A Convenient Synthesis of α-Vinyl-lactones by Photo-Deconjugation of α,β-Unsaturated γ- or δ-Lactones

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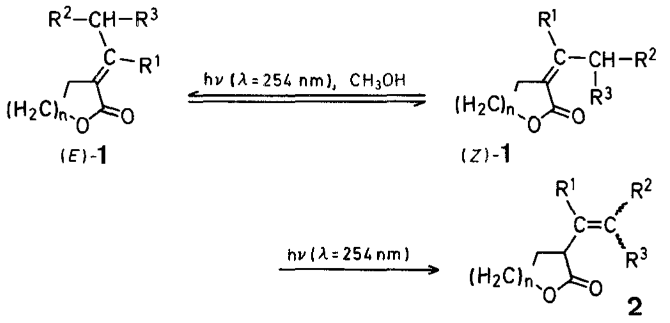
Recently, we required a convenient synthesis of α-vinyl-lactones **2**. These compounds have been relatively little studied and only a few methods are available for their preparation[1,2]. Since α-alkylidene-lactones **1** can be easily prepared[3,4,5], access to α-vinyl-lactones should be possible by isomerization.

It has been shown previously[6] that deconjugation of conjugated unsaturated ketones[7] and esters[8] can be realized by irradiation with U.V. light. Furthermore, the mechanism of photodeconjugation of 3-ethylidene-4,5-dihydro-2(3*H*)-furanone has been shown to involve a photodienol intermediate[9]. We have found that this type of isomerization reaction can be applied to prepare *α*-vinyl-lactones **2** in very high yields.

Irradiation at 254 nm of a methanolic solution of the *α*-alkylidene-butyrolactone **1a–f** or the valerolactone **1g** results in the complete disappearance of the educts and nearly quantitative transformation into the corresponding 3-alkenyl compound **2**.

The starting materials are selectively excited at this wavelength, whereas the deconjugated compounds **2** are almost unreactive under the reaction conditions (e.g., *ε* at 254 nm; **1a**: 261; **2a**: 6). The (*Z*)⇄(*E*) photoisomerization of compounds **1** is very fast, thus, the formation of **2** is independent on the initial geometry of the double bond. The deconjugation is sensitive to the solvent; the best yields of **2** are obtained in methanol.



1,2	n	R¹	R²	R³
a	1	H	H	H
b	1	H	H	CH_3
c	1	H	H	C_2H_5
d	1	H	CH_3	CH_3
e	1	CH_3	H	H
f	1	$-(CH_2)_4-$		H
g	2	H	H	H

Table. Photochemical Preparation of *α*-Vinyl-Lactones **2**

Educt	Product	Yield [%][a]	(*E*/*Z*) ratio	b.p. [°C]/torr	Molecular formula[b]	I.R. (solvent) *ν* [cm⁻¹]	¹H-N.M.R. ($CDCl_3$/TMS) *δ* [ppm]	M.S. *m/e* (M^+)
(*E*)-**1a**	**2a**	75 (90)	—	41–42°/0.5	$C_6H_8O_2$[c] (112.1)	935, 1022, 1157, 1646, 1772, 3087 (CCl_4)	2.32 (m, 2H); 3.20 (m, 1H); 4.93–5.23 (m, 2H); 5.05–6.10 (m, 3H)	112
(*Z*)-**1a**	**2a**	80 (95)	—					
(*E*)-**1b**	**2b**	72 (89)	60/40	67–68°/0.4[d]	$C_7H_{10}O_2$ (126.2)	(*E*): 965, 1028, 1160, 1675, 1770, 3040 (CCl_4) (*Z*): 710, 1025, 1150, 1660, 1780, 3030 (CS_2)	(*E*)[e]: 1.75 (t, 3H, *J* = 5.3 Hz); 2.32 (m, 2H); 3.25 (m, 1H); 4.25 (m, 2H); 5.92 (m, 1H); 6.19 (m, 1H) (*Z*)[e]: 1.75 (t, 3H, *J* = 6.3 Hz); 2.31 (m, 2H); 3.52 (q, 1H); 4.37 (m, 2H); 5.40 (m, 1H); 5.80 (m, 1H)	126 126
(*Z*)-**1b**	**2b**	73 (90)	62/38					
(*E*)-**1c**	**2c**	74 (92)	55/45	49–50°/0.07[d]	$C_8H_{12}O_2$ (140.2)	(*E*): 960, 1025, 1160, 1685, 1765, 3030 (CCl_4) (*Z*): 710, 1028, 1160, 1660, 1776, 3030 (CCl_4)	(*E*)[e]: 1.0 (t, 3H, *J* = 7 Hz); 2.15 (m, 4H); 3.22 (m, 1H); 4.40 (m, 2H); 5.46 (m, 1H); 5.71 (m, 1H) (*Z*)[e]: 1.0 (t, 3H, *J* = 7 Hz); 2.31 (m, 4H); 3.25 (q, 1H); 4.37 (m, 2H); 5.33 (m, 1H); 5.71 (m, 1H)	140 140
(*Z*)-**1c**	**2c**	72 (92)	60/40					
(*E*)-**1d**	**2d**	80 (90)	—	67–68°/0.4	$C_8H_{12}O_2$ (140.2)	839, 1024, 1156, 1679, 1769 ($CHCl_3$)	1.70 (dd, 6H, *J* = 4.5 Hz, 1.2 Hz); 1.86–2.8 (m, 2H); 3.28 (m, 1H); 4.18 (m, 2H); 4.98 (m, 1H)	140
(*Z*)-**1d**	**2d**	70 (90)	—					
1e	**2e**	72 (94)	—	44–45°/0.1	$C_7H_{10}O_2$ (126.2)	905, 1005, 1022, 1160, 1650, 1771, 3090 ($CHCl_3$)	1.87 (s, 3H); 2.35 (m, 2H); 3.27 (t, 1H, *J* = 7 Hz); 4.30 (m, 2H); 5.00 (m, 2H)	126
1f	**2f**	77 (94)	—	54–55°/0.08	$C_{10}H_{14}O_2$ (166.2)	795, 810, 1025, 1155, 1665, 1775, 3050 (CS_2)	1.37–1.82 (m, 4H); 1.82–2.50 (m, 6H); 3.15 (t, 1H, *J* = 12 Hz); 4.27 (m, 2H); 5.66 (m, 1H)	166
(*E*)-**1g**	**2g**	70 (90)	—	38–40°/0.1	$C_7H_{10}O_2$ (126.2)	922, 999, 1157, 1657, 1747, 3047, 3107 ($CHCl_3$)	1.93 (m, 4H); 3.17 (m, 1H); 4.25 (m, 2H); 4.98 (m, 1H); 5.10 (m, 1H); 5.93 (m, 1H)	126
(*Z*)-**1g**	**2g**	83 (93)	—					

[a] Yield of isolated product after distillation; value in bracket is the crude yield as estimated by ¹H-N.M.R. spectroscopy.

[b] Satisfactory microanalysis obtained: C ±0.14, H ±0.09; exception **2g**: C −0.59; determined on the (*E*/*Z*) mixture after distillation.

[c] Identical in all respects with an authentic sample; Ref.[9].

[d] b.p. measured for the mixture of (*E*)- and (*Z*)-isomers.

[e] The chemical shifts (*δ*) of the olefinic protons were determined by calculation after decoupling experiments as were the coupling constants: (*E*)-**2b**, *J* = 16 Hz; (*Z*)-**2b**, *J* = 10.65 Hz; (*E*)-**2c**, *J* = 15.6 Hz; (*Z*)-**2c**, *J* = 10.40 Hz.

If R^2 and R^3 are different, two geometrical isomers of **2** can be isolated with an observed stereoselectivity leading to the preferred formation of (*E*)-**2**. The stereochemistry is attributed on the basis of I.R. and ^{1}H-N.M.R. data with special reference to decoupling experiments[9].

^{1}H-N.M.R. spectra were determined on a Bruker CW 80 instrument. Chemical shifts are given in δ units [ppm] relative to tetramethylsilane as internal standard. I.R. spectra were determined on a Philips SP 2000 spectrophotometer and mass spectra were determined on a Jeol D 300 Mass spectrometer.

The starting materials were prepared according to the literature: Ref.[4]: **1a–d, 1g**; Ref.[3]: **1f**; Ref.[5]: **1e.**

3-(1-Propenyl)-tetrahydro-2-furanone (2b); Typical Procedure:

A methanol solution (500 ml) of the (*E*)- or (*Z*)-isomer of 3-propylidene-4,5-dihydro-2(3*H*)-furanone (**1b**; 500 mg, 3.96 mmol) is purged with argon and irradiated at 254 nm in an apparatus equipped with 12 Philips TUV 15-lamps. The deconjugation reaction is followed by analytical T.L.C. on silica gel (Merck) using a mixture of petroleum ether/ethyl acetate (7/3) as eluent. The total conversion is obtained after 6.5 h. Then the solvent is evaporated under reduced pressure. As examined by ^{1}H-N.M.R. on the crude mixture, the chemical yield of **2b** is almost quantitative.

The (*E*)- and (*Z*)-stereoisomers were separated on silica gel T.L.C. plates containing silver nitrate (10%) using a petroleum ether/ethyl acetate mixture (1/1).

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