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THE PHOTOCHEMICAL BEHAVIOUR OF CYCLIC OXA-ENONES†

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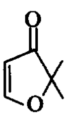
Abstract—Photodimerization of the title compounds **1** and **2**, as well as photoaddition to polarized olefins, proceed in a regiospecific manner. Product analysis by NMR is facilitated because of the simple spectra of the oxa-enones. A reaction pathway for the photoaddition of **1** to 2-butene is suggested.

In a recent review on enone photoannelation the author[1] pointed out that there are still several questions to be answered; for instance, detailed studies on the stereochemistry of the adducts are missing. In order to investigate this problem, the photoaddition reactions of oxa-enones[2,3] **1** and **2** have been studied.



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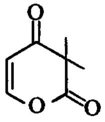

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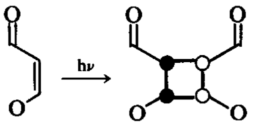
RESULTS

$n\pi^*$-Excitation of **1** and **2** leads to the following reactions:

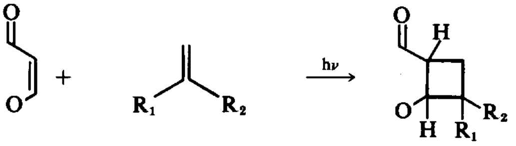
1. *Photodimerization.* Only one photodimer, the head-to-head *cis-anti-cis* isomer is formed on irradiation of **1** or **2** in various solvents (Eq. 1).



1; 2 3; 4 (1)

2. *Photoaddition to olefins.* (a) Photoaddition of **1** to tetramethylethylene gives the cyclobutane **5**, whilst **2** adds to the same olefin to yield a 1 : 1 mixture of the *cis-* and *trans-*fused products **6c** and **6t**. No oxetane formation was observed, neither here, nor in the following photoadditions.

(b) Photoaddition of **1** and **2** to isobutene, ketene dimethylacetal and ethyl–vinyl ether results in the regiospecific formation of the cyclobutane derivatives **7–12** (Eq. 2).

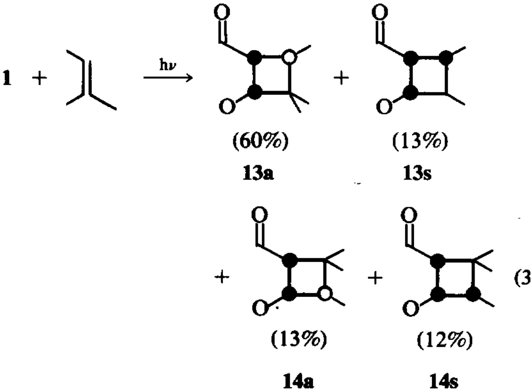


1; 2	$R_1 = R_2 = Me$	**7; 8c, 8t**
	$R_1 = R_2 = OMe$	**9; 10**
	$R_1 = H, \quad R_2 = OEt$	**11a, 11s; 12a, 12s**
	Tetramethylethylene	**5; 6c, 6t**

(2)

2 yields only *cis-*fused oxabicyclooctanes with the alkoxyolefins, but a 1 : 1 mixture of *cis-* and *trans-*fused products is obtained with isobutene. In contrast, **1** yields only *cis-*fused oxabicycloheptanes with each olefin.

(c) Photoaddition of **1** to 2-methyl-2-butene yields a mixture of the four isomers **13** and **14**. The reaction is regioselective with the predominant orientation of addition being the same as for the olefins mentioned above (Eq. 3). The addition of **2** proceeds in a similar fashion and the eight isomers formed were partially separated by chromatography on neutral silica-gel. The main product **15a** has the same stereochemistry as **13a**.



(60%) **13a** (13%) **13s** (13%) **14a** (12%) **14s** (3)

(d) Photoaddition of **1** and **2** to *cis-* or *trans-*2-

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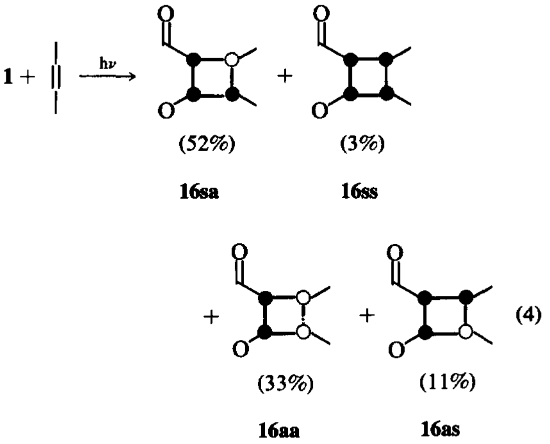
butene leads to a mixture of four and eight isomers respectively. Each oxa-enone affords an identical mixture of isomers starting from either the *cis*- or the *trans*-olefin (Eq. 4).



16sa **16ss** **16aa** **16as**

The NMR and other physical data of the new compounds are tabulated.

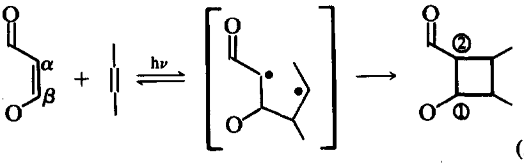
DISCUSSION

Oxa-enones have the following advantages over alicyclic enones:

(1) According to CNDO-2 calculations[4] the charge distribution in the C—C double bond in the ground state is larger. The exclusive formation of only one photodimer, as well as the regiospecificity observed in the photoaddition reactions suggests that the difference in electron densities of the reaction centres in the excited state is larger than that for cyclohexenone.[5]

(2) Product analysis by NMR is greatly facilitated due to the simple spectra of the oxa-enones, which only exhibit resonances due to the unequivalent olefinic protons and the Me-protons.

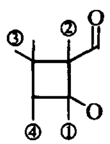
On the basis of the observed product distribution (Eq. 4) the following reaction pathway (Eq. 5) for the addition of **1** to *cis*- or *trans*-2-butene is suggested.



This reaction pathway consists of two steps: (a) addition of the olefin to C_β in **1** leading to an approximately 1 : 1 mixture of *syn*- and *anti*-adducts with respect to H①, (b) slow ring closure on C_α, resulting in a marked preference for the formation of *anti*-products with respect to H②. The fact that no olefin isomerization could be detected, (as ob-

Physical data

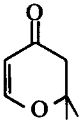
Compound	m.p. (°)	IR (CCl_4)		NMR	($CDCl_3$)	(ppm)	(Hz)	
	(b.p.)	$\nu'_{C=O}$(cm^{-1})	δ_1	δ_2	J_{12}	J_{23}	J_{14}	J_{34}
3	136[a]	1768 + 1750[e]	4·53	3·20	4·8	4·3	0·1	4·8
4	238[b]	1750 + 1725[e]	5·32	3·90	10·0[f]			
5	(75/12 mm)	1750	4·14	2·80	5·0			
6c	102[c]	1748 + 1710[e]	4·65	3·15	6·5			
6t	—	—	4·20	2·75	11·5			
7	(60/12 mm)	1752	4·18	3·06	5·0	9·5; 7·5		
8c	103[a]	1748 + 1715[e]	4·80	3·46	8·5	9·0; 5·5		
8t	119[c]	1768 + 1722[e]	4·03	3·13	11·5	10·0; 8·0		
9	(98/12 mm)	1758	4·62	2·98	6·0	10·0; 6·0		
10	84[c]	1742 + 1714[e]	4·90	3·08	9·0	9·0; 2·0		
11a	[d]	1752	4·59	3·18	7·0	11·2; 4·6	2·4	7·5; 6·3
11s	[d]	1758 + 1750	4·78	2·90	4·0	—	4·0	7·5; 6·5
12a	[d]	1765 + 1724	4·92	—	8·0	9·0; 3·0	4·0	3·0; 1·1
12s	[d]	1765 + 1725	4·78	—	10·2	10·0; 2·8	5·8	9·0; 8·4
13a	[d]	1755 + 1747	4·04	2·56	5·0	7·5		
15a	122[c]	1737 + 1708[e]	4·67	3·02	6·5	7·0		
16sa	[d]	1750	4·55	2·63	4·0	7·5	4·5	
16ss	[d]	1750	—	—	—	—	—	
16aa	[d]	1750	4·25	—	4·5	6·0	1·8	
16as	[d]	1750	4·15	3·08	6·0	9·0	1·0	



[a] Recrystallized from pentane.
[b] Recrystallized from acetone/diisopropylether.
[c] Recrystallized from ether/pentane.
[d] Isolated by GLPC.
[e] In KBr.
[f] In DMSO.

served by Corey[5]), indicates that the intermediate undergoes almost exclusively ring closure in preference to reverting to the starting materials.

Furthermore, cyclic oxa-enones should be of help in solving the problem of *trans*-product formation because of the ease of product analysis. Unfortunately the addition products of **2** are somewhat thermally unstable, so that product separation becomes difficult. At the moment, the photoaddition of **17** to various olefins is being investigated.[6] This 6-membered ring oxa-enone **17**, structurally analogous to **1**, gives *trans*-fused products which are sufficiently thermally stable to permit gas-chromatographic separation.



17

EXPERIMENTAL

General procedure for the photochemical reactions: Solns of the oxa-enone (2 g) and olefin (20 ml) in pentane (100 ml) were irradiated under N_2 at room temp in a pyrex glass apparatus with a (Philips) HPK-125W lamp. Reaction was complete after 15–18 hr.

Products **3**, **4**, **5**, **7**, **9** and **10** were isolated and purified by recrystallization or distillation.

Products **11**, **12** **13**, **14** and **16** were separated and isolated by GLPC using a capillary glass column (25 m, polypropyleneglycol). **6c** was obtained by chromatography of the product from the irradiation of **2** and tetramethylethylene through a basic alumina column; **6t** was not isolated pure.

Irradiation of **2** and isobutene led to the precipitation of **8t**; chromatography of the filtrate through a basic alumina column yielded pure **8c**. Similarly, irradiation of **2** and 2-methyl-2-butene led to the precipitation of **15a**, but only partial separation of the other isomers by chromatography on neutral silica-gel was accomplished.

The NMR spectra were recorded using a Varian HA-100 spectrometer.

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