83. Photooxygenation of 3,3-Dialkylsubstituted Allyl Alcohols. Occurrence of Syn Preference in the Ene Addition of $^1O_2$ at *E/Z*-Isomeric Allyl Alcohols

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Summary

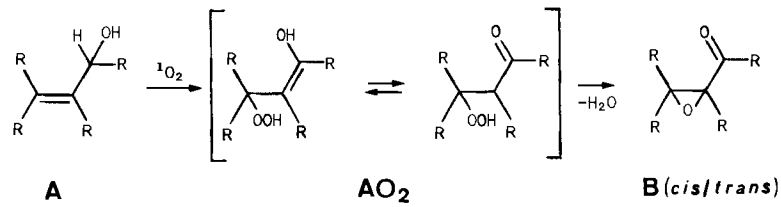
Dye-sensitized photooxygenation ($^1O_2$-reaction) of the symmetrically 3,3-dialkyl-substituted allyl alcohols **1–6** (**A**, *Table 1*) and the *E*- and *Z*-isomers of the 3-methyl-3-alkylsubstituted allyl alcohols **7–11** (**A**^{1}, *Table 2*) has been studied. The α,β-epoxy-aldehydes **B** and **B**^{1} and the β-hydroperoxy-homoallyl alcohols **C**, **C**^{1} and **D**^{1} were practically the sole oxygenation products formed. The rate and selectivity of the $^1O_2$ additions were found to be markedly dependent on the degree of substitution (*i.e.* H-availability) at the allyl position which is *Z*-orientated to the carbinol group. The allyl alcohols with a *Z*-3-methyl group, **1** and the *E*-isomers of **7** to **10**, showed practically the same reactivity towards $^1O_2$ and formed only the two oxygenation products of type **B**^{1} and **C**^{1} (ratio close to 60:40). In contrast, the allyl alcohols with a *Z*-3-methylene group, **2** and the *Z*-isomers of **7** to **9**, reacted more slowly with $^1O_2$ and yielded all the three possible products **B**^{1}, **C**^{1} and **D**^{1} in a very different ratio of ~80:10:10. However, from both the *E*- and *Z*-isomers of the alcohols **7** to **10** the formations of the two oxygenation products were always strongly favoured (85–100%) which result from $^1O_2$ additions at the disubstituted side of the double bond. This behaviour is thus completely analogous to that of the corresponding trisubstituted olefins previously studied [1][1]) and follows a new selection rule, termed *syn*-preference [1], in the ene addition of $^1O_2$.

Allyl alcohols possessing either tri- or tetraalkylsubstituted double bonds react with $^1O_2$ like the corresponding olefins by ene addition [6–9]. A significant directing effect of the α-hydroxyl group on the course of the $^1O_2$ addition is unknown. In general $^1O_2$ reaction involves all the allylic H-atoms – including those of the carbinol group – provided that they are suprafacially transferable [9]. H-Abstraction from the carbinol group leads to the unstable β-hydroperoxy carbonyl derivative **AO**$_2$

[1]) The same side-specific selectivity in $^1O_2$ ene additions to several *E/Z*-isomeric and deuterium-labelled olefins has also been described recently by *C. M. Stephenson et al.* [2] (we thank Dr. *V. Rautenstrauch* and Prof. *C. W. Jefford* for informing us about this work). The similar behaviour of enol ethers, which react with $^1O_2$ preferentially at the RO-substituted side, had been observed earlier by *C. S. Foote et al.* [3] and extended to numerous derivatives by *J. M. Conia et al.* [4] [5].

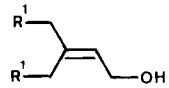
(Scheme 1), which is identical to the intermediate in the base-catalyzed H_2O_2-epoxidation of α,β-unsaturated carbonyl compounds (*Weitz-Scheffer* reaction [10] [11]) and thus rapidly converted to the α,β-epoxycarbonyl derivative **B**.

Scheme 1

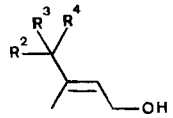


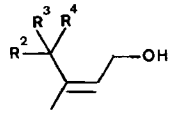
Up to now, the formation of **B** by $^1O_2$-oxygenation has only been observed [6] or used synthetically [8] with secondary allyl alcohols, primary allyl alcohols appearing not to undergo this reaction. No α,β-epoxyaldehydes were found for instance in the oxygenation products obtained from 21-hydroxy-17(20)-pregnene derivatives [12] or thujopsenol [13].

Scheme 2



A	R^1	R^1
1	H	H
2	CH_3	CH_3
3	$-(CH_2)_2-$	
4	$-(CH_2)_3-$	
5	$-(CH_2)_5-$	
6	$-(CH_2)_9-$	





(*E*)-A[1]	R^2	R^3	R^4	(*Z*)-A[1]	R^2	R^3	R^4
(*E*)-**7**	CH_3	H	H	(*Z*)-**7**	CH_3	H	H
(*E*)-**8**	$(CH_2)_2C(CH_3)=CH_2$	H	H	(*Z*)-**8**	$(CH_2)_2C(CH_3)=CH_2$	H	H
(*E*)-**9**	$(CH_2)_2C(CH_3)_2$	H	H	(*Z*)-**9**	$(CH_2)_2C(CH_3)_2$	H	H
(*E*)-**10**	CH_3	CH_3	H	(*Z*)-**10**	CH_3	CH_3	H
(*E*)-**11**	CH_3	CH_3	CH_3	(*Z*)-**11**	CH_3	CH_3	CH_3

We have now established that 3,3-dialkylsubstituted allyl alcohols of type **A** and (*E/Z*)-A[1] *(Scheme 2)* in general constitute excellent reaction partners for the ene addition of $^1O_2$ and that in practically all examples so far studied (**1** to **11**, *Table 1*

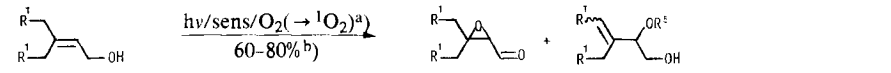
[2] The photooxygenation of *E*- and *Z*-γ-monocyclofarnesol leading to comparable results has already been described in another connection [14].

and *2*)[2]) they form the α,β-epoxyaldehydes **B** or **B**[1] as the principal products, together with the β-hydroperoxy-homoallyl alcohols **C** or **C**[1] and **D**[1]. In order to obtain further insight into the product forming process and the molecular factors governing the course of these $^1O_2$ ene additions at allyl alcohol double bonds oxygenation of the pure *E*- and *Z*-isomers of **A**[1] was investigated in more detail.

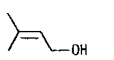
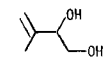
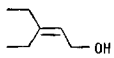
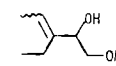
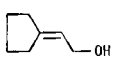
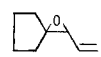
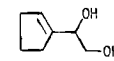
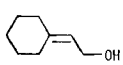
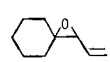
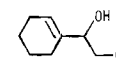
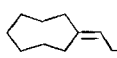
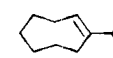
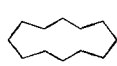
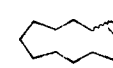
Results and discussion. – The oxygenations of the allyl alcohols **1** to **11** were carried out with photochemically generated $^1O_2$ [9] in methanol containing Na-acetate (~1%) and water (~5%) at 15–20°. In almost all cases there was nearly complete conversion with uptake of one equivalent of oxygen *(Tables 1* und *2)*. After reductive treatment of the oxygenation mixtures by standard procedures ($(CH_3)_2S$ or triphenylphosphine, 0–10°), α,β-epoxyaldehydes (**B** and **B**[1]) and diols (**E**, **E**[1] and **F**[1]), were the only volatile products isolated.

The product distributions determined by GC.-analysis of both the crude reduced oxygenation solutions and the product mixtures obtained after distillation (yields:

Table 1. *Dye-sensitized photooxygenation of the symmetrically 3,3-dialkylsubstituted allyl alcohols* **1-6** **(A)**



A **B** **C** (R^5=OH) **E** (R^5=H)

A		Reactivity[b]) β (M)	Conversion[c]) %	Products and product distribution (relat.)[c]) **B**	%	**E**	%
	**1**	0.14	93		**12** 56		**13** 44
	**2**	0.25	97		**14** 80		**15**[d]) 20
	**3**	0.02	100		**16** 54		**17** 46
	**4**	0.43	70		**18** 87		**19** 13
	**5**	0.06	92		**20** 59		**21** 41
	**6**	0.34	88		**22** 64		**23**[e]) 36

[a]) Conditions: 0.05 mol A/90 ml CH_3OH/5 ml H_2O/750 mg CH_3COONa/100 mg Rose Bengale/Pyrexapp. [15]/*Philips* HPK 125 W-lamp/20°.

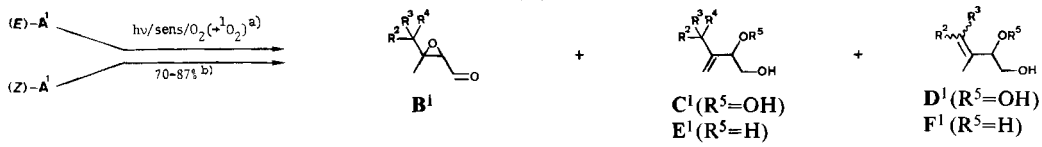
[b]) For determination of individual yields and β-values see experimental part.

[c]) Determined by GC.-analysis of the oxygenation mixture after reduction with $(CH_3)_2S$.

[d]) *E*/*Z* 15:5.

[e]) *E*/*Z* 20:16.

Table 2. *Dye-sensitized photooxygenation of the (E)- and (Z)-3-methyl-3-alkyl allyl alcohols* **7**–**11** *((E)-/(Z)-*$\mathbf{A}^1$*)*



(*E*)-/(*Z*)-$\mathbf{A}^1$	Reactivity[b] β (M)	Conversion[c] %	Products and product distribution (relat.)[c]					
			$\mathbf{B}^1$	%	$\mathbf{E}^1$	%	$\mathbf{F}^1$	%
(*E*)-7	0.13	100	24[d]	58	25	40	26	≤2
(*Z*)-7	0.19	100		82		11		7
(*E*)-8	0.15	95	27[d]	62	28	36	29[e]	≤2
(*Z*)-8	0.21	95		79		12		9
(*E*)-9	0.14	98	30[d]	58	31	42	32[e]	≤2
(*Z*)-9	0.23	90		80		11		9
(*E*)-10	0.14	92	33	58	34	40	35	≤2
(*Z*)-10	0.23	90		85		13		≤2
(*E*)-11	0.09	100	36	45	37	55	—	
(*Z*)-11	0.95	70		46		54		

[a]–[c]) See *Table 1* and experimental part; [d]) *cis/trans*-Mixture ~40:60; [e]) Only the (*E*)-isomers were observed.

60–87%, *Table 1* and *2*) did not vary significantly with the degree of conversion during an oxygenation run (GC.-analysis) and were reproducible to ± 5%[3]).

Preparatively the α,β-epoxyaldehydes **B** or $\mathbf{B}^1$ could be efficiently separated from the accompanying diols **E** or $\mathbf{E}^1$ and $\mathbf{F}^1$ by distillation through a short *Vigreux*

[3]) It should be noted however that the product distributions so determined only reflect the course of the $^1O_2$ reaction with the allyl alcohols **A** or $\mathbf{A}^1$ (*i.e.* addition selectivity) if all the β-hydroperoxy enols $\mathbf{AO}_2$ primarily formed (see *Scheme 1*) are completely transformed into α,β-epoxyaldehydes **B** or $\mathbf{B}^1$ and if work-up losses are the same for each of the products **B**, $\mathbf{B}^1$, **C**, $\mathbf{C}^1$ and $\mathbf{D}^1$.

column. The mixture of the remaining diols was then chromatographed for separation and final purification.

Separation of the *cis/trans* mixtures of the α,β-epoxyaldehydes **24**, **27** and **30** has so far only been achieved in the case of 2,3-epoxy-α-citronellal (**27**) using GC. but GC. indicated the presence of similar isomer ratios (40% *cis*: 60% *trans*) for **24** and **30**. From the highly branched allyl alcohols **10** and **11** only the formation of the *trans* isomers of the α,β-epoxyaldehydes **33** and **36** was observed[4]).

We found both the possible *E*- and *Z*-isomers of the diols **15**, **23** and **26** among the reduced oxygenation products of **2**, **6** and **7** respectively. In contrast, from **8** and **9** practically only the *E*-isomers of the diols **29** and **32** were formed.

The identification of all compounds was possible from their spectra and, in part, by comparison with authentic samples.

The reactivity of the allyl alcohols **A** and **A**[1] towards $^1O_2$, measured under standard conditions (see experimental part) and expressed by their β-values [18] [19], was on average only about one half of the reactivity of the corresponding trisubstituted olefins [1] [9], but generally high enough for preparative purposes[4]). Except for **4** and (*Z*)-**11**, which only reacted up to 70% conversion[5]), all allyl alcohols studied were easily and almost completely oxygenized with $^1O_2$ (>90%, see *Tables 1* and *2*).

The alcohols with a cyclopentylidene, cyclooctylidene or an *E*-orientated *t*-butyl group (**3**, **5** and (*E*)-**11**) exhibit unusually high reactivity towards $^1O_2$, even exceeding that of 3,3-dimethyl allyl alcohol (**1**), which might have been expected to have the greatest reactivity, on account of the two geminal methyl groups thus providing optimum H-availability [9]. The higher reactivity of **3** and **5** may be due to the fact that the allylic H-atoms on the 5- and 8-membered rings are stabilized in a conformation favourable for the occurrence of $^1O_2$ ene additions [9], thus counteracting the deactivating effect of the allylic OH group. For (*E*)-**11** it can be similarly assumed that the H-atoms of the *Z*-orientated 3-methyl group are also fixed in a favourable conformation due to the steric hindrance of the geminal *t*-butyl group. This behaviour parallels the fact that all three allyl alcohols **3**, **5** and (*E*)-**11** form relatively high percentages of the β-hydroxy-homoallyl alcohols **17** (46%), **21** (41%) and **37** (55%) respectively.

Furthermore it is also striking that the differences in reactivity between the *E*- and *Z*-isomers of each of the allyl alcohols **7**–**10** lie in the same direction. Whereas the *E*-isomers are converted by $^1O_2$ at about the same rate as 3,3-dimethyl allyl alcohol (**1**), all their corresponding *Z*-isomers react more slowly with $^1O_2$ and display about the same reactivity as 3,3-diethyl allyl alcohol (**2**). The results obtained with (*E*)- and (*Z*)-**10** show this trend to be unchanged even if there is only one H-atom present in the *syn* allyl position. A distinctly greater divergence of reactivity is only observed if all the *syn* allylic H-atoms are substituted by methyl

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[4]) To our knowledge none of these α,β-epoxyaldehydes has been described previously, implying difficulties with their syntheses following classical procedures [16] [17]. The oxygenation of 3,3-dialkylsubstituted allyl alcohols by $^1O_2$ thus provides a valuable alternative method for the preparation of β,β-dialkyl-α,β-epoxy propanals.

[5]) The reasons for this are not known, **4** and (*Z*)-**11** recovered from an initial exposure reacted again and in the same manner.

groups; the *t*-butyl derivative (*Z*)-**11** exhibiting a 5-fold decrease in reactivity towards $^1O_2$ with respect to all the other (*Z*)-**A**[1] studied.

Another interesting feature of the $^1O_2$ reaction with the allyl alcohols **7–10** is revealed by the significantly different orientation of the $^1O_2$ addition to their pure *E*- and *Z*-isomers. Whereas the *E*-isomers of **7–10** reacted to form only the α,β-epoxyaldehydes **B**[1] and the β-hydroperoxy-homoallyl alcohols **C**[1] in nearly equal amounts ($\sim 60:40$), the corresponding *Z*-isomers yielded the α,β-epoxyaldehydes **B**[1] together with the two possible β-hydroperoxy-homoallyl alcohols of type **C**[1] and **D**[1] in a very different ratio of $\sim 80:10:10$ *(Table 2)*. In comparison with the addition behaviour of 3,3-dimethyl allyl alcohol (**1**), it appears that the presence of one or more substituents at the *E*-methyl group (*anti* allyl position) thus brings about no marked change in the orientation of the $^1O_2$ addition. The ratios of the oxygenation products formed from all the *E*-isomers of **7–11** are very similar and practically the same as for **1** *(Table 2)*.

Significant changes from the addition behaviour of **1** towards $^1O_2$ first occur when the situation at the *Z*-methyl group (*syn* allyl position) is altered by alkyl substitution. Introduction of one alkyl substituent results in an increase in the yield of the α,β-epoxyaldehyde **B**[1] of about 20% (examples **2** and (*Z*)-**7** to (*Z*)-**9**). A second alkyl substitution causes a further increase up to 85% (*e.g.* **33** from (*Z*)-**10**). Finally if all the H-atoms in the *syn* allyl position are replaced by alkyl groups, a counter influence to the course of the $^1O_2$ addition becomes dominant. The *t*-butyl derivative (*Z*)-**11** only yields 46% of the α,β-epoxyaldehyde **36**, and the β-hydroperoxy-homoallyl alcohol of type **C**[1] constitute the principal oxygenation product (54%, isolated as the diol **37** after reduction).

If the *syn* allyl position is incorporated into an cycloaliphatic ring, additional conformational effects come into operation. The orientation of $^1O_2$ addition to the four cyclic allyl alcohols **3–6** show a clear dependence on ring size. For the alcohols with 5- and 8-membered rings, **3** and **5**, a product distribution of about 54–59% of α,β-epoxyaldehydes and 41–46% of β-hydroperoxy-homoallyl alcohols was observed; this is typical for the *E*-isomers of the allyl alcohols **A**[1]. In contrast, cyclohexylidene methanol (**4**) behaved differently and gave the highest proportion of α,β-epoxyaldehyde (**18**, 87%) of all the 3,3-dialkyl allyl alcohols investigated. The reason for this may be connected with the particular situation of the allylic H-atoms in the cyclohexane ring, known to be in an unfavourable conformation to attain the cyclic transition state needed for $^1O_2$ additions [20] [21].

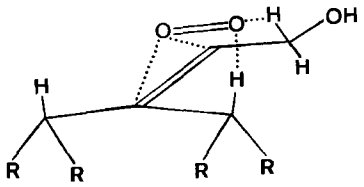
Conclusion. – Consideration of this and earlier work [1] lead to the following conclusions: Apart from diminishing the reactivity of the double bond ($\sim$25–30% on average), the presence of a primary C(1)-hydroxyl group in 3,3-dialkyl-prop-2-enes does not cause any greater change in the addition selectivity of $^1O_2$. The average product distributions found for the *E*- and *Z*-isomers of **7–9** (**B**[1]:**C**[1] $\sim 60:40$ and **B**[1]:**C**[1]:**D**[1] $\sim 80:10:10$ respectively) are generally close to those obtained from comparable *E*- and *Z*-isomeric olefines ($\sim 55:45$ and $\sim 75:15:10$ respectively [1]). Thus the primary carbinol group may be regarded as being roughly equivalent to a methyl or a methylene group in competing as H-donors in $^1O_2$ ene reactions.

Similar conclusions hold for the new selection rule of *syn* preference in the ene addition of $^1O_2$ [1]. As for trisubstituted acyclic olefines a comparably high preference

of $^1O_2$ ene additions at the disubstituted side of the double bond in the allyl alcohols **7–10** is evident. Both the *E*- and *Z*-isomers of **7–10** react with $^1O_2$ to form almost exclusively (85–100%) those pairs of oxygenation products (*i.e.* $\mathbf{B}^1 + \mathbf{E}^1$ from (*E*)-**7–10** and $\mathbf{B}^1 + \mathbf{F}^1$ from (*Z*)-**7–10**, see *Table 2*), which prerequisite a *syn* approach of $^1O_2$ *(Scheme 3)* and in which H-abstractions from the two *Z*-orientated allyl positions are involved.

The product selectivity (measured as difference in product yield of $\mathbf{B}^1$, $\mathbf{C}^1$ or $\mathbf{D}^1$ from *E*- and *Z*-$\mathbf{A}^1$) due to this *syn* directing factor lies in the range of 10–35% and were similarly found for the corresponding olefins [1].

Scheme 3



From comparison of the oxygenation behaviour of the six differently *syn* allyl-substituted alcohols **2** and (*Z*)-**7** to (*Z*)-**11** it further can be concluded that there may exist a distinct relationship between the degree of substitution (H-availability) in the *syn* orientated allyl position and the occurrence of *syn* preference in $^1O_2$ ene additions. From all these alcohols only the *t*-butyl derivative (*Z*)-**11** bearing no *syn* allylic H-atoms, behaves markedly different and forms the products from *syn* and *anti* ene additions in nearly equal quantities. Its lower homologue (*Z*)-**10** possessing one *syn* allylic H-atom reacts as fast as the alcohols **2** and the *Z*-isomers of **7–9** and shows the same high preference for the *syn* ene addition (~85%). Although abstraction of this methine H-atom does not occur (the expected diol **35** is not found in the reduced oxygenation mixtures of either the *E*- or *Z*-isomer of **10**), already its presence seems to give rise to the *syn* effect. Thus from all allylic H-atoms suprafacially transferable in an olefinic $^1O_2$ acceptor of type **A** or $\mathbf{A}^1$, those situated *syn* to a further hydrogen carrying substituent are preferentially involved in the product forming process.

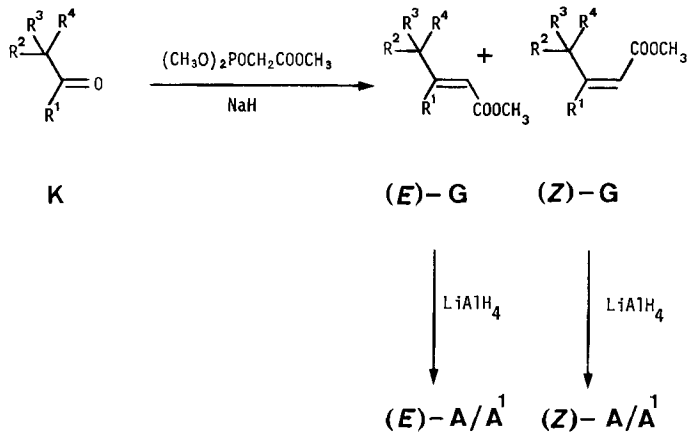
We thank Dr. *G. Ohloff*, Prof. *K. Gollnick*, Dr. *B. Maurer*, Dr. *A. F. Boschung* and Dr. *R. L. Snowden* for stimulating discussions.

Experimental Part

General. The apparatus for spectra has been described [1]. The gas chromatographic (GC.) separations were carried out both analytically and preparatively on Carbowax (15% on chromosorb 20 M) using a *Varian* gas chromatograph, type 700-A, and He as carrier gas. The ^{1}H-NMR. spectra were recorded in CCl_4 solutions with tetramethylsilane ($\delta = 0.00$ ppm) as internal standard unless otherwise stated. The multiplicities are given in brackets (*s* = singlet, *d* = doublet, *t* = triplet, *qa* = quadruplet, *m* = multiplet). The mass spectra (MS.) are given as the most intense fragment in each group (% of the most important fragment).

1. Starting materials. – *The 3,3-dialkylallyl alcohols* **1** and (*E*/*Z*)-**9** were obtained from *BASF*. Alcohols (*E*/*Z*)-**7** and (*E*/*Z*)-**8** were prepared from (*E*/*Z*)-3-methyl-3-pentenal [22] and α-citral [22] respectively by reduction with $LiAlH_4$. Compound **2**, the *E*/*Z*-isomers of **10** and **11**, and the cyclic substituted alcohols **3–6** were obtained by $LiAlH_4$ reduction of the corresponding esters **38–46** (**G**, *Scheme 4*), easily accessible from

Scheme 4



the ketones **K** by the *Horner-Wittig* reaction [23]. The *E*- and *Z*-isomers could in all cases be purified by distillation on a *Fischer* split ring column at the ester stage **G** or at the aldehyde stage for **7** and **8**.

1.1. *Preparation of the acrylates* **38–46**. – *General Procedure.* Methyldimethylphosphonoacetate (18.2 g, 0.1 mol) was added dropwise with stirring to a mixture of 2.5 g NaH *(Fluka)*, 10 g hexamethylphosphoric triamide (HMPT) and 100 ml di-isopropyl ether at 20–25° under N_2. After stirring for 2 h, ketone **K** (0.1 mol) in 20 ml di-isopropyl ether was added dropwise, and the mixture was heated for 3 h under reflux. After cooling and destruction of any remaining NaH with CH_3OH, the product was diluted with ether and washed with water to neutrality. The ether phase was dried (Na_2SO_4) and evaporated under vacuum, and the reaction product purified by distillation (*Fischer* split ring column).

Methyl 3-ethyl-2-pentenoate (**38**). Yield: 92%, b.p. 41°/7.5 Torr. – IR.: 1720 (C=O); 1640 (C=C). – ^{1}H-NMR.: 1.10 (2 *t*, *J* = 7, 2 CH_3CH_2); 3.63 (*s*, H_3C–O); 5.53 (*s*, H–C(2)). – MS.: 142 (M^+, 76), 127 (6), 111 (94), 95 (13), 81 (60), 67 (38), 55 (100), 41 (68), 27 (48).

*Methyl 3,4-dimethyl-2(*E*)-pentenoate* (**39**). Yield: 60%, b.p. 45°/8 Torr. – IR.: 1720 (C=O); 1640 (C=C). – ^{1}H-NMR.: 1.02 and 1.12 (2 *s*, $(H_3C)_2$–C(4)); 2.15 (*s*, H_3C–C(3)); 3.61 (*s*, H_3C–O); 5.61 (*s*, H–C(2)). – MS.: 142 (M^+, 50), 127 (50), 111 (59), 95 (51), 83 (100), 67 (58), 55 (86), 41 (77), 27 (31).

*Methyl 3,4-dimethyl-2(*Z*)-pentenoate* (**40**). Yield: 25%, b.p. 42°/8 Torr. – IR.: 1720 (C=O); 1640 (C=C). – ^{1}H-NMR.: 0.92 and 1.03 (2 *s*, $(H_3C)_2$–C(4)); 1.75 (*s*, H_3C–C(3)); 3.59 (*s*, H_3C–O); 5.5 (*s*, H–C(2)). – MS.: 142 (M^+, 62), 127 (50), 111 (62), 95 (56), 83 (100), 67 (65), 55 (87), 41 (65), 27 (34).

*Methyl 3,4,4-trimethyl-2(*E*)-pentenoate* (**41**). Yield: 40%, b.p. 81–83°/12 Torr. – IR.: 1715 (C=O); 1630 (C=C). – ^{1}H-NMR.: 1.11 (*s*, 3 H_3C–C(4)); 2,2 (*d*, *J* = 2, H_3C–C(3)); 3.7 (*s*, H_3C–O); 5,75 (*m*, H–C(2)). – MS.: 156 (M^+, 12), 141 (100), 125 (65), 109 (70), 97 (99), 81 (62), 55 (70), 41 (60).

*Methyl 3,4,4-trimethyl-2(*Z*)-pentenoate* (**42**) was prepared by irradiating **41** (3 g) in acetone (300 ml) under N_2 in a quartz apparatus [15] with a Hg vapour lamp (*Philips* HPK, 125 Watt) and was separated from **41** (*ca.* 50%) by distillation; b.p. 79–80°/12 Torr. – IR.: 1715 (C=O); 1630, 1615 (C=C). – ^{1}H-NMR.: 1.21 (*s*, $(H_3C)_3$–C(4)); 1.9 (*d*, *J* = 1.5, H_3C–C(3)); 3.7 (*s*, H_3C–O); 5.65 (*m*, H–C(2)). – MS.: 156 (M^+, 1), 141 (100), 125 (40), 109 (70), 97 (95), 81 (65), 55 (70), 41 (50).

Methyl cyclopentylidenacetate (**43**). Yield: 92%, b.p. 57°/8 Torr. – IR.: 1720 (C=O); 1670 (C=C). – ^{1}H-NMR.: 1.57–1.84 (*m*, 2 H–C(3′) and 2 H–C(4′)); 2.3–2.9 (*m*, 2 H–C(2′) and 2 H–C(4′)); 3.6 (*s*, H_3C–O); 5.75 (*m*, H–C(2)). – MS.: 140 (M^+, 100), 125 (12), 109 (85), 97 (8), 79 (85), 67 (48), 53 (52), 41 (56), 27 (47).

Methyl cyclohexylidenacetate (**44**). Yield: 91%, b.p. 65–66°/8 Torr. – IR.: 1710 (C=O); 1640 (C=C). – ^{1}H-NMR.: 1.63 (*m*, 2 H–C(3′–5′)); 2.2 and 2.82 (both 1 *m*, 2 H–C(2′) and 2 H–C(6′)); 3.58 (*s*, H_3C–O); 5.51 (*m*, H–C(2)). – MS.: 154 (M^+, 100), 139 (12), 123 (56), 111 (42), 95 (64), 80 (42), 67 (48), 53 (55), 39 (52), 27 (35).

Methyl cyclooctylidenacetate (**45**). Yield: 78%, b.p. 63°/0.1 Torr. – IR.: 1670 (C=O); 1645 (C=C). – ^{1}H-NMR.: 1.5 (*m*, 2 H–C(3'-7')); 2.25 and 2.27 (both 1 *m*, 2 × 2 H–C(2') and 2 H–C(8')); 3.58 (*s*, H_3C–O); 5.6 (*s*, H–C(2)). – MS.: 182 (M^+, 1), 168 (100), 151 (58), 140 (21), 138 (41), 108 (25), 93 (26), 81 (51), 67 (45), 55 (58), 41 (70), 29 (54).

Methyl cyclododecylidenacetate (**46**). Yield: 61%, m.p. 58–60° (cyclohexane). – IR. (KBr): 1710 (C=O); 1640 (C=C). – ^{1}H-NMR.: 1.3 (*m*, 2 H–C(3'-9')); 3.57 (*s*, H_3C–O); 5,63 (*s*, H–C(2)). – MS.: 222 (M^+, 0.5), 207 (22), 195 (0.5), 178 (2), 164 (50), 154 (13), 139 (23), 121 (21), 114 (100), 95 (45), 81 (52), 67 (49), 55 (73), 41 (85), 29 (32).

1.2. *Reduction of the Acrylates* **38–46**. *Allyl alcohols* **1–11**. The acrylates **38–46** (0.1 mol) in absolute diethyl ether (200 ml) were added dropwise at 0–10° under N_2, to a stirred mixture of $LiAlH_4$ (0.1 mol) in absolute ether (200 ml). Usual work-up yielded the alcohols **2** to **6** and the *E*- and *Z*-isomers of **10** and **11** (75–80%). All the allyl alcohols including the derivatives (*E*/*Z*)-**7** and (*E*/*Z*)-**8**, prepared from 3-methyl-2-pentenal [22] and α-citral [22], were separated into the *E*- and *Z*-isomers by distillation. The *E*-isomers always had the higher b.p. and longer retention times (GC.).

1.3. *Spectral Data for Allylalcohols* **1–11**.

3-Methyl-2-butenol (**1**, 'Prenol', *BASF*). – IR.: 3350 (OH); 1670 (C=C). – ^{1}H-NMR.: 1.63 and 1.72 (both 1*s*, $(H_3C)_2$–C(3)); 3.97 (*d*, *J* = 6, 2 H–C(1)); 5.29 (*m*, H–C(2)).

3-Ethyl-2-pentenol (**2**). – IR.: 3300 (OH); 1665 (C=C). – ^{1}H-NMR.: 0.98 and 1.02 (both 1 *t*, *J* = 6, 2 CH_3CH_2); 2.04 (*m*, 2 CH_2); 4.03 (*d*, *J* = 6, 2 H–C(1)); 5.26 (*t*, *J* = 6, H–C(2)). – MS.: 114 (M^+, 1), 128 (1), 114 (3), 96 (16), 85 (100), 67 (60), 55 (90), 41 (98).

2-Cyclopentylidene-ethanol (**3**). – IR.: 3300 (OH); 1670 (C=C). – ^{1}H-NMR.: 1.55 (*m*, $(CH_2)_2$); 2.22 (*m*, 2 H–C(4) and 2 H–C(7)); 3.96 (*d*, *J* = 6, 2 H–C(1)); 5.4 (*m*, H–C(2)). – MS.: 112 (M^+, 20), 94 (55), 79 (100), 67 (62), 55 (44), 41 (62).

2-Cyclohexylidene-ethanol (**4**). – IR.: 3350 (OH); 1670 (C=C). – ^{1}H-NMR.: 152 (*m*, $(CH_2)_3$); 2.15 (*m*, 2 H–C(4)) and 2 H–C(8)); 4.0 (*d*, *J* = 6, 2 H–C(1)); 5.27 (*t*, *J* = 6, H–C(2)). – MS.: 126 (M^+, 7), 108 (65), 93 (50), 79 (75), 67 (100), 55 (50), 41 (62). – (Lit.: [24]).

2-Cyclooctylidene-ethanol (**5**). – IR.: 3400 (OH); 1675 (C=C). – ^{1}H-NMR.: 1.53 (*m*, $(CH_2)_5$); 2.2 (*m*, H–C(4) and H–C(10)); 4.02 (*d*, *J* = 6, 2 H–C(1)); 5.33 (*t*, *J* = 6, H–C(2)). – MS.: 154 (M^+, 5), 136 (28), 121 (15), 108 (28), 93 (35), 81 (73), 67 (95), 55 (70), 41 (100).

2-Cyclododecylidene-ethanol (**6**). – IR.: 3380 (OH); 1660 (C=C). – ^{1}H-NMR.: 1.32 (*m*, $(CH_2)_9$); 2.1 (*m*, H–C(4) and H–C(14)); 4.1 (*d*, *J* = 6, 2 H–C(1)); 5.42 (*t*, *J* = 6, H–C(2)). – MS.: 210 (M^+, 3), 192 (7), 166 (4), 149 (6), 135 (8), 121 (10), 109 (22), 95 (44), 81 (65), 67 (70), 55 (95), 41 (100).

(E)-3-Methyl-2-pentenol ((E)-7). – IR.: 3350 (OH); 1670 (C=C). – ^{1}H-NMR.: 1.01 (*t*, *J* = 6, H_3C–C(4)); 1.63 (*d*, *J* = 2, H_3C–C(3)); 1.98 (*m*, 2 H–C(4)); 4.00 (*d*, *J* = 5, 2 H–C(1)); 5.28 (*t*, *J* = 6, H–C(2)). – MS.: 100 (M^+, 7), 71 (100), 53 (10), 43 (20), 41 (40). – (Lit. for (*E*/*Z*)-**7** [25]).

(Z)-3-Methyl-2-pentenol ((Z)-7). – IR.: 3350 (OH); 1665 (C=C). – ^{1}H-NMR.: 0.98 (*t*, *J* = 6, H_3C–C(4)); 1.70 (*d*, *J* = 1.5, H_3C–C(3)); 2.05 (*m*, 2 H–C(4)); 3.98 (*d*, *J* = 6, 2 H–C(1)); 5.29 (*t*, *J* = 6, H–C(2)). – MS.: 100 (M^+, 8), 71 (100).

(E)-3,7-Dimethylocta-2,7-dienol ((E)-8). – IR.: 3350 (OH); 3080, 1640 and 890 (C=CH_2); 1670 (C=C). – ^{1}H-NMR.: 1.56 and 1.64 (both 1*s*, H_3C–C(3) and H_3C–C(7)); 4.02 (*d*, *J* = 6, 2 H–C(1)); 4.62 (*m*, 2 H–C(8)); 5.33 (*t*, *J* = 6, H–C(2)). – MS.: 154 (M^+, 0.1), 136 (3), 121 (14), 96 (20), 83 (40), 69 (80), 55 (50), 41 (100). – (Lit. for **8** and **9** [26] [27]).

(Z)-3,7-Dimethylocta-2,7-dienol ((Z)-8). – IR.: 3350 (OH); 3090, 1645, 892 (C=CH_2); 1665 (C=C). – ^{1}H-NMR.: 1.69 and 1.7 (both 1 *m*, H_3C–C(3) and H_3C–C(7)); 3.98 (*d*, *J* = 6, 2 H–C(1)); 4.63 (*m*, 2 H–C(8)); 5.34 (*t*, *J* = 6, H–C(2)). – MS.: 154 (M^+, 1), 136 (5), 41 (100).

(E)-3,4-Dimethyl-2-octenol ((E)-9). – IR.: 3300 (OH); 1675 (C=C). – ^{1}H-NMR.: 0.87 (2 *d*, *J* = 7, 2 H_3C–C(7)); 1.63 (*d*, *J* = 2, H_3C–C(3)); 4.01 (*d*, *J* = 6, 2 H–C(1)); 5.3 (*t*, *J* = 6, H–C(2)). – MS.: 156 (M^+, 1), 138 (3), 123 (5), 109 (2), 95 (10), 81 (16), 71 (100), 55 (21), 41 (35).

(Z)-3,4-Dimethyl-2-octenol ((Z)-9). – IR.: 3350 (OH); 1670 (C=C). – ^{1}H-NMR.: 0.82 (2 *d*, *J* = 6, 2 H_3C–C(7)); 1.65 (*d*, *J* = 2, H_3C–C(3)); 4.00 (*d*, *J* = 6, 2 H–C(1)); 5.27 (*t*, *J* = 6, H–C(2)). – MS.: 156 (M^+, 0.1), 138 (4), 71 (100).

*(E)-3,4-Dimethyl-2-pentenol ((E)-**10**).* – IR.: 3350 (OH); 1675 (C=C). – ^{1}H-NMR.: 1.0 (2 *d*, J=6, 2 H_3C–C(4)); 1.61 (*d*, J=2, H_3C–C(3)); 2.2 (*m*, H–C(4)); 4.0 (*d*, J=6, 2 H–C(1)); 5.33 (*t*, J=6, H–C(2)). – MS.: 114 (M^+, 5), 96 (4), 83 (20), 71 (100), 55 (65), 43 (60).

*(Z)-3,4-Dimethyl-2-pentenol ((Z)-**10**).* – IR.: 3350 (OH); 1668 (C=C). – ^{1}H-NMR.: 0.98 (2 *d*, J=6, 2 H_3C–C(4)); 1.64 (*d*, J=2, H_3C–C(3)); 2.8 (*m*, H–C(4)); 4.0 (*d*, J=6, 2 H–C(1)); 5.34 (*m*, H–C(2)). – MS.: 114 (M^+, 1), 96 (25), 81 (30), 71 (100), 55 (82), 41 (75).

*(E)-3,4,4-Trimethyl-2-pentenol ((E)-**11**).* – IR.: 3300 (OH); 1645 (C=C). – ^{1}H-NMR.: 1.05 (*s*, 3 H_3C–C(4)); 1.69 (*s*, H_3C–C(3)); 4.20 (*d*, J=6, 2 H–C(1)); 5.45 (*t*, J=6, H–C(2)). – MS.: 128 (M^+, 3), 111 (2), 97 (70), 84 (50), 69 (39), 57 (92), 43 (95), 41 (100). – (Lit.: [26]).

*(Z)-3,4,4-Trimethyl-2-pentenol ((Z)-**11**).* – IR.: 3300 (OH); 1640 (C=C). – ^{1}H-NMR.: 1.1 (*s*, 3 H_3C–C(4)); 1.75 (*d*, J=2, H_3C–C(3)); 4.3 (*d*, J=6, 2 H–C(1)); 5.29 (*t*, J=6, H–C(2)). – MS.: 128 (M^+, 4), identical with that for (*E*)-**11**.

2. Photosensitized oxygenation of the 3,3-dialkyl allyl alcohols 1–11. – 2.1. *Equipment.* The photosensitized oxygenations ($^1O_2$-reactions) were carried out in a conventional *Pyrex* irradiation apparatus (capacity ~ 120 ml) [15], in pure oxygen by means of a centrally arranged, water cooled Hg-vapor lamp, *Philips* HPK 125 W. The oxygen was delivered from a volumetric storage flask and its consumption was recorded automatically. Irradiation temp.: ~ 16–20°.

2.2. *Oxygenation experiments.* Samples of 0.05 mol of allyl alcohols **1–11** in 90 ml methanol and 5 ml water together with 100 mg Rose bengal (RoBe) and 750 mg Na-acetate were photooxygenated. The O_2-uptake reached its maximum (V_{max}) in all cases after *ca.* 10% conversion and then fell continuously to 0.5 ml O_2/min. To avoid over-oxidation, after 90–98% conversion (GC.) the oxygenation was stopped. Average time needed for nearly total conversion of **1–11** under these conditions was 1–4 h. 2,5-Dimethylfuran, photooxygenated [28] [29] under identical conditions, gave a V_{max} = 62 ml O_2/min. Since this represents a quantum yield Q about *ca.* 0.8 mol/E [19], the β-values (M) for **1–11** were also calculable (*cf.* [18]) and are given in *Table 1* and *2*.

The allyl hydroperoxides **C/C**^{1} and **D**^{1} were reduced by adding dimethylsulfide (10 g) dropwise to the ice-cooled photooxygenation solution and stirring until the peroxide test (KI/acetic acid) was negative. Triphenylphosphine as reducing reagent [30] gave comparable results.

The resulting mixtures of the epoxy-aldehydes **B/B**^{1} and the diols **E/E**^{1} and **F**^{1} were isolated after evaporation of the solvent, the excess dimethylsulfide, and the dimethylsulfoxide by bulb distillation. Product distributions were determined by GC. analysis of the crude and distilled mixture on polar (Carbowax 20 M) or non-polar (Silicon SE30) columns. Undetectable means < 2% (GC. detection limit). Yields refer to the total after distillation.

2.3. *Individual experiments.* – *Oxygenation of* **1** (V_{max}: 20 ml O_2/min.; β = 0.15; conversion: 93%) gave a mixture of 50% of 2,3-epoxy-3-methyl-butanal (**12**), 38% of 3-methyl-3-butene-1,2-diol (**13**), 6% of starting compound (**1**) and about 6% of unidentified products. Since product losses could not be avoided during the work-up (azeotropic distillation of **12** and CH_3OH), preparative-scale photooxygenation of **1** was effected in acetone, to yield 72% of a product mixture (b.p. 25°/20 Torr (**12**) to 56°/0,1 Torr (**13**)) with practically the same product distribution.

Oxygenation of **2** (V_{max}: 13 ml O_2/min; β = 0.25; conversion: 97%) gave a mixture of 73% of 2,3-epoxy-3-ethyl-pentanal (**14**), 17% of (*E/Z*)-3-ethyl-3-pentene-1,2-diol (**15**, *E/Z* ~ 15:5, properties see below), 3% of starting compound (**2**) and 7% of unidentified products in 80% combined yield.

Oxygenation of **3** (V_{max}: 52 ml O_2/min; β = 0.02; conversion: 100%) gave a mixture of 53% of 1-oxa-spiro[4.2]heptane-2-carbaldehyde (**16**), 38% of 1′-cyclopenten-1′-yl-ethane-1,2-diol (**17**) and 9% of unidentified products in 88% combined yield.

Oxygenation of **4** (V_{max}: 8 ml O_2/min; β = 0.43; conversion: 70%) gave a mixture of 57% of 1-oxa-spiro[5.2]octane-2-carbaldehyde (**18**), 9% of 1′-cyclohexen-1′-yl-ethane-1,2-diol (**19**), 30% of starting compound (**4**) and 4% of unidentified products in 88% combined yield.

Oxygenation of **5** (V_{max}: 34 ml O_2/min; β = 0.06; conversion: 92%) gave a mixture of 54% of 1-oxa-spiro[7.2]decane-2-carbaldehyde (**20**), 37% of 1′-cycloocten-1′-yl-ethane-1,2-diol (**21**), 5% of starting compound (**5**) and 4% of unidentified products in 85% combined yield.

Oxygenation of **6** (V_{max}: 10 ml O_2/min; β = 0.34; conversion: 88%) gave a mixture of 57% of 1-oxa-spiro[11.2]tetradecane-2-carbaldehyde (**22**), of 1′-cyclododecen-1′-yl-ethane-1,2-diol (**23**), 8% of starting compound (**6**) and 6% of unidentified products in 86% combined yield.

Oxygenation of (E)-**7** (V_{max}: 21 ml O_2/min; $\beta = 0.13$; conversion: 100%) gave a mixture of 55% of 1,2-epoxy-3-methyl-pentanal (**24**), 40% of 3-methylidenepentane-1,2-diol (**25**) and 5% of unidentified products in 92% combined yield. 3-Methyl-3-pentene-1,2-diol (**26**) was not detectable.

Oxygenation of (Z)-**7** (V_{max}: 16 ml O_2/min; $\beta = 0.19$; conversion: 100%) gave a mixture of 78% of **24**, 10% of **25**, 6% of **26** and 6% of unidentified products in 88% combined yield.

Oxygenation of (E)-**8** (V_{max}: 19 ml O_2/min; $\beta = 0.15$; conversion: 95%) gave a mixture of 59% of 2,3-epoxy-3,7-dimethyl-7-octenal (**27**), 31% of 3-methylidene-7-methyl-7-octene-1,2-diol (**28**), 6% of starting compound ((*E*)-**8**) and 4% of unidentified products in 80% combined yield. 3,7-Dimethyl-3,7-octadiene-1,2-diol (**29**) was not detectable (see however (*Z*)-**8** below).

Oxygenation of (Z)-**8** (V_{max}: 15 ml O_2/min; $\beta = 0.21$; conversion: 95%) gave a mixture of 74% of **27**, 9% of **28**, 7% of (*E*)-**29**, 4% of starting compound ((*Z*)-**8**) and 6% of unidentified products in 82% combined yield.

Oxygenation of (E)-**9** (V_{max}: 20 ml O_2/min; $\beta = 0.14$; conversion: 98%) gave a mixture of 54% of 2,3-epoxy-3,7-dimethyloctanal (**30**), 38% of 3-methylidene-7-methyl-octane-1,2-diol (**31**) and 7% of unidentified products in 82% combined yield. 3,7-Dimethyl-3-octene-1,2-diol (**32**) was not detectable.

Oxygenation of (Z)-**9** (V_{max}: 14 ml O_2/min; $\beta = 0.23$; conversion: 90%) gave a mixture of 73% of **30**, 8% of **31**, 7% of (*E*)-**32**, 6% of starting compound ((*Z*)-**9**) and 6% of unidentified products in 89% combined yield.

Oxygenation of (E)-**10** (V_{max}: 20 ml O_2/min; $\beta = 0.14$; conversion: 92%) gave a mixture of 53% of 2,3-epoxy-3,4-dimethylpentanal (**33**), 33% of 2-methylidene-4-methylpentane-1,2-diol (**34**), 5% of starting compound ((*E*)-**10**) and *ca.* 9% of unidentified products in 93% combined yield. Diol **35** (3,4-dimethyl-3-pentene-1,2-diol) was not identified.

Oxygenation of (Z)-**10** (V_{max}: 14 ml O_2/min; $\beta = 0.23$; conversion: 90%) gave a mixture of 78% of **33**, 10% of **34**, 6% of unidentified products and 6% of starting compound ((*Z*)-**10**) in 85% combined yield. Diol **35** was not detectable (< 2%).

Oxygenation of (E)-**11** (V_{max}: 27 ml O_2/min; $\beta = 0.09$; conversion: 100%) gave a mixture of 40% of *trans*-2,3-epoxy-3,4,4-trimethylpentanal (**36**), 51% of 3-methylidene-4,4-dimethylpentane-1,2-diol (**37**) and 9% of unidentified products in 84% combined yield. The *cis* isomer of **36** was not detectable.

Oxygenation of (Z)-**11** (V_{max}: 4 ml O_2/min; $\beta = 0.95$; conversion: *ca.* 70%) gave a mixture of 28% of **36**, 33% of **37**, 32% of starting compound ((*Z*)-**11**) and 7% of unidentified compounds in 88% combined yield.

3. Identification and spectra of compounds 12–37. - With the exception of **35** all the compounds **12**–**37** were purified (> 98%) by prep. GC. and were identified from their spectra. The α,β-epoxyaldehydes **24**, **27** and **30** represented mixtures of *cis*/*trans*-isomers (ratio ~ 40:60) and only *cis*-**27** and *trans*-**27** were separated. The diols **15**, **23** and **26** consisted of mixture of *E*/*Z*-isomers. Their ratios (see below) were taken from ^{1}H-NMR.-spectra.

3.1. *α,β-Epoxyaldehydes* **B** *and* **B**[1]. *3-Methyl-2,3-epoxybutanal* (**12**). B.p. 25–27°/20 Torr. - IR.: 2750, 1720 (CHO). - ^{1}H-NMR.: 1.4 and 1.44 (2*s*, 2 H_3C–C(3)); 3.0 (*d*, $J = 5$, H–C(2)); 9.3 (*d*, $J = 5$, H–C(1)). - MS.: (M^+, 1), 85 (100), 60 (33), 43 (60), 41 (90).

3-Ethyl-2,3-epoxypentanal (**14**). - IR.: 2720, 1722 (CHO). - ^{1}H-NMR.: 0.93 and 0.1 (2*t*, $J = 7$, 2 CH_3CH_2); 1.70 (2*qa*, $J = 7$, 2 CH_2–C(3)); 3.04 (*d*, $J = 5$, H–C(2)); 9.4 (*d*, $J = 5$, H–C(1)). - MS.: 128 (M^+, 1), 99 (100), 85 (4), 69 (11), 55 (25), 41 (60).

1-Oxa-spiro[4.2]heptane-2-carbaldehyde (**16**). - IR.: 2700, 1615 (CHO). - ^{1}H-NMR.: 1.86 (*m*, $(CH_2)_4$); 3.36 (*d*, $J = 5$, H–C(2)); 9.25 (*d*, $J = 5$, H–C(1)). - MS.: 126 (M^+, 1), 111 (1), 97 (100), 79 (15), 67 (32), 55 (10), 41 (45), 27 (10).

1-Oxa-spiro[5.2]octane-2-carbaldehyde (**18**). - IR.: 2720, 1715 (CHO). - ^{1}H-NMR.: 1.61 (*m*, $(CH_2)_5$); 3.14 (*d*, $J = 5$, H–C(2)); 9.45 (*d*, $J = 5$, H–C(1)). - MS.: 140 (M^+, 1), 123 (1), 111 (15), 97 (100), 81 (25), 67 (12), 55 (17), 41 (24), 29 (7).

1-Oxa-spiro[7.2]decane-2-carbaldehyde (**20**). - IR.: 2710, 1615 (CHO). - ^{1}H-NMR.: 1.68 (*m*, $(CH_2)_7$); 3.2 (*d*, $J = 5$, H–C(2)); 9.48 (*d*, $J = 5$, H–C(1)). - MS.: 168 (M^+, 1) 153 (1), 137 (26), 125 (17), 109 (33), 97 (100), 84 (55), 67 (90), 55 (75), 41 (80), 29 (30).

1-Oxa-spiro[11.2]tetradecane-2-carbaldehyde (**22**). M.p. 49° (hexane). - IR.: 2710, 1725 (CHO). - ^{1}H-NMR.: 1.4 (*m*, $(CH_2)_{11}$); 2.94 (*d*, $J = 5$, H–C(2)); 9.37 (*d*, $J = 5$, H–C(1)). - MS.: 224 (M^+, 1), 206 (1), 193 (10), 181 (12), 153 (15), 139 (10), 121 (10), 109 (20), 97 (90), 83 (40), 55 (96), 41 (100), 29 (40).

3-Methyl-2,3-epoxypentanal (**24**) (*cis/trans*-mixture ~40:60). – IR.: 2720, 1725 (CHO). – ^{1}H-NMR.: 0.99 and 1.02 (both 1*t*, *J*=6, H_3C–C(4)); 1.38 and 1.42 (both 1*s*, H_3C–C(3)); 3.01 (*d*, *J*=5, H–C(2)); 9.33 (*d*, *J*=5, H–C(1)). – MS.: 114 (M^+, <1), 99 (18), 85 (100), 71 (8), 55 (35), 41 (62).

cis-*3,7-Dimethyl-2,3-epoxy-7-octenal* (*cis*-**27**). – IR.: 3080, 1650, 890 ($CH=CH_2$), 2720, 1720 (CHO). – ^{1}H-NMR.: 1.34 (*s*, H_3C–C(3)); 1.67 (*m*, narrow, H_3C–C(7)); 2.95 (*d*, *J*=5, H–C(2)); 4.62 (*m*, 2 H–C(8)); 9.32 (*d*, *J*=5, H–C(1)). – MS.: 168 (M^+, 1), 153 (1), 109 (24), 95 (26), 85 (75), 58 (80), 55 (82), 43 (82), 41 (100).

trans-*3,7-Dimethyl-2,3-epoxy-7-octenal* (*trans*-**27**). Larger GC. retention-time than *cis*-**27**. – IR.: 3080, 1645, 888 ($C=CH_2$), 1710, 1725 (CHO). – ^{1}H-NMR.: 1.42 (*s*, H_3C–C(3)); 1.65 (*m*, narrow, H_3C–C(7)); 2.98 (*d*, *J*=5, H–C(2)); 4.66 (*m*, 2 H–C(8)); 9.35 (*d*, *J*=5, H–C(1)). – MS.: identical to that for *cis*-**27**.

3,7-Dimethyl-2,3-epoxy-octanal (**30**) (*cis/trans*-mixture ~40:60). – IR.: 2720, 1725 (CHO). – ^{1}H-NMR.: 0.88 (2*d*, overlapping, *J*=6, 2 H_3C–C(7)); 1.4 or 1.42 (*s*, H_3C–C(3)); 3.17 (*d*, *J*=5, H–C(2)); 9.45 (*d*, *J*=5, H–C(1)). – MS.: 170 (M^+, 1), 155 (4), 139 (1), 123 (2), 109 (1), 95 (3), 85 (100), 71 (17), 55 (22), 43 (38), 41 (28).

trans-*3,4-Dimethyl-2,3-epoxypentanal* (33). – IR.: 2700, 1715 (CHO). – ^{1}H-NMR.: 0.92 and 1.05 (both 1*d*, *J*=6, 2 H_3C–C(4)); 1.37 (*s*, H_3C–C(3)); 3.16 (*d*, *J*=5, H–C(2)); 9.46 (*d*, *J*=5, H–C(1)). – MS.: 128 (M^+, 1), 113 (2), 85 (100), 69 (4), 55 (20), 43 (45), 41 (33).

3,4,4-Trimethyl-2,3-epoxypentanal (**36**). – IR.: 2710, 1710 (CHO). – ^{1}H-NMR.: 0.98 (*s*, 3 H_3C–C(4)); 1.42 (*s*, H_3C–C(3)); 3.38 (*d*, *J*=4, H–C(2)); 9.53 (*d*, *J*=4, H–C(1)). – MS.: 142 (M^+, <1), 127 (1), 113 (1), 95 (2), 85 (100), 69 (16), 57 (18), 43 (60), 41 (45).

3.2. *The diols* **E**, **E**^{1} *and* **F**^{1}. *3-Methyl-3-butene-1,2-diol* (**13**). – IR.: 3350 (OH), 3080, 1650, 895 (1810) ($C=CH_2$). – ^{1}H-NMR.: 1.68 (*s*, H_3C–C(3)); 3.55 (*m*, 2 H–C(1)); 4.05 (*m*, H–C(2)); 4.8 and 4.98 (2*m*, 2 H–C(4)). – MS.: 102 (M^+, 1), 71 (100). (Lit.: [31]).

(E/Z)-3-Ethyl-3-pentene-1,2-diol (**15**) (*E/Z*-mixture *ca.* 15:5). – IR.: 3350 (OH), 1660, 830 (C=CH). – ^{1}H-NMR.: 1.01 and 2.04 (*t*, *J*=6, and *m*, CH_3CH_2–C(3)); 1.67 (*d*, *J*=6, H_3C–C(4)); 3.55 (*m*, 2 H–C(1)); 4.17 (*m*, H–C(2)); 5.32 (*m*, H–C(4), typical of (*Z*)-**15**); 5.54 (*m*, H–C(4), typical of (*E*)-**15**). – MS.: 130 (M^+, 3), 112 (4), 99 (100), 79 (12), 69 (6), 55 (28), 43 (65), 41 (8).

1'-Cyclopenten-1'-yl-ethane-1,2-diol (**17**). M.p. 59–60° (hexane). – IR.: 3350 (OH), 1640 (C=C). – ^{1}H-NMR.: 1.91 (*m*, 2 H–C(4')); 2.3 (*m*, 2 H–C(3') and 2 H–C(5')); 3.6 (*m*, 2 H–C(1)); 4.31 (*m*, H–C(2)); 5.68 (*m*, H–C(2')). – MS.: 128 (M^+, 1), 119 (1), 110 (20), 97 (100), 79 (42), 67 (46), 55 (12), 41 (48).

1'-Cyclohexen-1'-yl-ethane-1,2-diol (**19**). – IR.: 3350 (OH). – ^{1}H-NMR.: 1.58 (*m*, 2 H–C(4') and 2 H–C(5')); 1.97 (*m*, 2 H–C(3')) and 2 H–C(6')); 3.56 (*m*, 2 H–C(1)); 4.05 (*m*, H–C(2)); 5.72 (*m*, H–C(2')). – MS.: 142 (M^+, 1), 124 (12), 111 (100), 93 (27), 81 (24), 67 (95), 55 (48), 43 (48), 29 (92).

1'-Cycloocten-1'-yl-ethane-1,2-diol (**21**). – IR.: 3350 (OH), 1645 (C=C). – ^{1}H-NMR.: 1.46 (*m*, narrow, 2 H–C(4'–7')); 2.15 (*m*, 2 H–C(3') and 2 H–C(8')); 3.55 (*m*, 2 H–C(1)); 5.67 (*t*, *J*=7, H–C(2')). – MS.: 170 (M^+, 7), 152 (10), 139 (100), 121 (70), 109 (22), 95 (98), 79 (68), 67 (80), 55 (70), 41 (85).

(E/Z)-1'-Cyclododecen-1-yl-ethane-1,2-diol (**23**). *E/Z*-mixture *ca.* 20:16. – IR.: 3350 (OH). – ^{1}H-NMR.: 1.38 (*m*, narrow, 2 H–C(4'–11')); 3.58 (*m*, 2 H–C(1)); 4.10 (*m*, H–C(2)); 5.52 (*t*, *J*=7, H–C(2')). – MS.: 226 (M^+, 1), 206 (8), 192 (3), 182 (8), 163 (7), 135 (15), 119 (22), 95 (40), 82 (60), 65 (55), 55 (68), 41 (100).

3-Methylidenpentane-1,2-diol (**25**). IR.: 3380 (OH), 3080, 1650, 905 ($C=CH_2$). – ^{1}H-NMR.: 1.03 (*t*, *J*=6, 3 H–C(5)); 1.97 (*m*, 2 H–C(4)); 3.52 (*m*, 2 H–C(1)); 4.1 (*m*, H–C(2)); 4.82 and 5.01 (both 1*m*, 2 H–C(3')). – MS.: 116 (M^+, <1), 98 (10), 85 (100), 67 (10), 57 (13), 43 (58), 41 (55), 29 (34).

(E/Z)-3-Methyl-3-pentene-1,2-diol (**26**) (*E/Z*-mixture *ca.* 4:1). – IR.: 3350 (OH). – ^{1}H-NMR.: 1.6 and 1.65 (*d* and *s* overlapping, H_3C–C(3) and 3 H–C(5)); 3.58 (*m*, 2 H–C(1)); 4.15 (*m*, H–C(2), typical of (*E*)-**26**; 4.65 (*m*, H–C(2), typical of (*Z*)-**26**); 5.30 and 5.52 (both 1*qa*, *J*=6, H–C(4); typical of (*Z*)- and (*E*)-**26**).

7-Methyl-3-methylidene-7-octene-1,2-diol (**28**). – IR.: 3350 (OH), 3080, 1645, 885, 900 (1810), (2 $C=CH_2$). – ^{1}H-NMR.: 1.67 (*s*, 3 H–C(8)); 3.5 (*m*, 2 H–C(1)); 5.08 (*m*, H–C(2)); 4.46 and 4.62 (both 1*m*, 2 H–C(8)); 4.81 and 5.02 (2*m*, 2 H–C(3')). – MS.: 170 (M^+, 1), 139 (20), 121 (28), 109 (17), 95 (55), 79 (38), 69 (54), 55 (75), 43 (90), 41 (100).

(E)-3,7-Dimethyl-3,7-octadiene-1,2-diol (**29**). – IR.: 3350 (OH), 3080, 1640, 890 (1810) (C=CH_2). – ^{1}H-NMR.: 1.65 and 1.68 (both 1*s*, H_3C–C(3) or H_3C–C(7)); 3.52 (*m*, 2 H–C(1)); 4.1 (*m*, H–C(2)); 4.6 and 4.72 (both 1*m*, 2 H–C(8)); 5.44 (*t*, *J* = 7, H–C(4)). – MS.: 170 (M^+, 1), 139 (15), 121 (20), 55 (75), 41 (100).

3-Methylidene-7-methyloctan-1,2-diol (**31**). – IR.: 3350 (OH), 3080, 1640, 895 (1800), (C=CH_2). – ^{1}H-NMR.: 0.85 (2*d*, overlapping, 2 H_3C–C(7)); 3.55 (*m*, 2 H–C(1)); 4.17 (*m*, H–C(2)); 4.91 and 5.11 (both 1*m*, 2 H–C(3')). – MS.: 172 (M^+, 1), 139 (1), 123 (1), 85 (12), 70 (11), 61 (16), 43 (92), 29 (100).

(E)-3,7-Dimethyl-3-octene-1,2-diol (**32**). – IR.: 3350 (OH). – ^{1}H-NMR.: 0.88 (2*d*, overlapping, 2 H_3C–C(7)); 1.6 (*s*, H_3C–C(3)); 3.56 (*m*, 2 H–C(1)); 4.1 (*m*, H–C(2)); 5.43 (*t*, *J* = 7, H–C(4), typical of (*E*)-**32**). – MS.: 172 (M^+, 1), 154 (2), 141 (64), 123 (50), 97 (30), 83 (36), 71 (95), 55 (56), 43 (100), 41 (80).

4-Methyl-3-methylidenepentane-1,2-diol (**34**). – IR.: 3350 (OH), 3080, 1640, 900 (1810) (C=CH_2). – ^{1}H-NMR.: 1.08 (2*d*, overlapping, 2 H_3C–C(4)); 2.21 (*m*, H–C(4)); 3.55 (*m*, 2 H–C(1)); 4.18 (*m*, H–C(2)); 4.92 and 5.1 (both 1*s*, 2 H–C(3')). – MS.: 130 (M^+, 1), 115 (5), 99 (100), 81 (55), 69 (15), 55 (33), 43 (95), 41 (30).

3-Methylidene-4,4-dimethylpentane-1,2-diol (**37**). – IR.: 3350 (OH), 3085, 1630, 905 (1820) (C=CH_2). – ^{1}H-NMR.: 1.11 (3*s*, overlapping, 3 H_3C–C(4)); 3.52 (*m*, 2 H–C(1)); 4.34 (*m*, H–C(2)); 5.1 and 5.2 (2*s*, 2 H–C(3')). – MS.: 144 (M^+, < 1), 129 (16), 113 (77), 99 (8), 83 (9), 69 (11), 57 (100), 41 (43).

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84. Influence de l'imidazole, de quelques sels métalliques et de mélanges imidazole/sel métallique sur des réactions de condensation «prébiotiques» induites par les polyphosphates en milieu aqueux

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Influence of imidazole, metal salts and mixtures of imidazole/metal salt on 'prebiotic' condensation reactions induced by polyphosphates in aqueous solution

Summary

In the presence of imidazole, aqueous solutions 0.1 M in glycine and 0.1 M in sodium trimetaphosphate, at pH 8.0–8.6 and room temperature, yield after 14 days up to 3% of triglycine. Addition of Cd^{2+} or Zn^{2+} decreases the yields, while Mg^{2+} increases them slightly.

The significance of the systems trimetaphosphate/imidazole and trimetaphosphate/imidazole/magnesium salt in the promotion of 'prebiotic' condensation reactions in aqueous solutions, especially the condensation of amino acids, is discussed.

Partant de l'hypothèse que les phosphates ont dû jouer un rôle important au cours de l'évolution chimique prébiologique, nous avons utilisé, avec un certain succès, l'énergie libre provenant de l'hydrolyse des liaisons P–O–P de polyphosphates minéraux linéaires ou cycliques, pour promouvoir la condensation

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