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STRUCTURE DETERMINATION OF PHOTOCYCLODIMERS OF 2-CYCLOALKENONES VIA ENANTIOSELECTIVE GAS CHROMATOGRAPHY AND GC/MS ANALYSIS

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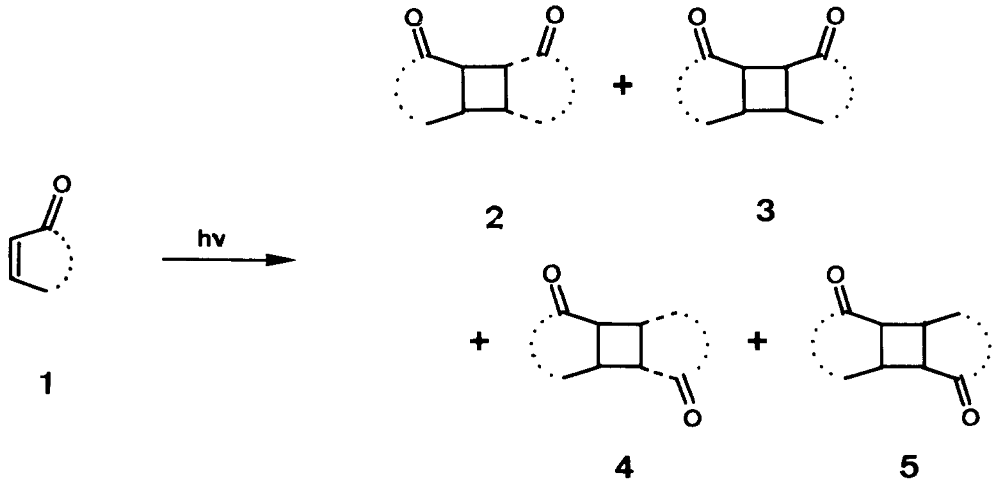
Summary. Enantioselective gas chromatography combined with GC/MS analysis allows the direct assignment of constitution and configuration of the photocyclodimers of cyclic enones <u>1a</u> - <u>1h</u> .

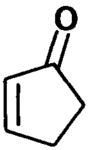
Light-induced reactions of α,β-unsaturated carbonyl compounds with olefins represent one of the most important synthetically useful photochemical reactions[1,2]. Photocyclodimers of enones have rarely been used as synthetic intermediates as an assignment of their constitution and configuration by conventional spectroscopic methods often remains ambiguous, although only the four *cis*-fused tricyclic dimers <u>2</u> - <u>5</u> are formed on irradiation of <u>1</u>.



Accounts on the structure of photocyclodimers of enones in the literature sometimes do coincide, as for 1a or 1b[3,4], or are in disagreement, as for 1c[5,6] or 1d[7,8]. On other occasions, as for 1e, they are missing[9]. For some other compounds as 1f[10], 1g[11], 1h[12], only one structural proposal has been advanced, usually after isolation of the dimers followed either by spectroscopic analysis or further chemical transformations.

We report here on a simple method allowing at the same time the qualitative and quantitative analysis of cyclobutanes 2 - 5 directly out of the reaction mixture. The method is based on the following two criteria: a) Only one head-head dimer (2) and only one head-tail dimer (5) are chiral. b) The head-head dimers (2,3) have a higher dipole moment than the head-tail dimers (4,5). Therefore gas chromatography on enantioselective phases[13] coupled with GC/MS-analysis allows to differentiate between the four isomers as the HH-dimers exhibit larger retention times than the HT-dimers, and only one HH-resp. HT-dimer (2, resp. 5) splits into antipodes on the chiral phase. The cyclobutane structures of the dimers are established by their mass spectra.

The experimental results of the reinvestigation of photocyclodimerisation of enones 1a - 1h are summarized in the Table. Our structural assignments for the dimers of 1a, 1b, 1f, 1g & 1h are in agreement with those reported in the literature. For 3-methyl-2-cyclopentenone 1c and isophorone 1d our results coincide with those described in references 6, resp. 8. The photodimer of 5,5-dimethyl-2-cyclohexenone[9] has the HT-anti-structure.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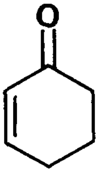
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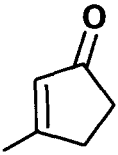
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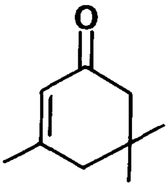
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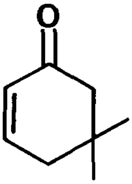
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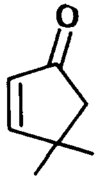
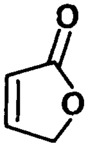

1f


1g

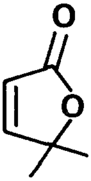

1h

Table. Photocyclodimerisation of 1 (10^{-1}M in acetonitrile, $\lambda > 340$ nm). Results of gas chromatography on chiral phases and of GC/MS analysis

Enone	product distribution (%) [a]	rel.retention times 2/4	separation factor α	column[b]/temp.[°C]
1a	2a(40), 4a(60)	1.3	2a: 1.014	A / 190
1b	2b(65), 4b(35)	1.2	2b: 1.019	B / 180
1c	2c(56), 3c(3), 4c(31), 5c(10)	2.4	2c: 1.012 5c: < 1.005	A / 190
1d	2d(59), 4d(23), 5d(18)	2.0	2d: 1.015 5d: 1.021	B / 200
1e	2e(45), 4e(55)	1.4	2e: 1.018	C / 190
1f	2f(20), 4f(80)	1.6	2f: 1.022	B / 170
1g	2g(55), 4g(45)	1.3	2g: 1.005	B / 200
1h	2h(50), 4h(50)	1.6	2h: 1.023	B / 180

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[a] determined from the peak areas in the gas chromatograms

[b] column A: 25 m glass capillary, coated with XE-60-L-valine-(R)-α-phenylethylamide[14]

column B: 15 m glass capillary, coated with XE-60-L-valine-(R)-α-phenylethylamide

column C: 15 m fused silica capillary, coated with XE-60-L-valine-(S)-α-phenylethylamide[14]

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