[5] überein. Die ^{13}C-NMR.-Spektren (vgl. Fig.) wurden mit einem *Varian*-XL-100-Spektrometer im PFT-Verfahren von 0,14 M Lösungen der Komplexe in D_2O/D_2SO_4 1:1 aufgenommen. Die chemische Verschiebung δ in ppm bezieht sich auf das Methylsignal von Methansulfonsäure als internem Standard. Unter den gleichen Bedingungen aufgenommen zeigt Glycin 2 Signale bei $\delta = 1{,}8$ und 130,5. Die Protonierung der Ligandatome N und O bewirkt demnach eine kleinere Verschiebung der ^{13}C-Signale nach tieferem Feld als die Koordination mit dem Co(III)-Zentralatom. Ausser den ^{13}C-NMR.-Spektren der reinen Komplexe wurden auch diejenigen von Gemischen beider Verbindungen aufgenommen. In allen Fällen waren beide Isomeren im Spektrum identifizierbar. Damit ist gezeigt, dass es sich bei den von *Ley & Winkler* isolierten kristallinen α- und β-Isomeren um reine Diastereomere handelt.

Wir danken Herrn Professor *J. F. M. Oth* für die Unterstützung dieser Arbeit.

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245. The Photochemical Behaviour of Endocyclic Oxa-enones with Substituents on the C-C Double Bond[1])

(Preliminary Communication)

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(8. X. 74)

Summary. Alkyl substituents on C_β of the C—C double bond hinder both photodimerization of endocyclic oxa-enones (**1**–**4**) and their photocycloaddition to olefins, and they cause a loss of regiospecificity in dimerization in unpolar solvents. The oxa-enone **3** which like the bicyclic compound **4** fails to dimerize at all, is shown to incorporate deuterium at the tertiary isopropyl carbon atom in CD_3OD solution as a consequence of a bimolecularly initiated photoenolization.

Several stereochemical and mechanistic aspects of the photochemical behaviour of unsubstituted cyclic oxa-enones, *inter alia* **1**, have been discussed in previous papers [1]. The present work concerns an investigation into the effects of substituents on the C–C double bond. In order to first minimize the electronic effects of the substituent, the oxa-enones **1**–**4** have been chosen. Photodimerization and photoaddition to charge-symmetric olefins (cyclopentene as a sterically unhindered and 2,3-

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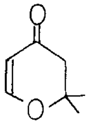
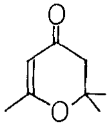
[1]) Presented at the Vth IUPAC Symposium on Photochemistry, Enschede, The Netherlands, July 1974.

dimethyl-2-butene as a hindered olefin) were studied. All irradiations were carried out at room temperature unless specified otherwise.



1



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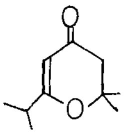

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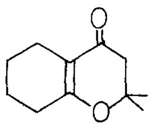
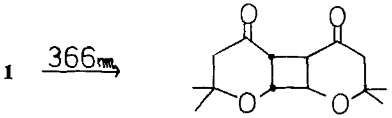


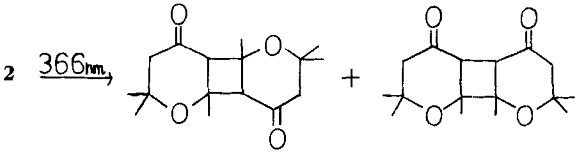
4

Compound **1** dimerizes exclusively to **5** independent of the solvent used (eq. 1). In contrast, the reaction of **2** is solvent dependent as illustrated in eq. 2[2], and compounds **3** and **4** do not dimerize at all.



5

(1)



6 **7**

(2)

product ratio 65 : 35 hexane
0 : 100 acetonitrile

The tricyclic nature of products **5**–**7** is evident from the mass (M^+, $M/2^+$), IR. (saturated 6-membered ring ketone), and NMR. spectra (absence of olefinic protons). The complete steric and substitutional pattern of the cyclobutane in **5** could be established by NMR.; ($AA'XX'$: $J_{AX} = 5.9$ Hz, $J_{AA'} = 8.5$ Hz, $J_{XX'} = 0.7$ Hz). These data correlate closely with those of the analogous product which had been obtained previously [1] by photodimerization of a five-membered cyclic oxa-enone. The constitution of the dimers **6** (head-to-tail) and **7** (head-to-head) was also determined by NMR. The H–H coupling constant of the low field ^{13}C–H satellite of the cyclobutyl proton was found to be $J = 0$ Hz for **6** and $J = 8$ Hz for **7**, in accordance with this assignement. The *cis*-ring junctions and *anti*-configurations are ascribed to **6** and **7** on the following basis. Both products remain unchanged on treatment with basic alumina (the same is valid for **5**) and should therefore represent the more stable ring fusion. Furthermore the *anti*-configuration is assumed to be sterically less crowded also in these dimers which are consequently assigned the same structural type as the well established compound **5**.

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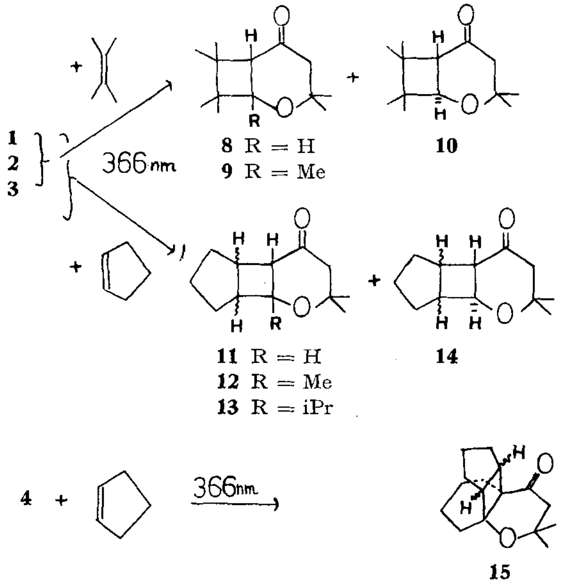
[2] *Yates & McGregor* [2] found only the head-to-head orientation in the photodimerization of 2,6-dimethyl-2,3-dihydro-4-pyrone in an unspecified 'variety of solvents'. It appears, however, unlikely that the additional methyl group in **2** exerts an important directional influence on the orientation of the dimerization, the more so as the solvent-dependent product selectivity of this oxa-enone parallels that of 3-methyl-2-cyclopentenone [3] [4].

For the difference in behaviour of **1** and **2** the following interpretation can be advanced. As the alkyl substituent reduces the difference in charge densities in the C–C double bond of the excited molecule, dipole-dipole interactions of the ground state, as suggested by *Wagner* [5] and *Herndon* [6] become predominant in unpolar solvents, leading to the preferential formation of **6**. In polar solvents the dipole-dipole interactions are sufficiently weakened for the influence of the charge separation to prevail and effect a regiospecific dimerization to **7**.

The addition to cyclopentene proceeds smoothly for all oxa-enones, whereas only **1** (*cf.* [1]) and **2** add to 2,3-dimethyl-2-butene (eq. 3). The cycloaddition of the non-substituted compound **1** afforded in both runs *cis*- and *trans*-fused products, **8**/**11** and **10**/**14** respectively. While the bicyclic *trans*-product **10** is sufficiently stable to be isolated, the tricyclic analog **14** could only be detected by analytical gas chromatography, but did not survive under preparative conditions of separation. In the reaction mixtures of the substituted oxa-enones **2** and **3** no *trans*-fused adducts were found.



(3)

The *cis*- and *trans*-configurations of products **8** and **10** (ratio = 60:40) derive from the vicinal coupling constants of 5.0 and 10.7 Hz, respectively, of the cyclobutane protons and are confirmed by the fact that the *trans*-adduct isomerizes to the *cis*-isomer on contact with basic alumina. The *cis*-structure of the cyclopentene adduct **11** (89%) is supported by the same NMR. evidence ($J = 6.5$ Hz), whereas the stability of products **9**, **12** and **13** towards basic alumina serves as the only proof for their *cis*-fusion[3]). In the mixture of adducts **11** and **14** (11%) the latter was converted to the isomer **11** by the same treatment. No attempt has been made to determine the configuration of adduct **15**.

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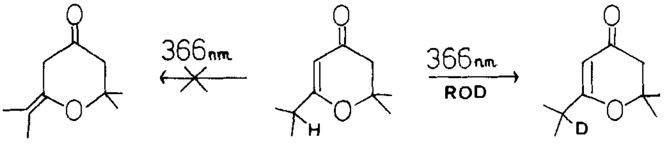
[3]) **12** is a mixture (80:20) as well as **13** (77:23). The major products are expected to have *anti*-configurations.

The differences in the results of cycloaddition (eq. 3) are already satisfactorily explained using a purely steric argument based on the degree of olefinic substitution in both oxa-enone and alkene. A second interpretation introduces additionally the concept that the choice of the site of primary bond formation (*cf.* [1]) responds to the steric conditions. Thus, the addition to cyclopentene would occur at C_α of all four oxa-enones whereas photodimerization and addition to 2,3-dimethyl-2-butene would be initiated at C_β of **1** and **2**, and the bulkier substituents of **3** and **4** would prevent the addition step altogether.

A plausible assumption to account for the apparent failure of **2** and **3** to furnish trans-fused products as does **1** can be seen in different conformations of the 6-membered ring in the 1,4-diradical intermediate owing to the double bond substitution. In other words, the activation entropy of ring closure to the *trans*-product can be expected to be more negative in the case of the alkylated oxa-enones [1]. This argument is of course only valid unless, contrary to expectation, *trans*-products should have formed in even greater proportions from **2** and **3** than from **1** and escaped detection entirely.

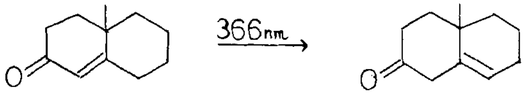
Finally it is interesting to note that no photochemical double bond migration could be observed for **2**, **3** and **4** even at –40° (see, *e.g.*, eq. 4).



16

(4)

As the quantum yield for this process [7] is relatively important ($\Phi = 2.10^{-2}$ in C_6F_6) for compound **17** (eq. 5), it could have been expected that this reaction might also occur with the alkylated oxa-enones and thus account in the case of **3** and **4** – which do not dimerize for steric reasons – for a 'chemical path' of energy dissipation and return to the ground state. A hydrogen transfer from a ground state to an excited molecule has been proposed [7] [8] to initiate the photochemical deconjugation, followed by a back transfer of hydrogen to afford a dienol which finally ketonizes to either or both the α,β- and β,γ-unsaturated ketone.



17

(5)

On the basis of this mechanism, however, the oxygen substitution on C_β in the oxa-enones would increase the negative charge density on C_γ of the dienolate anion produced in the course of an analogous photoreaction. It could thus sufficiently favour protonation on C_γ and regeneration of starting material to exclude any formation of the double-bond-migrated isomer. In order to probe this possibility experimentally **3** was irradiated in a CD_3OD/hexane 1:10. The NMR. analysis of the photolyzed ketone showed that indeed deuterium was incorporated at the tertiary isopropyl carbon (*cf.* **16**).

Financial support of this work by the *Fonds National Suisse de la Recherche Scientifique* (grant n. 2.8220.73) and *Firmenich* SA, Geneva, is gratefully acknowledged.

Experimental Part

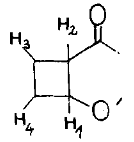
Compounds. The oxa-enones have been described: **1** [9], **2** [10], **3** [11], **4** [12]. Before use **1–3** were distilled and **4** was crystallized to constant m.p.; purity control by VPC. and spectral data. Of the solvents used for photolysis, hexane was spectroscopic grade and acetonitrile (*Fluka*) puriss. p.a. A generous gift of 2,3-dimethyl-2-butene – vacuum distilled at 30° – by Dr. *R. Rienäcker, Max Planck* Inst. f. Kohlenforschung in Mülheim/Ruhr, is gratefully acknowledged. Cyclopentene was puriss. *Fluka.*

Photolysis. Were carried out with a *Philips* HPK 125W mercury lamp through a filter solution with a cut-off at 340 nm. Before irradiation the solutions were flushed with Ar or N_2 although no difference in reactivity of non-deaereated solutions was observed. In all experiments $5 \cdot 10^{-2}$M solutions of oxa-enones were irradiated for 48 h (dimerizations) or 24 h (cycloadditions in the presence of $5 \cdot 10^{-1}$M olefin). The dimers were obtained directly in crystalline form and the other adducts were isolated by VPC. (**9**, **11**, **12**, **13** and **15**: 180°, 2% SE on Chromosorb G-AW-DMCS. **8** and **10**: 120°, 5% SF 96 on Silicon oil).

Details on experimental procedures and results will be reported in a full paper.

Table. *Selected Data of Photoproducts*

Compound	M.p.	IR. (CCl_4) ν' C=O (cm^{-1})	NMR. ($CDCl_3$)[a]) δ_{H_1}	δ_{H_2}	J_{12}	J_{23}	J_{14}
5	127°	1725	4.27	3.30	5.9	8.5	0.7
6	183°	1710		2.72			
7	127°	1700		2.96			
8		1710	3.82	2.52	5.0		
9		1705		2.35			
10		1725	3.67	2.49	10.7		
11		1710	4.02	2.90	6.5	6.5	2.8
12		1705		2.80		b)	
13		1705		2.70		b)	
15		1700					

a) 

J in Hz

b) *J* not determined.

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246. Reaction of Singlet Oxygen with 2-Methylnorborn-2-ene, 2-Methylidenenorbornane, and their 7,7-Dimethyl Derivatives. The Transition State Geometry for Hydroperoxidation.

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(9. VIII. 74)

Summary. The dye-sensitized photo-oxygenation of 2-methylnorborn-2-ene (**3**), 2-methylidenenorbornane (**4**) and their 7,7-dimethyl derivatives (**5** and **6**) has been studied. In all cases allylically rearranged hydroperoxides were formed, except that **4** also gave a little norbornanone (presumably from the dioxetane) and **5** gave some *endo*-3,7,7-trimethylnorbornan-2-one as a secondary photoproduct. It was found that the *exo*/*endo* attack ratios by singlet oxygen on **3** and **5** are 66 and 0.19. By exploiting the C (3) monodeuteriated derivatives, **4** and **6** showed ratios of 28 and 0.67.

Rates of reactivity of the olefins **3** and **4** were compared to methylidenecyclopentane, 1-methylcyclopentene and 1-methylcyclohexene as monocyclic standards. Additionally, comparative rates between the 7,7-dimethyl olefins and their parents were measured. When further comparison was made of the rate ratios partitioned for *exo* and *endo* attack, it was seen that oxygen experienced a 500- to 1000-fold rate retardation on approach to the *endo* side of **3** compared to that for its monocyclic analogue. *Exo* rates between the parent norbornene **3** and its 7,7-dimethyl derivative **5** showed a 250-fold decrease. Although four times smaller than the difference reported for epoxidation, the evidence clearly pointed to a one-step cyclic process as the rate determining step for photo-oxygenation. The steric evidence, taken with the low values found for the intermolecular isotope effects of 1.14 ± 0.01 and 1.02 ± 0.01 observed for *exo* and *endo*-3-deuterio-2-methylidenenorbornanes, permits the deduction that the transition state is largely dipolar. In the early stages of the addition bonding between one end of the oxygen molecule and the terminal vinyl carbon is advanced. At the same time positive charge is dispersed by hyperconjugation between the central carbon atom and the allylic carbon-hydrogen bond. At a later stage the anionic oxygen atom abstracts the loosened allylic hydrogen atom to create the hydroperoxide. No evidence for the formation of a discrete perepoxide intermediate was obtained.

Introduction. – The dye-sensitized photo-oxygenation of mono-olefins can follow two distinct courses [1]. The reagent, singlet oxygen, can either attack the double bond directly to give a dioxetane, or the allylic C–H bond can be involved as well, when an allylically rearranged hydroperoxide is formed. Which of the two courses is actually followed for a particular olefin depends mainly on the nature of the allylic part. Dioxetanes are usually formed from strained or electron-rich double bonds [2]. However, the production of hydroperoxides requires not only the presence of an allylic C–H bond, but that it effectively conjugates with the adjacent double bond [3].