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CHIRAL INDUCTION IN PHOTOCHEMICAL REACTIONS-XII.[1] SYNTHESIS OF CHIRAL CYCLOBUTANE DERIVATIVES FROM (+)-5-MENTHYLOXY-2-[5H]-FURANONE AND ETHYLENE

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Abstract - The temperature dependence of the diastereoselectivity in the photochemical [2 + 2]-cycloaddition of (+)–5-menthyloxy-2-[5H]-furanone to ethylene is investigated and the preparative isolation of the pure (1R, 4S, 5S)- as well as (1S,4S,5R)-4-(+)-menthyloxy-3-oxa-2-oxobicyclo-[3.2.0]-heptane is described.

Continuing our investigations of the diastereoselective course of photochemical [2 + 2]-cycloadditions[2] we used the chiral lactone **1**(5S) [mp 79°C, $[\alpha]_D^{25}$= + 133.7°(c = 1, $CHCl_3$), Lit.[4] mp 74.2 - 74.4°C, $[\alpha]_D^{20}$= + 139.7° (c = 1, $CHCl_3$)], which is readily accessible from pseudomaleicaldehyde acid[3] and (+)-menthol in the acetone sensitized[6] reaction with ethylene. A diastereomeric mixture of **2** and **3**[7] is obtained in high chemical yield. In this way we extend our former investigations with racemic 5-alkoxy-2-[5H]-furanones.[5] The ul - attack is preferred (Fig. 1). According to our experiences[8] about the asymmetric control of bimolecular photochemical reactions, the relatively low de-values observed are due to the fact that the bond formation proceeds in an early transition state at high energy of the diabatic reaction coordinate.

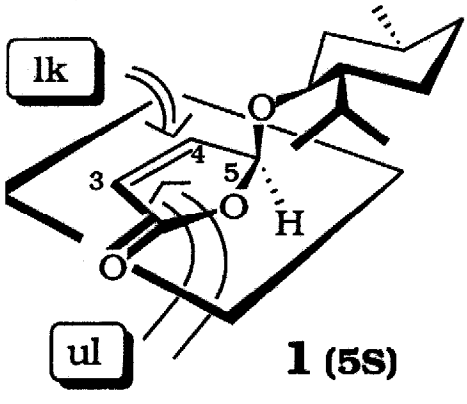

Fig. 1

The relative configuration of the isomers **2** and **3** were determined by the coupling constants of the acetal proton at position 4 (Fig. 2) with the proton at 5 from the ^1H NMR spectrum.[7] The represented absolute configurations base on Feringa's structure specifications for **1**.[4] By decreasing of the temperature the diastereoselectivity can be improved (Tab. 1). Recrystallization yields pure **2**.[7]

T/°C	de/%	Conversion/%	Chemical Yield/%
- 85	47	80	75
- 75	46	90	85
- 55	43	100	98
+ 14	29	100	98

Tab.1: Dependence of the de-value on temperature. The de-values are obtained from ^{13}C NMR spectra.

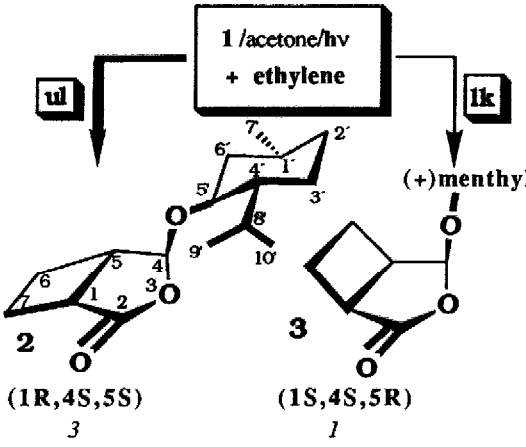

Fig. 2

Despite of the relatively low diastereoselection, however the described reaction is a preparative simple method to synthesize diastereomerically pure cyclobutane derivatives, since the two obtained diastereomers have quite different physical properties and thus are easily separated from each other by simple crystallization. NMR spectroscopy also shows the large differences of their physical properties. The obtained cyclobutane derivative is a valuable chiral building block for natural product synthesis, because chemical yield and conversion allow to produce it in large amounts.

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7. 4 g of **1** dissolved in 250 ml acetone are irradiated (HPK-125; Philips; Pyrex immersion well with vacuum jacket) while the solution is flushed with ethylene until the conversion reaches 80 to 100%. The solvent is removed. After determination of the de-value, the reaction product **2** is recrystallized from pentane [mp 116-117°C, $[\alpha]_D^{22} = +116°$ (c = 0.5, $CHCl_3$)]. **3** is purified by HPLC [15% ethyl acetate/ cyclohexane, sirup, $[\alpha]_D^{22} = +199°$ (c = 0.5, $CHCl_3$)]. - ^{1}H NMR (300 MHz, $CDCl_3$) (**2**): δ = 5.47 (s, H-4), 3.54 (d/t, J = 4.0/10.8 Hz, H-5'), 3.14(m), 2.96 (m, (H-5,-1), 2.57 (m), 2.29 (m, CH_2), 2.1 (m, H-6eq), 2.02 (sept/d, J = 7/2.4 Hz, H-8'), 1.6-1.7 (m, H-2'eq,-3eq), 1.39 (m, H-1'), 1.19 (m, H-4'), 1.01 (m, H-6'ax), 0.8 - 0.9 (m, H-2'ax, -3'ax), 0.93 (d, J = 6.4 Hz, CH_3-7'), 0.86, 0.78 (2d, J = 7.0 Hz, CH_3-9', –10') ppm. - ^{1}H NMR (300 MHz, $CDCl_3$) (**3**): δ = 5.77 (d, J = 5.7 Hz, H-4), 3.62 (d/t, J = 4.0/10.8 Hz, H-5'), 3.11 (m, H–5, –1), 2.4 - 2.6 (m, CH_2), 2.26 (sept/d, J = 7/2.4 Hz, H-8'), 2.1 (m, H-6'eq), 1.6-1.7 (m, H-2'eq, -3'eq), 1.40 (m, H-1'), 1.30 (m, H-1'), 1.03 (m, H-6'ax), 0.8-0.9 (m, H-2'ax, -3'ax), 0.93 (d, J = 6.4 Hz, CH_3-7'), 0.92, 0.96 (2d, J = 7.0 Hz, CH_3-9', –10') ppm. - ^{13}C NMR (75 MHz, $CDCl_3$) (**2**): δ = 179.88 (C-2), 104.10 (C-4), 76.25 (C-5'), 47.78 (C-4'), 39.88 (C-6'), 40.24, 37.72 (C-1, -5), 34.37 (C-2'), 31.39 (C-1'), 25.44 (C-8'), 23.22 (C-3'), 23.36 (C-7), 22.26 (C-7'), 21.78 (C-6), 20.87, 15.70 (C-9',-10') ppm. - ^{13}C NMR (75 MHz, $CDCl_3$) (**3**): δ = 178.42 (C-2), 101.20 (C-4), 77.89 (C-5'), 47.90 (C-4'), 39.83 (C-6'), 39.67, 37.86 (C-1, -5), 34.55 (C-2'), 31.40 (C-1'), 25.65 (C-8'), 23.20 (C-3'), 22.77 (C-7), 22.27 (C-7'), 17.95 (C-6), 20.97, 15.90 (C–9', -10') ppm.
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