CYCLOADDITION REACTIONS OF ARYLMETHYLENEMALONALDEHYDES WITH OLEFINS

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A series of 2,4-disubstituted 3,4-dihydro-2*H*-pyran-5-carboxaldehydes *II – XIX* was prepared by reaction of substituted arylmethylenemalonaldehydes *I* with 2-methylpropane, 1,1-diphenylethylene, styrene, ethyl vinyl ether, 1,1-dimethoxyethylene and 1,1-bis(methylthio)ethylene. In the case of the reaction with ethyl vinyl ether the dependence of the ratio of the arising *cis*- and *trans*- 2-ethoxy-4-aryl-3,4-dihydropyran-5-carboxaldehydes *VII – XIV* on the substituent on the aromatic nucleus was studied. Information on the mechanism of this reaction was obtained and conformational equilibria of 2-ethoxy-4-aryl-3,4-dihydro-pyran-5-carboxaldehydes in solution were studied by ^{1}H NMR spectroscopy. The stucture of *trans*-2-etho-xy-4-(4-chlorophenyl)-3,4-dihydropyran-5-carboxaldehyde (*trans-VIII*) was confirmed by X-ray analysis of the corresponding carboxylic acid *trans-XXII*.
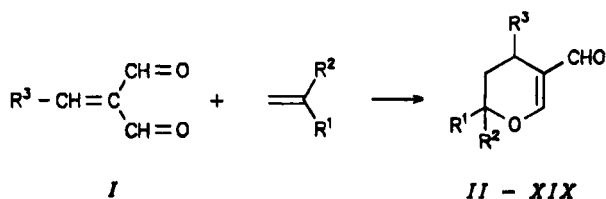
The cycloaddition of α,β-unsaturated carbonyl compounds to olefins represents a well known and widely used method of preparation of dihydropyrans[1]. Introduction of a second carbonyl group into the α-position in α,β-unsaturated carbonyl compounds enhances considerably the reactivity of these compounds as heterodienes[2,3]. These cycloadditions are regioselective and, in some cases of intramolecular course, also considerably stereospecific[4]. Arylmethylenemalonaldehydes[5], which can be considered to be such activated systems, in preliminary experiments also showed high reactivity in reactions with olefins and some dienes[6]. In this paper we present a more detailed study of cycloaddition reactions of arylmethylenemalonaldehydes with some olefins.

The study involves a series of compounds with variously activated C=C bond, going from hydrocarbons represented by 2-methylpropene, 1,1-diphenylethylene and styrene,

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via ethyl vinyl ether to very electron-rich 1,1-bis(methylthio)ethylene and 1,1-dimetho-xyethylene. In all cases, these olefins react with arylmethylenemalonaldehydes *I* to give substituted 3,4-dihydro-2*H*-pyran-5-carboxaldehydes *II – XIX* (Scheme 1 and Table I).

The rate of the cycloaddition of arylmethylenemalonaldehydes is considerably influenced by the nature of the olefinic component. Whereas the reaction with hydro-carbons proceeds very sluggishly even at elevated temperatures (several weeks), the reaction of arylmethylenemalonaldehydes with ethyl vinyl ether is a matter of several hours and 1,1-bis(methylthio)ethylene and 1,1-dimethoxyethylene react practically instantly. We are thus dealing with a typical cycloaddition reaction with "reversed

|	R^1	R^2	R^3
II	C_6H_5	C_6H_5	4-ClC_6H_4
III	C_6H_5	C_6H_5	$4\text{-CH}_3OC_6H_4$
IV	C_6H_5	C_6H_5	2-thienyl
V	CH_3	CH_3	4-ClC_6H_4
VI	H	C_6H_5	4-ClC_6H_4
VII	H	OCH_2CH_3	$4\text{-NO}_2C_6H_4$
VIII	H	OCH_2CH_3	4-ClC_6H_4
IX	H	OCH_2CH_3	C_6H_5
X	H	OCH_2CH_3	$4\text{-CH}_3OC_6H_4$
XI	H	OCH_2CH_3	$4\text{-(CH}_3)_2NC_6H_4$
XII	H	OCH_2CH_3	$2,4,6\text{-(CH}_3)_3C_6H_2$
XIII	H	OCH_2CH_3	2-thienyl
XIV	H	OCH_2CH_3	3-thienyl
XV	OCH_3	OCH_3	4-ClC_6H_4
XVI	OCH_3	OCH_3	$4\text{-CH}_3OC_6H_4$
XVII	OCH_3	OCH_3	2-thienyl
XVIII	SCH_3	SCH_3	4-ClC_6H_4
XIX	SCH_3	SCH_3	2-thienyl

SCHEME 1

TABLE I
Yields, melting (boiling) points, and analytical data of dihydropyrans $II - XIX$

Compound	Yield %	M.p., °C (b.p., °C/25 Pa)[a]	Formula M. w.	Calculated/Found		
				%C	%H	%N
II	87[b]	138 – 142	$C_{24}H_{19}ClO_2$ (374.9)	76.89 76.72	5.12 4.99	9.46[c] 9.48
III	67[b]	122 – 124	$C_{25}H_{22}O_3$ (370.5)	81.04 80.83	6.00 5.97	– –
IV	50[b]	165 – 166	$C_{22}H_{18}O_2S$ (346.5)	76.40 76.82	5.25 5.24	9.25[d] 9.19
V	56[e]	(140) (250.7)	$C_{14}H_{15}ClO_2$	67.06 66.61	6.04 5.89	14.14[c] 14.16
VI	84[f]	103 – 108[g] (298.5)	$C_{18}H_{15}ClO_2$	72.36 72.64	5.06 4.95	11.87[c] 12.01
VII	85[e]	105 – 107[g] (160)[h]	$C_{14}H_{15}NO_2$ (277.3)	60.65 60.30	5.45 5.79	5.05[j] 5.02
VIII	92[e]	68 – 70[i] 94 – 98[g] (135)[h]	$C_{14}H_{15}ClO_3$ (266.5)	63.03 62.81	5.63 5.62	13.32[c] 13.11
IX	73[e]	47 – 54[i] (120)[h]	$C_{14}H_{16}O_3$ (232.3)	72.39 72.08	6.94 6.95	– –
X	86[e]	87 – 89[g] (130 – 135)[h]	$C_{15}H_{18}O_4$ (262.3)	68.69 68.63	6.92 7.21	– –
XI	84[e]	102 – 106[g] (160)[h]	$C_{16}H_{21}NO_3$ (275.4)	69.79 69.45	7.69 7.60	5.09[j] 4.93
XII	98[f]	127 – 130[i] 84 – 88[g]	$C_{17}H_{22}O_3$ (274.4)	74.42 74.37	8.08 7.74	– –
XIII	56[e]	75 – 76[g] (115 – 120)[h]	$C_{12}H_{14}O_3S$ (238.3)	60.48 60.57	5.92 5.95	13.34[d] 13.27
XIV	60[f]		$C_{12}H_{14}O_3S$ (238.3)	– –	– –	– –
XV	91[e]	96 – 99 (145 – 150)	$C_{14}H_{15}ClO_4$ (282.5)	59.49 59.42	5.31 5.33	13.01[c] 13.05
XVI	92[e]	(155 – 160)	$C_{15}H_{18}O_5$ (278.3)	64.74 64.88	6.52 6.40	– –
XVII	88[e]	(120 – 125)	$C_{12}H_{14}O_4S$ (254.3)	56.67 56.30	5.55 5.33	12.61[d] 12.60
XVIII[k]	67[b]	103 – 105	$C_{14}H_{15}ClO_2S_2$ (314.5)	53.40 53.34	4.76 4.70	11.29[c] 11.12
XIX	84[b]	86 – 91	$C_{12}H_{14}O_2S_3$ (286.4)	50.32 50.39	4.93 4.91	33.58[d] 33.28

[a] Bath temperature; [b] crystallized product; [c] % Cl; [d] % S; [e] distilled product; [f] after chromatography; [g] trans-isomer; [h] mixture of isomers; [i] cis-isomer; [j] % N; [k] % S: 20.35/20.13.

electron demands". The reaction rate is also strongly influenced by the character of the substituent on the aromatic nucleus. Thus, e.g., in the preparative arrangement (cf. Experimental) the reaction of 4-nitrophenylmethylenemalonaldehyde with ethyl vinyl ether is finished during several minutes, the reaction of unsubstituted phenylmethylenemalonaldehyde takes several hours whereas the (uncatalyzed) reaction of 4-dimethylaminophenylmethylenemalonaldehyde is not finished even after several days. The cycloaddition reactions of arylmethylenemalonaldehydes can be catalyzed by Lewis acids. For the preparative execution the catalyst of choice is zinc iodide. This procedure was used for the preparation of cycloadducts of arylmethylenemalonaldehydes with 2-methylpropene and styrene, the reaction being finished at room temperature during 24 – 48 h, depending on the components used.

Reaction of arylmethylenemalonaldehydes with compounds containing monosubstituted C=C bond affords a mixture of *cis*- and *trans*-isomers of the corresponding dihydropyran of the general formula *XX* and *XXI*. These isomeric 2-substituted 3,4-dihydro-4-aryl-2*H*-pyran-5-carboxaldehydes can be easily separated by chromatography; the minor isomers are chromatographically more mobile and crystallize more readily than those arising as the main products. On the basis of analogy with a similar reaction of substituted 2-methylenindane-1,3-diones with ethyl vinyl ether studied by Polansky[2], the predominant formation of the *cis*-isomer could be expected.

XX XXI $trans-XXII$ $cis-XXII$
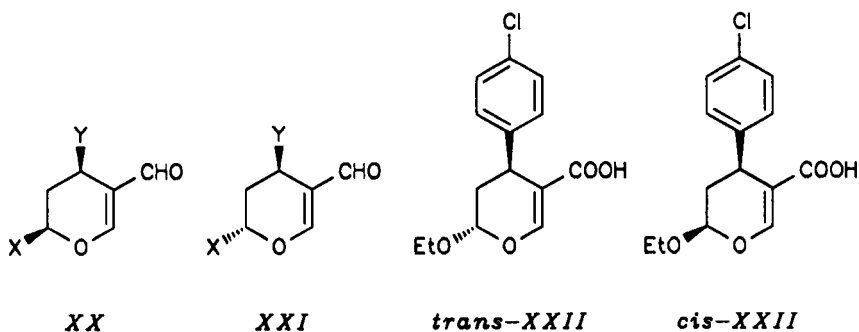
Because of conformational mobility of the obtained dihydropyrans, it was not possible to assign unequivocally the configuration to the individual isomers by use of ^1H and ^{13}C NMR spectroscopy. We employed therefore X-ray diffraction analysis to determine the configuration of the chromatographically more mobile minor product (with better crystallization properties) arising by reaction of 4-chlorophenylmethylenemalonaldehyde with ethyl vinyl ether *VIII*. Because the aldehyde easily underwent air oxidation, we subjected to the X-ray analysis the corresponding acid which appeared to be the *trans*-isomer *XXII*. In addition to oxidation with air oxygen, this compound as well as its isomer *cis-XXII* were obtained by oxidation of the corresponding isomeric aldehydes with potassium permanganate in pyridine. Since the compound obtained by

oxidation of the more mobile fraction was in all respects (m.p., ^{1}H NMR) identical with the material used for the X-ray analysis and the character of its ^{1}H NMR spectrum corresponded unequivocally to the starting dihydropyran aldehyde, we take it as proven that *trans*-2-ethoxy-4-aryl-3,4-dihydro-2*H*-pyran-5-carboxaldehyde arises as the minor product in the reaction of 4-chlorophenylmethylenemalonaldehyde with ethyl vinyl ether. On the basis of analogous ^{1}H NMR and chromatographic behaviour the more mobile minor isomers of compounds *VI, VII, IX – XIV* were assigned the *trans*-configuration whereas the predominating less mobile isomers are regarded as *cis*-isomers.

We studied in detail the formation of isomeric dihydropyrans using the reaction of arylmethylenemalonaldehydes with ethyl vinyl ether. This reaction is kinetically controlled and in the reaction mixture, which can be analyzed by GLC or ^{1}H NMR spectroscopy, the thermodynamically less stable *cis*-isomer *XX* predominates. The *cis/trans* isomer ratio is practically independent on the character of the substituent on the aromatic nucleus (Table II). The effect of solvent on the *cis/trans* ratio was studied on the reaction of 4-chlorophenylmethylenemalonaldehyde with ethyl vinyl ether. This ratio was the same (about 3 : 1 in favour of the *cis*-isomer) in benzene, acetonitrile, pyridine and dimethylformamide. The same isomer ratio was also observed in the zinc iodide catalyzed reaction in benzene at room temperature (under these conditions the product is not isomerized).

On heating in the presence of an acid catalyst (ZnI_2, $ZnCl_2$) the obtained isomer mixture is isomerized in favour of the thermodynamically more stable *trans*-isomer *XXI*. The same process was observed already earlier by Polansky[2] in reaction of substituted 5-methylene-2,2-dimethyl-1,3-dioxane-4,6-diones with ethyl vinyl ether. In the case of cycloadducts of arylmethylenemalonaldehydes with ethyl vinyl ether the isomer ratio clearly depends on the electron effect of substituents on the aromatic nucleus. Electron acceptors increase the relative content of the *cis*-isomer whereas electron donors decrease its population (Table II). For the 2,4,6-trimethylphenyl derivative we found a relatively high proportion of the *cis*-isomer which is apparently connected with capability of this isomer to assume the diequatorial conformation which, thanks to the sterically very bulky substituent, in this case is relatively more stable than in other *cis*-derivatives.

For the reaction of 4-chlorophenylmethylenemalonaldehyde with ethyl vinyl ether we tried to obtain information on the reaction mechanism. The cycloaddition reaction of arylmethylenemalonaldehyde with an olefin may be assumed to proceed by a concerted mechanism or by a two-step process with formation of a dipolar intermediate *XXIII* (Scheme 2). In this respect, an important information is given by determination of the effect of solvent polarity on the reaction rate. This approach has been used e.g. by Huisgen[7] in the study of reaction of tetracyanoethylene with enol ethers. In the cited case that concerns a two-step process, the ratio of rate constants $k_{(acetonitrile)}/k_{(cyclohexane)}$ is $10^3 - 10^4$. In a concerted process, this ratio is by several orders of magnitude lower.

Thus, e.g., for the dimerization of cyclopentadiene[8] the ratio $k_{(nitrobenzene)}/k_{(benzene)} = 3$ and Polansky, who investigated cycloaddition of some 1,1-dicarbonylethylenes, found for reaction of 2-(3-methyl-1-butenylidene)indane-1,3-dione with 1,1-dimethoxyethylene the value of $k_{(acetonitrile)}/k_{(toluene)}$ approximating 10 which may be considered as support of an assumed concerted process. For the reaction of 4-chlorophenylmethylene-malonaldehyde with ethyl vinyl ether we found that $k_{(acetonitrile)}/k_{(cyclohexane)} = 2.4$, also corresponding to a concerted reaction course.

I   *XXIII*   *II – XIX*
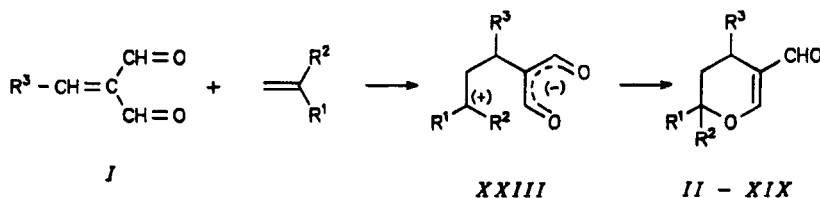
SCHEME 2

Stereochemistry of the Obtained Dihydropyrans

The character of ^1H NMR spectra of compounds *VI – XIII* (Table V) enabled a stereochemical study of the heterocyclic fragment. Because of the presence of double bond, the 3,4-dihydro-2*H*-pyran molecule can assume four conformations – the half-chair conformations HC^2 and HC_2 and the boat forms $B_{1,4}$ and $B^{1,4}$ (Fig. 1), the two former being more probable in the light of previous studies[9]. The population of the individual forms is influenced mainly by two factors: the anomeric effect stabilizing the

TABLE II
Dependence of relative amount of isomeric 2-ethoxy-2,3-dihydro-4*H*-pyrans on the type of substitution in the starting arylmethylenemalonaldehyde in toluene (for other conditions see Experimental)

	Reaction control			
Substituent	kinetic		thermodynamic	
	cis, %	*trans*, %	*cis*, %	*trans*, %
4-NO$_2$C$_6$H$_4$	73	27	29	71
4-ClC$_6$H$_4$	77	23	23	77
C$_6$H$_5$	76	24	18	82
4-CH$_3$OC$_6$H$_4$	77	23	16	84
4-(CH$_3$)$_2$NC$_6$H$_4$	82	18	10	90
2,4,6-(CH$_3$)$_3$C$_6$H$_4$	64	36	27	73
2-Thienyl	64	36	11	89
3-Thienyl	73	27	14	86

alkoxy group in the axial position, and the aryl substituent in position 4 which tends to occupy the pseudoequatorial position in which it is less destabilized by the nonbonding 1,3-interactions.

Analysis of the ^{1}H NMR spectra afforded approximate values of geminal and vicinal coupling constants between the protons H-2, H-3, H-3' and H-4 which were further refined by a simulation-iterative calculation. The obtained values served as a basis for conformational analysis of the individual compounds.

For the derivative *VI*, deviating from the studied group of compounds because of character of substitution at C-2, in the spectrum of the *cis*-isomer we observed two large diaxial coupling constants of proton H-3 with protons H-2 and H-4, $J(2,3) = J(3,4) = 10$ Hz, an about half as large constant $J(3',4) = 5.8$ Hz, and finally a small constant for coupling between the protons H-2 and H-3'. These values are very close to those described by De Boer[10] for 4-tert-butyl-3,4-dihydro-2H-pyran in a half-chair conformation. This means that in solution also the *cis*-isomer of compound *VI* exists practically exclusively in conformation HC^2 with both substituents in the energetically most advantageous pseudoequatorial positions.

In the case of the *trans*-isomer of this compound we found only one diaxial coupling constant $J(2,3') = 12$ Hz, the second coupling constant in the multiplet due to the proton
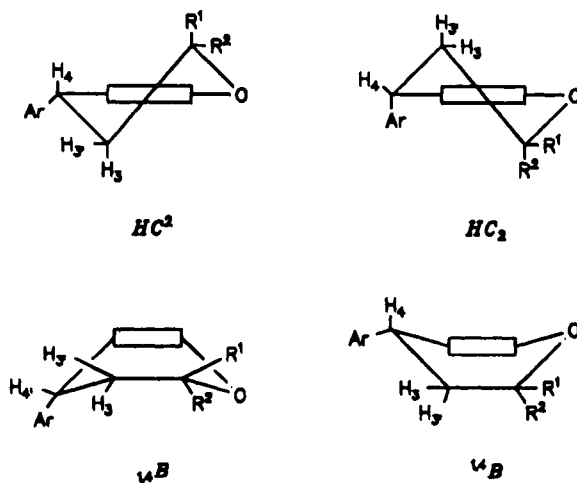
	R^1	R^2
cis	H	OEt, Ph
trans	OEt, Ph	H

Fig. 1
Possible conformations of dihydropyran ring

H-2 being only 2.2 Hz. The coupling constants of proton H-4 are $J(3,4)$ = 1.8 Hz and $J(3',4)$ = 5.6 Hz, the former for the diequatorial and the latter for the axial–equatorial coupling. From these values we can derive that in solution the *trans*-isomer of compound *VI* exists in the HC_2 conformation. Somewhat surprising is the fact that the conformation is determined exclusively by the aromatic substituent in position 2 whereas the at least equally bulky substituent in position 4 in the *trans*-isomer remains pseudoequatorial.

As already mentioned, the conformation of compounds *VII – XIII* is determined both by the anomeric effect of the ethoxy group and the aryl substituent in position 4. However, from the values of coupling constants $J(2,3)$, $J(2,3')$ and $J(3,4)$ one cannot directly make conclusions about the preferred conformation of these compounds in solution. For this reason we made use of a graphical evaluation, employed by Cook and Desimoni[11] for 2,3-dihydropyrano(2,3-*c*)pyrazoles. This procedure allows an estimate of conformer population in solution from estimation of limit values of the coupling constants $J(2,3)$, $J(2,3')$ and $J(3,4)$ (for the diaxial and diequatorial orientation of proton). Whereas for the *cis*-isomers the diaxial coupling constants are $J(2,3)$ and $J(3,4)$, in the *trans*-series these constants are $J(2,3')$ and $J(3,4)$ (see Fig. 1). We can then write the following equations:

$$J(3,4) \; = \; x(J(3\text{ax},4\text{ax}) - J(3\text{eq},4\text{eq})) + J(3\text{eq},4\text{eq}) \qquad (1)$$

$$J(2,3) \; = \; x(J(2\text{ax},3\text{ax}) - J(2\text{eq},3\text{eq})) + J(2\text{eq},3\text{eq}) \qquad (2)$$

$$J(2,3') \; = \; x(J(2\text{eq},3'\text{eq}) - J(2\text{ax},3'\text{ax})) + J(2\text{ax},3'\text{ax}) \, , \qquad (3)$$

where x is the molar fraction of conformer HC^2 and Eqs (*1*) and (*2*) hold for the *cis*-isomers and Eqs (*1*) and (*3*) hold for the *trans*-isomers. The evaluation proper of the experimental data is carried out in two phases. First a graph is constructed whose y-axis is calibrated in Hz whereas the x-axis is so far not calibrated. Using the estimated limit values of $J(3\text{ax},4\text{ax})$ and $J(3\text{eq},4\text{eq})$ a straight line is constructed corresponding to Eq. (*1*), on which the measured values of $J(3,4)$ are plotted. In the second phase the experimental values of $J(2,3)$ and $J(2,3')$ are plotted into the same graph, the coordinate x being given by the position of the corresponding point on the already constructed straight line. Now, straight lines corresponding to Eqs (*2*) and (*3*) are interpolated through these points using the least-squares method. Under assumption[12] that $J(2,3) \approx J(2,3')$, these straight lines cross each other just at the point $x = 0.5$. On the basis of this assumption the x-axis can be calibrated. The abscissae on the y-axis for $x = 0.0$ and $x = 1.0$ give the values of $J(3\text{ax},4\text{ax})$, $J(3\text{eq},4\text{eq})$, $J(2\text{ax},3\text{ax})$, $J(2\text{eq},3\text{eq})$, $J(2\text{ax},3'\text{ax})$ and $J(2\text{eq},3'\text{eq})$. From the experimental values of coupling constants and the obtained limit values $(J(2\text{ax},3\text{ax})$ = 9.9, $J(2\text{eq},3\text{eq})$ = 2.1, $J(2\text{ax},3'\text{ax})$ = 12.0, $J(2\text{eq},3'\text{eq})$ = 0.4,

$J(3ax,4ax)$ = 12.5 and $J(3eq,4eq)$ = 1.15) we estimated the probable population of the conformer HC^2 (Table II). The achieved correlation coefficient in the cis-series was 0.94, for the trans-series 0.98.

Compound *XII* differs from the other prepared 2-ethoxy-4-aryl-3,4-dihydro-2*H*-pyrans by the presence of the bulky 2,4,6-trimethylphenyl substituent in position 4. Its steric demands result in a conformationally distinct behaviour of this compound. The signal of the axial proton H-3 in the cis-isomer has two large diaxial coupling constants $J(2,3)$ = 9.6 and $J(3,4)$ = 11.4 Hz and the H-3' proton has constants $J(2,3')$ = 2.4 and $J(3'4)$ = 7.6 Hz. This situation is best compatible with the HC^2 conformation, similarly as in the case of compound *VI* (see Table II). In the ^{1}H NMR spectrum of the trans-isomer the proton H-2 appears as a triplet with two practically identical coupling constants $J(2,3) \approx J(2,3') \approx 2.2$ Hz. The proton H-4 shows a diaxial coupling constant with H-3 ($J(3',4)$ = 10.8 Hz) and an axial–equatorial constant with H-3' ($J(3,4)$ = 8.2 Hz). These values indicate that compound *XII* exists in solution in conformation HC^2 with axial ethoxy group and equatorial aromatic substituent (see Table III).

Another important argument for conclusions about the preferred conformation of 3,4-dihydro-2*H*-pyran ring is also the long-range coupling constant[4] $J(4,6)$. As reported by Chalmers[12] for 2,3,4-trisubstituted 3,4-dihydro-2*H*-pyrans, the existence of HC_2 conformation was manifested by signal broadening and could be proved only by a decoupling experiment whereas for the HC^2 conformation the coupling constant reached the value of $1 - 2$ Hz.

Also in our study, the spectrum of cis-isomer of compound *VI* exhibited $J(4,6)$ = 1.2 Hz (HC^2 conformation) whereas for the trans-isomer this coupling was not observed (HC_2 conformation). Similarly, for both isomers of compound *XII* the value is close to 2 Hz (HC^2 conformation). Also for compounds *VII* – *XI* and *XIII* the found values of $J(4,6)$ confirm the above conclusions about their conformation.

TABLE III
Population of conformation HC^2 (in %) for compounds *VII* – *XIII* and *XXII*

Compound	Mole fraction, %	
	cis-isomer	trans-isomer
VII	26	51
VIII	47	35
IX	48	32
X	48	34
XI	55	29
XII	93	85
XIII	37	21
XXII	29	27

The signals in the ^{13}C NMR spectrum of compounds *VI – XIII* (Table VI) were assigned on the basis of their comparison with those of the model 3,4-dihydro-2*H*-pyran, published by Burfitt[13], additive increments accessible in the literature[14], and signal multiplicity. The differences in the chemical shifts of the carbon atoms C-2, C-3 and C-4 in the isomer pairs reflect not only configurational but also conformational effects. Thus, the difference between the chemical shifts of the signals of C-2, C-3 and C-4 in the spectrum of compound *VI* amounts to about 3.5 ppm, the signal of the *cis*-isomer being invariably downfield. On the contrary, in the series *VII – XI* and *XIII* the chemical shift differences are small because of the existing equilibrium between both the half-chair forms. Finally, similarly to the case of compound *VI*, the marked change in the steric situation in compound *XII* manifests itself also by the different ^{13}C NMR shifts of the C-2, C-3 and C-4 signals.
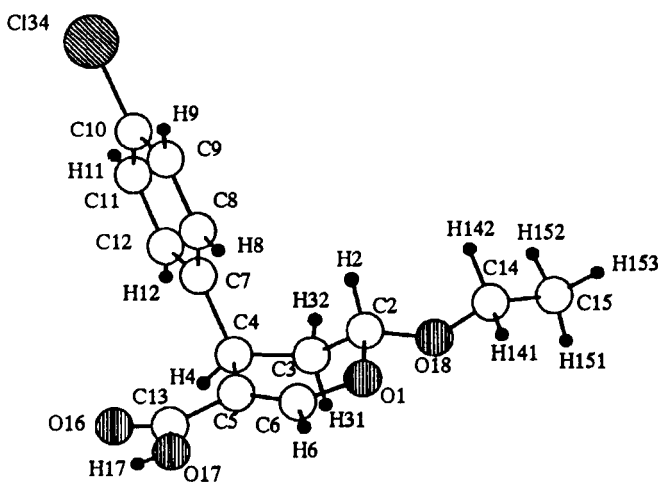

FIG. 2

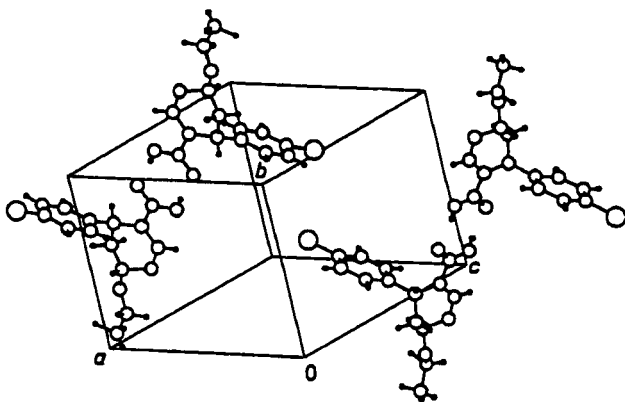Molecular structure of *trans-XXII*

FIG. 3

Arrangement of molecules of *trans-XXII* in the unit cell

The conclusions on the conformation of the studied compounds in solution obtained by the ^{1}H NMR analysis were confronted with the X-ray diffraction experiment. The molecular structure of *trans-XXII* is depicted in Fig. 2 and the arrangement of molecules in the unit cell in Fig. 3. Fractional coordinates of the atoms are given in Table VIII, the selected interatomic distances in Table IX. As follows from the calculated dihedral angles (Table X), in the solid state the compound exists in conformation HC_2. Contrariwise, the analysis of its ^{1}H NMR spectrum leads to the conclusion that, similarly to other compounds in solution, the anomeric effect of the ethoxy group in position 2 is also operating and the conformational behaviour of *trans-XXII* is not clearcut. The mentioned findings also support the assumption that the conformation of the studied compounds in solution is considerably influenced by the character of the substituent in position 2.

EXPERIMENTAL

The melting points were determined on a Kofler block. Analytical samples were dried at 25 °C and 25 Pa for 24 h over phosphorus pentoxide. Infrared spectra were recorded on a Zeiss UR 20 spectrometer. ^{1}H NMR spectra were measured on TESLA BS-467 (60 MHz; in CW node) and Varian XL-200 (200 MHz; in FT mode) instruments, ^{13}C NMR spectra were obtained with a Varian XL-200 (50.3 MHz) instrument using the APT technique[15]. The ^{1}H NMR chemical shifts and coupling constants of compounds *II – V* and *XV – XIX* (Table IV) were determined by the first order analysis, NMR chemical shifts and coupling constants of protons H-2, H-3, H-3' and H-4 in compounds *VI – XIII* and *XXII* (Table V) were refined by a simulation-iterative calculation (a modified program LAOCOON[16] for PC Olivetti M24). Pure *cis*- and *trans*-isomers for the NMR measurements (Tables V and VI) were isolated from the isomer mixtures by chromatography on silica gel in hexane–ethyl acetate. UV spectra were measured on a Specord UV-VIS spectrometer, mass specra on an AEI MS-902 instrument. GLC analyses were performed on an HP 5890 chromatograph.

Overall yields, elemental analyses and melting or boiling points of the studied compounds are given in Table I, the ^{1}H and ^{13}C NMR parameters in Tables IV – VI, the IR data in Table VII.

Crystal Structure Determination of *trans*-4-(4-Chlorophenyl)-2-ethoxy-3,4-dihydro-2*H*-pyran-5-carboxylic Acid (*trans-XII*)

Radiation wavelength 0.71073 Å (Nb-filter); monocrystal dimensions 0.3 × 0.3 × 0.4 mm; space group $P\bar{1}$; lattice parameters a = 10.570(2), b = 10.658(2), c = 12.783(3) Å, α = 94.98(2)°, β = 106.23 (2)°, γ = 94.39(1)°; V = 1 369.7(4) Å^3; Z = 4; M = 282.7, theoretical density ρ = 1.37 g/cm^3; absorption coefficient μ = 2.82 cm^{-1}; for the 3 550 observed reflections R = 0.059, wR = 0.083, S = 1.75. The measurement was carried out on a Hilger & Watts four-ring diffractometer at room temperature. The lattice parameters were determined by the least squares method from 54 intensive reflexions (7° < θ < 19°). Intensities were measured using the θ – 2θ scan technique. Stability of the measurement was checked by monitoring three standard reflections (005, 500, 060); during the whole time of measurement their intensity fluctuated less than six per cent. Of the 4 834 measured reflections were 3 550 considered observed (I > 1.96σ(I)). The data were corrected for the Lorentz and polarization effects, the effect of absorption was considered unimportant because of small absorption coefficient. The structure was solved and refined using the programs MULTAN80[17] and SDS system[18]. All calculations were performed on a Siemens 7356 computer. Atomic positions, together with anisotropic temperature parameters of nonhydrogen atoms were refined by the least squares method. The isotropic temperature parameters of hydrogen atoms were fixed. The atomic

TABLE IV
Selected ^{1}H NMR parameters of dihydropyrans *II – V* and *XV – XIX* in CDCl$_3$ (60 MHz)

Parameter	II	III[a]	IV	V[b]	XV[c]	XVI[d]	XVII[e]	XVIII[f]	XIX[g]
H-3	2.35 dd	2.35 dd	2.56 dd	1.67 dd	1.97 dd	1.99 dd	2.22	2.22 –	2.25 –
H-3'	3.13 dd	3.03 dd	3.13 dd	2.03 dd	2.30 dd	2.32 dd	2.33	– 2.70 m	– 2.90 m
H-4	3.55 bdd	3.52 bdd	3.93 bdd	3.68 bdd	3.87 bdd	3.83 bdd	4.23 bdd	3.90 bdd	4.28 bdd
H-6	8.02 d	7.67 d	7.62 d	7.41 d	7.38 d	7.34 d	7.28 d	7.34 d	7.28 d
H-13	9.18 s	9.19 s	9.20 s	9.21 s	9.30 s	9.31 s	9.31 s	9.28 s	9.29 s
J(3,4)	10.0	10.0	10.0	10.0	8.0	8.0			
J(3',4)	6.0	6.0	6.0	6.5	7.0	7.0			
J(4,6)	1.5	1.5	1.5	1.0	1.0	1.0	1.0	1.0	1.5

Other signals: [a] OCH$_3$ 3.75 s; [b] CH$_3$ 1.32 s 6 H; [c] OCH$_3$ 3.15 s, 3.35 s; [d] OCH$_3$ 3.14 s, 3.35 s; 4-CH$_3$OC$_6$H$_4$ 3.75 s; [e] OCH$_3$ 3.18 s, 3.35 s; [f] SCH$_3$ 2.12 s, 2.22 s; [g] SCH$_3$ 2.15 s, 2.22 s.

TABLE V
Selected ^{1}H NMR parameters of dihydropyrans *VI – XIII* and *XXII* in CDCl$_3$ (TMS, 200 MHz)

Parameter	*VI*[a]	*VII*	*VIII*	*IX*	*X*[d]	*XI*[e]	*XII*[f]	*XIII*	*XXII*
				cis-isomers					
H-2	5.04 ddd	5.28 dd	5.22 dd	5.18 dd	5.19 dd	5.17 dd	5.10 dd	5.24 dd	5.13 dd
H-3	1.94 dt	2.17 ddd	2.06 ddd	2.07 ddd	2.06 ddd	2.04 ddd	2.11 m	2.21 m	2.07 ddd
H-3'	2.38 ddd	2.27 ddd	2.21 ddd	2.23 ddd	2.23 ddd	2.24 ddd	2.16 m	2.24 m	2.19 ddd
H-4	3.87 ddd	3.96 ddd	3.79 dt	3.84 dt	3.81 dt	3.78 dt	4.22 ddd	4.15 dt	3.77 ddd
H-6	7.60 d	7.55 d	7.47 d	7.43 d	7.42 d	7.40 d	7.29 d	7.37 d	7.79 d
H-13	9.23 s	9.36 s	9.27 s	9.27 s	9.28 s	9.27 s	9.23 s	9.31 s	–
OCH$_2$CH$_3$	–	3.50 dq	3.51 dq	3.51 dq	3.55 dq	3.62 dq	3.71 dq	3.55 dq	3.45 dq
	–	3.82 dq	3.84 dq	3.85 dq	3.88 dq	3.99 dq	4.06 dq	3.86 dq	3.77 dq
	–	1.03 t	1.08 t	1.09 t	1.14 t	1.08 t	1.29 t	1.13 t	1.05 t
Arom. H	7.07 m[b]	7.32 m[b]	7.07 m[b]	7.09 –	6.78 m[b]	6.68 m[b]	6.71 m	6.87 m[b]	7.10 m[b]
	7.20 m[b]	8.09 m[b]	7.19 m[b]	– 7.29 m[c]	7.06 m[b]	7.04 m[b]	6.85 m	7.08 dd	7.18 m[b]
J(2,3)	10.16	4.06	4.95	5.75	5.85	6.53	9.60	3.85	4.29
J(2,3')	1.88	2.69	2.69	2.57	2.56	2.48	2.37	2.98	2.74
J(3,4)	10.01	4.13	6.79	6.72	6.71	7.10	11.35	5.97	4.59
J(3',4)	5.83	7.50	7.01	6.98	7.01	7.20	7.56	5.83	7.41
J(4,6)	1.2	1.0	1.1	1.2	1.2	1.2	1.9	1.1	1.10
J(3,3')	-12.84	-14.18	-13.98	-14.05	-14.10	-13.98	-13.96	-14.11	-14.03

TABLE V
(Continued)

Parameter	VI[a]	VII	VIII	IX	X[d]	XI[e]	XII[f]	XIII	XXII
				trans-isomers					
H-2	4.78 ddd	5.09 dd	5.01 dd	5.01 dd	5.01 dd	5.01 dd	5.32 t	5.13 dd	4.85 dd
H-3	2.01 ddd	1.98 ddd	1.99 ddd	2.06 ddd	2.03 m	2.04 m	2.00 m	2.21 ddd	1.96 ddd
H-3'	2.14 ddd	2.20 dt	2.11 ddd	2.10 ddd	2.07 m	2.05 m	2.06 m	2.06 ddd	2.10 ddd
H-4	3.96 ddd	4.03 dt	3.94 dt	3.96 dt	3.93 dt	3.96 dt	4.26 bdd	4.24 bdd	3.92 dt
H-6	7.63 d	7.50 d	7.47 d	7.47 d	7.45 d	7.45 d	7.20 d	7.39 s	7.74 d
H-13	9.31 s	9.31 s	9.31 s	9.31 s	9.31 s	9.32 s	9.23 s	9.33 s	–
OCH_2CH_3	–	3.62 dq	3.59 dq	3.57 dq	3.58 dq	3.57 dq	3.67 dq	3.62 dq	3.54 dq
	–	3.95 dq	3.95 dq	3.94 dq	3.96 dq	3.96 dq	3.88 dq	3.99 dq	3.92 dq
	–	1.24 t	1.22 t	1.21 t	1.22 t	1.22 t	1.25 t	1.24 t	1.20 t
Arom. H	7.06 m[b]	7.32 m[b]	7.09 m[b]	7.10 –	6.83 m[b]	6.69 m[b]	6.72 m	6.78 dt	7.14 m[b]
	7.18 m[b]	8.16 m[b]	7.27 m[b]	–7.35 m[c]	7.06 m[b]	7.01 m[b]	6.86 m	6.91 dd	7.26 m[b]
								7.14 dd	
J(2,3)	2.24	2.43	2.40	2.39	2.53	2.07	2.10	2.46	2.35
J(2,3')	12.06	6.40	7.73	8.15	8.11	9.02	2.30	9.26	8.35
J(3,4)	1.79	6.80	4.99	4.64	5.07	4.72	10.82	3.12	4.14
J(3',4)	5.59	6.18	6.27	5.83	5.31	4.79	8.16	5.72	6.11
J(4,6)	0.0	1.0	0.8	0.6	0.6	0.6	2.0	0.0	1.04
J(3,3')	–14.10	–13.93	–13.75	–13.75	–13.69	–13.82	–14.14	–13.79	–13.52

Other signals: [a] *cis*-C_6H_5 7.27 – 7.36 m 5 H; *trans*-C_6H_5 7.12 – 7.32 m 5 H; [b] intensity of 2 H; [c] intensity of 5 H; [d] *cis*-4-$CH_3OC_6H_4$ 3.76 s 3 H; *trans*-4-$CH_3OC_6H_4$ 3.77 s 3 H; [e] *cis*-4-$(CH_3)_2NC_6H_4$ 2.90 s; *trans* 4-$(CH_3)_2NC_6H_4$ 2.91 s; [f] *cis*-2,4,6-$(CH_3)_3C_6H_2$ 2.14 bs, 2.21 bs, 2.37 bs; *trans*-2,4,6-$(CH_3)_3C_6H_2$ 2.14 bs, 2.22 bs, 2.39 bs.

TABLE VI
^{13}C NMR chemical shifts of dihydropyrans VI – XIII and XXII in CDCl$_3$ (50.3 MHz)

Carbon	VI^a	VII	VIII	IX	X^b	XI^c	XII^d	XIII	XXII
					cis-isomers				
C-2	76.19 d	99.75 d	100.29 d	100.44 d	100.75 d	100.93 d	123.93 d	99.91 d	98.62 d
C-3	37.06 t	34.09 t	34.83 t	35.45 t	35.85 t	36.16 t	31.19 t	35.15 t	34.93 t
C-4	33.09 d	32.25 d	32.38 d	33.41 d	33.00 d	33.31 d	26.74 d	28.06 d	33.57 d
C-5	119.73 s	120.13 s	120.87 s	121.22 s	121.78 s	122.01 s	129.39 s	121.36 s	107.76 s
C-6	165.89 d	163.88 d	164.96 d	163.33 d	163.26 d	162.81 d	162.46 d	162.56 d	155.99 d
C-7	141.42 s	150.36 s	140.78 s	142.15 s	134.31 s	130.15 s	136.51 s	145.95 s	142.10 s
C-8	128.69 d	128.44 d	127.99 d	127.12 d	128.31 d	127.85 d	134.80 d	126.10 d	128.90 d
C-9	128.56 d	123.19 d	127.86 d	127.79 d	113.51 d	112.56 d	130.09 d	124.55 d	128.00 d
C-10	132.44 s	146.32 s	131.42 s	125.89 d	157.92 s	149.05 s	135.43 s	122.99 d	131.60 s
C-13	189.42 d	189.37 d	189.53 d	189.30 d	189.58 d	189.48 d	189.08 d	189.47 d	172.40 s
OCH$_2$CH$_3$	–	64.91 t	64.39 t	64.57 t	64.87 t	64.77 t	64.64 t	64.84 t	64.53 t
	–	14.74 q	14.71 q	14.62 q	14.88 q	14.86 q	15.04 q	14.74 q	14.84 q
					trans-isomers				
C-2	79.86 d	98.89 d	99.38 d	99.60 d	99.78 d	99.92 d	102.60 d	100.64 d	97.32 d
C-3	40.34 t	35.20 t	35.26 t	35.27 t	35.45 t	35.36 t	32.53 t	35.10 t	35.27 t
C-4	36.74 d	32.83 d	32.41 d	32.98 d	32.27 d	32.09 d	31.57 t	28.55 d	34.44 d
C-5	121.71 s	120.08 s	120.28 s	120.43 s	120.73 s	122.01 s	123.16 s	120.57 s	107.16 s
C-6	166.42 d	163.89 d	163.67 d	163.57 d	163.53 d	163.23 d	162.06 d	163.11 d	154.35 d

TABLE VI
(Continued)

Carbon	VI[a]	VII	VIII	IX	X[b]	XI[c]	XII[d]	XIII	XXII
C-7	141.00 s	150.49 s	141.10 s	142.52 s	134.60 s	130.15 s	136.08 s	146.37 s	142.72 s
C-8	128.43 d	128.21 d	128.06 d	127.30 d	128.32 d	127.65 d	134.40 d	126.80 d	128.54 d
C-9	128.04 d	123.83 d	128.06 d	128.49 d	113.98 d	112.13 d	130.14 d	124.55 d	128.19 d
C-10	131.77 s	146.68 s	132.32 s	126.53 d	158.25 s	149.05 s	135.56 s	123.75 d	131.60 s
C-13	189.03 d	188.90 d	189.04 d	189.17 d	189.32 d	189.48 d	188.52 d	188.87 d	168.38 s
OCH$_2$CH$_3$	—	65.37 t	65.34 t	65.27 t	65.35 t	65.23 t	65.58 t	65.46 t	64.67 t
	—	14.94 q	14.95 q	14.96 q	15.01 q	14.86 q	15.08 q	14.94 q	14.76 q

Other carbons: [a] cis-C$_6$H$_5$ 138.64 s, 125.98 d (2 × C), 129.01 d (2 × C), 128.52 d, $trans$-C$_6$H$_5$ 138.46 s, 125.76 d (2 × C), 128.49 d (2 × C), 128.43 d; [b] cis-4-CH$_3$OC$_6$H$_4$ 55.13 q, $trans$-4-CH$_3$OC$_6$H$_4$ 55.18 q; [c] cis-4-(CH$_3$)$_2$NC$_6$H$_4$ 40.64 q, $trans$-4-(CH$_3$)$_2$NC$_6$H$_4$ 40.64 q; [d] cis-2,4,6-(CH$_3$)$_3$C$_6$H$_2$ 20.47 q, 20.73 q, 21.05 q, $trans$-2,4,6-(CH$_3$)$_2$C$_6$H$_2$ 20.20 q, 20.72 q, 21.19 q.

scatter factors were taken from *International Tables for Crystallography*[19]. The greatest peaks on the final differential electron density map had the value of $\pm$ 0.4 eÅ^{-3}. The final fractional coordinates and selected interatomic distances for one molecule of *trans-XXII*, together with the standard deviations, are given in Tables VIII and IX, the calculated dihedral angles in Table X. Lists of all atomic coordinates and distances in the unit cell are available from the author (I. C.) on request. The molecular structure of *trans-XXII* is depicted in Fig. 2 and the arrangement of atoms in the unit cell in Fig. 3.

Preparation of Dihydropyrans *II – IV*

Anhydrous zinc iodide (35 mg, 0.11 mmol) was added to a solution of the dialdehyde (2 mmol) and 1,1-diphenylethylene (0.39 g, 2.18 mmol) in benzene (2 ml) and the solution was stirred at room temperature for 48 h. The reaction mixture was diluted with benzene (5 ml), washed with 1M-NaOH (2 ml), dried over magnesium sulfate and the solvent was evaporated in vacuo. Upon addition of ether (0.5 ml), the residue crystallized. The product was collected on filter, washed with a small amount of ether and crystallized from benzene–light petroleum.

Preparation of Dihydropyran *V*

Zinc iodide (56 mg, 0.175 mmol) and 2-methylpropene (2.13 g, 37 mmol) were added to 4-chlorophenyl-methylenemalonaldehyde (585 mg, 3 mmol) in nitromethane (3 ml). The solution was stirred in a sealed ampoule at room temperature for 30 h, the solvent was evaporated, the residue dissolved in dichloromethane (10 ml) and washed with 1M-NaOH (6 ml). The organic layer was separated, dried over magnesium sulfate, the solvent was evaporated and the product distilled.

TABLE VII
IR spectra (in cm^{-1}) of dihydropyrans *II – XIX* (tetrachloromethane)

Compound	CH=O		C=C
	C–H	C=O	
II	2 725, 2 825	1 688	1 629
III	2 721, 2 825	1 690	1 630
IV	2 725, 2 830	1 690	1 629
V	2 726, 2 827	1 685	1 624
VII [a]	2 730, 2 829	1 683	1 632
VIII [a]	2 726, 2 824	1 685	1 632
IX [a]	2 723, 2 835	1 688	1 633
X [a]	2 724, 2 823	1 688	1 633
XI [a]	2 722	1 689	1 634, 1 624
XIII [a]	2 732, 2 826	1 685	1 630
XV	2 729	1 691	1 637
XVI	2 728	1 691	1 636
XVII	2 728	1 681	1 647
XVIII	2 728, 2 830	1 691	1 629
XIX	2 727, 2 833	1 693	1 631

[a] Mixture of isomers.

TABLE VIII
Fractional atom coordinates for one molecule of *trans-XXII*. Standard deviations in parentheses

Atom	x	y	z
Cl34	0.1870(1)	0.4742(1)	0.3678(1)
O1	−0.3869(2)	0.0104(2)	0.4273(2)
C2	−0.3236(3)	−0.0006(3)	0.3396(3)
C3	−0.3780(3)	0.0838(3)	0.2548(3)
C4	−0.3620(3)	0.2222(3)	0.3035(2)
C5	−0.4066(3)	0.2275(3)	0.4052(2)
C6	−0.4163(3)	0.1251(3)	0.4554(3)
C7	−0.2235(3)	0.2848(2)	0.3208(2)
C8	−0.1277(3)	0.2948(3)	0.4214(3)
C9	−0.0023(3)	0.3514(4)	0.4346(3)
C10	0.0298(3)	0.3991(3)	0.3493(3)
C11	−0.0631(4)	0.3910(3)	0.2483(3)
C12	−0.1877(3)	0.3341(3)	0.2356(3)
C13	−0.4479(3)	0.3448(3)	0.4460(2)
C14	−0.2820(4)	−0.2153(3)	0.3555(3)
C15	−0.2890(6)	−0.3317(4)	0.2822(5)
O16	−0.4569(2)	0.4360(2)	0.3887(2)
O17	−0.4741(3)	0.3504(2)	0.5371(2)
O18	−0.3501(2)	−0.1240(2)	0.2917(2)
H2	−0.229(3)	0.026(3)	0.375(3)
H31	−0.468(3)	0.057(3)	0.225(3)
H32	−0.328(3)	0.073(3)	0.204(3)
H4	−0.417(3)	0.271(3)	0.254(3)
H6	−0.445(3)	0.120(3)	0.518(3)
H8	−0.151(3)	0.265(3)	0.480(3)
H9	0.061(3)	0.361(3)	0.498(3)
H11	−0.041(3)	0.419(3)	0.187(3)
H12	−0.252(3)	0.328(3)	0.172(3)
H141	−0.327(3)	−0.230(3)	0.406(3)
H142	−0.184(3)	−0.176(3)	0.388(3)
H151	−0.370(3)	−0.354(3)	0.262(3)
H152	−0.222(3)	−0.296(3)	0.261(3)
H153	−0.246(3)	−0.402(3)	0.320(3)
H17	−0.489(3)	0.410(3)	0.554(3)

Preparation of Dihydropyran *VI*

Styrene (0.4 ml) and zinc iodide (25 mg, 0.08 mmol) were added to a solution of 4-chlorophenyl-methylenemalonaldehyde (395 mg, 2 mmol) in benzene (2 ml). The stirred mixture was heated at 75 °C for 5 h, the solvent was evaporated and the residue chromatographed on silica gel in light petroleum–ethyl acetate (5 : 1). Yield 85 mg of the more mobile *trans*-isomer which was crystallized from light petroleum–ethyl acetate, 110 mg of an intermediate fraction and 313 mg of the less mobile *cis*-isomer.

Preparation of Dihydropyrans *VII – X* and *XII – XIV*

An excess of ethyl vinyl ether (0.2 – 0.5 ml, i.e. 2 – 5 mmol) was added to a solution of the arylmethylenemalonaldehyde (1 mmol) in acetonitrile (2 ml) and the mixture was set aside at room temperature (*VII* for 1 h, *VIII* for 2 h, others overnight). After the dialdehyde had reacted (the yellow coloration of the solution disappeared), the solvent and the excess ethyl vinyl ether were evaporated and the residue distilled in vacuo or the pure isomers were obtained by chromatography on silica gel (30 – 60 μm, 40 g/mmol, light petroleum–ethyl acetate 5 : 2), the *trans*-isomer being obtained as the more mobile fraction. Crystalline isomers were crystallized from hexane–ethyl acetate.

Preparation of Dihydropyran *XI*

Ethyl vinyl ether (1 ml, 10.5 mmol) was added to a stirred mixture of 4-dimethylaminophenyl-methylenemalonaldehyde (0.21 g, 1 mmol), zinc iodide (35 mg, 0.11 mmol) and dry benzene (3 ml). The

TABLE IX
Selected interatomic distances and their standard deviations for molecule of *trans-XXII*

Atoms	Distance, Å	Atoms	Distance, Å
Cl34–C10	1.732(4)	C2–H2	0.99(3)
O1–C2	1.458(5)	C3–H31	0.93(3)
O1–C6	1.329(4)	C3–H32	0.94(4)
C2–C3	1.489(4)	C4–H4	0.95(3)
C2–O18	1.375(3)	C6–H6	0.93(4)
C3–C4	1.528(4)	C8–H8	0.93(4)
C4–C5	1.500(5)	C9–H9	0.89(3)
C4–C7	1.511(4)	C11–H11	0.94(4)
C5–C6	1.324(5)	C12–H12	0.90(3)
C5–C13	1.457(4)	C14–H141	0.92(4)
C7–C8	1.386(4)	C14–H142	1.04(3)
C7–C12	1.380(5)	C15–H151	0.83(3)
C8–C9	1.373(5)	C15–H152	0.90(4)
C9–C10	1.356(6)	C15–H153	1.00(3)
C10–C11	1.377(5)	O17–H17	0.70(3)
C13–O16	1.261(4)		
C13–O17	1.268(4)		
C14–C15	1.472(6)		
C14–O18	1.431(4)		

mixture was stirred at room temperature for 1 h, diluted with benzene (5 ml) and washed with 1M-NaOH (5 ml). The organic layer was separated, dried over magnesium sulfate, the solvent was evaporated and the residue was distilled or chromatographed as described for the other cycloadducts with ethyl vinyl ether.

Preparation of Dihydropyrans *XV – XVII*

To solution of arylmethylenemalonaldehyde (2 mmol) in acetonitrile (2 ml) was added 1.6M solution of 1,1-dimethoxyethylene in acetonitrile (2 ml). After decoloration of the reaction mixture (several minutes) the solvent and the remaining reagent were evaporated and the residue was distilled in vacuo.

Preparation of Dihydropyrans *XVIII* and *XIX*

The corresponding arylmethylenemalonaldehyde (1 mmol) was added to a solution of 1,1-bis(methylthio)-ethylene (123 mg, 1.025 mmol) in dry benzene (4 ml) and the mixture was stirred until the aldehyde dissolved. After standing at room temperature (*XVIII* for 1 h, *XIX* overnight), the solvent was evaporated in vacuo and ether (0.5 ml) was added to the residue. After several hours the crystalline product was filtered, washed with a small amount of ether and purified by crystallization from cyclohexane.

Preparation of *cis-* and *trans*-4-(4-Chlorophenyl)-2-ethoxy-3,4-dihydro-2*H*-pyran-5-carboxylic Acids (*cis-XXII* and *trans-XXII*)

A solution of potassium permanganate (0.180 g, 1.138 mmol) in a mixture of pyridine (2.3 ml) and water (1 ml) was added dropwise at –10 °C to a solution of *cis-VIII* (0.438 g, 1.64 mmol) in pyridine (4 ml). The mixture was kept at this temperature for 15 min, allowed to warm to room temperature, filtered through Celite and the filtrate was taken down in vacuo. The residue was dissolved in 10% sodium carbonate solution and this solution was twice extracted with ether and then acidified with 10% hydrochloric acid. The liberated acid was taken up in dichloromethane and the extract dried over magnesium sulfate. Evaporation of solvent afforded 0.136 g (29%) of the crude acid *cis-XXII* which was purified by chromatography on silica gel in light petroleum–ethyl acetate (5 : 1) and crystallized from hexane–ethyl acetate; m.p. 142 – 143 °C. For $C_{14}H_{15}ClO_4$ (282.7) calculated: 59.48% C, 5.31% H, 12.55% Cl; found: 59.76% C, 5.12% H, 12.62% Cl.

Similarly, oxidation of *trans-VIII* (0.365 g, 1.37 mmol) afforded 0.222 g (51%) of crude acid *trans-XXII*, practically pure according to TLC, which upon crystallization from hexane–ethyl acetate melted at 185 – 187 °C. For $C_{14}H_{15}ClO_4$ (282.7) calculated: 59.48% C, 5.31% H, 12.55% Cl; found: 59.30% C, 5.33% H, 12.47% Cl.

TABLE X
Calculated dihedral angles in the molecule of *trans-XXII*

Atoms	Angle, °	Atoms	Angle, °
H2–C2–C3–H32	69	C13–C4–C3–H31	–165
H2–C2–C3–H31	–179	C13–C4–C3–H32	–42
H31–C3–C4–H4	–34	H6–C6–C5–C4	–176
H32–C3–C4–H4	89	O1–C2–C3–C4	67
C13–C4–C3–C2	63		

Determination of Isomeric Composition in Dihydropyrans *VII – XIV*

The isomer ratio was determined by GLC (capillary 50 m × 0.2 mm × 0.33 μm; 5% MePh silicone; carrier gas He, flow rate 27.5 ml/min; injection 270 °C, detector 230 °C. In the case of compound *XI* this method failed and the isomer ratio was determined from integrals of the aldehydic proton signals in ^{1}H NMR spectrum.

A) Kinetically controlled reaction. To a solution of the corresponding arylmethylenemalonaldehyde (0.1 mmol) in toluene (1 ml) was added a trace amount of pyridine (to neutralize possible acidic impurities) and ethyl vinyl ether (0.05 ml, 0.52 mmol). After the end of the reaction (usually after standing overnight) the mixture was analyzed (Table I).

B) Isomer ratios under conditions of thermodynamic equilibrium. The procedure was the same as described for the kinetically controlled reaction except that pyridine was not added. After the reaction end (disappearance of the yellow coloration of the starting dialdehyde) the excess ethyl vinyl ether was evaporated, zinc iodide (10 mg, 0.073 mmol) was added to the residue and the mixture was heated at 100 °C for 1 h (on longer heating no further change in the isomer ratio was observed). After shaking with 10% potassium carbonate solution the mixture was analyzed (Table I).

C) Dependence of isomer ratio in the kinetically controlled reaction on the solvent used. The procedure was the same as described under *A*); no pyridine was added and, instead of toluene, an appropriate solvent – acetonitrile, benzene, pyridine or dimethylformamide – was used. The *cis/trans* ratio was the same in all cases, i.e. 77 : 33 (within the accuracy limits of ^{1}H NMR measurements).

Determination of Solvent Effect for Reaction of 4-Chlorophenylmethylenemalonaldehyde with Ethyl Vinyl Ether

The kinetic study was performed under conditions of a pseudomonomolecular reaction using about 5 000 times greater excess of ethyl vinyl ether. The decrease of 4-chlorophenylmethylenemalonaldehyde was followed spectroscopically at its λ_{max} = 308 nm. The measurement was performed in acetonitrile and in cyclohexane at 22 °C and the obtained values were processed using linear regression. The initial concentrations of ethyl vinyl ether in acetonitrile was 0.281 mol/l, of the dialdehyde 4.96 . 10^{-5} mol/l, the respective initial concentrations in cyclohexane were 0.247 mol/l and 4.90 . 10^{-5} mol/l. The rate constants in acetonitrile and cyclohexane were 1.131 . 10^{-3} l/mol min and 4.68 . 10^{-4} l/mol min, respectively. The ratio of reaction rates in both solvents is thus 2.4.

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