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INVESTIGATION OF CHIRAL INDUCTION IN PHOTOCHEMICAL OXETANE FORMATION

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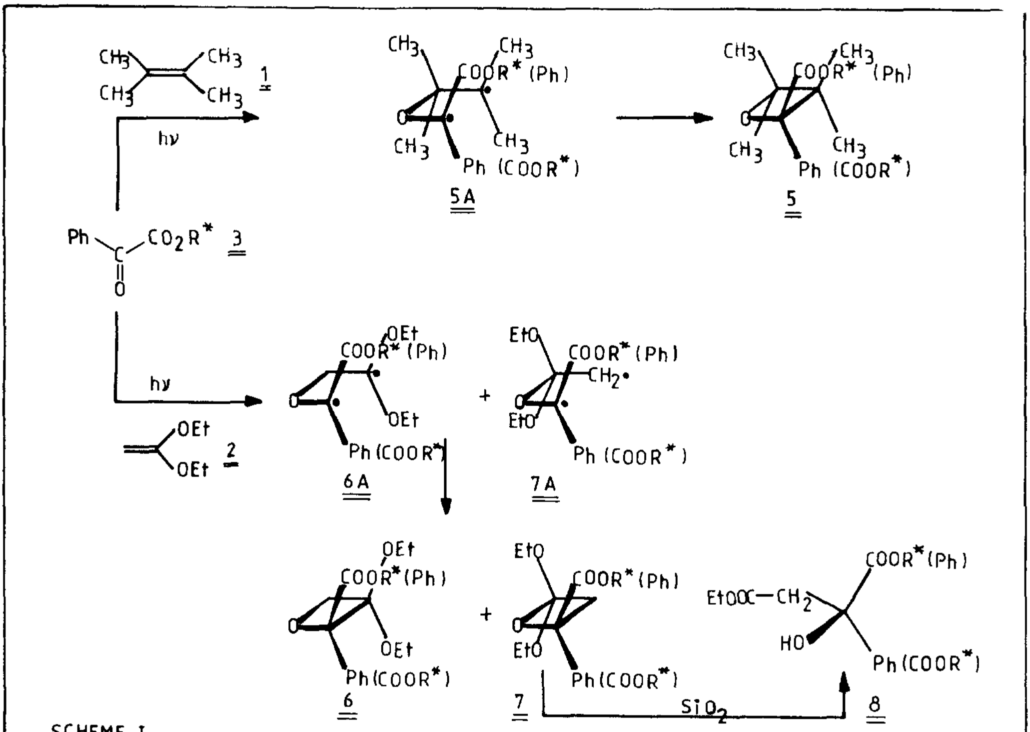
Summary: The formation of oxetanes from photochemical addition of tetramethylethylene (TME) or diethylketeneacetal with phenylglyoxylic acid esters in the "concave" position5) leads to high diastereomeric excess (d_e).

Until now only a few cases of high chiral induction in photochemical [2+2] cycloadditions in solution have been reported1-3). In contrast to the successful investigations of the chiral Diels-Alder reaction4), systematic investigations and criterion, which make high induction plausible, are lacking for photochemical cycloadditions. In order to gain better knowledge about chiral induction in photochemical reactions we chose as a model reaction, the formation of oxetanes from phenylglyoxylic acid 3 and tetramethylethylene 1 or diethylketeneacetal 2 (Scheme I). As chiral moieties we chose secondary alcohols4a,c,e) of the weakly "concave" and distinctly "concave" tpyes5) in order to correlate induction with increasing side differentiation of the prochiral carbonyl group. The results, which are collected in Table 1, render the following statements possible:



SCHEME I

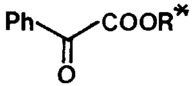
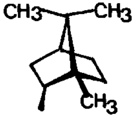
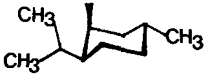
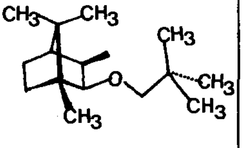
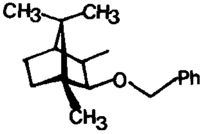
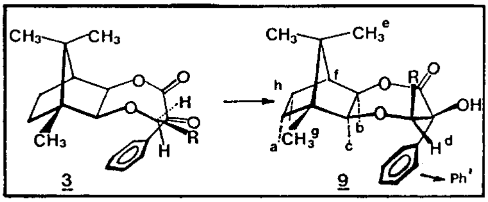
chiral alcohol	3  R*	mp °C	α_D^{22} (EtoH)	reaction-products[10]										
				5			9	6			8		$\frac{6}{7}$ [14] Ratio H^1-NMR	chem. yield % 6 + 7
				% d_e HPLC	% d_e C^{13}NMR	% chem. yield[13]	a) % d_e C^{13}NMR b) chem. yield	% d_e HPLC	% d_e C^{13}NMR	chem. yield %	% d_e C^{13}NMR	chem. yield %		
a		42-43	-26° c=0.989	16	19	59	–	–	3	50	9	20	73:27	70
b		oil	+33,4° c=1.001	15	13	43	–	–	21	48	11	24	76:24	71
c		74	-43.6° c=0.945	47	54[11]	49	–	39[12]	41	46	28	20	72:28	67
d		88-89	- 6.6° c=1.097	>96	>96	42	–	91	90	56	76	22	73:27	78
e		oil	+4.1° c=1.106	>96 –	>96[15] –	38 –	a)>96 b) 26 a)>96 b) 21.6	–	>96	36.5	>96	16	71:29	(9+6+7) 74
f		oil	-8.8° c=1.051	30	31	25	a)>96 b) 45	–	–	–	–	–	–	–

Table I

I) The diastereomeric excess (d_e) of 3b and 3c follows the results of the Prelog-atrolactinic acid analysis[6)], whereby chiral, equatorial cyclohexanols show higher induction than the axial conformers.

II) The esters 3d and 3e obviously possess in all three cases (5, 6, 8) a large degree of "concave" screening, which leads to high induction.

III) Suitable expectation suggests, that 3f would likewise have brought good results. However, the modest production of the oxetane 5f and the surprisingly high diastereoselective formation of only one of the four possible cycloaddition products obtained via carbon-carbon-sigma bond formation, indicates a special conformation of the excited ketoester (Scheme II). The proximity of the screening ethermethylene group to the prochiral keto group should be responsible for the formation of 9e and 9f.[7)]



Scheme II

3e 9e R = t-Bu

3f 9f R = Ph"

9e mp. = 142 °C α_D^{22} = +12.1° EtOH c = 0.954

9f mp. = 222 °C α_D^{22} = +75.5° EtOH c = 0.96

	H^1-NMR (90 MHz) δ/ppm 9e	9f
a	0.4-0.6	0.4-0.6
b	3.37 (d) 8Hz	3.43 (d) 8Hz
c	3.57	3.58
d	4.11	5.65
e	1.17	1.30
f	1.79 (d) 5Hz	1.95 (d)
g	0.91	0.84
h	1.2-1.7	1.3-1.8

notes: 1) If the Ph' is below the bornane ring system, positions a) are shifted to high field. - 2) The Eu(FoD)$_3$ shift experiments show a distinctly low field shift of CH_3^e and that the proton d) is syn to OH. - 3) If the Ph" has no influence of the bornane ring protons (a) but a small influence on the CH_3^e protons, the structure 9 can be concluded.

This highly diastereomeric cyclisation becomes understandable, if a cisoid conformation of the carbonyl group is envisaged (Scheme II, 3). Furthermore, in the oxetane formation the neopentyl group 5e clearly shows a better side differentiation than the benzyl group 5f. These results are in accordance with the observations of the chiral Diels-Alder reaction[4c)].

IV) The generally higher induction of the 3-ketaloxetanes 6 over the regioisomers 2-ketal oxetanes 7[8)] corresponds to the stabilising capability of the intermediate 1,4-diradical (6A, 7A)[9a)] and is in agreement with a diabatic reaction[9b)]. Contrarily, the product 9 probably is formed via an adiabatic reaction pathway. It can be further concluded from analysis of the phosphorescence spectra of compounds 3, that the geometry of the excited state is similar to ground state geometry; therefore, the model of "concave" screening in ground state reactions remains valid also to these photochemical processes.

References and notes

1) H. Gotthard, W. Lenz, Angew. Chem. 91 (1979), 926

2) B.S. Green, A.T. Hagler, Y. Rabinsohn, M. Rejtö; Isr. J. Chem. 15 (1976/77), 124-130

3) L.M. Tolbert, M.B. Ali; J. Amer. Chem. Soc. (1981) 104, 1742-44

4) a) G. Helmchen, R. Schmierer; Angew. Chem. 93 (1981), 208

b) E.J. Corey, C.A. Parnell, H.E. Ensley; J. Org. Chem. 43 (1978), 610

c) W. Oppolzer, C. Chapius, G.M. Dao, D. Reichlin, T. Godel; Tetrahedron Lett. 23 (1982) 4781-8

d) B.M. Trost in Asymmetric Reaction and Processes in Chemistry, ACS Symposium Series 185, Washington D.C., 1982, 1-20

e) W. Oppolzer, M. Kurth, D. Reichlin, C. Chapius, M. Mohnhaupt, F. Moffatt; Helv. Chim. Acta 64 (1981), 2802-2807

5) This terminology was introduced by G. Helmchen and V. Prelog; see 4a)

6) V. Prelog, H.C. Meier; Helv. Chim. Acta 40 (1953); 320-325; H.B. Kagan Stereochemistry Vol. 3, 39, Georg Thieme Publishers, Stuttgart 1977

7) a) According to ref. 2); the two analogs, (-)-2,3-di-O-methyl-L-erythritol 1,4-di-trans-cinnamate and (-)-2,3-O-isopropyliden-L-erythritol 1,4-di-trans-cinnamates were irradiated in benzene solution. Intramolecular $[2+2]$ cycloaddition occurredin both derivatives (d_e= 85 %, 6 %). - b) Under the following conditions compound 9 can be formed exclusively: 6 mmol 3f or 3e / 250 ml benzene / 110 min HPK 125 W/hν / 72 % 9f, 78 % 9e

8)The regioisomer ratio is comparable with that obtained when acetone is used as the ketone. S.H. Schröder, C.H. Orlando; J. Org. Chem. 34 (1969), 1181-87

9) a) N.J. Turro, Modern Molecular Photochemistry, Benjamin/Cummings Publishing Co. Inc. Chapter 11 (1978) 2727 Sand Hill Road, Menlo Park, California 94025;

b) H.-D. Scharf, J. Fleischhauer in Houben-Weyl, Bd. 4/5a (1976) 20, Georg Thieme Verlag, Stuttgart 1976

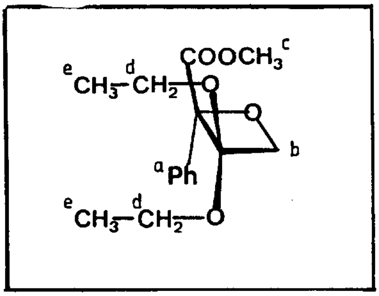
1o) Preparation: For 3: analogous to ref. 6), purification of 3b, 3e, 3f via chromatography 5 % EtOAc/hexane,yield 72-88 %. For 5: 7 mmol 1, 3 mmol 3, 250 ml benzene/hν, HPK 125 W / N_2 / 100 min. For 6 and 8: 5 ml 2, 5 mmol 3, 250 ml benzene/hν, HPK 125 W / N_2 / 210 min.

11) According to ref. 1): 53 % d_e determined by GC

12) According to ref. 1): with dimethylketeneacetal only 6 is formed (37 % d_e)

13) All reported chem. yields refer to the isolated product after separation by preparative HPLC (5 % EtOAc/hexane,Li-Chrosorb Merck, 7μ)

14) The ratio of compounds 6 and 7 were determined using H^1 NMR. The H^1 NMR spectrum of 6 ($R=CH_3$, isolated by HPLC) is as follows:



	δ/ppm	Int.	
a	7.20-7.5o	3	(m)
	7.70-7.90	2	(m)
b	4.45	1	J = 6 Hz (d)
	4.7o	1	J = 6 Hz (d)
c	3.80	3	(s) →
d	3.37	2	J = 7 Hz (q)
	3.4-3.7	2	(diastereotop)
e	1.22	3	J = 7 Hz (t)
	1.78	3	J = 7 Hz (t)

15) α_D^{22}= -19.71°, c = 0.982, EtOH, mp. = 57-61 °C

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