Pergamon

Tetrahedron Vol. 50, No. 38, pp. 11167-11186, 1994

0040-4020/94 $7.00+0.00

0040-4020(94)00704-7

Chiral Induction in Photochemical Reactions - 15.[1] Detection of Stereoelectronic Effects by Temperature Dependent Measurements of the Diastereoselectivity in the Photosensitized [2+2]-Cycloaddition

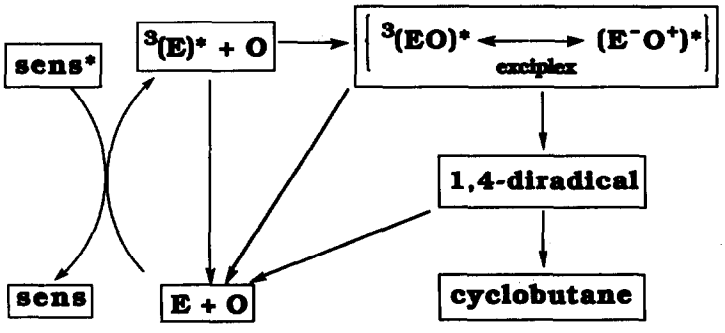
Norbert Hoffmann, Helmut Buschmann, Gerhard Raabe and Hans-Dieter Scharf*

Institut für Organische Chemie der RWTH Aachen
Prof.-Pirlet-Str. 1, D-52056 Aachen, Germany

Abstract:. The mechanism of the diastereoselection in the photosensitized [2 + 2]-cycloaddition reaction of ethylene to 5-alkoxy-2(5*H*)-furanones is investigated. The dependence of product ratio on the reaction temperature as well as on structural features of the enone system is measured. The structure dependent activation parameter differences ($\Delta\Delta H^{\neq}$, $\Delta\Delta S^{\neq}$) obtained by this method (modified Eyring plot) are used as a tool to characterize the stereoelectronic factors, which are responsible for the diastereoselection. In detail these factors involve: pyramidalization of the β-carbon, homoanomeric effect, and the steric requirements of the alkoxy substituent in the relaxed ($^3\pi\pi^*$)-excited furanones.

Introduction

The mechanism of the [2 + 2]-photocycloaddition (photochemical formation of cyclobutanes) as well as its application in natural product synthesis has been a well investigated topic for several years.[2,3] We were interested in the stereoselection mechanism of the [2 + 2]-photocycloaddition of ethylene and 5-alkoxy-2(5*H*)-furanones. Recently we have made use of this reaction in the synthesis of both enantiomers of grandisol, as well as several structural analogues.[4] α,β–Unsaturated lactones may easily be excited to the T_1 sate by photosensitization (Scheme 1).[5,6] In the presence of an

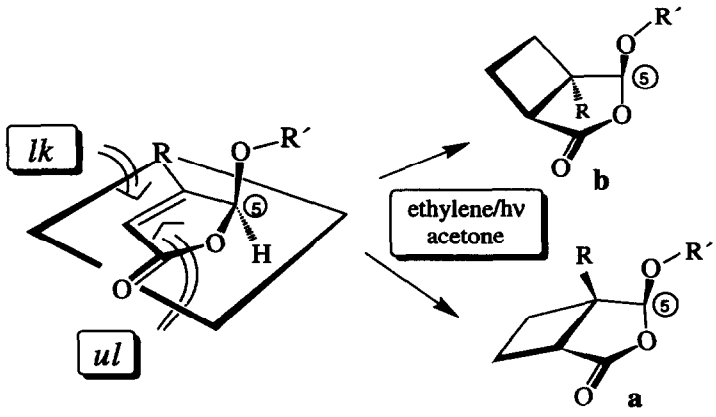


Scheme 1: Mechanism of the photosensitized [2 + 2]-cycloaddition; sens: sensitizer, E: enone, O: olefin

olefinic partner they form reversibly an exciplex according to the Corey-de Mayo mechanism. Hitherto in many cases the exciplex is not directly detectable. Therefore in these cases many authors have assumed the direct formation of the diradical from the excited enone.[2,3,9,10] The 1,4-diradical intermediate can then recombine to form cyclobutanes. Recently the diradicals have been be trapped by an intermolecular H abstraction from H_2Se as hydrogen donor.[10] In the mechanistic cycle the exciplex as well as the 1,4-diradical intermediate may resplit to the starting products.

One of the subjects of our investigation is the relevance of these partial steps for the observed stereoselection. The importance of selectivity dependence on the temperature, to detect the relevant factors of the mechanism was initiated by Pracejus et al.[11] for ground state reactions.

For the Paternò-Büchi reaction we have demonstrated, that depending on the different temperature region particular steps of the mechanism control mainly the stereoselection.[1,12] Information on the factors which influence the selection are obtained from its temperature dependence. In this paper this instrument is applied to the diastereoselective photosensitized [2 + 2]-cycloaddition of 5-alkoxy-2(5*H*)-furanones and ethylene (Scheme 2). These results as well as the dependence of the product ratio on structural features give information on the stereoelectronic effects. Furthermore, the stereoelectronic effects can be correlated to the activation parameters ($\Delta\Delta H^{\neq}$, $\Delta\Delta S^{\neq}$).



	R		R'	*ul*	*lk*
1	H	A	Me	a	b
2	Me	B	Et		
3	Et	C	iPr		
4	iPr				
5	Ph				
6	Tol				

Scheme 2: Competing stereochemical pathways of the photosensitized [2 + 2]-cycloaddition of ethylene to 5-alkoxy-2(5*H*)-furanones.

Results

The furanones (Scheme 2) were irradiated with ethylene in acetone as solvent and sensitizer. The ratios of diastereomeric cyclobutane products were determined by ^{13}C-NMR spectroscopy as described in ref. [12a]. In order to enable an unique interpretation of the results of all investigated systems (reaction partners) the product ratios were calculated according to equation 1. The diastereomeric excess is now defined by equation 2 (I: signal intensity in the ^{13}C NMR spectra).

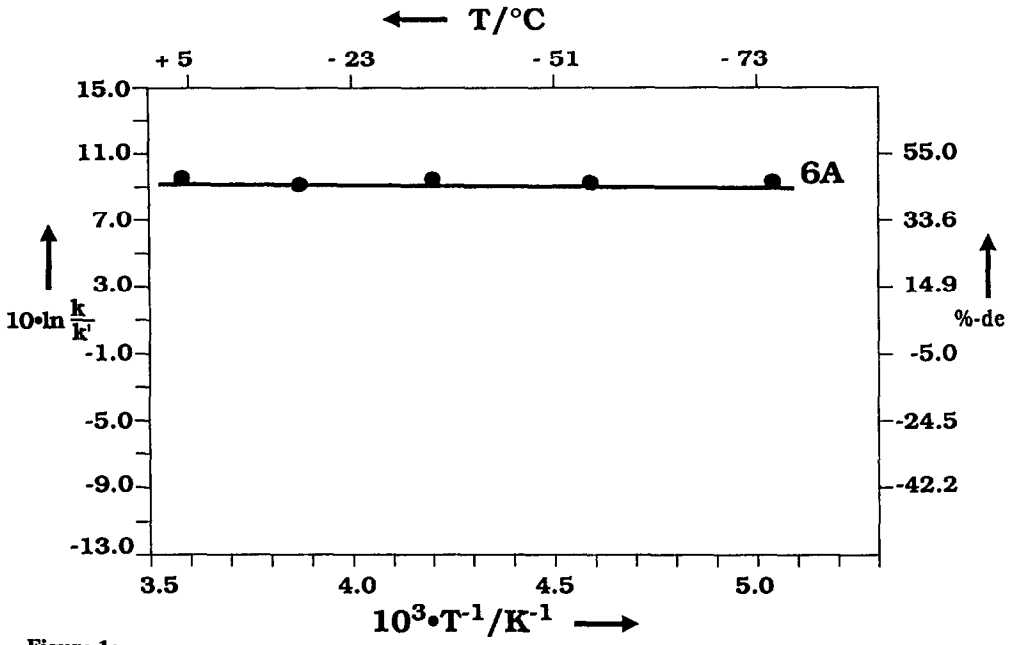


Figure 1e

Figure 1: Modified Eyring plots for the diastereoselectivity of photosensitized [2 + 2]-cycloaddition of ethylene to 5-alkoxy-2(5*H*)-furanones (see Scheme 2, equation 4).

$$P = \frac{I_{ul}}{I_{lk}} \qquad \text{(eq.1)} \qquad\qquad de\ (\%) = \frac{I_{ul} - I_{lk}}{I_{ul} + I_{lk}} \qquad \text{(eq.2)}$$

Furanones were used in racemic form. The diastereoselectivity obtained with racemic substrates is comparable with that observed by using enantiomerically pure substrates, since the interaction of chiral substrates and products is negligible.[13] The diastereoselectivity is independent of the initial concentration and of the progress of the conversion. The logarithms of the product ratios are plotted against the reciprocal of the absolute temperature (Figure 1). From this plots the differences in activation parameters $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$ for the overall reaction (Table 1) are calculated (equation 3).[14]

In the temperature region investigated a linear dependence of the ln*P*-values from T^{-1} is observed for all systems. This is in remarkable contrast to the photo-oxetane formation, which have two linear functions with an inversion point of selectivity (ln*P*-values). The latter results could be explained in terms of the principle of isoinversion[12] as follows: Enthalpy or entropy respectively dominates in a different temperature region, since the two relevant partial selection steps were influenced in two different ways by the enthalpy ($\Delta\Delta H^{\neq}$) and entropy ($\Delta\Delta S^{\neq}$).[1,12] The selectivity observed is controlled complementarily by the enthalpic and entropic contributions.

The diastereoselectivity of the photocyclobutane formation however described in this paper depends predominantly on the achiral substituent R. The influence of R′ is only of minor importance despite the corresponding chiral centre (acetal, position 5) is the origin of the stereoinduction. For furanones with R = H, Me (**1A, 1B, 1C, 2A, 2B, 2C**) the *ul*-attack dominates (de-values > 0 according to equation 1, 2). In the case of **3A, 3B** (R = Et) an inversion of the preferred

Table 1: Activation parameter differences for the diastereoselective photosensitized [2 + 2]-cycloaddition of ethylene to 5-alkoxy-2(5*H*)-furanones.

			$\Delta\Delta H^{\neq}$	$\Delta\Delta S^{\neq}$
			kJ•mol^{-1}	J•mol^{-1}K^{-1}
R: H	R': Me	**1A**	- 0.95	+ 3.97
	R': Et	**1B**	- 1.61	+ 1.27
	R': iPr	**1C**	- 4.19	- 4.19
R: Me	R': Me	**2A**	+ 0.54	+ 5.35
	R': Et	**2B**	+ 0.53	+ 5.59
	R': iPr	**2C**	+ 0.70	+ 5.57
R: Et	R': Me	**3A**	+ 3.23	+ 12.88
	R': Et	**3B**	+ 2.70	+ 11.10
	R': iPr	**3C**	+ 0.26	+ 0.84
R: iPr	R': Me	**4A**	+ 4.74	+ 13.54
	R': Et	**4B**	+ 3.67	+ 9.13
	R': iPr	**4C**	+ 3.17	+ 7.41
R: Ph	R': Me	**5A**	- 0.31	+ 6.19
R: Tol	R': Me	**6A**	+ 0.08	+ 8.20

$$\ln P = \ln \frac{k}{k'} = \frac{-\Delta\Delta H^{\neq}}{RT} + \frac{\Delta\Delta S^{\neq}}{R} \qquad \textbf{(eq.3)}$$

direction of attack is caused by the variation of temperature. Despite of the steric demand of the aromatic substituents in **5A** and **6A** (R = Ph, p-Tol) in this cases again, positive de-values are obtained surprisingly as observed for compounds **4A, 4B, 4C** (R = H). The calculated $\Delta\Delta H^{\neq}$- and $\Delta\Delta S^{\neq}$-parameters are plotted against each other in a compensation diagram for all investigated systems (Figure 2).

For the total number of systems only an unsatisfied correlation is observed. However, much better results are obtained for furanones with the same substituent R but different R´. Furthermore the furanones **5A** and **6A** (R = Ph, p-Tol) belong to the same correlation, which is found for the compounds **1A, 1B,1C**. In the case of **2A, 2B, 2C** such a compensation is not observed. From the slope of the compensation line the isoselective temperature T_{iso} is calculated by equation 4.[15]

$$\frac{\partial\Delta\Delta H^{\neq}}{\partial\Delta\Delta S^{\neq}} = T_{iso} \qquad (\partial\Delta\Delta G^{\neq} = 0) \qquad \textbf{(eq 4)}$$

An isoselective temperature T_{iso} characterizes an ensemble of systems and is identical with the temperature at the intersection point of the corresponding Eyring plots. At this temperature all participating systems produce the same selectivity.[15a] Table 2 shows that all isoselective temperatures are in the same region as a result of the near parallelism of the compensation lines (Figure 2).

Remarkable differences in the enthalpic and entropic determination for the formation of the excess diastereomer are observed in the reaction of the enones carrying an isopropyl substituent (**4Ab, 4Bb, 4Cb**) with ethylene compared with the enones carrying an aryl substituent (**5Aa, 6Aa**) and the enones without β-substitution. In the upper case the *lk*-attack (de-values <0) is favoured by an enthalpy control (negative slope in the modified Eyring diagram) and enthropically disfavoured (positive ordinate intercept). Therefore the *ul*-attack is favoured. In the sequence of the enones with 5-methoxy- (**4A**), 5-ethoxy- (**4B**), 5-isopropyloxysubstitution (**4C**), the enthalpy preference for the major isomer

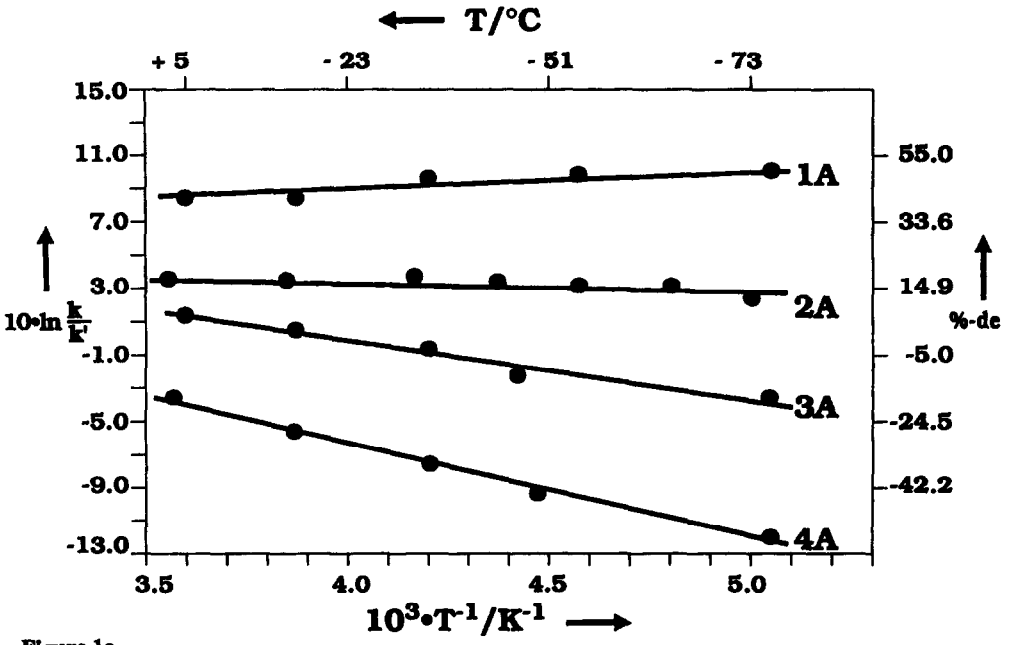


Figure 1a

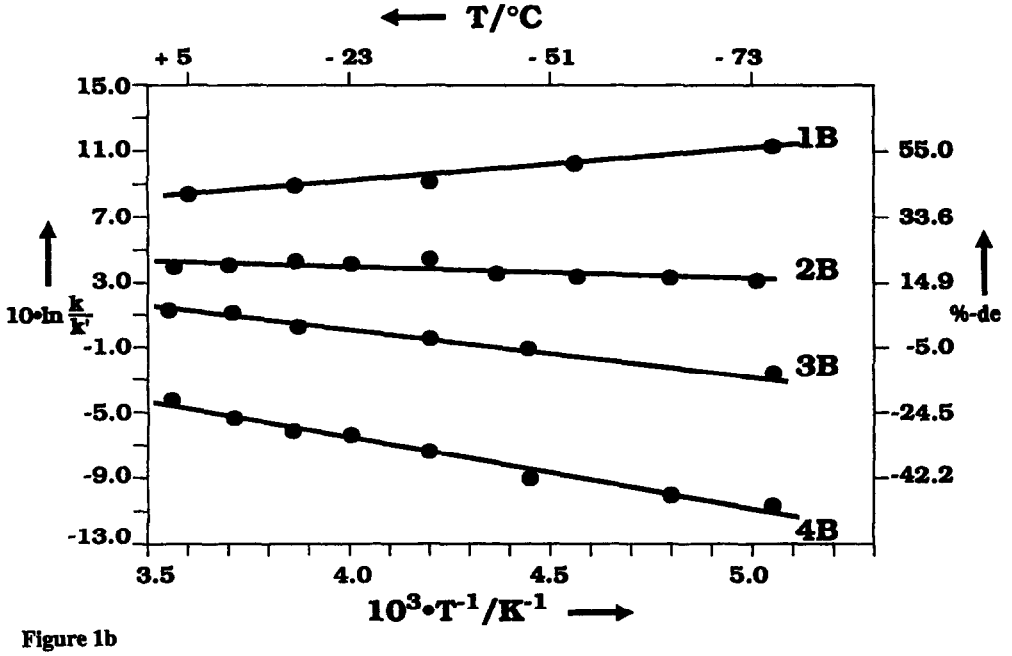


Figure 1b

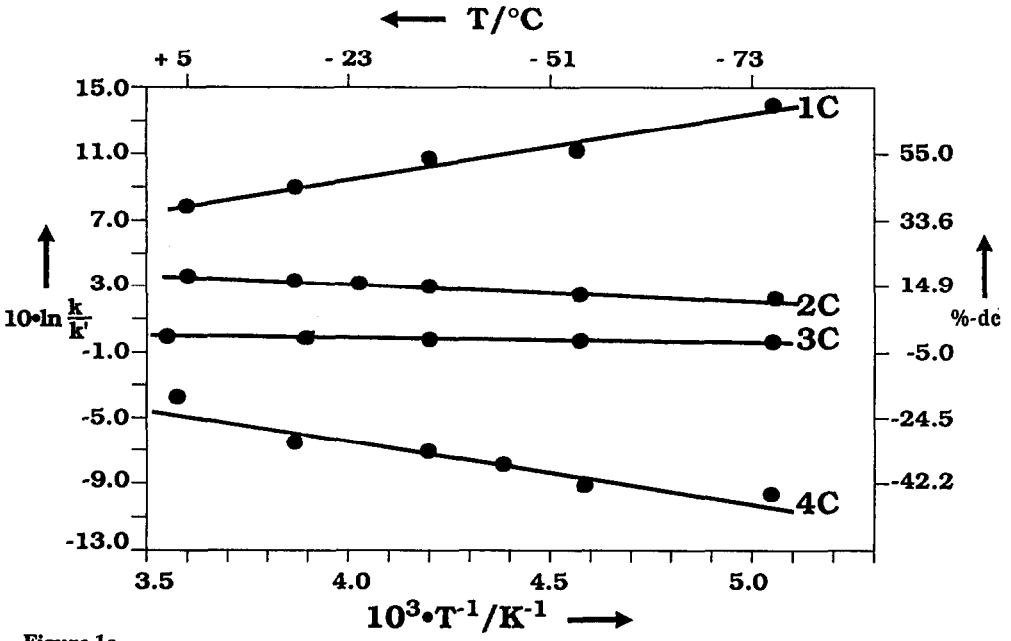


Figure 1c

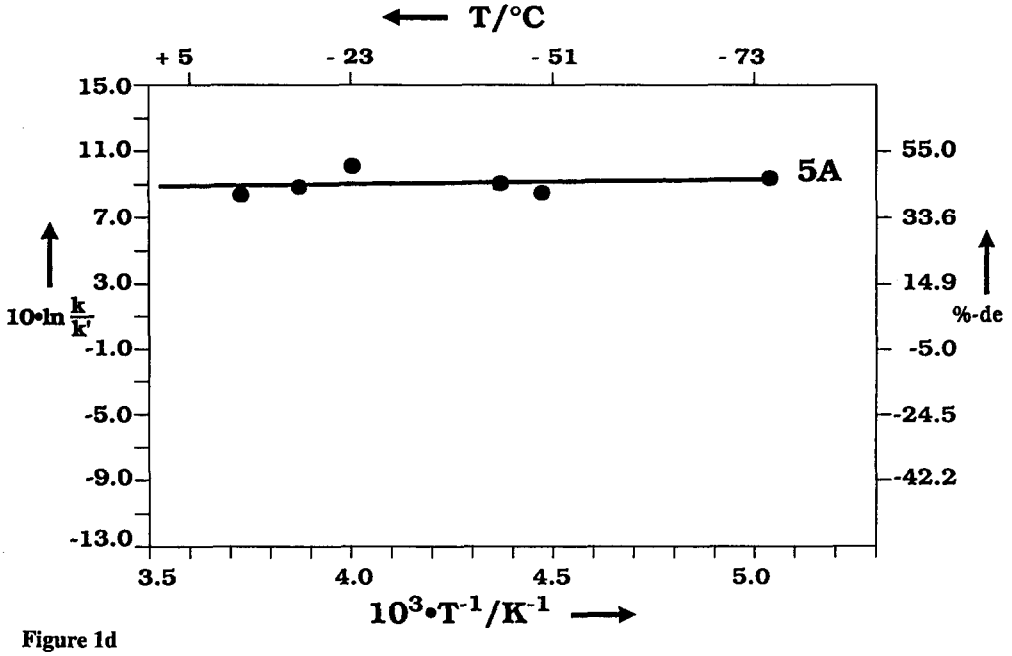


Figure 1d

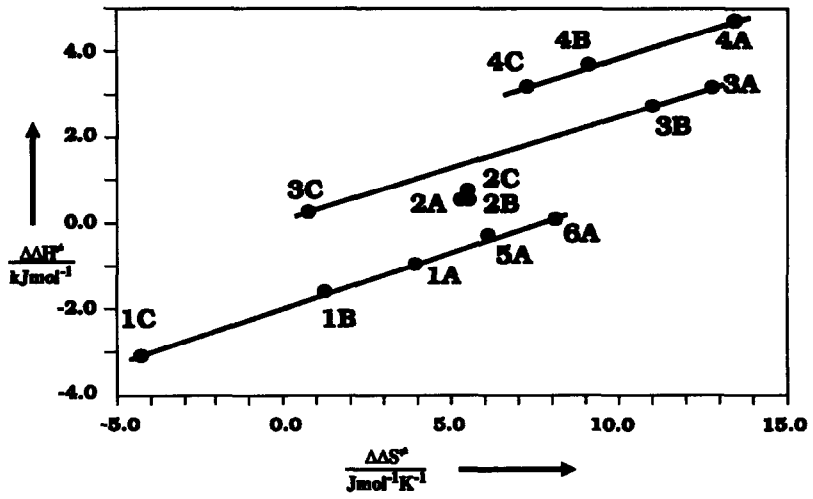


Figure 2: Isoselective relationships in the photosensitized [2 + 2]-cycloaddition of ethylene to 5-alkoxy-2(5*H*)-furanones (see: figure 1, equation 4).

Table 2: Isoselective temperatures for different groups of 5-alkoxy-2(5*H*)-furanones in the diastereoselective [2 + 2]-cycloaddition to ethylene.

		T_{iso} K (°C)
R: iPr	**4A, B, C**	254 (-19)
R: Et	**3A, B, C**	244 (-29)
R: H, Ph, Tol	**1A, B, C**	260 (-13)

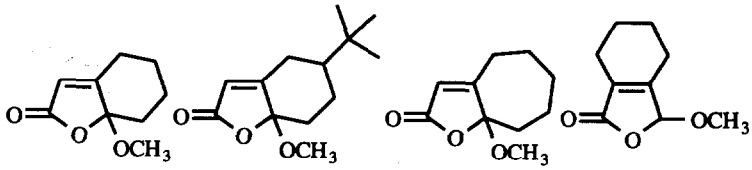
decreases. Correspondingly the entropy preference for the *ul*-attack (formation of the minor isomer) increases in the series: **4Aa, 4Ba, 4Ca**. Alkoxy substituents with a large number of degrees of freedom of rotation and vibration cause a dominant influence of the entropy in the transition states according to the principle of Price and Hammett.[16] In this case, from a larger number of configurations the favoured one has to be selected. Consistently, the influence of enthalpy in the transition state decreases. In an extreme case the enthalpy determination for the formation of the major isomer changes to an entropic one. As in the cases of **4A, 4B, 4C** the *ul*-attack on the β–unsubstituted furanones **1A, 1B** is also entr favoured. The *ul*-attack of the ethylene is also slightly enthalpically favoured (positive slope).

In this sense, the isopropyl substituted furanone **1C** is an exception because the *ul*-attack is enthalpically and the *lk*-attack entropically favoured. This is again a consequence of the Price-Hammett principle[16] for mainly entropic determined selection, if an isoselective relationship exists.

For the aryl substituted furanones **5A, 6A** the *ul*-selection is strongly entropically determinated. The formation of **5Aa** (major isomer from *ul*-attack) additionally has a small enthalpy preference, while in the case of the tolylfuranone **6A** a little preference for the *lk*-attack is observed.

Furthermore, we have converted the bicyclic furanones **7A, 8A, 9A** and **10A** under the same conditions at -55 °C. While the furanones **7A, 8A, 9A** produce cyclobutanes with nearly identical selectivity, the bicyclic furanone **10A** reacts without diasteroselectivity (Table 3).

Table 3: Diastereoselectivity of the photosensitized [2 + 2]-cycloaddition of bicyclic furanones to ethylene.

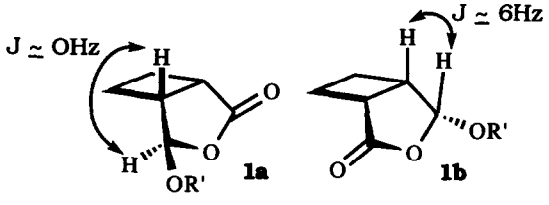


7A **8A** **9A** **10A**

	7A	8A	9A	10A
de (%)	+ 47	+ 46	+ 51	0

Structure Determination of the Cyclobutanes

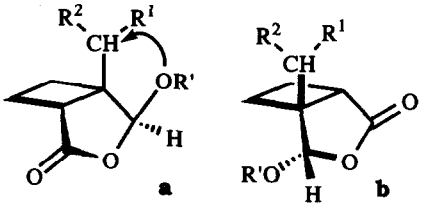
The relative configuration of the bicyclic photoadducts was determinated by their NMR data. For compounds **1a** and **1b** the configuration could be found by comparison of ^{1}H-NMR coupling constants of the acetal proton, since the dihedral angles differ significantly in the two diasteromers (Scheme 3). Similar examples are descriped in literature.[5a,6]



1a **1b**

R' = Me, Et, i-Pr

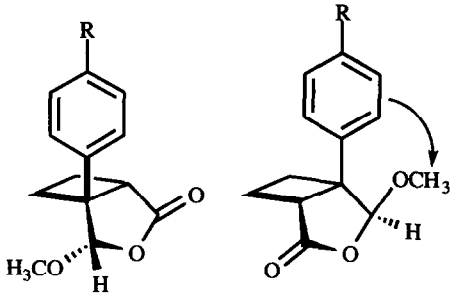
Scheme 3: NMR coupling constants of the diastereomeric cyclobutanes **1a** and **1b**.



a **b**

Scheme 4: NMR γ-effects of the alkoxy group the diastereomeric cyclobutanes **a** and **b**.

The structure of the cycloadducts of the 4-alkyl substituted furanones could be determined by observation of the γ–effect[17] of the alkoxy groups (Scheme 4).



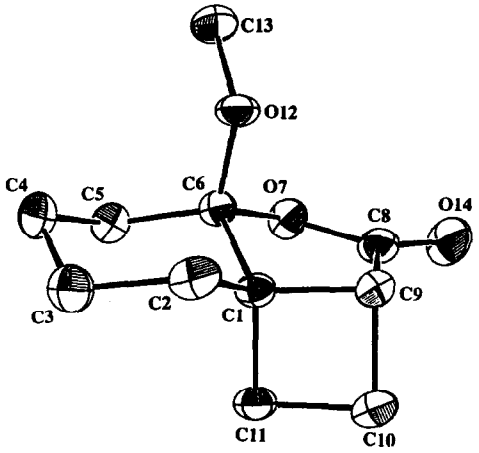
5 Ab (R = H) **5 Aa** (R = H)
6 Ab (R = CH_3) **6 Aa** (R = CH_3)

Scheme 5: Aryl anisotropic effect in the NMR spectroscopy of cyclobutane diastereomers.

For the adducts with structure **a** the ^{13}C-NMR signals are high field shifted by 2.2 to 5.4 ppm when they are compared with the isomeric structure **b**. Further comparison of NMR data of the isomers **1a** or **1b** confirm this structure assignment. Another verification of structure was given by the application of a 4-methyl substituted furanone in the synthesis of grandisol.[4]

The arylanisotropic effect of 0.1 ppm (high field) on the chemical shift of the methoxy protons could be used additionally to determine the structure of **5Aa** and **6Aa** (Scheme 5).

The structure of the cyclobutane isomer **7Aa** could be solved by single crystal X-ray analysis (Scheme 6). Therefore we were able to determine the structures of the other tricyclic ethylene adducts by analogy considerations.



Scheme 6: Single crystal X-ray analysis of compound **7Aa**[48]. Displacement ellipsoids plotted at 30% probability

Discussion

The observed activation parameters $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$ results of the overall reaction. Consequently, they are composed in a complex manner of the contributions of all elementary reactions. On the other hand, it is well accepted, however, that only a few steps of a complex mechanism determine the selectivity predominantly. Therefore our statement is: The $\Delta\Delta H^{\neq}$- and $\Delta\Delta S^{\neq}$-values are influenced mainly by these relevant steps.

The linearity in the Eyring plot (Figure 1) for the whole investigated temperature region is explained by the dominance of only one partial selection step in the case of ethylene as olefinic partner. This is in contrast to the Paternò-Büchi reaction.[12] At the first glance, the mechanistic pattern of the photosensitized cyclobutane formation (Scheme 1) on one hand and that of the Paternò-Büchi reaction[18,21] on the other hand seem to be close to each other. In both cases the reaction path is running via 1,4-diradical intermediate. As for the Paternò-Büchi reaction[18], the 1,4-diradical intermediate has been detected by inter- and intramolecular trapping reactions.[2,7,8,10,19,20] There are, however, remarkable differen-ces between both reactions, which is clearly demonstrated by the results of these investigations. In the Paternò-Büchi reaction the primarily formed (C-O)-bond in the 1,4-diradical intermediates undergoes facile heterolytical retrocleavage[21], which represents the second selection level in terms of the isoinversion principle.[12]

In the case of the decay of biradicals with longer chain between the radical positions, there exists a competition of the molecular dynamic, the intersystem crossing and structural features (chain length, substitution) as rate limiting factors.[22] The corresponding mechanistic steps have different Arrhenius-parameters too.

For the [2 + 2]-photocycloaddition, the (C-C)-bond in the 1,4-diradical intermediate is more stable versus

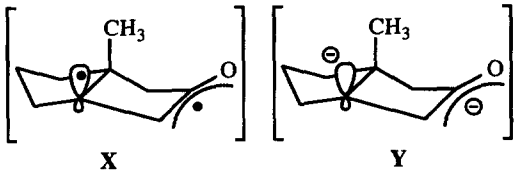
retrocleavage. The competition between cyclization and fragmentation is of minor importance for the diastereoselectivity (contrary to the regioselectivity[9b,10]). As a consequence the stereoselection is controlled mainly by one level, which means the approach of the ethylene to the excited furanone from one or the other side. No inversion points are observed in the modified Eyring plot (see also[23]).This is in line with the observation, that double stereodifferentiation in the photocyclobutane formation reaction reveal, that the energy difference (responsible for the observed stereoselection) is a result of the energy differences for single inductions (addition principle).[24] This also supports the assumption of an unique one-step-mechanism as long as the stereoselection is concerned. On the basis of these facts we consider,the addition of ethylene to the furanone by the formation of the 1,4-diradical intermediate as the dominant part in the selection step (Scheme 1).

Moreover, exciplexes as precursors in our systems seem to be of minor importance for the selection in this case. Only with polarizable olefinic partners have exciplexes been detected by their luminescence.[25] For similar systems, Wolff et al. [26] observed inversion points on the modified Eyring diagrams (compare eq. 8) for the head-to-tail/head-to-head selectivity. They explain their results with the exciplex rather than the 1,4-biradical as relevant intermediate for the selectivity (competition between product formation and decay to the substrates from the exciplex). Ethylene is, however, a rather unpolarizable olefin. Thus relatively stable exciplexes with this olefin are unlikely.

The relaxed excited furanones, which are responsible for the selection, are energy rich. As a consequence of this, the two diastereomeric transition states are situated near the initial point of the potential surface according to the reactivity-selectivity principle (rsp).[27,28] Consequently, the selection is the result of the stereoelectronic properties of the excited furanones.

The excited state of the furanone is achieved by acetone sensitization and has triplet character.[5,6] By Stern-Volmer investigations of similar systems (enones and alkyl substituted olefins), it could be demonstrated that the T_1 state has predominantly ($\pi\pi^*$)-character.[9] In the reaction of electron rich olefins with enones carrying electron withdrawing substituents, oxetane formation occurs additionally. This side reaction gives evidence to a stronger ($n\pi^*$)-character of the excited state (T_1).[29] ($^3\pi\pi^*$)-Excited enones can relax vibrationally by twisting of the (C=C)-double bond or by pyramidalization at the β-C-atom or by both.[9,30,31] The pyramidalization is mainly observed in the reaction of bicyclic enones. Evidence for the relaxation mechanism is obtained from transient analytical investigations.[32] A higher reactivity at the β-C-atom may also be induced by this pyramidalization (spin density orientation). As the result the generation of the 1,4-diradical intermediates should occur by bond formation at the β-position of the enone.[2,20c,33] Olefinic partners with substituents of higher steric demand may diminish the reactivity of the β-position favouring α-reactivity.[9,10]

The importance of pyramidalization at the β-carbon for the stereodifferentiation in the [2 + 2]-photocycloaddition reactions was first pointed out by Wiesner et al.[30] The authors compared these results with the stereoselection in the reduction of α,β-unsaturated carbonyl compounds with Li/NH_3. In this case a carbanion **Y** is formed instead of the pyramidalized radical **X** in β-position (Scheme 7). The carbanion **Y** is protonated during the reaction.

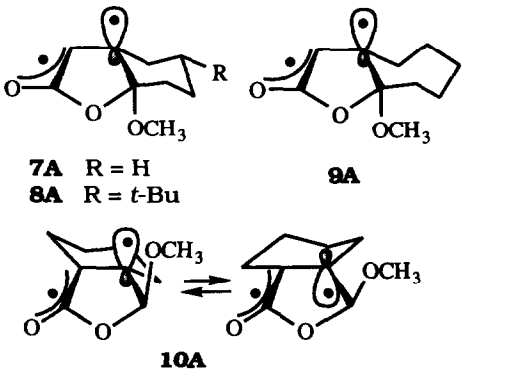


Scheme 7 **X** **Y**

In our case, we can not decide definitely whether the 1,4-biradical intermediate is formed by a (C-C)-bond in the α- or β-position of the excited furanone. But the various substituents at the β-carbon have a decisive influence on the diastereoselection. For this reason, we describe the biradical intermediate with a (C-C)-bond in the β-position . The

observed ste-reoelectronic effects of the side differentiation should also be active to a certain extent in the α-position. Consequently, the formation of the biradical with a (C-C)-bond in the α-position should give similar diastereoselectivities in the cyclobutane products.

The orientation of the spin density is controlled by the substitution of the enone. The olefin predominantly attacks the enone from the side carrying the higher spin density. The side differentiation caused by this electron distribution in the [2+2]-photocycloaddition (excited enone) differs significantly from that in the Michael addition reaction (ground state reaction of the enone).[34] The de-values of relatively high level obtained in the reaction of the enones **7A**, **8A** and **9A** with ethylene can be explained with the pyramidalization effect. The ($^3\pi\pi^*$)-excited bicyclic furanones in the relaxed state have a higher spin density on the *ul*-side as a consequence of the chair conformation. Therefore cyclobutanes of type **a** are formed predominantly. No stable chair conformation excists for the relaxed ($^3\pi\pi^*$)-excited state of the enone **10A**. As a consequence of this, no detectable diastereoselectivity is observed (Scheme 8).

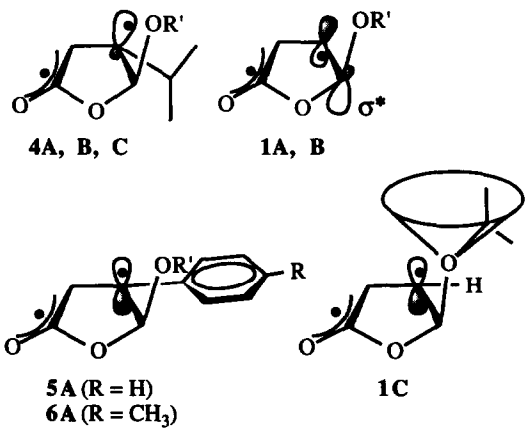


7A R = H
8A R = *t*-Bu

9A

10A

Scheme 8: Relaxed ($^3\pi\pi^*$)-excited states of bicyclic furanones.



4A, B, C **1A, B**

5A (R = H)
6A (R = CH_3)

1C

Scheme 9: Relaxed ($^3\pi\pi^*$)-excited states of 5-alkoxy-2(5*H*)-furanones.

In the case of the furanones **4A, 4B, 4C** the spin density is syn orientated to the alkoxy group because of the repulsing interactions of the isopropyl and OR′-substituents (Scheme 9). Therefore in this case, the *lk*-attack is favoured (positive de-values). Considering the activation parameters, this *lk*-attack is enthalpically favoured ($\Delta\Delta H^{\neq} > 0$) and entropically disfavoured ($\Delta\Delta S^{\neq} > 0$).

In scheme 11 two characteristically different potential surfaces for the formation of the 1.4-diradical intermediates are shown. If *lk*-attack occurs, the force constant for the bond being formed in the transition state is comparatively high (high spin and high electron density). As a consequence only a few vibration states can be occupied (Figure 3b). Such a reaction channel is favoured by the enthalpy and disfavoured by the entropy.[28,35,36,15c] In the case of the *ul*-attack the spin density is low and therefore the force constant of the forming bond in the transition state is low. More vibration states can be occupied (Figure 3c). As a consequence the *ul*-attack is entropically favoured and enthalpically disfavoured.

For the furanones **1A, 1B, 1C** the *ul*-attack is favoured (positive de-values). This selection is mainly determined by steric hindrance of the alkoxy group. Such selection processes are generally dominated by the entropy.[36] Indeed, an entropically favoured *ul*-attack is observed for **1A, 1B**. Furthermore this attack is slightly favoured by enthalpy, which

can be explained by the homoanomeric effect. A slight pyramidalization in β-position is caused by the overlapping of the σ*-orbital of the (C-O)-bond in the alkoxy group with the orbital in β-position carrying the radical. This interaction is called homoanomeric effect as it is observed for the preferred conformation of glycosyl radicals.[37] The homoanomeric effect causes, in the case of the *ul*-attack, a greater force constant in the transition state for the forming bond in the corresponding 1,4-diradical (close to the potential surface shown in figure 3b).

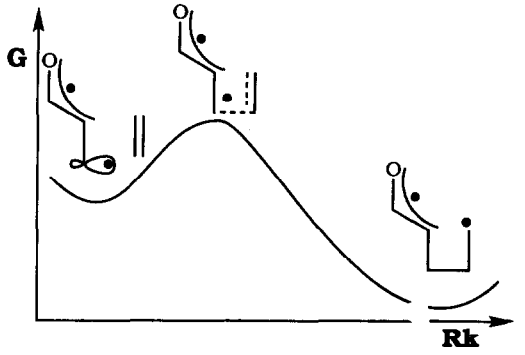


Figure 3a

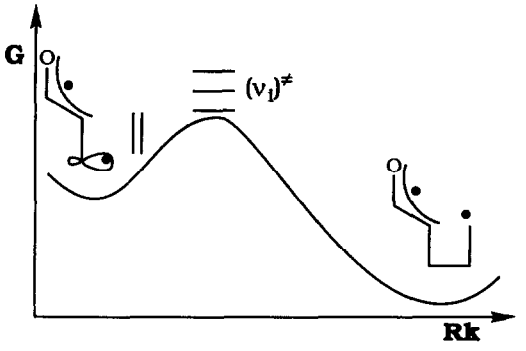


Figure 3b

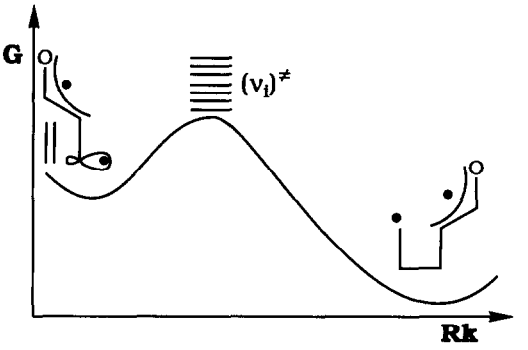


Figure 3c

Figure 3: Potential surfaces for the formation of 1,4-diradical intermediates from the relaxed ($^3\pi\pi^*$)-excited 5-alkoxy-2(5*H*)-furanones with pyramidalization in the β-position. 3b shows the *lk*-attack of ethylene to the furanone (eg. formation of **3Aa**). 3c shows the *ul*-attack (eg. formation of **3Ab**).

The homoanomeric effect is compensated by the β-aryl substitution because of the delocalization of the radical position. The structure of the β-carbon is now a trigonal planar one. As a consequence of this the *ul*-attack is entropically favoured (steric effect of the alkoxy group). No significant enthalpy contribution is observed.

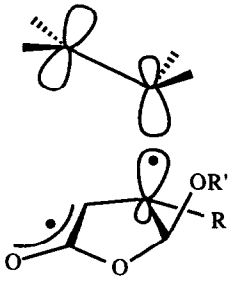
In the case of **1C** the approach of the ethylene is strongly hindered by the rotation cone of the isopropyl substituent. The distance of the reaction partners in both diastereomeric transition states is quite different. Therefore the force constants for the relevant transition states for the *ul*- and *lk*-reaction channel is also quite different. Because of these relationships, the *ul*-attack is now enthalpically favoured and correspondingly the *lk*-attack is favoured by the entropy. A reverse of influence of enthalpy and entropy by substituents with a large number of rotational and vibrational degrees of freedom is described by the Price-Hammett principle.[16] The furanones **4A, 4B, 4C, 5A, 6A** belong to the same isoselective relationship. This is a criterion for a unique selection process.[15c] As a consequence the selection controlling

factors are related to each other. The existance of different isoselective relationships for the furanones **4A, 4B, 4C** (R = i–Pr), **3A, 3B, 3C** (R = Et) and **1A, 1B, 1C, 5A, 6A** (R = H, Ph, p-Tol) (Figure 2) as well as the extremely different de-values give evidence for different structures of the relaxed ($^3\pi\pi^*$)-excited states. In the cases of **4A, 4B, 4C** the pyramidalization of the β-carbon is dominant, whereas the selection for the furanones **1A, 1B, 1C, 5A, 6A** is controlled by the twisted (C=C)-bond, which implies a dominant influence of the steric hindrance of the alkoxy substiuent. For furanones **2A, 2B, 2C** (R = Me) both effects are superposed and no isoselective relationship is observed.

Giese[15c,38] has also described different isoselective relationships for radical reactions. For π-radicals and σ-radicals two different isoselective relationships are observed.

A linearity in the modified Eyring diagrams (no inversion temperatures of the diastereoselectivity) is also observed for concerted or nearly concerted reactions. Shaik and Epiotis[39] describe a concerted mechanism for cyclization of a triplet excited enone with an olefinic partner in the ground state. The molecular dynamic of the transition state (influenced by stereoelectronic effects) must be such that intersystem crossing occurs during the cyclization process. Twisting and pyramidalization in the (C=C)-bond of the enone are of such. In scheme 10 a possible transition state for the cyclization of ($^3\pi\pi^*$)-excited 5-alkoxy-2(5*H*)-furanones and ethylene in terms of a pyramidalization dynamic is shown. Ethylene has no significant sterical requirements and therefore it may favour this reaction pathway.

Molecular dynamics, which accelerate the intersystem crossing, are discussed as stereochemical determining factors for cyclization of diradicals in the triplet state.[1,40] The results of transient analytical investigations of excited enones are also discussed in terms of pyramidalization and twisting, which catalyzes intersystem crossing. The life times of these enones is significantly influenced by these effects.[32,41]



Scheme 10: Possible transition state of the [2 + 2]-cycloaddition of ethylene to a triplet excited 5-alkoxy-2(5*H*)-furanone.

Conclusion

The stereoelectronic effects, which are responsible for the diastereoselectivity in the photosensitized [2 + 2]-cycloaddition of ethylene to 5-alkoxy-2(5*H*)-furanones were analyzed by temperature dependent measurements of the selectivity as well as by the structure variation in the furanone partner. For the investigated systems the diastreoselection is dominated by only one mechanistical step, which is the approach of the ethylene to the vibrationally relaxed ($^3\pi\pi^*$)-excited furanone. Other steps seem to be of minor importance for the selectivity. The remarkable dependence on the β-substitution (positive and negative de-values) correlates with the stereoelectronic effects of the excited furanone (pyramidalization of the β-carbon, homoanomeric effect, steric requirements of the alkoxy substituent), which were characterized by the activation parameter differences $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$ and which are different to those of the groundstate furanones.

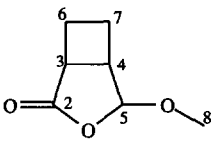
Experimental Section

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian VXR-300 in $CDCl_3$ as solvent and TMS as internal standard. 5-Alkoxy-2(5*H*)-furanones were synthesized by Mannich condensation of aldehydes with glyoxylic acid hydrate[42], photooxygenation of furfural[43] and by reduction of a corresponding carboxylic anhydride (for **10A**).[44] Full acetalation was carried out by heating the hemiacetals with an eight fold excess of corresponding alcohol in toluene (35 mL for 0.1 mole hydroxyfuranone and catalytic amount of p-toluene sulfonic acid). In the case of **1A, 1B, 1C** an equimolar quantity of alcohol was used. These reactions were carried out in $CHCl_3$ as solvent.[5c,42,45] **8A** and **10A** were synthesized by a modified Noyori method.[46,47]

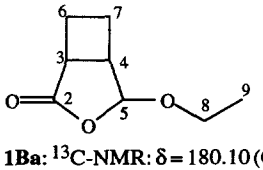
The structure was solved by means of direct methods as implemented in the *XTAL 3.2* program package[49], employing *Gensin*[50] to generate structure invariant relationships and *Gentan*[51] for the tangent phasing procedure. The molecular drawing was generated using the *Ortep*[52] set of routines.

Irradiation of 5-Alkoxy-2(5H)-furanones with Ethylene in Acetone

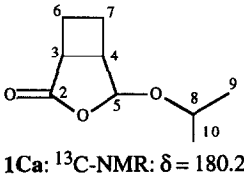
The solution of 5 mmol of the alkoxyfuranone in 250 ml acetone was filled in a photoreactor (quartz immersion well with vacuum jacket) and saturated with ethylene. The apparatus was slowly thermostatisated. The solution was irradiated (high pressure mercury lamp, HPK 150 W) untill the conversion was complet (TLC, silica, 20 % ethyl acetate/cyclohexane; reaction time: about 8 h). **7A, 8A, 9A** and **10A** were irradiated at -55 °C. The solvent was evaporated. The diastereomeric ratio was determined by ^{13}C-NMR from crude material (chemical purity: > 90 %). Yield: quantitative.



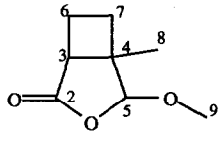
1Aa: ^{1}H-NMR: δ = 5.23 (s, H-5), 3.46 (s, H-8) ppm.
1Ab: ^{1}H-NMR: δ = 5.43 (d, J = 6.0 Hz, H-5), 3.60 (s, H-8) ppm.
The following signals ot the spectrum of the diastereomeric mixture couldn't be assigned: ^{1}H-NMR: δ = 3.15 (m, H-3, 4, 6, 7), 3.02 (m, H-3, 4, 6, 7), 2.0 - 2.7 (m, H-3, 4, 6, 7) ppm.
1Aa: ^{13}C-NMR: δ = 179.99 (C-2),109.07 (C-5), 56.15 (C-8), 39.91 (C-3,4), 37.57 (C-3,4), 23.27 (C-6,7), 21.82 (C-6,7) ppm.
1Ab: ^{13}C-NMR: δ = 178.45 (C-2),106.31 (C-5), 58.11 (C-8), 39.42 (C-3,4), 37.40 (C-3,4), 22.59 (C-6,7), 17.65 (C-6,7) ppm.



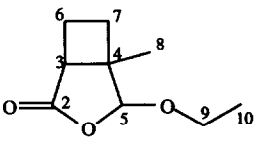
1Ba: ^{1}H-NMR: δ = 5.33 (s, H-5), 3.85 (d/q, J = 9.5/7.0 Hz, H-8), 3.60 (d/q, J = 9.5/7.0 Hz, H'-8), 1.21 (t, J = 7.0 Hz, H-9) ppm.
1Bb: ^{1}H-NMR: δ = 5.58 (d, J = 6.0 Hz, H-5), 3.95 (d/q, J = 9.5/7.0 Hz, H-8), 3.71 (d/q, J = 9.5/7.0 Hz, H'-8), 1.27 (t, J = 7.0 Hz, H-9) ppm.
The following signals ot the spectrum of the diastereomeric mixture couldn't be assigned: ^{1}H-NMR: δ = 3.15 (m, H-3, 4, 6, 7), 3.00 (m, H-3, 4, 6, 7), 2.0 - 2.67 (m, H-3, 4, 6, 7) ppm.
1Ba: ^{13}C-NMR: δ = 180.10 (C-2), 107.95 (C-5), 64.67 (C-8), 40.05 (C-3,4), 37.68 (C-3,4), 23.26 (C-6,7), 21.86 (C-6,7) 14.95 (C-9) ppm.
1Bb: ^{13}C-NMR: δ = 179.62 (C-2),105.10 (C-5), 66.54 (C-8), 39.42 (C-3,4), 37.53 (C-3,4), 22.61 (C-6,7), 17.77 (C-6,7), 14.99 (C-9) ppm.



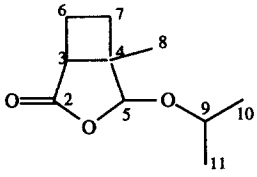
1Ca: ^{1}H-NMR: δ = 5.42 (s, H-5), 3.99 (sep, J = 6.0 Hz, H-8), 1.20 (d, J = 6.0 Hz, H-9, 10), 1.18 (d, J = 6.0 Hz, H-9, 10) ppm.
1Cb: ^{1}H-NMR: δ = 5.68 (d, J = 5.5 Hz, H-5), 4.03 (sep, J = 6.0 Hz, H-8), 1.29 (d, J = 6.0 Hz, H-9, 10), 1.20 (d, J = 6.0 Hz, H-9, 10) ppm.
The following signals ot the spectrum of the diastereomeric mixture couldn't be assigned: ^{1}H-NMR: δ = 3.15 (m, H-3, 4, 6, 7), 2.97 (m, H-3, 4, 6, 7), 2.0 - 2.68 (m, H-3, 4, 6, 7) ppm.
1Ca: ^{13}C-NMR: δ = 180.22 (C-2), 106.51 (C-5), 71.33 (C-8), 40.31 (C-3,4), 37.83 (C-3,4), 23.33 (C-9,10), 23.24 (C-6,7), 21.87 (C-6,7), 21.58 (C-9,10) ppm.
1Cb: ^{13}C-NMR: δ = 178.83 (C-2),103.77 (C-5), 73.00 (C-8), 39.50 (C-3,4), 37.83 (C-3,4), 23.11 (C-9,10), 22.61 (C-6,7), 21.78 (C-9,10) 17.84 (C-6,7) ppm.



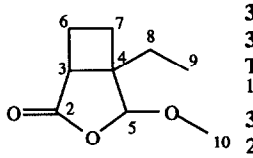
2Aa: ^{1}H-NMR: δ = 5.02 (s, H-5), 3.48 (s, H-9), 1.31 (s, H-8) ppm.
2Ab: ^{1}H-NMR: δ = 5.06 (s, H-5), 3.59 (s, H-9), 1.34 (s, H-8) ppm.
The following signals ot the spectrum of the diastereomeric mixture couldn't be assigned: ^{1}H-NMR: δ = 1.6 -2.8 (m, H-3,6,7) ppm.
2Aa: ^{13}C-NMR: δ = 179.89 (C-2),109.68 (C-5), 56.50 (C-9), 44.91 (C-4), 42.22 (C-3), 29.49 (C-7), 20.80 (C-6), 17.06 (C-8) ppm.
2Ab: ^{13}C-NMR: δ = 178.03 (C-2), 110.97 (C-5), 58.32 (C-9), 53.97 (C-4), 44.21 (C-3), 24.66 (C-7), 21.19 (C-8), 19.59 (C-6) ppm.



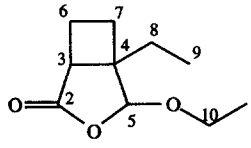
2Ba: ^{1}H-NMR: δ = 5.12 (s, H-5), 3.86 (d/q, J = 9.5/7.0 Hz, H-9), 3.75 (d/q, J = 9.5/7.0 Hz, H'-9), 1.31 (s, H-8), 1.21 (t, J = 7.0 Hz, H-10) ppm.
2Bb: ^{1}H-NMR: δ = 5.16 (s, H-5), 3.94 (d/q, J = 9.5/7.0 Hz, H-9), 3.69 (d/q, J = 9.5/7.0 Hz, H'-9), 1.33 (s, H-8), 1.27 (t, J = 7.0 Hz, H-10) ppm.
The following signals ot the spectrum of the diastereomeric mixture couldn't be assigned: ^{1}H-NMR: δ = 1.6 - 2.75 (m, H-3,6,7) ppm.
2Ba: ^{13}C-NMR: δ = 180.04 (C-2), 108.60 (C-5), 64.93 (C-9), 44.89 (C-4), 42.38 (C-3), 29.50 (C-7), 20.81 (C-6), 17.16 (C-8), 14.86 (C-10) ppm.
2Bb: ^{13}C-NMR: δ = 178.19 (C-2), 109.76 (C-5), 66.67 (C-9), 53.97 (C-4), 44.20 (C-3), 24.75 (C-7), 21.09 (C-8), 19.63 (C-6), 14.98 (C-10) ppm.



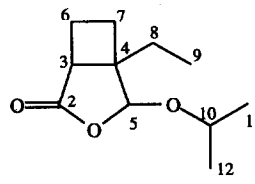
2Ca: ^{1}H-NMR: δ = 5.21 (s, H-5), 3.96 (sep, J = 6.0 Hz, H-9), 1.29 (s, H-8), 1.20 (d, J = 6.0 Hz, H-10,11), 1.16 (d, J = 6.0 Hz, H-10,11) ppm.
2Cb: ^{1}H-NMR: δ = 5.24 (s, H-5), 3.98 (sep, J = 6.0 Hz, H-9), 1.31 (s, H-8), 1.26 (d, J = 6.0 Hz, H-10,11), 1.18 (d, J = 6.0 Hz, H-10,11) ppm.
The following signals ot the spectrum of the diastereomeric mixture couldn't be assigned: ^{1}H-NMR: δ = 1.6 - 2.75 (m, H-3,6,7) ppm.
2Ca: ^{13}C-NMR: δ = 180.20 (C-2), 107.40 (C-5), 71.70 (C-9), 44.96 (C-4), 42.52 (C-3), 29.54 (C-7), 23.25 (C-10,11), 21.57 (C-10,11), 20.85 (C-6), 17.32 (C-8) ppm.
2Cb: ^{13}C-NMR: δ = 178.36 (C-2), 106.42 (C-5), 73.08 (C-9), 44.33 (C-4), 44.19 (C-3), 24.78 (C-7), 23.04 (C-10,11), 21.74 (C-10,11), 20.78 (C-8), 19.69 (C-6), 19.69 (C-8) ppm.



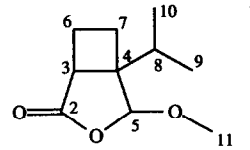
3Aa: ^{1}H-NMR: δ = 5.04 (s, H-5), 3.48 (s, H-10), 0.92 (t, J = 7.0 Hz, H-9) ppm.
3Ab: ^{1}H-NMR: δ = 5.11 (s, H-5), 3.59 (s, H-10), 0.92 (t, J = 7.0 Hz, H-9) ppm.
The following signals ot the spectrum of the diastereomeric mixture couldn't be assigned: ^{1}H-NMR: δ = 2.28 - 2.82 (m, H-3,6,7,8) ppm.
3Aa: ^{13}C-NMR: δ = 180.07 (C-2), 109.15 (C-5), 56.51 (C-10), 48.88 (C-4), 41.33 (C-3), 26.32 (C-6,7,8), 23.40 (C-6,7,8), 21.45 (C-6,7,8), 8.45 (C-9) ppm.
3Ab: ^{13}C-NMR: δ = 178.24 (C-2), 109.90 (C-5), 58.06 (C-10), 48.07 (C-4), 42.38 (C-3), 27.97 (C-6,7,8), 22.14 (C-6,7,8), 19.96 (C-6,7,8), 8.17 (C-9) ppm.



3Ba: ^{1}H-NMR: δ = 5.13 (s, H-5), 3.88 (d/q, J = 9.5/7.0 Hz, H-10), 3.57 (d/q, J = 9.5/7.0 Hz, H'-10), 1.21 (t, J = 7.0 Hz, H-11), 0.92 (t, J = 7.0 Hz, H-9) ppm.
3Bb: ^{1}H-NMR: δ = 5.21 (s, H-5), 3.92 (d/q, J = 9.5/7.0 Hz, H-10), 3.69 (d/q, J = 9.5/7.0 Hz, H'-10), 1.26 (t, J = 7.0 Hz, H-11), 0.92 (t, J = 7.0 Hz, H-9) ppm.
The following signals ot the spectrum of the diastereomeric mixture couldn't be assigned: ^{1}H-NMR: δ = 1.9 - 2.8 (m, H-3,6,7,8), 1.90 - 2.15 (m, H-3,6,7,8), 1.58 - 1.85 (m, H-3,6,7,8) ppm.
3Ba: ^{13}C-NMR: δ = 180.22 (C-2), 107.99 (C-5), 64.97 (C-10), 48.83 (C-4), 41.50 (C-3), 14.87 (C-11), 8.40 (C-9) ppm.
3Bb: ^{13}C-NMR: δ = 178.40 (C-2), 108.66 (C-5), 66.50 (C-10), 48.07 (C-4), 42.40 (C-3), 15.01 (C-11), 8.40 (C-9) ppm.
The following signals ot the spectrum of the diastereomeric mixture couldn't be assigned: ^{13}C-NMR: δ = 27.94 (CH_2), 26.34 (CH_2), 23.49 (CH_2), 22.24 (CH_2), 21.46 (CH_2), 20.02 (CH_2) ppm.



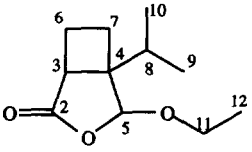
3Ca: ^{1}H-NMR: δ = 5.23 (s, H-5), 3.96 (sep, J = 6.0 Hz, H-10), 1.22 (d, J = 6.0 Hz, H-11,12), 1.18 (d, J = 6.0 Hz, H-11,12), 0.91 (t, J = 7.0 Hz, H-9) ppm.
3Cb: ^{1}H-NMR: δ = 5.31 (s, H-5), 4.01 (sep, J = 6.0 Hz, H-10), 1.28 (d, J = 6.0 Hz, H-11,12), 1.20 (d, J = 6.0 Hz, H-11,12), 0.93 (t, J = 7.0 Hz, H-9) ppm.
The following signals ot the spectrum of the diastereomeric mixture couldn't be assigned: ^{1}H-NMR: δ = 2.25 - 2.80 (m, H-3,6,7,8), 1.58 - 1.90 (m, H-3,6,7,8) ppm.
3Ca: ^{13}C-NMR: δ = 180.31 (C-2), 107.37 (C-5), 71.57 (C-10), 48.85 (C-4), 41.69 (C-3), 20.08 (C-8), 8.30 (C-9) ppm.
3Cb: ^{13}C-NMR: δ = 178.51 (C-2), 106.46 (C-5), 73.05 (C-10), 48.12 (C-4), 42.48 (C-3), 22.26 (C-8), 8.21 (C-9) ppm.
The following signals ot the spectrum of the diastereomeric mixture couldn't be assigned: ^{13}C-NMR: δ = 27.80 (CH_2), 26.28 (CH_2), 23.47 (CH_2), 23.32 (CH_3), 23.13 (CH_3), 21.81 (CH_3), 21.47 (CH_2), 21.44 (CH_3) ppm.



4Aa: ^{1}H-NMR: δ = 5.00 (s, H-5), 3.48 (s, H-11), 0.96 (d, J = 7.0 Hz, H-9,10), 0.86 (d, J = 7.0 Hz, H-9,10) ppm.
4Ab: ^{1}H-NMR: δ = 5.13 (s, H-5), 3.58 (s, H-10), 1.10 (d, J = 7.0 Hz, H-9,10), 0.82 (d, J = 7.0 Hz, H-9,10) ppm.
The following signals ot the spectrum of the diastereomeric mixture couldn't be assigned: ^{1}H-NMR: δ = 2.84 (m, H-3,6,7,8), 2.48 - 2.60 (m, H-3,6,7,8), 1.74 - 2.44 (m, H-3,6,7,8) ppm.

4Aa: ^{13}C-NMR: δ = 180.27 (C-2), 109.73 (C-5), 56.53 (C-11), 52.12 (C-4), 40.23 (C-3), 26.83 (C-8), 22.90 (C-6,7), 22.60 (C-6,7), 17.85 (C-9,10), 16.69 (C-9,10) ppm.

4Ab: ^{13}C-NMR: δ = 178.40 (C-2), 108.47 (C-5), 57.85 (C-11), 51.35 (C-4), 41.29 (C-3), 32.18 (C-8), 20.30 (C-6,7), 19.83 (C-6,7), 16.69 (C-9,10), 16.30 (C-9,10) ppm.

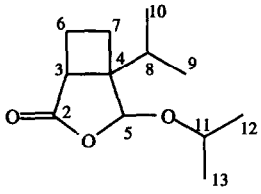


4Ba: ^{1}H-NMR: δ = 5.11 (s, H-5), 3.88 (d/q, J = 9.5/7.0 Hz, H-11), 3.56 (d/q, J = 9.5/7.0 Hz, H'-11), 1.21 (t, J = 7.0 Hz, H-12), 1.10 (d, J = 7.0 Hz, H-9,10), 0.82 (d, J = 7.0 Hz, H-9,10) ppm.

4Bb: ^{1}H-NMR: δ = 5.25 (s, H-5), 3.94 (d/q, J = 9.5/7.0 Hz, H-11), 3.69 (d/q, J = 9.5/7.0 Hz, H'-11), 1.26 (t, J = 7.0 Hz, H-12), 0.96 (d, J = 7.0 Hz, H-9,10), 0.87 (d, J = 7.0 Hz, H-9,10) ppm.

The following signals ot the spectrum of the diastereomeric mixture couldn't be assigned: ^{1}H-NMR: δ = 2.83 (m, H-3,6,7,8), 2.51 - 2.66 (m, H-3,6,7,8), 1.75 - 2.46 (m, H-3,6,7,8) ppm.

4Ba: ^{13}C-NMR: δ = 180.42 (C-2), 108.56 (C-5), 64.99 (C-11), 52.06 (C-4), 40.37 (C-3), 26.91 (C-8), 22.98 (C-6,7), 22.59 (C-6,7), 17.84 (C-9,10), 16.61 (C-9,10), 14.85 (C-12) ppm.



4Bb: ^{13}C-NMR: δ = 178.53 (C-2), 107.26 (C-5), 66.30 (C-11), 51.34 (C-4), 41.33 (C-3), 32.17 (C-8), 20.39 (C-6,7), 19.90 (C-6,7), 16.75 (C-9,10), 16.32 (C-9,10), 15.04 (C-12) ppm.

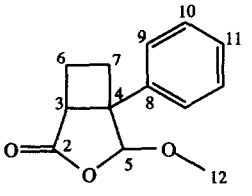
4Ca: ^{1}H-NMR: δ = 5.21 (s, H-5), 3.97 (sep, J = 6.0 Hz, H-11), 1.22 (d, J = 6.0 Hz, H-12,13), 1.18 (d, J = 6.0 Hz, H-12,13), 1.09 (d, J = 7.0 Hz, H-9,10), 0.81 (d, J = 7.0 Hz, H-9,10) ppm.

4Cb: ^{1}H-NMR: δ = 5.36 (s, H-5), 4.03 (sep, J = 6.0 Hz, H-11), 2.58 (d/d/d/d, J = 12.5/9.0/8.0/1.5 Hz, H-6), 1.28 (d, J = 6.0 Hz, H-12,13), 1.21 (d, J = 6.0 Hz, H-12,13), 0.96 (d, J = 7.0 Hz, H-9,10), 0.87 (d, J = 7.0 Hz, H-9,10) ppm.

The following signals ot the spectrum of the diastereomeric mixture couldn't be assigned: ^{1}H-NMR: δ = 2.81 (m, H-3,6,7,8), 1.73 - 2.42 (m, H-3,6,7,8) ppm.

4Ca: ^{13}C-NMR: δ = 180.52 (C-2), 107.17 (C-5), 71.51 (C-11), 52.07 (C-4), 40.52 (C-3), 26.79 (C-8), 23.35 (C-12,13), 22.95 (C-6,7), 22.62 (C-6,7), 21.34 (C-12,13), 17.88 (C-9,10), 16.48 (C-9,10) ppm.

4Cb: ^{13}C-NMR: δ = 178.65 (C-2), 105.93 (C-5), 72.98 (C-11), 51.36 (C-4), 41.39 (C-3), 32.16 (C-8) 23.20 (C-12,13), 21.82 (C-12,13), 20.48 (C-6,7), 19.96 (C-6,7), 16.85 (C-9,10), 16.37 (C-9,10) ppm.



5Aa: ^{1}H-NMR: δ = 5.29 (s, H-5), 3.31 (s, H-12) ppm.

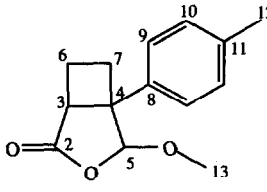
5Ab: ^{1}H-NMR: δ = 5.19 (s, H-5), 3.57 (s, H-12) ppm.

The following signals ot the spectrum of the diastereomeric mixture couldn't be assigned: ^{1}H-NMR: δ = 7.20 - 7.42 (m, H-9,10,11), 3.35 - 3.50 (m, H-3,6,7), 2.05 - 2.73 (m, H-9,6,7) ppm.

5Aa: ^{13}C-NMR: δ = 179.21 (C-2), 138.35 (C-8), 128.36 (C-9), 126.91 (C-10), 125.37 (C-11), 108.93 (C-5), 56.52 (C-12), 53.14 (C-4), 41.71 (C-3), 31.27 (C-7), 21.63 (C-6) ppm.

5Ab: ^{13}C-NMR: δ = 177.51 (C-2), 141.72 (C-8), 128.36 (C-9), 127.32 (C-11), 127.01 (C-10), 110.77 (C-5), 58.29 (C-12), 51.58 (C-4), 41.71 (C-3), 31.27 (C-7), 21.63 (C-6) ppm.

6Aa: ^{1}H-NMR: δ = 5.27 (s, H-5), 3.31 (s, H-13), 2.15 (s, H-12) ppm.

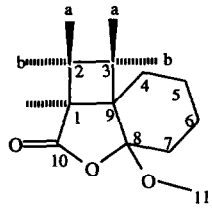


6Ab: ^{1}H-NMR: δ = 5.17 (s, H-5), 3.56 (s, H-13), 2.34 (s, H-12) ppm.

The following signals ot the spectrum of the diastereomeric mixture couldn't be assigned: ^{1}H-NMR: δ = 7.10 - 7.25 (m, H-9,10,11), 3.40 (m, H-3,6,7), 3.01 (m, H-3,6,7), 2.0 - 2.7 (m, H-9,6,7) ppm.

6Aa: ^{13}C-NMR: δ = 179.32 (C-2), 137.00 (C-8), 136.62 (C-11), 129.08 (C-10), 126.86 (C-9), 108.97 (C-5), 56.48 (C-13), 52.87 (C-4), 41.79 (C-3), 31.27 (C-7), 21.62 (C-6), 21.00 (C-12) ppm.

6Ab: ^{13}C-NMR: δ = 177.59 (C-2), 138.71 (C-8), 135.30 (C-11), 129.62 (C-10), 125.34 (C-9), 110.97 (C-5), 58.28 (C-13), 51.34 (C-4), 43.99 (C-3), 29.25 (C-12), 25.35 (C-7), 20.42 (C-6) ppm.



2g of **7Aa,b** was chromatographed (210 ml silica gel, 10 % ethyl acetate/cyclohexane). The product from the first fraction **7Aa** was recrystallized from n-hexane. F: 80.5 °C.

Major isomer **7Aa**: ^{1}H-NMR: δ = 3.27 (s, H-11), 2.79 (d/d/t, $J_{1/2a}$ = 1.0 Hz, $J_{1/2b}$ = 8.2 Hz, $J_{1/3a}$ = 1.0 Hz, $J_{1/3b}$ = 4.1 Hz, H-1), 2.37 (d/d/d/d, J = 10.8/10.3/9.2/8.2 Hz, H-2b), 2.23 (m, H-3a), 2.15 (m, H_{eq}-7), 2.00 (t/d/d, J = 12.5/4.0/1.6 Hz, H_{eq}-4), 1.86 (m, H-3b), 1.84 (m, H-2a), 1.76 (m, H_{ax}-4), 1.60 (m, H_{ax}-7), 1.15 - 1.55 (m, H-5, 6) ppm.

NOE: H-1 (2.79 ppm) --> H-2b (2.37 ppm)
H-11 (3.27 ppm) --> H-7 (2.16 ppm)

H-11 (3.27 ppm) --> H-4 (2.05 ppm)

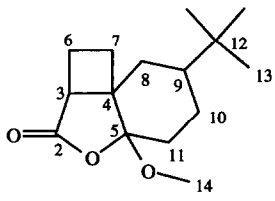
^{13}C-NMR: δ = 180.00 (C-10), 108.93 (C-8), 51.75 (C-9), 48.72 (q, J(C,H) = 143 Hz, C-11), 41.88 (d, J(CH) = 150 Hz, C-1), 29.32 (t, J(CH) = 137 Hz, C-3), 27.00 (t, J(CH) = 130 Hz, C-4), 23.18 (t, J(CH) = 130 Hz, C-7), 21.65 (C-5,6), 21.07 (t, J(C,H) = 139 Hz, C-2), 20.15 (t, J(C,H) = 126 Hz, C-5,6) ppm.

Minor isomer **7Ab:** ^{1}H-NMR: δ = 3.46 (s, H-11), 2.85 (H-1), 2.72 (H-3a), 2.46 (H-7), 2.38 (H-2b), 2.10 (H-4), 1.93 (H-2a), 1.70 (H-5,6), 1.60 (H-5,6), 1.56 (H-4), 1.52 (H-3b), 1.27 (H-7,5,6) ppm. $J_{1/2a}$ = 1.7 Hz, $J_{1/2b}$ = 8.9 Hz, $J_{1/3a}$ = 1.1 Hz, $J_{1/3b}$ = 3.8 Hz, $J_{2a/2b}$ = 11.8 Hz, $J_{2a/3a}$ = 8.8 Hz, $J_{2a/3b}$ = 2.6 Hz, $J_{2b/3a}$ = 10.4 Hz, $J_{2b/3b}$ = 9.6 Hz, $J_{3a/3b}$ = 12.3 Hz.

NOE: H-1 (2.85 ppm) --> H-3b (1.52 ppm)

H-11 (3.46 ppm) --> H-7 (2.46 ppm)

^{13}C-NMR: δ = 177.67 (C-10), 109.98 (C-8), 51.76 (q, J(C,H) = 146 Hz, C-11), 48.76 (C-9), 43.45 (d, J(CH) = 146 Hz, C-1), 30.03 (t, J(CH) = 128 Hz, C-7), 29.58 (t, J(CH) = 127 Hz, C-4), 26.90 (t, J(C,H) = 130 Hz, C-3), 22.26 (t, J(C,H) = 126 Hz, C-5,6), 21.54 (t, J(C,H) = 130 Hz, C-5,6), 20.76 (t, J(C,H) = 139 Hz, C-2) ppm.



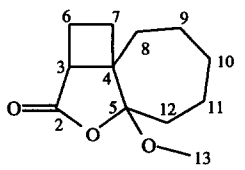
8Aa: ^{1}H-NMR: δ = 3.27 (s, H-14), 0.90 (s, H-13) ppm.

8Ab: ^{1}H-NMR: δ = 3.45 (s, H-14), 0.90 (s, H-13) ppm.

The following signals ot the spectrum of the diastereomeric mixture couldn't be assigned: ^{1}H-NMR: δ = 1.0 - 2.9 (m) ppm.

8Aa: ^{13}C-NMR: δ = 181.03 (C-2), 108.78 (C-5), 51.77 (C-4), 48.67 (C-14), 42.18 (C-3,9), 42.16 (C-3,9), 27.85 (C-13) ppm.

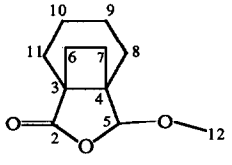
8Ab: ^{13}C-NMR: δ = 176.73 (C-2), 109.78 (C-5), 51.69 (C-4), 48.14 (C-14), 44.15 (C-3,9), 43.75 (C-3,9), 27.44 (C-13) ppm.



The following signals ot the spectrum of the diastereomeric mixture couldn't be assigned: ^{13}C-NMR: δ = 32.33, 32.14, 30.90, 30.13, 29.89, 26.94, 22.92, 22.67, 21.06, 20.77 ppm. ^{1}H-NMR: δ = 3.43 (s, H-13, **b**), 3.34 (s, H-13, **a**), 1.2 - 2.9 (m, H-3,6,7,8,9,10,11,12) ppm.

9Aa: ^{13}C-NMR: δ = 180.22 (C-2), 112.45 (C-5), 52.55 (C-4), 49.32 (C-13), 44.96 (C-3), 27.96 (CH_2), 27.34 (CH_2), 25.85 (CH_2), 24.66 (CH_2), 23.58 (CH_2), 20.89 (CH_2) ppm.

9Ab: ^{13}C-NMR: δ = 178.13 (C-2), 113.30 (C-5), 51.61 (C-4), 50.85 (C-13), 45.23 (C-3), 31.95 (CH_2), 30.02 (CH_2), 29.30 (CH_2), 23.90 (CH_2), 22.43 (CH_2), 19.28 (CH_2) ppm.



10A,a,b: ^{1}H-NMR: δ = 5.13 (s, H-5), 5.03 (s, H-5), 3.59 (s, H-12), 3.48 (s, H-12), 1.2 - 2.5 (m, H-6,7,8,9,10,11) ppm.

^{13}C-NMR: δ = 182.89 (C-2), 180.89 (C-2), 109.91 (C-5), 108.59 (C-5), 58.32 (C-12), 56.93 (C-12), 45.65 (C-3,4), 44.81 (C-3,4), 44.04 (C-3,4), 43.60 (C-3,4), 29.77 (CH_2), 28.78 (CH_2), 28.08 (CH_2), 27.24 (CH_2), 24.35 (CH_2), 23.38 (CH_2), 23.23 (CH_2), 22.23 (CH_2), 21.21 (CH_2), 21.09 (CH_2), 20.77 (CH_2) ppm.

Acknowledgements - Our thanks are directed to the Fonds der Chemischen Industrie for supporting this work. We are grateful to Dr. J. Runsink for his assistance in the interpretation of NMR data.

References

1. Buschmann, H.; Hoffmann, N.; Scharf, H.-D. *Tetrahedron Asymm.* **1991**, *2*, 1429.
2. a) Baldwin, S.W.; *Organic Photochemistry* **1981**, *5*, 123; b) Oppolzer, W.; *Acc. Chem. Res.* **1982**, *15*, 135; c) Weedon, A.C.; *Synthetic Organic Photochemistry;* Horspool, W.M.: Plenum Press, New York, 1983; p. 61; d) Crimmins, M.T. *Chem. Rev.* **1988**, *88*, 1435; e) P.A. Wender, *Photochemistry in Organic Synthesis;* Coyle, J.D.: Royal Society of Chemistry, London, 1986; p. 163; f) Horspool, W.M. *Photochemistry in Organic Synthesis;* Coyle, J.D.: Royal Society of Chemistry, London, 1986; p. 210; g) Demuth, M.; Mikhail, G. *Synthesis* **1989**, 145; ; h) Crimmins, M.T. *Comprehensive Organic Synthesis* (Trost, B.M.; Fleming, I. ; Ed.), Vol. 5, Pergamon Press, Oxfort **1991**, p. 123.
3. Becker, D.; Haddad, N. *Organic Photochem.* **1989**, *10*, 1.
4. Hoffmann, N.; Scharf, H.-D. *Liebigs Ann. Chem.* **1991**, 1273.
5. see for example: a) Tada, M.; Kokubo, T.; Sato, T. *Tetrahedron* **1972**, *28*, 2121; b) Kosugi, H.; Sekiguchi, S.; Sekita, R.; Uda, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 520; c) Scharf, H.-D.; Janus, J.; Müller, E. *Tetrahedron* **1979**, *35*, 25; d) Pearlman, B.A. *J. Am. Chem. Soc.* **1979**, *101*, 6398, 6404.

6. a) Getty, S.J.; Berson, J.A. *J. Am. Chem. Soc.* **1991**, *113*, 4607; b) Alibés, R.; Bourdelande, J.L.; Font, J. *Tetrahedron Asymm.* **1991**, *2*, 1391.
7. Corey, E.J.; Bass, J.D.; Le Mathieu, R.; Mitra, R.B.; *J. Am. Chem. Soc.* **1964**, *86*, 5570.
8. Loutfy, R.O.; de Mayo, P. *J. Am. Chem. Soc.* **1977**, *99*, 3559.
9. a) Schuster, D.I. *The Chemistry of the Enones;* Patai, S.; Rappoport, Z.: J. Wiley & Sons Ltd. Chichester, UK, 1989; p. 623; b) Schuster, D.I.; Lem, G.; Kaprinidis, N.A. *Chem. Rev.* **1993**, *93*, 3.
10. a) Hastings, D.J.; Weedon, A.C. *J. Am. Chem. Soc.* **1991**, *113*, 7311; b) Maradyn, D.J.; Sydnes, L.K.; Weedon, A.C. *Tetrahedron Lett.* **1993**, *34*, 2413; c) Andrew, D.; Hastings, D.J.; Oldroyd, D.L.; Rudolf, A.; Weedon, A.C.; Wong, D.F.; Zhang, B. *Pure Appl. Chem.* **1992**, *64*, 1327. Steric and electronic effects which control the structure of the biradical intermediate are described by: d) Winkler, J.D.; Shao, B. *Tetrahedron Lett.* **1993**, *34*, 3355; Fischer, E.; Gleiter, R; *Angew. Chem.* **1989**, *101*, 925; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 925; f) Gleiter, R; Fischer, E.; *Chem. Ber.* **1992**, *125*, 1899.
11. Pracejus, H. *Liebigs Ann. Chem.* **1960**, *634*, 23.
12. a) Buschmann, H.; Scharf, H.-D.; Hoffmann, N.; Plath, M.W.; Runsink, J. *J. Am. Chem. Soc.* **1989**, *111*, 5367; b) Buschmann, H.; Scharf, H.-D.; Hoffmann, N.; Esser, P. *Angew. Chem.* **1991**, *103*, 480; *Angew. Chem., Int. Ed. Eng.* **1991**, *30*, 477.
13. a) Kagan, H.B.; Fiaud, J.C. *Top. Stereochem.* **1978**, *10*, 175;b) Wynberg, H.; Feringa, B.; *Tetrahedron* **1976**, *32*, 2831.
14. a) Glasstone, S.; Laidler, K.J.; Eyring, H. *The Theory of Rate Processes;* Mc Graw-Hill Book Co., London, 1941; b) Pracejus, H. *Fortschr. Chem. Forsch;* Vol. 8/4, Springer-Verlag, Berlin, 1967; p. 493.
15. a) Pracejus, H.; Tille, A. *Chem. Ber.* **1963**, *96*, 854; b) Exner,O.; Giese, B. *Angew. Chem.* **1978**, *90*, 816; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 775; c) Giese, B. *Acc. Chem. Res.* **1984**, *17*, 438; For a recent example of a compensation relationship in photochemical *cis/trans*-isomerisation see: d) Inoue, Y.; Yamasaki, N.; Yokoyama, T.; Tai , A. *J. Org. Chem.* **1992**, *57*, 1332.
16. a) Price, F.P., Jr.; Hammett, L.P. *J. Am. Chem. Soc.* **1941**, *63*, 2387; b) Schaleger, L.L.; Long, F.A. *Adv. Phys. Org. Chem.* **1963**, *1*, 1.
17. a) Lambert, J.B.; Vagenas, A.R. *Org. Magn. Reson.* **1981**, *17*, 265,270; b) Duddeck, H.; *Top. Stereochem.* **1986**, *16*, 219; c) Wilson, N.K.; Sothers, J.B. *Top. Stereochem.* **1974**, *8*, 1.
18. a) Ryang, H.-S.; Shima, K.; Sakurai, H. *J. Am. Chem. Soc.* **1971**, *93*, 5270; b) Turro, N.J.; Shima, K.; Chung, C.-J.; Tanielan, C.; Kanfer, S. *Tetrahedron Lett.* **1980**, *21*, 2775; c) Wilson, R.M. *Org. Photochem.* **1985**, *7*, 339; d) Gersdorf, J.; Mattay, J; Görner, H. *J. Am. Chem. Soc.* **1987**, *109*, 1203; e) Gersdorf, J.; Mattay, J.; Buchkremer, K. *Chem. Ber.* **1987**, *120*, 307; f) Candrell, T.S.; Allen, A.C. *J. Org. Chem.* **1989**, *54*, 135; g) Adam, W.; Grabowski, S.; Wilson, R.M. *Acc. Chem. Res.* **1990**, *23*, 165.
19. Rudolf, A.; Weedon, A.C. *Can. J. Chem.* **1990**, *68*, 1590.
20. a) Eaton, P.E. *Acc. Chem. Res.* **1968**, *1*, 50; b) Candrell, T.S.; Haller, W.S.; Williams, J.C. *J. Org. Chem.* **1969**, *34*, 509; c) Becker, D.; Nagler, M.; Sahali, Y.; Haddad, N. *J. Org. Chem.* **1991**, *56*, 4537; d) Becker, D.; Haddad, N. *Tetrahedron* **1993**, *49*, 947.
21. a) Freilich, S.C.; Peters, K.S. *J. Am. Chem. Soc.* **1981**, *103*, 6255; b) Freilich, S.C.; Peters, K.S. *J. Am. Chem. Soc.* **1985**, *107*, 3819.
22. a) Zimmt, M.B.; Doubleday, C., Jr.; Turro, N.J. *J. Am. Chem. Soc.* **1986**, *108*, 3618; b) Wang, J.; Doubleday, C., Jr.; Turro, N.J. *J. Am. Chem. Soc.* **1989**, *111*, 3962; c) Doubleday, C., Jr.; Turro, N.J.; Wang, J. *Acc. Chem. Res.* **1989**, *22*, 199.
23. Linear dependencies of ln P from the pressure without inversion points were observed for the diastereoselectivity in the reaction of cyclopentenone with less polarizable olefinic partners: Buback, M.; Bünger, J.; Tietze, L.F. *Chem. Ber.* **1992**, *125*, 2577. For the correspondence of p (pressure) and T^{-1} see ref. 12b and the references cited therein.
24. a) Herzog, H.; Koch, H.; Scharf, H.-D.; Runsink, J. *Chem. Ber.* **1987**, *120*, 1737; see also: b) Tolbert, L.M.; Ali, M.B. *J. Am. Chem. Soc.* **1982**, *104*, 1742; c) Tolbert, L.M.; Ali, M.B. *J. Am. Chem. Soc.* **1984**, *106*, 3806.
25. a) Caldwell, R.A.; Creed, D. *Acc. Chem. Res.* **1980**, *13*, 45; b) Mattes, S.L.; Farid, S. *Acc. Chem. Res.* **1982**, *15*, 80; c) Kuzmin, M.G.; Soboleva, I.V. *Prog. React. Kinetics* **1986**, *14*, 157.
26. Wolff, T.; Schmidt, F.; Volz, P. *J. Org. Chem.* **1992**, *57*, 4255.
27. a) Hammond, G.S. J. *Am. Chem. Soc.* **1955**, *77*, 334; b) Giese, B. *Angew. Chem.* **1977**, *89*, 162; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 125; c) Pross, A. *Adv. Phys. Org. Chem.* **1977**, *14*, 69; d) Johnson, C.D. *Tetrahedron* **1980**, *36*, 3461; e) Tedder, J.M. *Angew. Chem.* **1982**, *94*, 433; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 401; f) Jencks, W.P. *Chem. Rev.* **1985**, *85*, 511.
28. Gould, I.R.; Turro, N.J.; Butcher, J., Jr.; Doubleday, C., Jr.; Hacker, N.P.; Lehr, G.F.; Moss, R.A.; Cox, D.P.; Guo,

W.; Munjal, R.C.; Perez, C.A.; Fedorynski, M. *Tetrahedron* **1985**, *41*, 1587.
29. a) Desobry, V.; Magareta, P. *Helv. Chim. Acta* **1975**, *58*, 2161; b) Thi, G.V.; Magareta, P. *Helv. Chim. Acta* **1976**, *59*, 2236; c) Cruciani, G.; Rathjen, H.-J.; Magareta, P. *Helv. Chim. Acta* **1990**, *73*, 856.
30 a) Wiesner, K. *Tetrahedron* **1975**, *31*, 1655; b) Matini-Bettòlo, G.; Sahoo, S.P.; Poulton, G.A.; Tsai, T.Y.R.; Wiesner, K. *Tetrahedron* **1980**, *36*, 719; c) Blound, J.F.; Gray, G.D.; Atwal, K.S.; Tsai, T.Y.R.; Wiesner,K. *Tetrahedron Lett.* **1980**, *21*, 4413.
31. For theoretical and specroscopical investigations see:
a) Kearns, D.R.; Marsh, G.; Schaffner, K. *J. Chem. Phys.* **1968**, *49*, 3316; b) Cargill, R.L.; Miller, A.C.; Pond, D.M.; de Mayo, P.; Tchir, M.F.; Neuberger, K.R.; Saltiel, J. *Mol. Photochem.* **1969**, *1*, 301; c) Mc Cullough, J.J.; Ohorodnyk, H.; Santry, D.P. *J. Chem. Soc. Chem. Commun.* **1969**, 570; d) Marsh, G.; Kearns, D.R.; Schaffner, K. *J. Am. Chem. Soc.* **1971**, *93*, 3129; e) Cargill, R.L.; Bundy, W.A.; Pond, D.M.; Sears, A.B.; Saltiel, J.; Winterle, J. *Mol. Photochem.* **1971**, *3*, 123; f) Devaquet, A.; Salem, L. *Can. J. Chem.* **1971**, *49*, 977; g) Devaquet, A. *J. Am. Chem. Soc.* **1972**, *94*, 5160; h) Jones, C.R.; Kearns, D.R. *J. Am. Chem. Soc.* **1977**, *99*, 344; i) Yamauchi, S.; Hirota, N.; Higuchi, J. *J. Phys. Chem.* **1988**, *92*, 2129; j) Caldwell, R.A.; Tang, W.; Schuster, D.I.; Heibel, G.E. *Photochem. Photobiol.* **1991**, *53*, 159; k) Blok, P.M.L.; Dekkers, H.P.J.M. *Photochem. Photobiol.* **1991**, *53*, 421.
32. a) Bonneau, R. *J. Am. Chem. Soc.* **1980**, *102*, 3816; b) Schuster, D.I.; Bonneau, R.; Dunn, D.A.; Rao, J.M.; Joussot-Dubien, J. *J. Am. Chem. Soc.* **1984**, *106*, 2706; c) Kelly, J.M.; Mc Murry, T.B.H.; Work, D.N. *J. Chem. Soc. Perkin Trans. 2*, **1990**, 981; d) Schuster, D.I.; Dunn, D.A.; Heibel, G.E.; Brown, P.B.; Rao, J.M.; Woning, J.; Bonneau, R. *J. Am. Chem. Soc.* **1991**, *113*, 6245.
33. a) Dilling, W.L.; Tabor, T.E.; Boer, F.P.; North, P.P. *J. Am. Chem. Soc.* **1970**, *92*, 1399; b) Peet, N.P.; Cargill, R.L.; Bushey, D.F. *J. Org. Chem.* **1973**, *38*, 1218.
34. a) Seebach, D.; Zimmermann, J.; Gysel, U.; Ziegler, R.; Ha, T.-K. *J. Am. Chem. Soc.* **1988**, *110*, 4763; b) Seebach, D.; Maetzke, T.; Petter, W.; Klötzer, B.; Plattner, D.A. *J. Am. Chem. Soc.* **1991**, *113*, 1781.
35. Skell, P.S.; Cholod, M.S. *J. Am. Chem. Soc.* **1969**, *91*, 7131.
36. Blackadder, D.A.; Hinshelwood, C. *J. Chem. Soc.* **1958**, 2728.
37. a) Giese, B.; Dupuis, J. *Tetrahedron Lett.* **1984**, *25*, 1349; b) Dupuis, J.; Giese, B.; Rüegge, D.; Fischer, H.; Korth, H.-G.; Sustmann, R. *Angew. Chem.* **1984**, *96*, 887; *Angew. Chem., Int. Ed. Eng.* **1984**, *23*, 896; c) Korth, H.-G.; Sustmann, R.; Dupuis, J.; Giese, B. *J. Chem. Soc. Perkin Trans. 2*, **1986**, 1453; d) Korth, H.-G.; Sustmann, R.; Gröninger, K.S.; Witzel, T.; Giese, B. *J. Chem. Soc. Perkin Trans. 2*, **1986**, 1461; e) Korth, H.-G.; Sustmann, R.; Gröninger, K.S.; Leisung, M.; Giese, B. *J. Org. Chem.* **1988**, *53*, 4364; f) Giese, B. *Angew. Chem.* **1989**, *101*, 993; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 969; g) Korth, H.-G.; Praly, J.-P.; Somsák, L.; Sustmann, R. *Chem. Ber.* **1990**, *123*, 1155; h) Korth, H.-G.; Sustmann, R.; Giese, B.; Rückert, B.; Gröninger, K.S. *Chem. Ber.* **1990**, *123*, 1891; i) Rajan Babu, T.V. *Acc. Chem. Res.* **1991**, *24*, 139; for a modified FMO treatment see also: Huang, X.L.; Dannenberg, J.J.; Duran, M.; Bertrán, J. *J. Am. Chem. Soc.* **1993**, *115*, 4024.
38. Giese, B. *Angew. Chem.* **1976**, *88*, 159, 161, 723; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 173, 174, 688.
39. a) Shaik, S.S. *J. Am. Chem. Soc.* **1979**, *101*, 3184; b) Shaik, S.; Epiotis, N.D. *J. Am. Chem. Soc.* **1978**, *100*, 18; c) Epiotis, N.D. *Theory of Organic Reactions*; Springer Verlag, Berlin, 1978.
40. a) Salem, L.; Rowland, C. *Angew. Chem.* **1972**, *84*, 86; *Angew. Chem., Int. Ed. Eng.* **1972**, *11*, 92; b) Wagner, P.J.; Meador, M.A.; Zhou, B.; Park, B.-S. *J. Am. Chem. Soc.* **1991**, *113*, 9630, and references cited therein; c) Griesbeck, A.G.; Stadtmüller, S. *J. Am. Chem. Soc.* **1991**, *113*, 6923; d) Griesbeck, A.G.; Mauder, H.; Peters, K.; Peters, E.-M.; von Schnering, H.G. *Chem. Ber.* **1991**, *124*, 407; e) Griesbeck, A.G.; Stadtmüller, S. *Chem. Ber.* **1990**, *123*, 357; f) Griesbeck, A.G.; Stadtmüller, S.; Busse, H.; Bringmann, G.; Buddrus, J. *Chem. Ber.* **1992**, *125*, 933, g) Ramamurthy, V.; Corbin, D.R.; Johnston, L.J. *J. Am. Chem. Soc.* **1992**, *114*, 3870.
41. Caldwell, R.A. *Kinetics and Spectroscopy of Carbenes and Biradicals;* Platz, M.S.: Plenum Press, New York, 1990; p. 77.
42. a) Bourguignon, J.J.; Wermuth, C.G. *J. Org. Chem.* **1981**, *46*, 4889; b) Laugrand, S.; Guingant, A.; d'Angelo, J. *J. Org. Chem.* **1987**, *52*, 4788; c) Schreiber, J.; Wermuth, C.G.; Meyer, A. *Bull. Soc. Chim. Fr.* **1973**, 625; d) Yu, W.; Ching-Sheng, H. *Hua Hsueh Hsueh Pao* **1960**, *26*, 84 (C.A. *59* 5032); e) Mondon, A.; Menz, H.-U.; Zander, J. *Chem. Ber.* **1963**, *96*, 826.
43. Bolz, G.; Wiersdorff, W.-W. (BASF) *Ger. Offen.* No. 2111119 (1972).
44. a) Canonne, P.; Plamondon, J.; Akissira, M. *Tetrahedron* **1988**, *44*, 2903; b) Knight, D.W.; Pattenden, G. *J. Chem. Soc. Perkin Trans 1*, **1979**, 62.
45. a) Schenk, G.O. *Ger. Offen.* No. 881193 (1953); b) Schenk, G.O. *Liebigs Ann. Chem.* **1953**, *584*, 156; c) Pattenden, G.; Weedon, B.C.L. *J. Chem. Soc. (C)* **1968**, 1984.
46. a) Tsunoda, T.; Suzuki, M.; Noyori, R. *Tetrahedron Lett.* **1980**, *21*, 1357; b) Noyori, R.; Murata, S.; Suzuki, M. *Tetrahedron* **1981**, *37*, 3899.

47. Hoffmann, N.; *Dissertation, RWTH Aachen* **1992.**
48. Details regarding the crystal structure analysis are available from the *Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH*, D-76344, Eggenstein-Leopoldshafen, on quoting the depository number CSD 58309, the names of the authors, and the journal.
49. Hall, S.R.; Flack, H.D.; Stewart, J.M. *XTAL3.2 Reference Manual.* Universities of Western Australia, Geneva and Maryland **1992.**
50. Subramanian, V.; Hall, S.R.; *XTAL3.2 Reference Manual.* Eds. Hall, S.R.Stewart, J.M.Universities of Western Australia, Geneva and Maryland, p. 131 **1992.**
51. Hall, S.R.; *XTAL3.2 Reference Manual.* Eds. Hall, S.R.Stewart, J.M.Universities of Western Australia, Geneva and Maryland, p. 139 **1992.**
52. Johnson, C.K.; *ORTEP.* A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations. Oak Ridge National Laboratory; Report ORNL-3794, Oak Ridge, Tennessee, USA.

(*Received in Germany* 27 *August* 1993; *revised* 9 *August* 1994; *accepted* 10 *August* 1994)