186. Light-Induced Dehydrodimerization of Pyrroles

Preliminary Communication

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(2. VIII. 83)

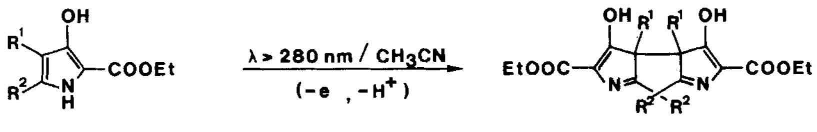
Summary

Irradiation ($\lambda > 280$ nm) of 3-hydroxypyrroles **1** in acetonitrile leads to the formation of 3,3′-bi-3*H*-pyrroles **2** in reasonable to good yields.

Some examples of oxidative 2,2′-coupling of pyrroles by means of either $Pb(OAc)_4$ or $K_3Fe(CN)_6$ have been reported in [1] [2]. We now present preliminary results on the photochemical oxidative coupling of pyrroles **1** leading to the formation of a novel class of compounds, the 3,3′-bi-3*H*-pyrroles **2**.

Irradiation ($\lambda > 280$ nm) of a 10^{-2} M solution of **1** in thoroughly degassed CH_3CN gives **2** as inferred from the mass spectra (M^+), the chemical shift of the CH_3- and CH_2-groups in the ^{1}H-NMR spectra (indicating the 3,3′-coupling pattern) and the likeness of the UV and IR spectra of all compounds **2**. The formation of **2** can be plausibly explained as occuring *via* electron transfer from excited **1** to the solvent followed either by deprotonation of the radical cation and dimerization of the so-formed radical, or by dimerization of the radical cation and subsequent deprotonation of the dication. Traces of oxygen give rise to complex product mixtures, presumably by trapping the radical intermediate. The spectroscopic data for the new compounds **1** and for compounds **2** are summarized in the *Table*.

Scheme



1 **2**

a $R^1, R^2 = H$
b $R^1, R^2 = CH_3$
c $R^1 = CH_2{=}CH{-}CH_2, R^2 = CH_3$
d $R^1 = CH_2{=}CH{-}CH_2{-}CH_2, R^2 = CH_3$
e $R^1, R^2 = (CH_2)_4$

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[1]) Part of the planned doctoral thesis, University of Hamburg.

Table. *Physical and Spectroscopic Data for* **1c**, **1d** *and* **2a–e**

Compound[a])	Yield[b]) (diastereom. ratio)	M.p.	UV (CH_3CN)	IR (KBr)	^{1}H-NMR ($CDCl_3$)	MS (M^+)
1c	36%	107°	273 (4.18)	3470, 3300, 3070, 1670	5.90 (*m*, 1 H); 5.00 (*m*, 2 H); 4.32 (*q*, 2 H); 3.14 (*m*, 2 H); 2.15 (*s*, 3 H); 1.35 (*t*, 3 H)	209, *135*
1d	40%	85°	274 (4.23)	3450, 3270, 3060, 1660	5.84 (*m*, 1 H); 5.00 (*m*, 2 H); 4.33 (*q*, 2 H); 2.46 (*m*, 2 H); 2.28 (*m*, 2 H); 2.19 (*s*, 3 H); 1.34 (*t*, 3 H)	223, *136*
2a	45% (1:1)	166°	305 (4.02)	3370, 1740, 1680	8.11 and 8.10 (*d*, 2 H); 5.15 and 5.14 (*d*, 2 H); 4.25 (*q*, 4 H); 1.25 (*t*, 6 H)	308, *155*
2b	75%	179°	309 (4.08)	3400, 1740, 1690, 1610	4.20 (*q*, 4 H); 2.19 (*s*, 6 H); 1.49 (*s*, 6 H); 1.21 (*t*, 6 H)	364, *183*
2c	65% (2:1)	95°	311 (3.95)	3400, 1740, 1690, 1600	5.69 (*m*, 2 H); 4.89 (*m*, 4 H); 4.21 and 4.07 (*q*, 4 H); 2.74 and 2.89 (*m*, 4 H); 2.15 (*s*, 6 H); 1.20 and 1.11 (*t*, 6 H)	416, *209*
2d	63% (2:1)	34°	309 (4.04)	3400, 1740, 1690, 1600	5.72 (*m*, 2 H); 4.95 (*m*, 4 H); 4.23 and 4.07 (*q*, 4 H); 2.18 and 2.15 (*s*, 6 H); 2.04 (*m*, 8 H); 1.20 and 1.11 (*t*, 6 H)	444, *136*
2e	75% (3:2)	145°	309 (4.00)	3350, 1740, 1690, 1580	4.26 and 4.10 (*q*, 4 H); 2.53 (*m*, 4 H); 2.14 and 1.89 (*m*, 4 H); 1.68 (*m*, 8 H); 1.24 and 1.17 (*t*, 6 H)	416, *209*

[a]) All new compounds gave satisfactory elemental analyses.

[b]) Yields of isolated and purified products *(cf. Exper. Part).*

It is interesting to note that **2a** does not tautomerize to a 3,3′-bi-1*H*-pyrrole. One such compound (5,5′-bis(ethoxycarbonyl)-2,2′,4,4′-tetramethyl-3,3′-bi-1*H*-pyrrole) has been reported as being formed *via Ullmann*-reaction of the corresponding 3-iodopyrrole [3] and its spectral data differ totally from the one indicated in this work.

Further studies with *O*- and *N*-alkyl and acyl derivatives of **1** are in progress to elucidate whether the conversion **1** → **2** is restricted to the 3-hydroxy derivatives.

Financial support by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* is gratefully acknowledged.

Experimental Part

General. Absorptions in the UV spectra are given in nm (logε) and in the IR spectra in cm^{-1}. Chemical shifts in the 400-MHz ^{1}H-NMR spectra are given in ppm relative to TMS (= 0 ppm) as internal standard.

Starting Materials. Pyrroles **1a** [4], **1b** and **1e** [5] were synthesized according to the references indicated; **1c** (m.p. 107 °, 36%[2])) and **1d** (m.p. 85°, 40%[2])) were prepared in an analogous reaction sequence as **1b**.

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[2]) Overall yield for two steps from the corresponding 3-alkyl-ethylacetoacetate.

Preparation of **2**. A solution of 10^{-3} mol **1** in 100 ml CH_3CN is thoroughly degassed with Ar and then irradiated through *Pyrex* for 48 h with a 250-W Hg-lamp. The degree of conversion is $\geq 80\%$ (TLC). Evaporation of the solvent, chromatography (SiO_2, CH_2Cl_2/CH_3OH 95:5) and recrystallization from cyclohexane affords **2** as a mixture of diastereoisomers.

REFERENCES

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