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Journal of Photochemistry and Photobiology A: Chemistry 105 (1997) 35–38

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A:CHEMISTRY

Photochemistry of *N*-acyl-1*H*-pyrrol-2(5*H*)-ones [1]

Matthias N. Wrobel, Paul Margaretha *

Institut für Organische Chemie der Universität Hamburg, M.L. King Platz 6, D-20146 Hamburg, Germany

Received 1 November 1996; revised 11 December 1996; accepted 2 January 1997

Abstract

On direct irradiation (254 nm) in acetonitrile, the *N*-acylpyrrolones **2a–2d** are converted into the parent (*N*-unsubstituted) lactam **1** in addition to undergoing photodegradation to polymeric material. The relative rates of formation of **1** indicate that **2a–2d** undergo cleavage of the exocyclic N–C(O) bond, followed by disproportionation of the radical pair.

On sensitized irradiation (300 nm) in hexadeuterioacetone, pyrrolones **2** are cleanly converted into 1:1 mixtures of the *cis–transoid–cis*-cyclobutadipyrrolediones **3** and **4**, contrary to similar irradiations in (hexaprotio)acetone, where competitive H abstraction from the solvent, with the subsequent formation of 2H and RH addition products of **2**, only allows for low yields of tricyclic dimers. © Elsevier Science S.A.

Keywords: Hexadeuterioacetone as sensitizer and solvent; Radical pair disproportionation; Semicyclic imides

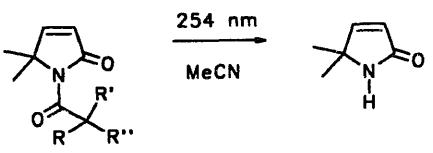
1. Introduction

In a recent investigation on the photochemistry of five-membered α,β-unsaturated lactams, we found that 5,5-dimethyl-1*H*-pyrrol-2(5*H*)-one (**1**) gave only low yields of cyclodimers, on both direct (254 nm) and acetone-sensitized (300 nm) irradiation, due to photodegradation in the former and competing photoreduction and reductive solvent addition in both sets of experiments [1]. For the *N*-acetyl derivative **2a**, we observed that these bimolecular triplet state reactions seemed to occur preferentially in sensitized irradiations since, on direct excitation, **2a** was converted into **1**, possibly via α cleavage and subsequent H transfer or intramolecular H abstraction followed by ketene elimination. In this study, we have prepared the *N*-acyl derivatives **2b–2d**, and have investigated their photochemical behaviour together with that of **2a** in order to understand this reaction more clearly. We report the results of these investigations and the advantage of using hexadeuterioacetone instead of acetone as sensitizer/solvent for the photocyclodimerization of these semicyclic imides and related *N*-acylcarbamates.

2. Results

Direct irradiation (254 nm) of imides **2a–2d** in acetonitrile gives lactam **1** (Scheme 1) in low yields (less than 40%), minor amounts of dimeric products which undergo photodegradation and polymeric material. Comparative data on these reactions **2** → **1**, summarized in Table 1, were obtained by performing irradiations in CD_3CN in a merry-go-round set-up and monitoring the formation of **1** by ^1H NMR spectroscopy.

On monitoring the sensitized photodimerization of **2a–2d** by ^1H NMR in $(CD_3)_2CO$, we observed that the conversion to dimers (invariably a 1:1 mixture of **3** and **4** (Scheme 2)) occurred cleanly and in near-quantitative yield for 3×10^{-1} M solutions, contrary to similar experiments in acetone, where lower yields of dimers were obtained due to the competitive formation of dihydro compounds, RH adducts as well as hydrodimers, all arising via H abstraction from ground state acetone. We therefore extended this method to **1** and the *N*-boc-protected lactam **5**, both undergoing nearly quantita-



1

	R	R'	R''
2a	H	H	H
2b	H	H	CH_3
2c	H	CH_3	CH_3
2d	CH_3	CH_3	CH_3

Scheme 1.

* Corresponding author. Tel.: +49 40 4123 4316; fax: +49 40 4123 2893; e-mail: margpaul@chemie.uni-hamburg.de

[1] Dedicated to Professor Dr. Hans Paulsen, University of Hamburg, on the occasion of his 75th birthday.

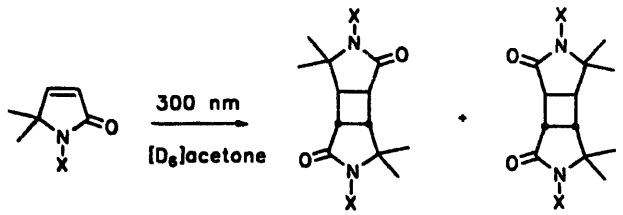
PII S1010-6030(97)00010-5

Table 1
Relative rates of formation of **1** on irradiation (254 nm) of **2a–2d** (10^{-1} M) in CD_3CN: (A) measured rates; (B) statistically corrected values for α-H abstraction step only

Compound	A	B
2a	6.9	1.0 (1/3 CH_3)
2b	9.9	2.3 (1/2 CH_3CH_2)
2c	6.5	2.8 (1/1 $(CH_3)_2CH$)
2d	1.0	–

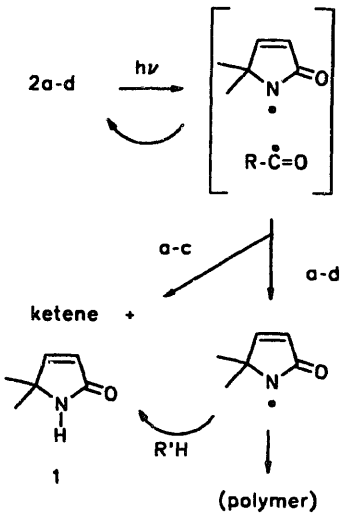
tive dimerization to 1:1 mixtures of **6** and **7** and **8** and **9** respectively. Typical product ratios (dimers to reduction products) for 3×10^{-1} M solutions of pyrrolones are 84:16 in hexadeuterioacetone and 55:45 in acetone; for 1×10^{-1} M solutions, these values decrease to 75:25 and 38:62 respectively.

Competitive type I and II cleavage processes have been discussed by Machida et al. [2] for the formation of pyrrolidin-2-one on irradiation of *N*-acetyl-, propionyl- and butyryl-pyrrolidinones in acetonitrile. Although no differentiation between these alternative mechanisms has been proposed, it is evident that so-called "semicyclic" imides undergo α cleavage between the N atom and the external carbonyl group. The relative selectivities for the abstraction of primary vs. secondary vs. tertiary hydrogens by the oxygen of an excited carbonyl group [3] are roughly 1:20:100, comparable with those observed for abstractions by tert-butoxy radicals [4] (1:8:36 at 25 °C). The corresponding values (Table 1) found for the conversion of compounds **2** to lactam **1** do not fit with those given above, but rather with those reported for H abstraction by nitrogen in excited 2-alkyl-quinolines [5] (1:2.3:2.5) or imidyl radicals [6]; this suggests that singlet excited compounds **2** undergo α cleavage only, the acceleration of the formation of **1** observed for **2a**, **2b** and **2c** reflecting the rate of disproportionation of the radical pair [7] to **1** and a ketene compared with recombination (to starting material) and dissociation to free radicals (Scheme 3).



	X		
2a	$COCH_3$	3a	4a
2b	COC_2H_5	3b	4b
2c	$COCH(Me)_2$	3c	4c
2d	$COC(Me)_3$	3d	4d
1	H	6	7
5	$COOC(Me)_3$	8	9

Scheme 2.



Scheme 3.

Deuterium atom abstraction from alkanes or alkylbenzenes by radicals, e.g. Cl˙ or tert-BuO˙, is about 5–10 times slower than the corresponding H atom abstraction [8], and this k_H/k_D ratio is reflected in the (intermolecular) reaction of triplet excited **2** (or **1**, **5**) with acetone as H atom donor. Despite its relatively high price, hexadeuterioacetone can advantageously replace acetone as solvent/sensitizer in reactions in which H atom abstraction from acetone becomes competitive and where the solvent can be recovered by distillation, i.e. where neither starting material(s) nor product(s) are low boiling compounds.

3. Experimental details

IR and UV spectra were obtained using Perkin–Elmer 1720 X and 552 spectrometers respectively. ^{1}H NMR (500 MHz), ^{13}C NMR (100.63 MHz) and mass (MS) (70 eV) spectra were obtained. Photolyses were performed in a Rayonet RPR-100 photoreactor (λ = 254 nm and 300 nm). Acetone-d_6 (99.8 at.% D) was purchased from E. Merck. Chromatographic separation of the photoproducts was performed on silica gel (0.040–0.063 mm).

3.1. Starting materials

5,5-Dimethyl-1*H*-pyrrol-2(5*H*)-one (**1**) [1] and 1-acetyl-5,5-dimethyl-1*H*-pyrrol-2(5*H*)-one (**2a**) [1] were synthesized according to literature procedures.

3.2. N-Acyl-5,5-dimethyl-1H-pyrrol-2(5H)-ones 2b–2d

To a solution of 1.11 g (10^{-2} mol) of **1** in 50 ml of tetrahydrofuran (THF) under N_2 was added 240 mg (10^{-2} mol) of NaH. The mixture was stirred until all NaH had reacted (clear solution). At room temperature, 10^{-2} mol of acid chloride in 50 ml of THF was added dropwise and the mixture was stirred at 60 °C for 16 h. After cooling, 500 ml

of CH_2Cl_2 and 10 ml of H_2O were added, and the organic phase was separated, washed with aqueous $NaHCO_3$ and saturated aqueous NaCl solution and then dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by chromatography with diethyl ether as eluent.

3.2.1. 5,5-Dimethyl-1-propanoyl-1H-pyrrol-2(5H)-one (2b)

Yield, 81%; m.p., 38 °C. IR (KBr) ν: 1719, 1691 cm^{-1} (C=O). UV (CH_3CN) λ_{max} (log ϵ): 229 nm (3.79). ^1H NMR ($CDCl_3$) δ: 1.15 (t, J=7.1 Hz, 3H), 1.56 (s, 6H), 2.96 (q, J=7.1 Hz, 2H), 5.99 (d, J=6.1 Hz, 1H), 7.11 (d, J=6.1 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 8.2 (q), 23.6 (q), 31.3 (t), 66.2 (s), 123.2 (d), 159.6 (d), 170.3 (s), 174.1 (s). MS (70 eV) m/z (%): 167 (3) [M^+], 96 (100). $C_9H_{13}NO_2$ (167.2): calculated: C, 64.65%; H, 7.84%; N, 8.38%; found: C, 64.42%; H, 7.80%; N, 8.19%.

3.2.2. 5,5-Dimethyl-1-isobutyryl-1H-pyrrol-2(5H)-one (2c)

Yield, 74%; m.p., 33 °C. IR (KBr) ν: 1729, 1697 cm^{-1} (C=O). UV (CH_3CN) λ_{max} (log ϵ): 231 nm (3.79). ^1H NMR ($CDCl_3$) δ: 1.15 (d, J=7.1 Hz, 6H), 1.55 (s, 6H), 3.84 (sept., J=7.1 Hz, 1H), 5.99 (d, J=6.1 Hz, 1H), 7.11 (d, J=6.1 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 18.8 (q), 23.6 (q), 34.2 (d), 66.4 (s), 123.3 (d), 159.7 (d), 169.8 (s), 177.8 (s). MS (70 eV) m/z (%): 181 (14) [M^+], 112 (100). $C_{10}H_{15}NO_2$ (181.2): calculated: C, 66.27%; H, 8.34%; N, 7.73%; found: C, 65.88%; H, 8.36%; N, 7.62%.

3.2.3. 5,5-Dimethyl-1-pivaloyl-1H-pyrrol-2(5H)-one (2d)

Yield, 83%; m.p., 55 °C. IR (KBr) ν: 1724, 1681 cm^{-1} (C=O). UV (CH_3CN) λ_{max} (log ϵ): 239 nm (3.78). ^1H NMR ($CDCl_3$) δ: 1.36 (s, 9H), 1.53 (s, 6H), 5.95 (d, J=6.1 Hz, 1H), 7.06 (d, J=6.1 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 24.1 (q), 26.4 (q), 42.5 (s), 67.8 (s), 123.4 (d), 159.4 (d), 168.8 (s), 179.6 (s). MS (70 eV) m/z (%): 195 (0.5) [M^+], 140 (100). $C_{11}H_{17}NO_2$ (195.3): calculated: C, 67.66%; H, 8.76%; N, 7.17%; found: C, 67.21%; H, 8.83%; N, 7.18%.

3.3. tert-Butyl-2,5-dihydro-5,5-dimethyl-2-oxo-1H-pyrrole-1-carboxylate (5)

Compound **5** was obtained from $(boc)_2O$ and the sodium salt of **1** in THF under Ar according to Ref. [1]. Purification was performed by chromatography (Et_2O). Yield, 95%; m.p., 92 °C. ^1H NMR ($CDCl_3$) δ: 1.53 (s, 6H), 1.59 (s, 9H), 5.98 (d, J=6.1 Hz, 1H), 7.01 (d, J=6.1 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 24.1 (q), 28.2 (q), 65.4 (s), 82.8 (s), 123.5 (d), 149.5 (s), 157.8 (d), 169.3 (s). MS (70 eV) m/z (%): 211 (0.1) [M^+], 57 (100). $C_{11}H_{17}NO_3$ (211.3): calculated: C, 62.54%; H, 8.11%; N, 6.63%; found: C, 62.41%; H, 8.16%; N, 6.59%.

3.4. Direct irradiation (254 nm) of imides 2

Solutions of 0.01 mmol of **2a**, **2b**, **2c** and **2d** in 1 ml of CD_3CN containing 0.002 mmol of undecane as internal standard were irradiated in quartz NMR tubes in a "merry-go-round" set-up. Every 3 min, ^1H NMR spectra were recorded to monitor the conversion **2** → **1**. After 30 min, about 50% of the starting material had disappeared. The relative rates of formation of **1** are summarized in Table 1.

3.5. Comparative sensitized irradiation (300 nm) in acetone-d_6 and acetone

Solutions containing **1**, **2a**, **2b** or **2c** (3×10^{-1}–5×10^{-2} M) were irradiated in hexadeuterioacetone and acetone (1 ml) using a merry-go-round set-up for 3 h. After evaporation of the solvent, the relative amount of tricyclic dimers vs. reduction (H abstraction) products was determined by ^1H NMR spectroscopy in $CDCl_3$ by measuring the integrals of the ring methyl protons of the different photoproducts.

3.6. Preparative runs in acetone-d_6

Ar-degassed solutions of 3 mmol of **2a–2d**, **5** or **1** in 10 ml of acetone-d_6 were irradiated for 4 h. After filtration of the precipitated pure *HT* dimer (**3**, **8** or **6**), the solvent was regained by distillation at 100 Torr. Acetone (3 ml) was added to the residual dimer mixture and cooled to 5 °C, leading to further precipitation of the pure *HT* dimer, which was again filtered. Evaporation of the solvent afforded the crude *HH* dimer (**4**, **9** or **7**) which was purified as described below. This work-up procedure was unsuccessful for the irradiation of **2b** because dimers **3b** and **4b** do not have different solubilities. The coupling constants for the cyclobutane (AA'XX') protons of the *HT* dimers **3**, **6** and **8** are the same (this also applies to the *HH* dimers **4**, **7** and **9**), and are therefore only given once. The crystal structures of **8** and **9** have been determined by X-ray analysis [9].

3.6.1. cis–transoid–cis-2,5-Diacetylperhydro-3,3,6,6-tetramethylcyclobuta[1,2-c:3,4-c']dipyrrole-1,4-dione (3a)

Yield: 30%; m.p., 229 °C. ^1H NMR (acetone-d_6) δ: 1.43 (s, 6H), 1.65 (s, 6H), 2.40 (s, 6H), 2.57 and 3.42 (AA'XX', J_{AX}=7.2 Hz, $J_{AA'}$=1.7 Hz, $J_{AX'}$=3.1 Hz, $J_{XX'}$=1.0 Hz, 4H). ^{13}C NMR (acetone-d_6) δ: 23.9 (q), 26.9 (q), 27.6 (q), 42.3 (d), 46.9 (d), 64.5 (s), 172.6 (s), 178.0 (s).

3.6.2. cis–transoid–cis-2,5-Diacetylperhydro-3,3,4,4-tetramethylcyclobuta[1,2-c:3,4-c']dipyrrole-1,6-dione (4a)

From pentane–acetone (3:1); yield, 20%; m.p., 108 °C. ^1H NMR (acetone-d_6) δ: 1.39 (s, 6H), 1.57 (s, 6H), 2.41 (s, 6H), 2.88 and 3.13 (AA'XX', J_{AX}=6.9 Hz, $J_{AA'}$=5.7 Hz, $J_{AX'}$=1.2 Hz, $J_{XX'}$=1.2 Hz, 4H). ^{13}C NMR (acetone-d_6) δ: 22.8 (q), 25.9 (q), 27.0 (q), 43.0 (d), 45.3 (d), 64.5 (s), 172.8 (s), 176.8 (s).

3.6.3. Mixture (1:1) of cis–transoid–cis-2,5-dipropanoyl perhydro-3,3,6,6-tetramethylcyclobuta[1,2-c:3,4-c']-dipyrrole-1,4-dione (3b) and cis–transoid–cis-2,5-dipropanoylperhydro-3,3,4,4-tetramethylcyclobuta-[1,2-c:3,4-c']dipyrrole-1,6-dione (4b)

Compound **3b**: ^{1}H NMR ($CDCl_3$) δ: 1.06 (t, J=7.1 Hz, 6H), 1.43 (s, 6H), 1.64 (s, 6H), 2.79 (m, 4H), 2.56 and 3.40 (AA'XX', 4H); ^{13}C NMR ($CDCl_3$) δ: 8.5 (q), 23.9 (q), 27.7 (q), 32.1 (t), 41.6 (d), 46.4 (d), 64.3 (s), 175.6 (s), 176.3 (s). Compound **4b**: ^{1}H NMR ($CDCl_3$) δ: 1.06 (t, J=7.1 Hz, 6H), 1.40 (s, 6H), 1.57 (s, 6H), 2.03 (m, 4H), 2.87 and 3.12 (AA'XX', 4H). ^{13}C NMR ($CDCl_3$) δ: 8.4 (q), 22.8 (q), 26.1 (q), 32.2 (t), 42.6 (d), 45.0 (d), 63.9 (s), 176.4 (s), 177.0 (s).

3.6.4. cis–transoid–cis-2,5-Diisobutyrylperhydro-3,3,6,6-tetramethylcyclobuta[1,2-c:3,4-c']dipyrrole-1,4-dione (3c)

Yield, 15%; m.p., 183 °C. ^{1}H NMR ($CDCl_3$) δ: 1.15 (d, J=6.6 Hz, 12H), 1.46 (s, 6H), 1.64 (s, 6H), 2.46 and 3.28 (AA'XX', 4H), 3.72 (sept., J=6.6 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 18.2 (q), 19.7 (q), 23.7 (q), 27.8 (q), 35.1 (d), 41.7 (d), 46.4 (d), 64.5 (s), 176.6 (s), 180.1 (s).

3.6.5. cis–transoid–cis-2,5-Diisobutyrylperhydro-3,3,4,4-tetramethylcyclobuta[1,2-c:3,4-c']dipyrrole-1,6-dione (4c)

Chromatography (pentane–acetone, 10:1) afforded the compound in 85% purity only. ^{1}H NMR ($CDCl_3$) δ: 1.15 (d, J=7.1 Hz, 6H), 1.16 (d, J=7.1 Hz, 6H), 1.41 (s, 6H), 1.50 (s, 6H), 2.59 and 3.15 (AA'XX', 4H), 3.76 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 18.0 (q), 19.9 (q), 22.5 (q), 26.3 (q), 35.2 (d), 42.5 (d), 45.0 (d), 64.0 (s), 175.1 (s), 180.3 (s).

3.6.6. cis–transoid–cis-2,5-Dipivaloylperhydro-3,3,6,6-tetramethylcyclobuta[1,2-c:3,4-c']dipyrrole-1,4-dione (3d)

Yield, 37%; m.p., 259 °C. ^{1}H NMR ($CDCl_3$) δ: 1.33 (s, 18H), 1.46 (s, 6H), 1.48 (s, 6H), 2.48 and 3.20 (AA'XX', 4H). ^{13}C NMR ($CDCl_3$) δ: 22.5 (q), 27.2 (q), 28.9 (q), 41.4 (d), 43.8 (s), 46.7 (d), 65.0 (s), 175.8 (s), 185.1 (s).

3.6.7. cis–transoid–cis-2,5-Dipivaloylperhydro-3,3,4,4-tetramethylcyclobuta[1,2-c:3,4-c']dipyrrole-1,6-dione (4d)

Purified by chromatography (pentane–acetone, 10:1); yield, 28%; m.p., 53 °C. ^{1}H NMR ($CDCl_3$) δ: 1.31 (s, 18H), 1.34 (s, 6H), 1.46 (s, 6H), 2.63 and 3.07 (AA'XX', 4H). ^{13}C NMR ($CDCl_3$) δ: 21.1 (q), 27.1 (q), 27.4 (q), 42.0 (d), 43.8 (s), 45.7 (d), 64.6 (s), 174.3 (s), 185.2 (s).

3.6.8. cis–transoid–cis-Perhydro-3,3,6,6-tetramethylcyclobuta[1,2-c:3,4-c']dipyrrole-1,4-dione (6) and cis–transcid–cis-perhydro-3,3,4,4-tetramethylcyclobuta-[1,2-c:3,4-c']dipyrrole-1,6-dione (7)

Compound **6**: yield, 52%. Compound **7**: yield, 15%. NMR spectral data are given in Ref. [1].

3.6.9. Di-tert-butyl-cis–transoid–cis-perhydro-3,3,6,6-tetramethyl-1,4-dioxocyclobuta[1,2-c; 3,4-c']dipyrrole-2,5-dicarboxylate (8)

Yield, 42%; m.p., 196 °C. ^{1}H NMR ($CDCl_3$) δ: 1.41 (s, 6H), 1.56 (s, 6H), 1.62 (s, 18H), 2.53 and 3.21 (AA'XX', 4H). ^{13}C NMR ($CDCl_3$) δ: 24.2 (q), 28.1 (q), 28.3 (q), 41.5 (d), 45.7 (d), 63.3 (s), 83.4 (s), 150.3 (s), 175.2 (s).

3.6.10. Di-tert-butyl-cis–transoid–cis-perhydro-3,3,4,4-tetramethyl-1,6-dioxocyclobuta[1,2-c; 3,4-c']dipyrrole-2,5-dicarboxylate (9)

From pentane–acetone (3:1); yield, 10%; m.p., 193 °C. ^{1}H NMR ($CDCl_3$) δ: 1.37 (s, 6H), 1.49 (s, 6H), 1.56 (s, 18H), 2.65 and 3.12 (AA'XX', 4H). ^{13}C NMR ($CDCl_3$) δ: 22.3 (q), 26.6 (q), 28.1 (q), 41.9 (d), 45.7 (d), 62.7 (s), 83.4 (s), 150.3 (s), 173.3 (s).

Acknowledgements

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

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