108. Synthesis and Photochemistry of 5,5-Dimethyl-1*H*-pyrrol-2(5*H*)-one and of Some *N*-Substituted Derivatives

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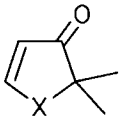
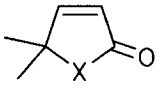
In two steps, 5,5-dimethyl-1*H*-pyrrol-2(5*H*)-one (**3a**) was prepared from 5,5-dimethylpyrrolidine-2,4-dione (= dimethyltetramic acid; **4**) in 71% overall yield (*Scheme 1*) and further converted to *N*-substituted derivatives **3b–f** *via* acylation, alkylation, or methoxycarbonylation of its anion (*Scheme 2*). The substitutents on the N-atom exert a strong influence on the photochemical reactivity ([2 + 2] photocycloaddition to 2,3-dimethylbut-2-ene, photocyclodimerisation, photoreduction) of these aza-enones **3** (*Scheme 3*). In general, *N*-alkyl compounds react much slower and with less efficiency than either the (*N*-unsubstituted) title compound **3a** or its *N*-acetyl and *N*-(methoxycarbonyl) derivatives **3e** and **3f**, respectively. These compounds behave similarly to the corresponding lactone, 5,5-dimethyl-2(5*H*)-furanone, studied previously.

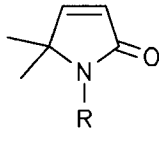
Introduction. – In the course of our investigations on the photochemistry of cyclic α,β-unsaturated carbonyl compounds [1] [2], we had emphasized on the synthesis of several heteropentacyclic enones such as **1** and **2** with a geminal dimethyl group adjacent to the heteroatom to prevent tautomerization to a 2- or 3-hydroxy-substituted heterocycle. We had shown that both 3(2*H*)- and 2(5*H*)-furanones **1a** and **2a** and 3(2*H*)-thiophenone **1b** exhibit photochemistry typical for cyclopent-2-enone itself [3–5] and that 2(5*H*)-thiophenones, *e.g.* **2b**, behave differently in undergoing light-induced ring-opening reactions in hydroylic solvents [6] [7]. Finally, while 1*H*-pyrrol-3(2*H*)-one **1c** is photoinert [8], the corresponding *N*-(ethoxycarbonyl) derivative **1d** again exhibits typical enone behavior [9]. We now report on a new – large-scale – synthesis of the 'missing link' in this



1a X = O
b X = S
c X = NH
d X = NCOOEt



2a X = O
b X = S



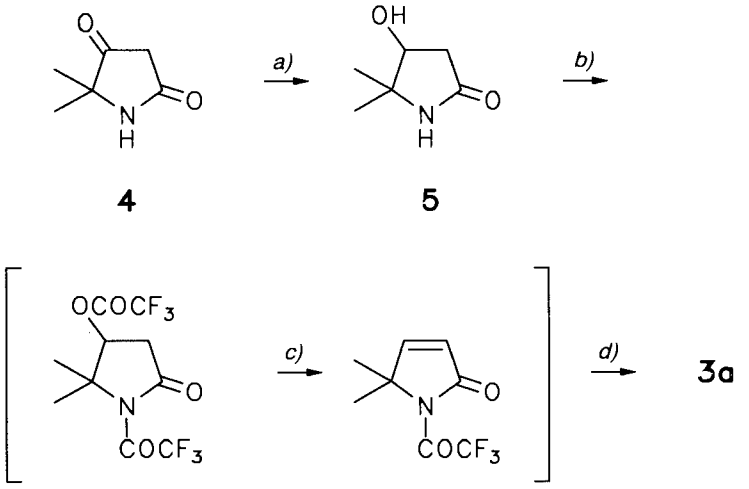
3a R = H
b R = Me
c R = $CH_2CH{=}CH_2$
d R = $(CH_2)_{12}$-**3**
e R = COMe
f R = COOMe

[1]) Ph. D. Thesis, University of Hamburg, 1992.

series, 5,5-dimethyl-1*H*-pyrrol-2(5*H*)-one (**3a**), on the preparation of some novel *N*-substituted derivatives thereof (**3b–f**), and on the photochemical behavior of these five-membered cyclic α,β-unsaturated lactams.

Results. – Lactam **3a** was previously synthesized from 5-cyano-3,4-dihydro-2,2-dimethyl-2*H*-pyrrole 1-oxide in a multistep sequence [10] [11], one photochemical step – the preparation of a bicyclic oxaziridine intermediate – requiring chromatographic workup. Searching for a procedure which would allow a large-scale preparation of **3a**, we found that 5,5-dimethylpyrrolidine-2,4-dione (= dimethyltetramic acid; **4**), readily accessible from ethyl 2-amino-2-methylpropanoate and ethyl (chloroformyl)acetate [12], could easily be reduced to 4-hydroxy-5,5-dimethylpyrrolidin-2-one (**5**) *via* catalytic hydrogenation. Subsequent *O*,*N*-bis(trifluoroacetylation), elimination of trifluoroacetic acid, and hydrolysis [13] afforded lactam **3a** in 71% yield (*Scheme 1*).

Scheme 1



a) Raney-Ni, H_2. *b)* $(CF_3CO)_2O$. *c)* Et_3N. *d)* $NaHCO_3$.

We found next that the most convenient way of deprotonating **3a** was to use NaH in tetrahydrofuran, as the sodium salt **6** is soluble in this solvent. By this route, **3a** reacted with iodomethane, 3-bromoprop-1-ene, 1,12-diiodododecane, and methyl chloroformate – the reaction with acetyl chloride requiring no added base – to afford the *N*-substituted derivatives **3b–f**, respectively, in good yields (*Scheme 2*).

The substituent at the N-atom of compounds **3b–f** has pronounced effects on their spectroscopic (ground-state) properties. The UV absorption maxima (MeCN) are shifted to longer wavelengths and the ε values decrease with increasing electron-donor property of the substituent R (*Table 1*). Similarly, the chemical shifts of both the olefinic H–C(4) and the geminal Me groups at C(5) are affected.

On photolysis of the aza-enones **3**, the products resulting from bimolecular (triplet) reactions, in general, were rarely formed in more than 50% yield (isolated) as photopoly-

Scheme 2

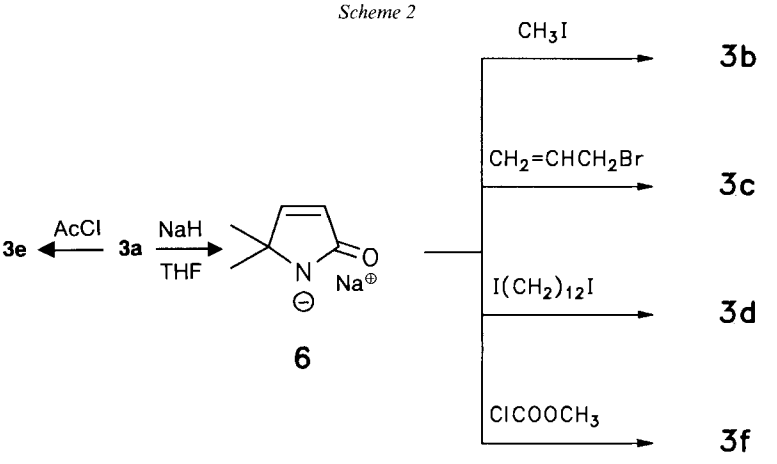


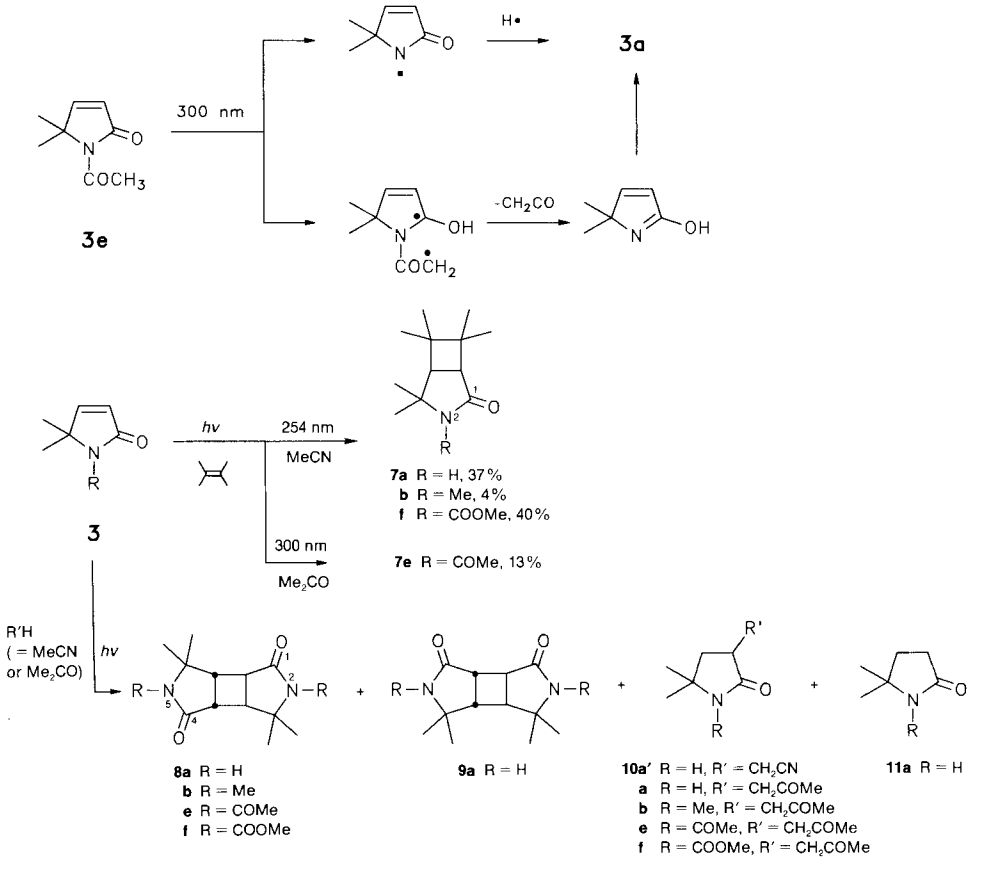
Table 1. *Selected Spectroscopic Data of Compounds* **3**

	3f (R = COOMe)	**3e** (R = COMe)	**3a** (R = H)	**3b** (R = Me)	**3c** (R = CH_2=$CHCH_2$)
UV (MeCN)					
λ_{max}	< 220	228	232	242	242
log ε	–	3.77	3.39	3.34	3.37
^{1}H-NMR ($CDCl_3$)					
H–C(4)	7.15	7.14	6.98	7.02	6.96
Me_2C(5)	1.57	1.57	1.38	1.29	1.31

merization interfered in both direct (254 nm) and xanthone- or acetone-sensitized (300 nm) irradiations. Also the rate of conversion of the *N*-alkyl compounds **3b–d** to identified products was much lower than that of either the parent **3a** or the *N*-acetyl and *N*-(methoxycarbonyl)derivatives **3e** and **3f**. For **3e**, such bimolecular triplet-state reactions occurred *only* in sensitized reactions, as on direct excitation, **3e** was converted from its S_1 state to **3a** either *via* α-cleavage and subsequent H-atom transfer or *via* intramolecular H-abstraction followed by ketene elimination and subsequent tautomerization (*Scheme 3*). Thus, irradiation of **3a,b,f,e** (0.1M soln. in MeCN) in the presence of a ten-fold molar excess of 2,3-dimethylbut-2-ene afforded perhydro-3,3,4,4,5,5-hexamethyl-1*H*-cyclobuta[*c*]pyrrol-1-ones **7a,b,f,e** in 4–40% isolated yield, depending on the substituent at the N-atom (*Scheme 3*).

The product yields on both direct and sensitized irradiations of compounds **3** in the *absence* of added alkene again depend on the substituent on the N-atom, but in addition, the product distribution is a function of both enone concentration and solvent, as photoreduction and reductive solvent addition compete efficiently with photocyclodimerization (*Scheme 3*). Thus, irradiation of **3a** afforded dimers **8a** and **9a** in a 5:1 ratio in *t*-BuOH and in a 1:1 ratio in MeCN. In this latter solvent, irradiation of a 10^{-1} M solution of **3a** gave **8a**/**9a**/**10a′**/**11a** in a 23:24:38:15 ratio, while on irradiation of a 1M solution, the relative yield of dimers **8a** and **9a** was up to 70%. On irradiation of **3a** in propan-2-ol, 5,5-dimethylpyrrolidin-2-one (**11a**) was formed selectively. Finally, acetone-

Scheme 3



sensitized irradiation of 10^{-1} M **3a** afforded a 5:1 mixture **8a**/**9a**, 5,5-dimethyl-3-(2-oxopropyl)pyrrolidin-2-one (**10a**), and **11a** in relative yields of 60:28:12, respectively. The behaviour of **3f** resembled that of **3a** regarding product distribution and yields, and the same applied to **3e**, but here again in acetone-sensitized reactions exclusively. As before, **3b** reacted much slower than **3a** affording only very low yields of isolated products, all

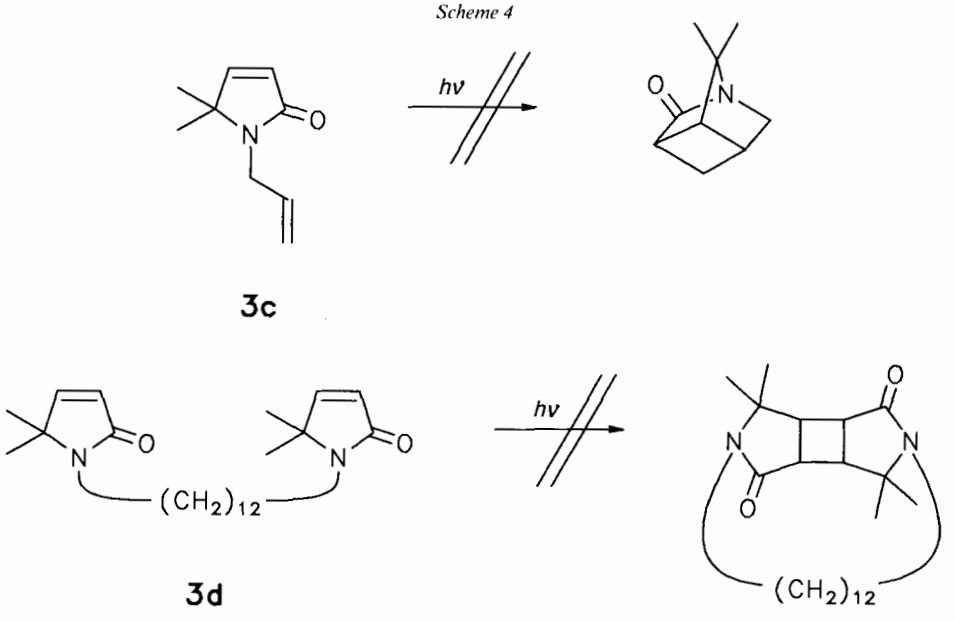
Table 2. *Isolated Yields of Photoproducts on Irradiation of* **3**

Product	3a	3b	3e	3f
8	25%[a])	6%[b])	16%[c])	22%[a])
9	9%[d])	–	–	–
10	10% (7%[e]))	1%[f])	2%[f])	11%[f])
11	60%[g])			

[a]) 1M in *t*-BuOH, 254 nm. [b]) 1M in *t*-BuOH, xanthone, 300 nm. [c]) 1M in acetone, 300 nm. [d]) 1M in MeCN, 254 nm. [e]) 0.01M in MeCN, 254 nm: product **10a**. [f]) 0.01M in acetone, 300 nm. [g]) 0.1M in propan-2-ol, 254 nm.

these results being summarized in *Table 2*. Regarding the nonreactivity of the *N*-alkyl compounds, no intramolecular cycloaddition products of either **3c** or **3d** were detected, neither on direct nor on sensitized irradiation of these bichromophoric aza-enones (*Scheme 4*).

Scheme 4



Discussion. – The reduction of 5,5-dialkylpyrrolidine-2,4-diones, *e.g.* tetramic acid (**4**), to 5,5-dialkyl-4-hydroxypyrrolidin-2-ones, *e.g.* **5**, their conversion to α,β-unsaturated lactams, *e.g.* **3a**, *via* elimination of CF_3COOH [13], and the subsequent *N*-functionalization in THF allows a general convenient access to 3,4-unsubstituted 5,5-dialkyl-1*H*-pyrrol-2(5*H*)-ones. Up to now, only some few directed syntheses of such compounds were published [11] [14] [15].

The photocycloaddition of a related bicyclic α,β-unsaturated lactam to ethylene in the presence of a fivefold excess of acetophenone as sensitizer was reported by *Meyers* and *Fleming* [16]. Unfortunately – to our knowledge – no report on the study of photocycloadditions of various bicyclic lactams to other olefins as a general method for synthesizing chiral cyclobutanes (ref. 9 in [16]) was published.

The fact that electron-withdrawing substituents on the N-atom increase the efficiency in photocycloadditions of cyclic vinylogous amides to alkenes, while (electron-donating) alkyl groups lower it drastically, was observed for dihydropyrrol derivatives [8] [9] and for the corresponding six-membered heterocycles [17]. We proposed [5] that *N*-alkyl compounds undergo efficient self-quenching *via* electron transfer between a ground-state and an excited-state molecule followed by electron back-transfer between the two ion radicals. An interesting – albeit speculative – alternative explanation for the observed overall nonreactivity of these *N*-alkyl-aza-enones would be that [2 + 2] photocycloadducts are indeed formed, but that they undergo cycloreversion initiated by reductive single-electron

transfer, as proposed for simple pyrimidine dimers in model studies on DNA enzymatic photorepair [18].

The overall photoreactivity of **3a** and **3f** parallels that of lactone **2a** [4] regarding the solvent-dependence in the orientation of addition in photocyclodimerization (head-to-tail *vs.* head-to-head dimers) and in the preferential formation of 3-R′-substituted derivatives **10** in the photoreductive solvent addition. The possible mechanisms involved in this latter reaction were discussed in detail, both for **2a** [4] and for 4,4-dialkylcycloalk-2-enones in general [19]. Photoreductive addition of acetone to the C=C bond of an excited cyclic α,β-unsaturated carbonyl derivative represents a novel type of reaction. To our knowledge, the 'RH addition' of acetone to the C=C bond of bicyclo[2.2.1]hept-2-ene [20] [21] is the only related example of such a reaction. The – singlet-state – photoreactivity of imide **3e** fits into the expected general behaviour of this class of compounds [22].

The default of intramolecular photocycloadditions of compounds **3c** and **3d** could be overcome by synthesizing *N*-COX-substituted derivatives **3**, with the N-atom bearing either an acryloyl side chain (X = CH=CH_2) or being linked to a second lactam moiety by a $COO(CH_2)_nOC(O)$ chain. Such studies are now in progress.

Experimental Part

1. *General.* Photolyses: *Rayonet-RPR-100* photoreactor equipped with 254 (*A*) or 300 nm (*B*) lamps. Qual. GC: 30-m *SE 30* capillary column. Prep. GC: 2-m 10% *QF 1* on *Chromosorb W-AW DMCS*. UV Spectra: in nm (log ε). IR Spectra: in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: at 400 and 100.63 MHz, resp.; chemical shifts in ppm rel. to TMS (= 0 ppm), coupling constants *J* in Hz. MS: at 70 eV; in *m/z* (rel. intensity in %).

2. *Synthesis. 4-Hydroxy-5,5-dimethylpyrrolidin-2-one* (**5**). To a soln. of tetramic acid [12] (**4**; 15 g, 0.118 mol) in dry EtOH (500 ml) is added *Raney*-Ni (5 g) and the mixture hydrogenated in a 1-l autoclave at 60°/100 bar for 12 h. Then, the solvent is evaporated and acetone (100 ml) added to the residue. Filtration, drying ($MgSO_4$), and evaporation afford 14.8 g (97%) of **5**. M.p. 102°. IR (KBr): 3407, 3200, 1685. ^{1}H-NMR ($CDCl_3$): 4.11 (*dd*, *J* = 6.2, 5.0); 2.75 (*dd*, *J* = 17.2, 6.2); 2.35 (*dd*, *J* = 17.2, 5.0); 1.24, 1.21 (2*s*, Me). ^{13}C-NMR (CD_3OD): 173.4 (*s*); 72.0 (*d*); 58.4 (*s*); 36.8 (*t*); 24.1 (*q*); 18.7 (*q*). MS: 129 (43, M^+), *58*.

*5,5-Dimethyl-1*H*-pyrrol-2(5*H*)-one* (**3a**). To **5** (7.4 g, 0.057 mol) is added dropwise trifluoroacetic anhydride (28 ml, 0.2 mol). The mixture is refluxed for 12 h. After evaporation of excess anhydride and CF_3COOH *in vacuo*, the residue is dissolved in CH_2Cl_2 (15 ml) to which is added a soln. of Et_3N (10 ml) in CH_2Cl_2 (15 ml). After stirring for 12 h, a soln. of $KHCO_3$ (15 g) in MeOH (30 ml) is added and stirring continued for 2 h. Addition of $CHCl_3$ (200 ml), washing with dil. HCl soln., H_2O, and aq. NaCl soln., drying ($MgSO_4$), filtering, evaporation, and subsequent chromatography (SiO_2, CH_2Cl_2/MeOH 9:1) afford 4.64 g (73%) of **3a**. M.p. 101–102° ([11]: 99–100°). ^{13}C-NMR ($CDCl_3$): 173.4 (*s*); 156.8 (*d*); 124.4 (*d*); 61.7 (*s*); 25.4 (*q*). MS: 111 (21, M^+), *96*.

Anion **6** *in THF Solution.* To a suspension of NaH (0.56 g, 0.023 mol) in THF (25 ml) at 0° is added a soln. of **3a** (2 g, 0.018 mol) in THF (25 ml), and stirring is continued at 0° for 30 min until a clear soln. is obtained.

*1,5,5-Trimethyl-1*H*-pyrrol-2(5*H*)-one* (**3b**). To the THF soln., of **6** is added, at 0°, MeI (4.3 g, 0.030 mol) in THF (10 ml). The mixture is then refluxed for 16 h. After evaporation, CH_2Cl_2 (50 ml) and H_2O (10 ml) are added to the residue. Separation of the aq. phase, drying of the org. phase ($MgSO_4$), evaporation, and subsequent chromatography (SiO_2, CH_2Cl_2/MeOH 9:1) afford 2.02 g (89%) of **3b**. M.p. 32°. IR (KBr): 1690, 1592. ^{1}H-NMR ($CDCl_3$): 7.02, 6.05 (*d*, *J* = 6.0); 2.86 (*s*, 3 H); 1.29 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): 169.9 (*s*); 154.2 (*d*); 124.7 (*d*); 64.0 (*s*); 23.4 (*q*); 22.5 (*q*). MS: 125 (3, M^+), *110*.

*5,5-Dimethyl-1-(prop-2-enyl)-1*H*-pyrrol-2(5*H*)-one* (**3c**). As described for **3b**, with 3-bromoprop-1-ene (3.6 g, 0.030 mol): **3c** in 61% yield. B.p. 110°/0.02 Torr. IR (film): 1685, 1597. ^{1}H-NMR ($CDCl_3$): 6.96, 6.02 (*d*, *J* = 6.0); 5.84 (*ddt*, *J* = 17.0, 10.2, 5.8); 5.22 (*dq*, *J* = 17.0, 1.5); 5.13 (*dq*, *J* = 10.2, 1.5); 3.99 (*dq*, *J* = 5.8, 1.5, 2 H); 1.31 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): 170.0 (*s*); 154.8 (*d*); 134.5 (*d*); 124.4 (*d*); 116.4 (*t*); 64.8 (*s*); 41.3 (*t*); 24.0 (*q*). MS: 151 (42, M^+), *41*.

*1,1′-(Dodecamethylene)-5,5,5′,5′-tetramethylbis(1*H*-pyrrole)-2,2′(5*H*,5′*H*)-dione* (**3d**). As 1,12-diiodododecane described for **3b**, with (2.5 g, 0.006 mol), and distilling off the excess of **3a** (300 mg) before chromatography: **3d**

in 56% yield. M.p. 36–39°. IR (KBr): 1680, 1594. ^{1}H-NMR ($CDCl_3$): 6.92, 6.02 (*d*, *J* = 5.8, 4 H); 3.26 (*m*, 4 H); 1.62 (*m*, 4 H); 1.31 (br. *s*, 16 H); 1.26 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): 170.3 (*s*); 154.1 (*d*); 124.9 (*d*); 64.6 (*s*); 39.3 (*t*); 29.5, 29.4, 29.2, 27.3 (4*t*); 24.0 (*q*).

*1-Acetyl-5,5-dimethyl-1*H*-pyrrol-2(5*H*)-one* (**3e**). A soln. of **3a** (2 g, 0.018 mol) in AcCl (10 ml) is heated at 80° for 24 h. Evaporation of the excess AcCl *in vacuo* at 50° for 3 h gives **3e** in quant. yield. M.p. 62°. IR (KBr): 1731, 1688. ^{1}H-NMR ($CDCl_3$): 7.14, 6.01 (*d*, *J* = 5.8); 2.54 (*s*, 3 H); 1.57 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): 170.3 (*s*); 170.1 (*s*); 159.7 (*d*); 123.1 (*d*); 66.1 (*s*); 26.3 (*q*); 23.5 (*q*). MS: 153 (1, M^+), *96*.

*Methyl 2,5-Dihydro-5,5-dimethyl-2-oxo-1*H*-pyrrole-1-carboxylate* (**3f**). To the THF soln. of **6** (see above) is added methyl chloroformate (1.7 g, 0.018 mol). The mixture is stirred for 24 h at r.t. and worked up as above: **3f** in 72% yield. M.p. 69–70°. IR (KBr): 1724, 1607. ^{1}H-NMR ($CDCl_3$): 7.15, 6.02 (*d*, *J* = 6.0); 3.90 (*s*, 3 H); 1.57 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): 168.5 (*s*); 158.7 (*d*); 151.6 (*s*); 123.2 (*d*); 65.8 (*s*); 53.0 (*q*); 23.6 (*q*). MS: 169 (0.1, M^+), *122*.

3. *Photochemistry*. 3.1. *Photocycloadditions to 2,3-Dimethylbut-2-ene*. An Ar-degassed soln. of **3** (0.002 mol) and 2,3-dimethylbut-2-ene (2.4 ml, 0.02 mol) in solvent (20 ml) is irradiated up to total conversion of starting material (GC monitoring). Evaporation and purification afford photocycloadduct **7**.

*Perhydro-3,3,4,4,5,5-hexamethyl-1*H*-cyclobuta[c]pyrrol-1-one* (**7a**). From **3a**, lamps *A*, MeOH, 8 h, purification by bulb-to-bulb distillation (125°/0.1 Torr); 37% yield. M.p. 99–100°. IR (KBr): 1684. ^{1}H-NMR ($CDCl_3$): 2.61, 2.31 (*d*, *J* = 7.6); 1.36, 1.24, 1.16, 1.13, 1.06, 1.02 (6*s*, Me). ^{13}C-NMR ($CDCl_3$): 178.3 (*s*); 58.2 (*s*); 51.7 (*d*); 49.2 (*d*); 41.8 (*s*); 40.0 (*s*); 32.5 (*q*); 27.2 (*q*); 27.1 (*q*); 23.2 (*q*); 23.1 (*q*); 20.5 (*q*). MS: 195 (16, M^+), *98*.

*Perhydro-2,3,3,4,4,5,5-heptamethyl-1*H*-cyclobuta[c]pyrrol-1-one* (**7b**). From **3b**, lamps *A*, MeCN, 52 h, purification by chromatography (SiO_2, AcOEt): 4% yield. Oil. IR (film): 1679. ^{1}H-NMR ($CDCl_3$): 2.71 (*s*, 3 H); 2.56, 2.28 (*d*, *J* = 7.4); 1.30, 1.15, 1.05, 1.00 (4*s*, Me). ^{13}C-NMR ($CDCl_3$): 175.0 (*s*); 61.3 (*s*); 50.1 (*d*); 48.4 (*d*); 41.7 (*s*); 40.1 (*s*); 27.6 (*q*); 27.1 (*q*); 27.0 (*q*); 24.0 (*q*); 23.1 (*q*); 21.7 (*q*); 20.3 (*q*). MS: 209 (15, M^+), *110*.

*2-Acetylperhydro-3,3,4,4,5,5-hexamethyl-1*H*-cyclobuta[c]pyrrol-1-one* (**7e**). From **3e**, lamps *B*, acetone, 19 h, purification by prep. GC: 13% yield. Oil. ^{1}H-NMR ($CDCl_3$): 2.63 (*d*, *J* = 8.0); 2.47 (*s*, 3 H); 2.23 (*d*, *J* = 8.0); 1.58, 1.28, 1.20, 1.13, 1.04, 1.02 (6*s*, Me). ^{13}C-NMR ($CDCl_3$): 172.3 (*s*); 170.3 (*s*); 64.6 (*s*); 50.5 (*d*); 48.7 (*d*); 28.4 (*q*); 27.1 (*q*); 26.8 (*q*); 23.4 (*q*); 22.8 (*q*); 20.1 (*q*). MS: 237 (7, M^+), *97*.

*Methyl Perhydro-3,3,4,4,5,5-hexamethyl-1-oxo-1*H*-cyclobuta[c]pyrrole-2-carboxylate* (**7f**). From **3f**, lamps *A*, MeCN, 6 h: 40% yield. Oil. IR (CCl_4): 1746, 1728. ^{1}H-NMR ($CDCl_3$): 3.87 (*s*, 3 H); 2.63, 2.27 (*d*, *J* = 7.8); 1.56, 1.31, 1.19, 1.15, 1.05, 1.02 (6*s*, Me). ^{13}C-NMR ($CDCl_3$): 175.5 (*s*); 152.6 (*s*); 64.0 (*s*); 53.1 (*q*); 50.4 (*d*); 48.7 (*d*); 42.2 (*s*); 41.4 (*s*); 28.4 (*q*); 27.0 (*q*); 26.8 (*q*); 23.3 (*q*); 22.7 (*q*); 20.0 (*q*). MS: 253 (3, M^+), *97*.

3.2. *Photocyclodimerization*. Solns. of **3** (0.002 mol) in solvent (2 ml) are irradiated up to total conversion of starting material; workup as described below.

cis-transoid-cis-*Perhydro-3,3,6,6-tetramethylcyclobuta[1,2-c:3,4-c']dipyrrole-1,4-dione* (**8a**). From **3a**, lamps *A*, *t*-BuOH, 8 h. After evaporation, the residue is treated with CH_2Cl_2 (2 ml) in which **8a** is insoluble and filtered: yield 25%. M.p. 174°. ^{1}H-NMR ($CDCl_3$): 3.23, 2.57 (*AA'XX'*, *J* = 8.1, 3.6, 2.3, 0.1); 1.39, 1.24 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): 179.8 (*s*); 59.2 (*s*); 48.6 (*d*); 43.7 (*d*); 31.3 (*q*); 24.7 (*q*).

cis-transoid-cis-*Perhydro-3,3,4,4-tetramethylcyclobuta[1,2-c:3,4-c']dipyrrole-1,6-dione* (**9a**). From **3a**, lamps *A*, MeCN, 9 h. A precipitate, consisting mainly of **8a**, is formed on irradiation and filtered off. The filtrate is evaporated and treated with Et_2O (2 ml) in which **9a** is insoluble and filtered: yield 9%. M.p. 248°. ^{1}H-NMR (CD_3OD): 3.00, 2.83 (*AA'XX'*, *J* = 6.5, 4.7, 1.6, 1.3); 1.26, 1.22 (*s*, 6 H). ^{13}C-NMR (CD_3OD): 178.7 (*s*); 58.4 (*s*); 47.1 (*d*); 44.1 (*d*); 29.9 (*q*); 22.7 (*q*).

cis-transoid-cis-*Perhydro-2,3,3,5,6,6-hexamethylcyclobuta[1,2-c:3,4-c']dipyrrole-1,4-dione* (**8b**). From **3b**, lamps *B*, *t*-BuOH containing 18.5 mg xanthone as sensitizer, 13 days. After evaporation, the residue is treated with CCl_4 (3 ml) in which **8b** is insoluble. Filtering and subsequent chromatography (SiO_2, CH_2Cl_2/MeOH 9:1) afford **8b**, yield 7%. M.p. 112°. IR (KBr): 1667. ^{1}H-NMR ($CDCl_3$): 3.11 (*m*, 2 H); 2.77 (*s*, 6 H); 2.52 (*m*, 2 H); 1.39, 1.16 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): 174.6 (*s*); 61.1 (*s*); 45.7 (*d*); 41.4 (*d*); 27.00 (*q*); 24.8 (*q*); 22.7 (*q*).

cis-transoid-cis-*2,5-Diacetylperhydro-3,3,6,6-tetramethylcyclobuta[1,2-c:3,4-c']dipyrrole-1,4-dione* (**8e**). From **3e**, lamps *B*, acetone, 40 h. After evaporation, the residue is treated with MeOH (2 ml). Filtering affords **8e** in 16% yield. M.p. 132°. IR (KBr): 1730, 1709. ^{1}H-NMR ($CDCl_3$): 3.18 (*m*, 2 H); 2.50 (*s*, 6 H); 2.48 (*m*, 2 H); 1.68, 1.45 (*s*, 6 H). ^{13}C-NMR (C_6D_6): 176.7 (*s*); 171.7 (*s*); 63.7 (*s*); 46.2 (*d*); 41.3 (*d*); 27.2 (*q*); 26.9 (*q*); 23.7 (*q*).

Dimethyl cis-transoid-cis-*Perhydro-3,3,6,6-tetramethyl-1,4-dioxocyclobuta[1,2-c:3,4-c']dipyrrole-2,5-dicarboxylate* (**8f**). From **3f**, lamps *A*, *t*-BuOH, 8 h. Dimer **8f** precipitates during the irradiation. It is filtered and washed with Et_2O: yield 22%. M.p. 141°. ^{1}H-NMR ($CDCl_3$): 3.89 (*s*, 6 H); 3.26 (*m*, 2 H); 2.58 (*m*, 2 H); 1.65, 1.44 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): 174.8 (*s*); 152.5 (*s*); 63.7 (*s*); 53.5 (*q*); 45.8 (*d*); 41.5 (*d*); 27.9 (*q*); 23.7 (*q*).

3.3. *Photoreductive Solvent Addition: Formation of Compounds* **10**. Irradiation of 10^{-2} M solns. of **3** in either MeCN (10 ml) or acetone (10 ml) and workup as described.

5,5-Dimethyl-2-oxopyrrolidine-3-acetonitrile (**10a'**). From **3a**, lamps *A*, MeCN, 4 h. Evaporation, addition of Et_2O (5 ml), filtration from the precipitate, and subsequent prep. GC afford **10a'** in 7% yield. M.p. 149°. IR (KBr): 2248, 1696. ^{1}H-NMR ($CDCl_3$): 2.93 (*dddd*, J = 10.8, 8.6, 8.4, 4.8); 2.81 (*dd*, J = 17.0, 4.8); 2.57 (*dd*, J = 17.0, 8.5); 2.32 (*dd*, J = 12.6, 8.5); 1.82 (*dd*, J = 12.6, 10.8); 1.37, 1.30 (2*s*, Me). ^{13}C-NMR ($CDCl_3$): 174.2 (*s*); 117.8 (*s*); 54.7 (*s*); 41.3 (*t*); 38.3 (*d*); 29.9 (*q*); 28.7 (*q*); 19.0 (*t*). MS: 152 (7, M^+), *137*.

5,5-Dimethyl-3-(2-oxopropyl)pyrrolidin-2-one (**10a**). From **3a**, lamps *B*, acetone, 12 h. Filtration from the precipitate formed, evaporation, and subsequent bulb-to-bulb distillation at 125°/20 Torr afford **10a** in 10% yield. Colorless oil. IR (film): 1720, 1690. ^{1}H-NMR ($CDCl_3$): 3.10 (*dd*, J = 18.0, 3.2); 3.00 (*dddd*, J = 10.4, 9.4, 8.4, 3.2); 2.48 (*dd*, J = 18.0, 9.4); 2.31 (*dd*, J = 12.4, 8.4); 2.17 (*s*, 3 H); 1.52 (*dd*, J = 12.4, 10.4); 1.30, 1.27 (2*s*, Me). ^{13}C-NMR ($CDCl_3$): 206.8 (*s*); 177.3 (*s*); 54.6 (*s*); 44.9 (*t*); 42.7 (*t*); 37.1 (*d*); 30.1 (*q*); 30.0 (*q*); 28.6 (*q*). MS: 169 (4, M^+), *43*.

1,5,5-Trimethyl-3-(2-oxopropyl)pyrrolidin-2-one (**10b**). From **3b**, lamps *B*, acetone, 30 h. Compound **10b** is present in traces (< 5%) in the mixture and analyzed by GC/MS: 183 (1, M^+), *168*.

1-Acetyl-5,5-dimethyl-3-(2-oxopropyl)pyrrolidin-2-one (**10e**). From **3e**, lamps *B*, acetone, 7 h. Compound **10e** is isolated by prep. GC in 2% yield. Colorless oil. IR (film): 1732, 1721, 1697. ^{1}H-NMR (C_6D_6): 2.66 (*dddd*, J = 12.5, 8.8, 8.0, 4.0); 2.54 (*dd*, J = 18.0, 4.0); 2.44 (*s*, 3 H); 1.91 (*dd*, J = 18.0, 8.0); 1.65 (*dd*, J = 12.4, 8.8); 1.42, 1.20 (2*s*, Me); 1.03 (*t*, 12.4).

Methyl 5,5-Dimethyl-2-oxo-3-(2-oxopropyl)pyrrolidine-1-carboxylate (**10f**). From **3f**, lamps *B*, acetone, 4 h. Evaporation and subsequent chromatography (SiO_2, Et_2O) afford **10f** in 11% yield. Colorless oil. IR (film): 1780, 1723. ^{1}H-NMR (C_6D_6): 3.46 (*s*, 3 H); 2.74 (*dddd*, J = 12.5, 8.6, 8.4, 4.0); 2.68 (*dd*, J = 18.0, 4.0); 1.91 (*dd*, J = 18.0, 8.5); 1.77 (*dd*, J = 12.5, 8.5); 1.63, 1.34, 1.18 (3*s*, Me); 1.04 (*t*, J = 12.5). ^{13}C-NMR ($CDCl_3$): 206.1 (*s*); 175.3 (*s*); 152.3 (*s*); 60.9 (*s*); 53.2 (*q*); 44.1 (*t*); 41.8 (*t*); 37.1 (*d*); 30.2 (*q*); 28.5 (*q*); 24.9 (*q*). MS: 227 (0.1, M^+), *43*.

3.4. *Irradiation of* **3a** *in Propan-2-ol: Formation of 5,5-Dimethylpyrrolidin-2-one* (**11a**). From **3a**, lamps *A*, propan-2-ol, 3 h. Evaporation and bulb-to-bulb distillation (110°/20 Torr) afford **11a** [23] in 60% yield.

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