Experimental part

Preparation of 1-(chloromethylthio)-1-alkynes **1**

a. From RC≡C–Li and $ClCH_2SC{\equiv}N$

To a solution of 0.10 mol of butyllithium in 70 ml of hexane and 100 ml of ether was added, with cooling below −10°, 0.10 mol of the alkyne (in the case of propyne and butyne a cold (−30°) solution of 0.12 mol of the alkyne in 30 ml of ether was added). Subsequently a mixture of 0.10 mol of chloromethyl thiocyanate[15] and 40 ml of ether was introduced at −30°/−40°. The cooling bath was then removed, and after an additional period of 20 minutes the mixture was hydrolysed with ice-water. Extraction with ether, drying over $MgSO_4$ and distillation gave the compounds **1**.
For yields and spectral data see Tab. I.

b. From $RC{\equiv}CLi,S_8$ and $BrCH_2Cl$

A suspension of 0.20 mol of an alkynyllithium was prepared by adding a mixture of 0.20 mol of an alkyne and 25 ml of THF (in the case of propyne and butyne cooled at −30°) to a cooled (−30°C), vigorously stirred solution of 0.20 mol of butyllithium in 140 ml of hexane. Subsequently 140 ml of dry THF were added. The cooling bath was removed and 0.20 mol of powdered and dry sulfur was added with vigorous stirring. The temperature was kept between 0° and 5°C for 45 minutes, and subsequently 0.40 mol of $BrCH_2Cl$ was introduced in one portion. The reaction was rather slow. After 6 h the brown solution was poured into 1 l of ice-water. The upper layer and three pentane extracts of the water layer were combined, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel). Distillation gave the compounds **1** in yields of 58–63%.

Reaction of the compounds **1** *with alkali metal sulfide, selenide and telluride. Preparation of the five-membered ring compounds* **2**

To a vigorously stirred solution of 0.20 at of sodium in 500 ml of liquid ammonia was added over 10 minutes 0.20 mol of powdered sulfur or 0.10 mol of powdered selenium or tellurium. After 1 h the ammonia was evaporated by warming the flask in a water bath of 40°. During this operation nitrogen was passed through in order to prevent oxidation of the sulfide, selenide and telluride. To the residue were successively added 250 ml of methanol, 50 ml of dimethylformamide and 0.05 mol of **1**. After 8–9 h 500 ml of ice-water were added to the dark reaction mixtures. The product was extracted with dichloromethane. After washing the extracts with water and drying over $MgSO_4$, the solvent was removed by evaporation in a water pump vacuum. The residue was subjected to column chromatography. Subsequent distillation afforded the heterocycles **2**. For physical data, spectra and yields see Tables II and III.

Reaction of **1** *(R = CH_3, t-C_4H_9) with sodium alkanethiolate NaSR' (R' = CH_3, C_2H_5) in liquid ammonia. Formation of the products* **3**

To a solution of 0.12 mol of sodium in 300 ml of liquid ammonia was added dropwise dimethyl disulfide or diethyl disulfide, until the blue colour had disappeared. Ethanol (50 ml) and compounds **1** (0.05 mol) were successively added. After three hours the ammonia was evaporated by placing the flask in a water bath of 50°. Ice-water was added to the residue and the products **3** were isolated by extraction with ether, drying over $MgSO_4$ and distillation (see Tab. IV).

Table IV Physical constants, yields and ^{1}H-NMR data of the compounds $RC{\equiv}C{-}S{-}CH_2{-}S{-}R'$, **3**.

Compound **3** R	R'	B.p. °C/mm Hg	n_D^{20}	Yield (%)	^{1}H-NMR δ(R)	δ(CH_2)	δ(R')
Me	Me	86/15	1.5662	83	1.93	3.80	2.20
Me	Et	95/12	1.5520	81	1.96	3.83	1.33; 2.70
t-Bu	Me	97/15	1.5223	95	1.20	3.76	2.20

$ZnCl_2$-catalysed cycloadditions between ketene acetals and α,β-unsaturated carbonyl compounds. A simple route to 2,2-dialkoxy-3,4-dihydropyrans*

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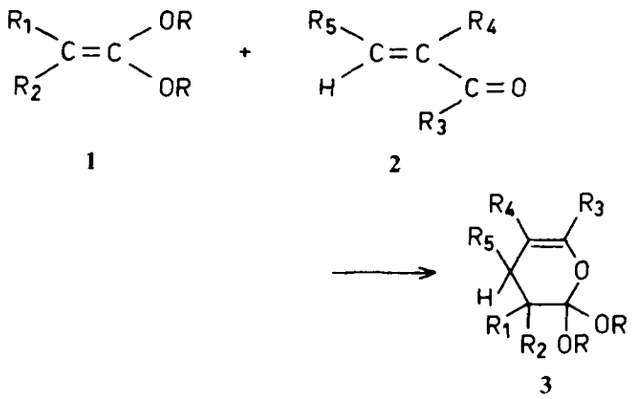
Abstract. 2,2-Dialkoxy-3,4-dihydropyrans (**3**) can be obtained under mild conditions and in good yields from ketene acetals (**1**) and α,β-unsaturated carbonyl compounds (**2**) in the presence of $ZnCl_2$. At low temperatures (< −20°C) the reaction between **1** and **2** proceeds as a (2 + 2)-cycloaddition, leading to an oxetane (**4**), which can sometimes be isolated by neutralisation of the Lewis acid. At higher temperatures, however, the oxetanes decompose into the starting compounds, eventually leading to the thermodynamically more stable dihydropyrans. The cycloadditions of tetramethoxyethene (**1a**) with **2**, having no substituents at the β-carbon atom, yield a cyclobutane derivative as the low temperature product; in cycloadditions of α,β-unsaturated esters this is the final product. Cycloadditions of 2-chloroketene acetal (**1e**) lead in some cases to 2 : 1 adducts. The deviating behaviour of **1a** and **1e** is discussed.

Recent literature presents several synthetic procedures[1], in which 2,2-dialkoxy-3,4-dihydropyrans (**3**) are used as starting compounds. The same compounds have also been used in mechanistic studies[2]. *Meerwein* has given[3] a useful

* This paper is considered as Part III in the series: Chemistry of ketene acetals. Part II: *J. W. Scheeren, F. J. M. Dahmen* and *C. G. Bakker*, Tetrahedron Lett. **1979**, 2925.

method for the preparation of mixed ortho esters, but application of this method to the synthesis of *cyclic* ortho esters such as **3** requires α-dihydropyrones, which are not generally accessible *via* simple methods.

Cycloadditions according to Scheme 1 could provide another method for the synthesis of **3**, as has been demonstrated in reactions of 1,1-diethoxyethene[4] (**1**, $R^1 = R^2 = H$, R = Et) and 1,1-dialkoxy-2-chloroethenes[5] (**1**, $R^1 = Cl$, $R^2 = H$) with several α,β-unsaturated carbonyl compounds (**2**). These conversions, however, required rather high temperatures (> 100°C) together with long



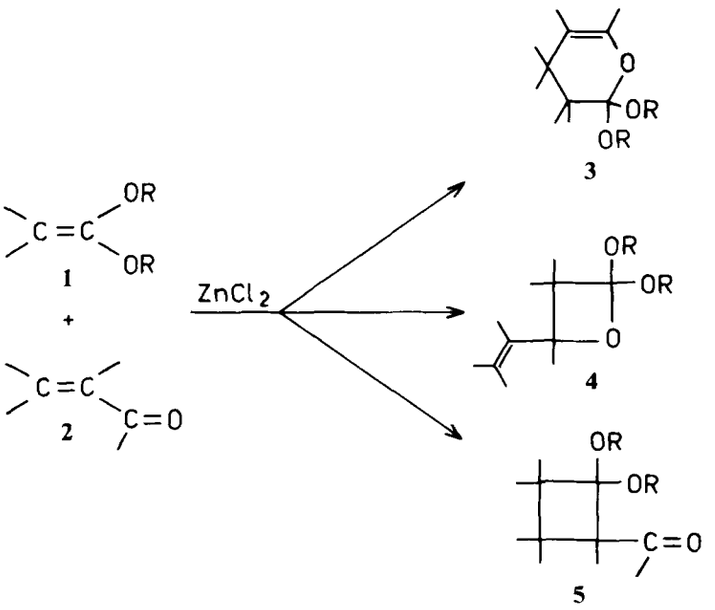
Scheme 1

reaction times, and the yields were mostly below 50%. With more substituted ketene acetals and less reactive α,β-unsaturated carbonyl compounds it might be expected that the yields would deteriorate or the reaction completely fail (compare ref. 6).

In previous investigations on cycloadditions of ketene acetals we have found that these olefins react under much milder conditions with aldehydes or ketones[7,8] and with acrylic esters[9], to give oxetanes and cyclobutanes, respectively, when a small amount of zinc chloride is used as catalyst. Ketene acetals appeared to be relatively stable against di- and polymerisation in the presence of this Lewis acid, so that satisfactory yields could be obtained in these (2 + 2)-cycloadditions. With these results in mind, we studied the reaction between ketene acetals and several α,β-unsaturated carbonyl compounds in the presence of $ZnCl_2$, as a possible method for the preparation of 2,2-dialkoxydihydropyrans.

A priori, reactions between **1** and **2** with $ZnCl_2$ as catalyst could lead to three types of cycloaddition products *viz.* dihydropyrans (**3**) *via* (4 + 2)-, together with oxetanes (**4**) and cyclobutanes (**5**) *via* (2 + 2)-cycloaddition (Scheme 2).

In this study the influence of structural factors and the effect of temperature on the course of the reaction is elucidated.



Scheme 2

Results

In Tab. I the ketene acetals used (**1a-e**) have been arranged horizontally according to their decreasing electron density and increasing polarisation. The unsubstituted ketene acetal ($R^1 = R^2 = H$) has not been included, because a previous study[7] of its reactivity towards simple aldehydes in the presence of $ZnCl_2$ revealed that rather complex reaction mixtures always arise from this compound. The α,β-unsaturated carbonyl compounds used in this study have been tabulated vertically, with the aldehydes (**2a-d**) prior to the ketones (**2e-g**). All products isolated from reactions between these compounds have been mentioned in the Table.

We found that in nearly all reactions studied dihydropyrans (**3**) could be obtained when solutions of **1** and **2** in acetonitrile, one of them containing 0.5–2 mol % $ZnCl_2$, were mixed at 60° and left at this temperature for some time. When the reactions were performed at a lower temperature (−20°C), with longer reaction times, oxetanes (**4**) instead of **3** appeared to be formed.

In general, the oxetanes were rather unstable; on heating (10–50°), especially in the presence of $ZnCl_2$, they decomposed into the starting compounds **1** and **2**, which could be distilled at reduced pressure. In most of the reactions with **2a** and **b** the oxetanes could be isolated by neutralisation of the Lewis acid with triethylamine at low temperature, followed by precipitation of the salt with pentane and evaporation of all volatile compounds from the reaction mixture *in vacuo*[7]. Samples thus obtained were sufficiently pure (> 90%) for identification by NMR. In general, the stability of the oxetanes from **2a** and **b** decreased from left to right across the Table: the oxetanes from the reactions between **2b**, **c** and **1a** appeared to be sufficiently stable for distillation under reduced pressure (80–100°C). Decomposition was only observed above 120° and led to complete polymerisation. This explains why **3** could not be obtained from these reaction mixtures. In cycloadditions with **2d-g** we did not succeed in isolating an oxetane (**4**); **3** was the only product obtained from these reactions.

The reactions of **1a** with **2a** and **2e** at low temperature (< −20°C) did not yield oxetanes (**4**), but gave instead mixtures of a cyclobutane (**5**) and a dihydropyran (**3**). The

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[1] *Ch. B. Chapleo, P. Hallett, B. Lythgoe* and *P. W. Wright*, Tetrahedron Lett. **1974**, 847; *R. J. Cave, B. Lythgoe, D. A. Metcalfe* and *J. Waterhouse*, J. Chem. Soc. Perkin I, **1977**, 1218; *Ch. B. Chapleo, P. Hallett, B. Lythgoe, J. Waterhouse* and *P. W. Wright*, J. Chem. Soc. Perkin I, **1977**, 1211; *Vu Moc Thuy*, Bull. Soc. Chim. **1970**, 4429; *T. Tsijikawa, Y. Nakagav* and *K. Tsukamara*, Heterocycles **6**, 261 (1977).

[2] *P. Deslongchamps, R. Chênevert, R. J. Taillefer, Cl. Moreau* and *J. K. Saunders*, Can. J. Chem. **53**, 1601 (1975).

[3] *H. Meerwein, P. Borner, O. Fuchs, H. J. Sasse, H. Schrodt* and *J. Spille*, Chem. Ber. **89**, 2060 (1956).

[4] *S. M. McElvain, E. D. Degginger* and *J. D. Behun*, J. Am. Chem. Soc. **76**, 5736 (1954).

[5] *A. Bélanger* and *P. Brassard*, J. Chem. Soc. Chem. Commun. **1972**, 863; Can. J. Chem. **53**, 195, 201 (1975).

[6] *S. S. Hall, G. F. Weter* and *A. J. Duggan*, J. Org. Chem. **43**, 667 (1978).

[7] *J. W. Scheeren, R. W. Aben, P. H. J. Ooms* and *R. J. F. Nivard*, J. Org. Chem. **42**, 3128 (1977).

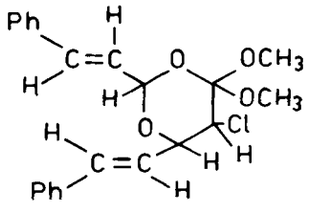
[8] *R. W. Aben* and *J. W. Scheeren*, Synthesis **1978**, 400.

[9] Unpublished results.

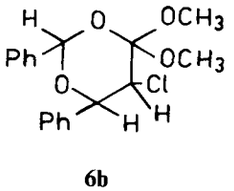
cyclobutanes could be separated from the reaction mixtures by neutralisation of the catalyst at −20°C followed by HPLC at room temperature. In this way **5** was obtained in 40–50% yield together with the corresponding (4 + 2)-adduct (**3**). The pure cyclobutanes were easily and quantitatively converted into dihydropyrans when $ZnCl_2$ was added at room temperature. Formation of the starting compounds **1** and **2** during this transformation could not be detected by NMR. When the cycloadditions between **1a** and **2a** or **2e** were performed at higher temperature (80°C) **3** was the only product obtained.

It is noteworthy that cyclobutanes (**5**) are the only cycloaddition products obtained from reactions between **1a** or **1d** and acrylic esters (**2**, R^3 = OAlk, $R^4 = R^5$ = H)[9]. Acryloyl chloride (**2**, R^3 = Cl, $R^4 = R^5$ = H) gave a similar result with **1a**, but its reaction with **1d** led to a complex mixture, the NMR spectrum of which indicated the presence of the (4 + 2)-cycloadduct (**3**, R^1 = Me, R^3 = Cl, $R^2 = R^4 = R^5$ = H) (δ 4.0–4.5, m, 1H, characteristic for HC=C(Cl)–O in dimethoxy-dihydropyrans).

The reactions of **1e** with **2b** and **c** also gave complex mixtures. In the reaction with cinnamaldehyde (**2c**) the mixture could be partially separated; an impure product was obtained, which was identified by NMR and mass spectroscopy as the 1 : 2 adduct **6a**. An analogous product **6b** was obtained from benzaldehyde and **1e**. Reaction of **1e** with **2e** in the presence of $ZnCl_2$, however, gave **3**. A similar result had been previously[5] obtained in the uncatalysed reaction.



6a



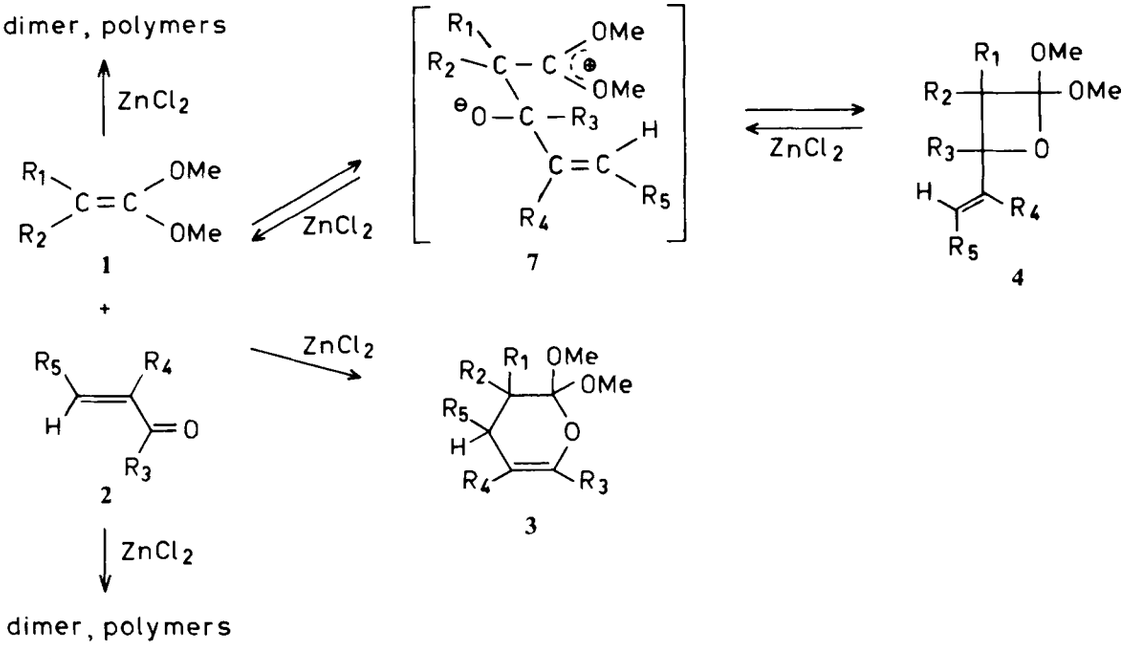
6b

Discussion

Insight into mechanistic details of cycloaddition reactions can be obtained by application of the Frontier Orbital theory[10-12], which uses the main interaction between the HOMO's and LUMO's of the reactants as a simple but useful method for describing the course of these reactions. In our case this main interaction concerns the overlap between the HOMO of the ketene acetal (**1**) and the LUMO of the carbonyl compound (**2**), since the energy gap between these MO's is the smaller one[10]; the energy of the HOMO of **1** is high as a consequence of the donating methoxy substituents; the LUMO of **2** is lowered by complexation with the catalyst. The effect of $ZnCl_2$, which should be comparable to that of protonation[11], leads not only to lowering of the energy of the LUMO (and HOMO) of **2**, but also causes an increase of the LUMO coefficients at the carbonyl carbon atom to a far greater extent than at C_β. This explains the general tendency for oxetane formation, which is observed at low temperature. In the reversible oxetane formation, bond formation at the carbonyl carbon of **2** will occur much faster than at the carbonyl oxygen, such that the reaction proceeds via strongly polar intermediate states (Scheme 3), probably via a $ZnCl_2$-complexed, dipolar intermediate (**7**). Bond formation at C_β, leading to a (4 + 2)-cycloaddition product, proceeds more slowly than at the carbonyl carbon and is only observed at higher temperature. This formation of a more stable six-membered ring compound, also catalysed by $ZnCl_2$, has a more concerted character.

The preference for the formation of an oxetane as the kinetically determined product is most clearly demonstrated in the reactions with α,β-unsaturated *aldehydes* without a substituent at C_α (R^4 = H). This is understandable because these compounds (**2a-c**) only occur in a transoid conformation, which is an additional handicap to (4 + 2)-cycloaddition. In the α,β-unsaturated *ketones* (**2e-g**) and also in the aldehyde **2d** cisoid and transoid conformations are in equilibrium to a greater extent. This favours the (4 + 2)-cycloaddition relative to the oxetane formation. In **2g** the methoxy substituent at C_β raises the LUMO energy, thus

[10] *K. N. Houk* in: "Pericyclic Reactions", Vol. II, Eds. *A. P. Marchand* and *R. E. Lehr*, Acad. Press, New York, 1977, p. 181.
[11] *I. Fleming*, "Frontier Orbitals in Organic Chemical Reactions", J. Wiley and Sons, London, 1976, p. 86.
[12] *K. Fukui*, "Theory of Orientation and Stereoselection", Springer Verlag, Berlin, 1975.



Scheme 3

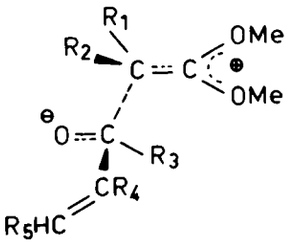
Table I Products isolated from reactions between ketene acetals (**1a-e**) *and α,β-unsaturated carbonyl compounds* (**2a-g**); **3** = *dihydropyran*, **4** = *oxetane*, **5** = *cyclobutane (see Scheme 2)*.

1 / 2	R^3	R^4	R^5	**a** OMe OMe	**b** OMe H	**c** Me Me	**d** Me H	**e** Cl H
a	H	H	H	5 → 3	4 → 3	4 → 3	4 → 3	3
b	H	H	Me	4	4 → 3	4 → 3	4 → 3	(1 : 2 adduct)
c	H	H	Ph	4		(see ref. 8)	4 → 3	(1 : 2 adduct)
d	H	Me	H			3	3	
e	Me	H	H	5 → 3		3	3	3
f	Ph	H	H	(4+2)-cyclo-adduct of **2f**		3	3	
g	Me	H	OMe	No reaction			3	

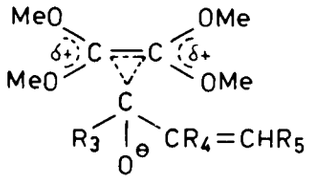
lowering reactivity of this compound. The substituent also enlarges the LUMO coefficient at this carbon atom; **3** might be the kinetically determined product in this case.

In reactions of acrylic esters (R^3 = OR) with ketene acetals neither an oxetane nor a dihydropyran is isolated. Both reactions imply bond formation at the carbonyl oxygen and should be accompanied by loss of conjugation in the ester function, which will lower the stability of such products. Addition of the ketene acetal occurs at the olefinic bond and leads to a cyclobutane derivative, which will be thermodynamically more stable.

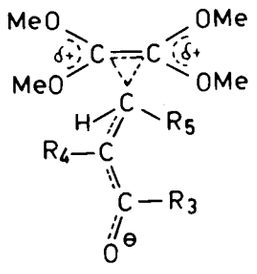
A similar cyclobutane formation was also observed in the reactions of **2a** and **2e** with **1a**. We tend to ascribe these results to the special nature of the dipolar intermediate in (2 + 2)-cycloadditions of the symmetrically substituted ketene acetal **1a**. In the oxetane formation from less symmetric ketene acetals the intermediate arises from $1^D_s + 1^A_s$ overlap (**7a**); in reactions with **1a**, $2^D_s + 1^A_s$ overlap, as indicated in **7b**, should be preferred[7].



7a



7b



7c

Table II Dipole moments (μ) *of ketene acetals in Debye units*[13].

		μ
R = Me	R^1 = H	1.37
R = Et	R^1 = H	1.50
R = Et	R^1 = Me	1.28
R = Et	R^1 = Cl	2.51

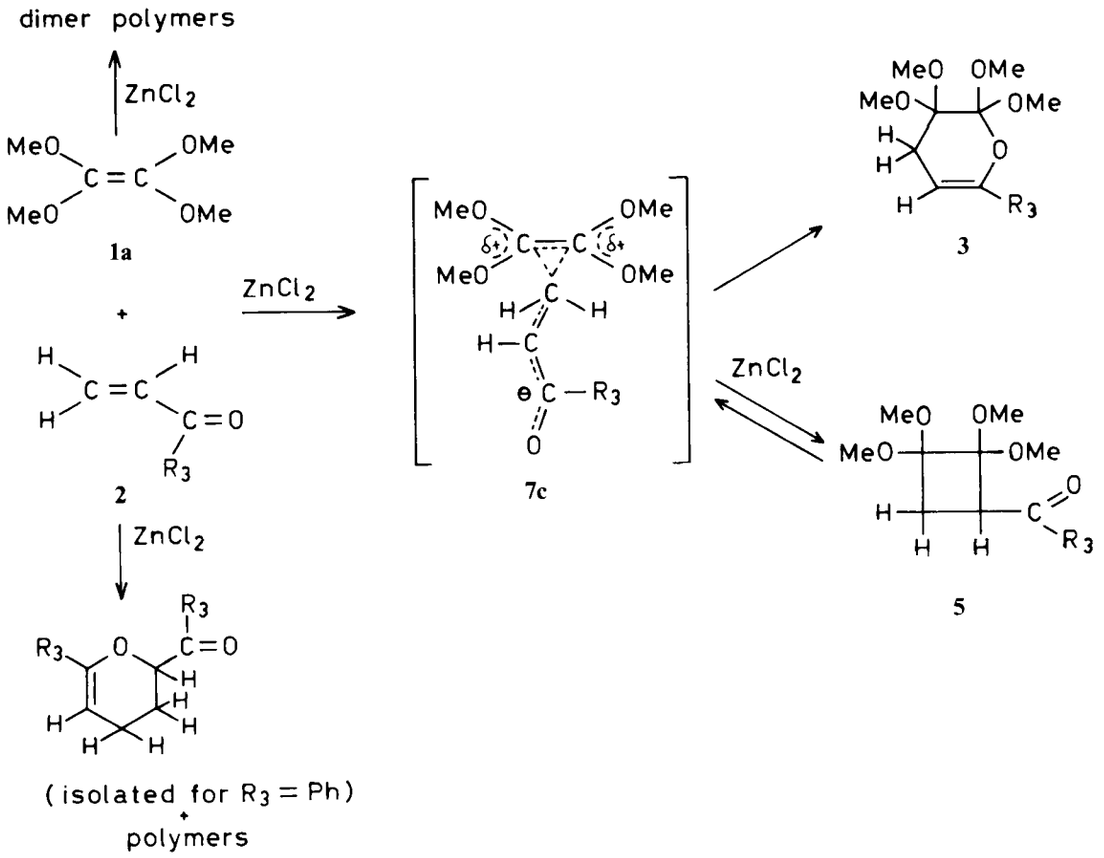
However, along this pathway serious crowding should occur especially in reactions with α,β-unsaturated ketones ($R^3 \neq$ H). In such cases formation of an adduct via bonding at C_β (**7c**; Scheme 4) is preferred, at least when C_β is unsubstituted (R^5 = H), as is the case in **2a** and **e**; with the ketones **2b** and **c** ($R^5 \neq$ H) this preference is not observed. Apparently **7c** is an intermediate state in the formation of a (2 + 2)- as well as a (4 + 2)-adduct in these reactions; at low temperature a mixture of **5** and **3** is obtained and the conversion of the less stable cyclobutane derivative **5** into a dihydropyran (**3**) does not seem to occur via complete decomposition of **5** into the starting compounds **1** and **2**.

Due to the low LUMO coefficient on oxygen in **2** three-centre interaction is more favourable than four-centre interaction, even in (4 + 2)-cycloadditions with the symmetrical tetramethoxyethylene.

The special behaviour of the ketene acetal **1e** must be connected with its high polarisation, which is evidenced by the dipole moments given in Tab. II.

It would be expected that the transition state in the cycloadditions of the ketene acetals gradually varies from **7b** to **7a** in going from **1a** to **1e**. Ketene acetals like **1e**, with largely different orbital coefficients at the olefinic carbon atoms and a high net polarisation, give rise to a transition

[13] *E. Taskinen, V. M. Mukkala* and *M. L. Pentikaïnen*, Tetrahedron **35**, 547 (1979).



Scheme 4

state which is close to a dipolar intermediate with high charge densities at the dimethoxymethylene carbon and oxygen atoms. They can be trapped by another molecule of the carbonyl compound, but this formation of a 1 : 2 adduct is apparently not the only reaction occurring since rather complex reaction mixtures are obtained. It is not completely clear why in the reactions of **1e** with **2a** or **e** this deviating behaviour is less apparent; in both reactions the normal dihydropyran derivative is obtained in good yield at higher temperature.

A more complex reactivity, as observed for **1e** in this investigation, has previously been found in our study[7] of cycloadditions of ketene acetals to simple carbonyl compounds in the presence of $ZnCl_2$. In that case also the most polar ketene acetal of the series used (**1a,b,d** and $H_2C{=}C(OMe)_2$) *viz.* dimethoxyethene, did not yield the expected oxetane but gave instead a complex mixture of products.

Experimental

Melting points are uncorrected. IR spectra were recorded on a Perkin Elmer 297 spectrophotometer. ^{1}HNMR spectra were measured using a Varian T60 and a Bruker 90 MHz spectrometer in CCl_4 or $CDCl_3$ solution, with tetramethylsilane ($\delta = 0$) as an internal standard. Mass spectra were obtained using a double focussing Varian Associates SM1-B spectrometer. HPLC on preparative scale was carried out on a Miniprep L.C. Jobin Yvon apparatus.

The α,β-unsaturated carbonyl compounds **2a,b,c,e** and **g** are commercially available. **2f** was prepared according to *Gras*[14] using paraformaldehyde instead of trioxane; **2d** was obtained according to *Fischer*[15].

Tetramethoxyethene[16] (**1a**), 1,1-dimethoxy-2-methylpropene[7] (**1c**) and 1,1-dimethoxypropene[7] (**1d**) were prepared according to the literature.

1,1,2-Trimethoxyethene (**1b**) was obtained from methoxyacetonitrile *via* the imino ester hydrochloride and 1,1,1,2-tetramethoxyethene as described for the corresponding triethoxyethene[17].

Chloromethyl methyl ether* (1 mol, 80.5 g) and cuprous cyanide (1 mol, 89.5 g) were mixed and refluxed with stirring for 3 h. Distillation gave methoxymethyl cyanide (80%, b.p. 120°C). The product (2.6 moles, 195 ml) was dissolved in a mixture of dry methanol (170 ml) and ether (390 ml) and cooled to 0°C. Dry hydrogen chloride (600 ml/min) was passed through the solution for 2 h, and after addition of more dry ether the mixture was kept at 0–5° for 3 days. The imino ester hydrochloride was filtered, washed with cold, dry ether, saturated with ammonia, and dried *in vacuo* at 0°.

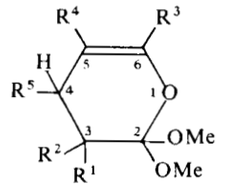
The product (1 mol) was added to a mixture of dry methanol (10 moles) and pentane (1000 ml) and stirred for 3 days at room temperature. The ammonium chloride was filtered off and the filtrate concentrated *in vacuo*. Pentane was added and the resulting precipitate filtered off. The procedure was repeated until no more precipitate was formed. The residue was then distilled, giving 1,1,1,2-tetramethoxyethane (65%, b.p. 42°C/12 mm Hg). The product (0.5 mole, 75 g) was added dropwise to aluminium *tert*-butoxide (0.6 mole, 47.5 g) at 170–180°, and the mixture was refluxed for 4 h. Part of the *tert*-butyl alcohol formed was distilled, the mixture cooled down to 50°C, and distillation continued at low pressure (12 mm Hg). The product was redistilled with a spinning band column; b.p. 37°C/12 mm Hg; yield 40%. NMR (CCl_4): δ 3.42 (s, 6 H), 3.61 (s, 3 H), 5.23 (s, 1 H).

2-Chloro-1,1-dimethoxyethene was prepared from 2-chlorovinyl methyl ether *via* 1,1-dichloro-1,2-dimethoxyethane by modification of the preparation of the corresponding diethoxy compound[18].

* Attention, the compound is carcinogenic.

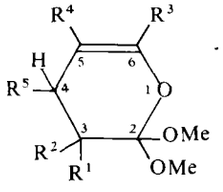
[14] *J. L. Gras*, Tetrahedron Lett. **1978**, 2955.
[15] *F. G. Fischer* and *K. Löwenberg*, Justus Liebigs Ann. Chem. **494**, 272 (1932).
[16] *J. W. Scheeren, R. J. F. M. Staps* and *R. J. F. Nivard*, Recl. Trav. Chem. Pays-Bas **92**, 11 (1973).
[17] *S. M. McElvain* and *J. W. Nelson*, J. Am. Chem. Soc. **64**, 1825 (1942); *S. M. McElvain* and *W. R. Davie*, J. Am. Chem. Soc. **73**, 1400 (1951).
[18] *S. M. McElvain* and *M. J. Curry*, J. Am. Chem. Soc. **70**, 3781 (1948).

Table III Preparative and physical data for 2,2-dimethoxy-3,4-dihydropyrans.

	PREPARATION METHOD	Reaction conditions			B.p. (°C/mmHg)	Yield (%)	n_D^{25}	NMR
		Temp. (°C)	Time (h)	$ZnCl_2$ (mol %)				
R^1 = Me; R^2 = R^3 = R^4 = R^5 = H	a	60	½	½	58–60/15	75–85	1.4420	$CDCl_3$: 0.97 (d, *J* 6.5, 3H, H_3C-C^3); 1.55–2.45 (m, 3H, H_2-C^4, $H-C^3$); 3.30 (s, 3H, H_3CO-C^2); 3.31 (s, 3H, H_3CO-C^2); 4.10–4.27 (m, 1H, $H-C^5$); 6.60–6.80 (m, 1H, $H-C^6$).
R^1 = R^5 = Me; R^2 = R^3 = R^4 = H	b	80	1	1	68–70/15	70–80	1.4430	$CDCl_3$: 0.70–1.10 (m, 6H, H_3C-C^3, H_3C-C^4); 1.30–2.10 (m, 2H, $H-C^3$, $H-C^4$); 3.20–3.30 (s, with splitting, 6H, H_3CO-C^2); 4.30–4.60 (m, 1H, $H-C^5$); 5.90–6.20 (m, 1H, $H-C^6$). (*cis-trans* mixture).
R^1 = R^4 = Me; R^2 = R^3 = R^5 = H	a	80	1	1	80–84/14[a]	70–75		CCl_4: 0.92 (d, *J* 6, 3H, H_3C-C^3); 1.51 (broad s, 3H, H_3C-C^5); 1.60–2.10 (m, 3H, $H-C^3$, H_2-C^4); 3.20 (s, 6H, H_3CO-C^2); 5.80–5.90 (m, 1H, $H-C^6$).
R^1 = R^3 = Me; R^2 = R^4 = R^5 = H	a	80	½	½	70–72/15	85–90	1.4426	$CDCl_3$: 0.95 (d, *J* 6.5, 3H, H_3C-C^3); 1.77 (broad s, 3H, H_3C-C^6); 1.80–2.35 (m, 3H, $H-C^3$, H_2-C^4); 3.30 (s, 3H, H_3CO-C^2); 3.31 (s, 3H, H_3CO-C^2); 4.40–4.55 (m, 1H, $H-C^5$).
R^1 = R^3 = Me; R^2 = R^4 = H; R^5 = OMe	b	80	5	2	101–103/15	40–50		CCl_4: {0.77 (d, *J* 6.5); 0.90 (d, *J* 6.5), 3H, H_3C-C^3}; 1.70 (broad s, 3H, H_3C-C^6); 1.80–2.50 (m, 1H, $H-C^3$); 3.10 (s, 3H, H_3CO-C^4); 3.17 (s, 3H, H_3CO-C^2); 3.25 (s, 3H, H_3CO-C^2); {3.40–3.60 (m); 3.70–4.00 (m), (1H, $H-C^4$)}; {4.30–4.50 (m), 4.55–4.80 (m); (1H, $H-C^5$)}. (*cis-trans* mixture).
R^1 = Me; R^2 = R^4 = R^5 = H; R^3 = Ph	a	80	1	1	93–94/0.2	70–80		CCl_4: 0.96 (d, *J* 6, 3H, H_3C-C^3); 2.10 (d, *J* 4, 2H, H_2-C^4); 1.90–2.20 (m, 1H, $H-C^3$); 3.23 (s, 6H, H_3CO-C^2); 5.17 (t, *J* 4, 1H, $H-C^5$).
R^1 = R^2 = Me; R^3 = R^4 = R^5 = H	a	60	2	1	85/14[a]	75–85		CCl_4: 0.93 (s, 6H, H_3C-C^3); 1.70–1.85 (dd, *J* 4, *J'* 2, 2H, H_2-C^4); 3.32 (s, 6H, H_3CO-C^2); 4.40–4.70 (dd, *J'* 2, *J''* 6, 1H, $H-C^5$); 5.90–6.10 (dd, *J''* 6, *J'* 2, 1H, $H-C^6$).
R^1 = R^2 = R^5 = Me; R^3 = R^4 = H	a	80	3	2	100/14[a]	65–75		CCl_4: 0.75 (s, 3H, H_3C-C^3); 0.94 (s, 3H, H_3C-C^3); 0.87 (d, *J* 7, 3H, H_3-C^4); 1.50–1.70 (m, 1H, $H-C^4$); 3.25 (s, 3H, H_3CO-C^2); 3.45 (s, 3H, H_3CO-C^2); 4.35–4.55 (dd, *J* 6, *J'* 2, 1H, $H-C^5$); 5.90–6.10 (dd, *J* 6, *J'* 2, 1H, $H-C^6$).
R^1 = R^2 = R^4 = Me; R^3 = R^5 = H	a	80	2	1	100/14[a]	60–70		CCl_4: 0.98 (s, 6H, H_3C-C^3); 1.57 (broad s, 3H, H_3C-C^5); 1.77 (broad s, 2H, H_2-C^4); 3.33 (s, 6H, H_3CO-C^2); 5.80–5.95 (m, 1H, $H-C^6$).

[a] Kugelrohr distillation.

Table III (cont.).

	PREPARATION METHOD	Reaction conditions			B.p. (°C/mmHg)	Yield (%)	n_D^{25}	NMR
		Temp. (°C)	Time (h)	$ZnCl_2$ (mol %)				
$R^1 = R^2 = R^3 = Me$; $R^4 = R^5 = H$	a	80	2	1	102/14[a]	70–80		CCl_4: 0.93 (s, 6H, H_3C-C^3); 1.73 (borad s, 3H, H_3C-C^6); 1.60–1.84 (m, 2H, H_2-C^4); 3.33 (s, 6H, H_3CO-C^2); 4.27–4.50 (m, 1H, $H-C^5$).
$R^1 = R^2 = Me$; $R^4 = R^5 = H$; $R^3 = Ph$	a	80	3	1	102–105/0.1	30–50		CCl_4: 1.02 (s, 6H, H_3C-C^3); 2.00 (d, J 4, 2H, H_2-C^4); 3.40 (s, 6H, H_3CO-C^2); 5.27 (t, J 4, 1H, $H-C^5$); 6.90–7.50 (m, 5H, $H_5C_6-C^6$).
$R^1 = Cl$; $R^2 = R^3 = R^4 = R^5 = H$	a	60	2	2	72–74/12	60–70		Neat: 2.50 (m, 2H, H_2-C^4); 3.30 (s, 3H, H_3CO-C^2); 3.32 (s, 3H, H_3CO-C^2); 4.32 (t, J 6, 1H, $H-C^3$); 4.75 (d t, J 3.5, J' 6, 1H, $H-C^5$); 6.25 (d t, J' 6, J'' 2.5, 1H, $H-C^6$).
$R^3 = Me$; $R^1 = Cl$; $R^2 = R^4 = R^5 = H$	a	80	2	2	90–92/12	85–90		CCl_4: 1.79 (m, 3H, H_3C-C^6); 2.45 (m, 1H, H_2-C^4); 3.32 (s, 3H, H_3CO-C^2); 3.37 (s, 3H, H_3CO-C^2); 4.22 (t, J 5.5, 1H, $H-C^3$); 4.52 (m, 1H, $H-C^5$).
$R^1 = OMe$; $R^2 = R^3 = R^4 = R^5 = H$	a	60	2	2	80–82/14	70–75		CCl_4: 2.00–2.30 (m, 2H, H_2-C^4); 3.20 (s, 3H, H_3CO-C^3); 3.28 (s, 6H, H_3CO-C^2); 3.30–3.40 (m, 1H, $H-C^3$); 4.30–4.60 (m, 1H, $H-C^5$); 5.90–6.10 (m, 1H, $H-C^6$).
$R^5 = Me$; $R^1 = OMe$; $R^2 = R^3 = R^4 = H$	a	80	3	2	100–105/14	50–60		CCl_4: {0.76 (d, J 7, H_3C-C^4); 0.95 (d, J 7, H_3C-C^4), tot. 3H}; 2.20–2.40 (m, 1H, $H-C^4$); 3.20 (s, 3H, H_3CO-C^3); 3.28 (s, 6H, H_3CO-C^2); 3.60–3.80 (m, 1H, $H-C^3$); 4.30–4.50 (m, 1H, $H-C^5$); 5.90–6.10 (m, 1H, $H-C^6$). (*cis-trans* mixture).
$R^1 = R^2 = OMe$; $R^3 = R^4 = R^5 = H$	a	80	2	2	50–52/0.1	70–75	1.4490	$CDCl_3$: 2.28 (dd, J 4, J' 2, 2H, H_2-C^4); 3.34 (s, 6H, H_3CO-C^3); 3.44 (s, 6H, H_3CO-C^2); 4.60–4.80 (m, 1H, $H-C^5$); 6.10–6.20 (m, 1H, $H-C^6$).
$R^3 = Me$; $R^1 = R^2 = OMe$; $R^4 = R^5 = H$	a	80	2	2	64–65/0.1	80–85	1.4519	$CDCl_3$: 1.81 (broad s, 3H, H_3C-C^6); 2.20–2.40 (m, 2H, H_2-C^4); 3.39 (s, 6H, H_3CO-C^3); 3.48 (s, 6H, H_3CO-C^2); 4.40–4.60 (m, 1H, $H-C^5$).

[a] Kugelrohr distillation.

a. Chloroacetaldehyde dimethyl acetal was decomposed by heating with potassium pyrosulfate[19] in a round-bottomed flask, which was provided with a Vigreux column (150 × 2 cm), washed with triethylamine in ether. The mixture of 2-chlorovinyl methyl ether and methanol, which evaporated, was collected in a receiver containing 5% aqueous sodium carbonate solution. The organic layer was separated, washed four times with 3% sodium hydroxide solution, dried over Na_2SO_4/Na_2CO_3, and then distilled.
2-Chlorovinyl methyl ether (yield 80–85%, b.p. 78–79°)was obtained as a mixture of *cis* and *trans* isomers. NMR (CCl_4): δ 3.53 (s, 3 H), 5.37 and 6.60 (AB, 2 H, *J* 11 Hz) *(trans)*; 3.68 (s, 3 H), 5.00 (d, 1 H, *J* 4 Hz), 6.13 (d, 1 H, *J* 4 Hz) *(cis)*.
b. The previous product (1 mol, 92.5 g) was added to a solution of sodium methoxide (54g) in methanol (128 g), which was cooled in dry ice/acetone. Chlorine was passed through the solution at −80°C. The mixture was poured into a cold, concentrated sodium carbonate solution (500 ml), and the organic layer was separated and dried (Na_2SO_4). *1,1-Dichloro-2,2-dimethoxyethene* was distilled; yield 70%; b.p. 161–162°; NMR (CCl_4): δ 3.42 (s, 6 H), 4.33 (d, 1 H, *J* 6 Hz), 5.44 (d, 1 H, *J* 6 Hz).
c. 1,1-Dichloro-2,2-dimethoxyethane (0.5 mol, 60 g) was added to a solution of potassium *tert*-butoxide (0.6 moles, 68 g) in *tert*-butanol (500 ml). *Tert*-butanol was evaporated by distillation through a Vigreux column (100 × 2 cm), after which *2-chloro-1,1-dimethoxyethene* was distilled from the residue under reduced pressure (60–80 mm Hg). Yield 65%; b.p. 140–141°/730 mm Hg; NMR (CCl_4): δ 3.60 (s, 3 H), 3.68 (s, 3 H), 4.79 (s, 1 H).

General procedure for the preparation of 2,2-dimethoxy-3,4-dihydropyrans (**3**)

An α,β-unsaturated carbonyl compound (**2**, 125 mmoles) dissolved in acetonitrile (25 ml) was added to a heated solution (60–80°) of a ketene acetal (**1**, 100 mmoles) in the same solvent (25 ml), containing 0.5–2 mol % $ZnCl_2$. The mixture was maintained at 60–80° for the time given in Table III (procedure *a*). In reactions with ketene acetals, which quickly polymerise in the presence of $ZnCl_2$, a ketene acetal solution was added to a solution of the carbonyl compound, containing the catalyst (procedure *b*).

For work up the reaction mixture was cooled to room temperature, triethylamine (1 ml) was added, and the mixture concentrated *in vacuo*. On addition of pentane (50 ml) the product **3** dissolved, but the catalyst precipitated as a zinc chloride/triethylamine complex and could be filtered off. The filtrate was distilled under reduced pressure. Yields and physical data are given in Tab.III.

Procedure for the preparation of 2,2-dimethoxyoxetanes (**4**)

Similar solutions as used in the previous procedure were cooled to −50°C, then mixed and left for 24 h at −20°C. Triethylamine was then added to the reaction mixture. Oxetanes which are stable at room temperature were obtained with a purity between 80 and 90% (NMR) by precipitation of the catalyst by addition of pentane[7] and evaporation of the solvents *in vacuo*. They were identified by mass spectroscopy (molecular ion equal to calculated molecular weight within 0.003 mass units). Yields and NMR data (CCl_4) of the vinylic and characteristic H−C−O ring protons are given below. In one case: ($R^1 = R^2 = OCH_3$, $R^5 = CH_3$) the product could be distilled at low pressure.
4 ($R^1 = CH_3$; $R^2 = R^3 = R^4 = R^5 = H$). Yield ~ 75%; vinylic-H: 5.40–5.60 (m, 3 H); $R^3 = H$: 3.90–4.15 (m, 1 H).
4 ($R^1 = R^5 = CH_3$; $R^2 = R^3 = R^4 = H$). Yield ~ 80%; vinylic-H: 5.40–5.60 (m, 2 H); $R^3 = H$: 3.95–4.15 (m, 1 H).
4 ($R^1 = R^2 = CH_3$; $R^3 = R^4 = R^5 = H$). Yield ~ 80%; vinylic-H: 5.40–5.60 (m, 3 H); $R^3 = H$: 3.90–4.15 (m, 1 H).
4 ($R^1 = R^2 = R^5 = CH_3$; $R^3 = R^4 = H$). Yield ~ 85%; vinylic-H: 5.45–5.65 (m, 2 H); $R^3 = H$: 4.00–4.20 (m, 1 H).
4 (R^1 = OMe; $R^2 = R^3 = R^4 = R^5 = H$). Yield ~ 70%; vinylic-H: 5.40–5.70 (m, 3 H); $R^3 = H$: 4.00–4.30 (m, 1 H).
4 (R^1 = OMe; $R^5 = CH_3$, $R^2 = R^3 = R^4 = H$). Yield ~ 80%; vinylic-H: 5.40–5.70 (m, 2 H); $R^3 = H$: 4.00–4.30 (m, 1 H).
4 ($R^1 = R^2$ = OMe; $R^3 = R^4 = H$; $R^5 = CH_3$). Yield 45–60% after distillation; b.p. 94–95°C/0.5 mm Hg; NMR (CCl_4): 1.70–1.80 (R^5, m, 3 H); 3.34 (R^1, s, 3 H); 3.36 (R^2, s, 3 H); 3.45 (OMe, s, 6 H); 4.61 (R^3, d, 1 H, *J* 7 Hz); 5.75–5.95 (m, 2 H, vinyl).

1,1,2,2-Tetramethoxycyclobutanes (**5**)

The procedure given for the preparation of oxetanes yielded mixtures of a cyclobutane (**5**) and a dihydropyran derivative (**3**) from the reactions between **1a** and **2a** or **2d**. After removal of the catalyst as described, the mixtures could be separated by HPLC on silicagel using diisopropyl ether/hexane (1 : 1) as the eluent. In the mass spectra of the products strong peaks for M^+, $M - 15$, $M - 30$ and for products from a retro reaction, were observed. The IR spectra showed strong carbonyl absorptions (1750–1770 cm^{-1}).

5: ($R^1 = R^2$ = OMe; $R^3 = R^4 = R^5 = H$); yield 40–50%; NMR (CCl_4): 2.20–2.60 (m, 2 H); 2.65–3.00 (m, 1 H); 3.15–3.40 (s, 12 H, 4 OMe); 9.49 (d, *J* 4, HC=O).

5: ($R^1 = R^2$ = OMe; $R^3 = CH_3$; $R^4 = R^5 = H$); yield 40–50%; NMR (CCl_4): 2.12 (s, 3 H, acetyl); 2.30–2.80 (m, 2 H); 3.00–3.50 (m, 1 H); 3.14, 3.24, 3.29, 3.47 (4 s, 12 H, OMe).

Isolation of the 1,3-dioxane derivatives (**6**)

Application of the procedure, given for the preparation of dimethoxydihydropyrans, to **1e** and **2c**, yielded mainly 5-chloro-6,6-dimethoxy-2,4-distyryl-1,3-dioxane, which was isolated after a reaction time of ½ h using the method previously described. The crude product was purified by chromatography on a silica column using toluene as the solvent. However, the product thus obtained did not appear to be completely pure. The compound was identified by mass spectroscopy (*m/e:* 386/388 (7%), 354/356 (6%), 254/256 (12%), 247 (14%) and 205 (100%), and NMR (CCl_4): δ 3.13 (s, 3 H, OMe); 3.20 (s, 3 H, OMe); 3.79 (d, H−CCl, *J* 10 Hz); 4.50 (dd, H−C(4), *J* 10 Hz, *J'* 5.5 Hz); 5.40 (d, H−C(6), *J* 5.5 Hz); 6.04 (dd, 2 H, $H-C_\alpha$, *J'* 5.5 Hz, *J* 15 Hz); 6.67 (d, 2 H, $H-C_\beta$, *J* 15 Hz); 7.10–7.36 (m, 10 H, phenyl).

Under similar conditions **1e** and benzaldehyde gave 5-chloro-6,6-dimethoxy-2,4-diphenyl-1,3-dioxane, m.p. 106–107° (crystallized from methanol); *m/e:* 334/336 (2%); 228/230 (2%), 212/214 (10%), 197/199 (26%), 138/140 (100%); NMR (CCl_4): δ 3.41 (s, 6 H, OMe); 3.98 (d, 1 H, H−CCl, *J* 10 Hz); 4.83 (d, 1 H, H−C(4), *J* 10 Hz); 5.85 (s, 1 H, H−C(2)); 7.24 (m, 10 H, phenyl).

[19] *J. F. Arens, J. Vegter* and *T. de Boer*, Recl. Trav. Chim. Pays-Bas **77**, 753 (1958).