=CHOCH_3)OCOR$, could be isolated. The latter compounds could not be separated completely from traces of acylals XI and 1-alkenyloxy-alkyl carboxylates V, even with a spinning band column, but their purity was at least 90%. Boiling points were about the same as those of their isomers XVII.

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