Photocycloisomerization of Boc-Protected 5-Alkenyl-2,5-dihydro-1*H*-pyrrol-2-ones

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Dedicated to Professor *William C. Agosta* on the occasion of his 70th birthday

On irradiation (254 nm), the newly synthesized Boc-protected 5-alkenyl-2,5-dihydro-1*H*-pyrrol-2-ones **13** undergo regioselective intramolecular [2+2] photocycloadditions. While the allyl derivatives **13a**–**13c** afford mainly azatricyclo[3.3.0.$0^{2,7}$]octanones, *i.e.*, *crossed* cycloadducts, the butenyl- and pentenyl-substituted compounds **13d** and **13e** isomerize preferentially to *straight* cycloadducts.

Introduction. – Intramolecular enone + alkene [2+2] photocycloadditions, *i.e.*, light-induced cycloisomerizations of α,β-unsaturated carbonyl compounds bearing an additional C=C bond [1][2], have attracted the attention of organic chemists as a powerful method for assembling polycyclic molecules. Well-known examples are the carvone → carvonecamphor conversion [3] and a key step in the synthesis of cubane [4]. Regarding the regioselectivity of such reactions, the number of atoms between the two reactive C=C bonds has turned out as being a decisive factor: many examples wherein the two C=C bonds are separated by one, two, or three additional atoms, are governed by the so-called '*rule of five*', which states that '*if triplet cyclizations can lead to rings of different size, the one formed by 1,5-cyclization is preferred kinetically*' [5][6].

While the behavior of five- and six-membered cyclic enones bearing an alkenyl side chain either at C(2) or C(3) has been extensively investigated, detailed results on 4-alkenyl-substituted cyclopent-2-enones and related heterocyclic enones are scarce. As expected, irradiation of cyclopentenone **1** affords the tricyclic ketone **2** in a '*crossed*' addition mode [7], while, under similar conditions, enone **3** affords ketone **4**, now in a '*straight*' addition mode [8]. Similarly, on irradiation, the 5-allyl-2(5*H*)-furan-2-one (**5**) isomerizes predominantly to the *crossed* tricyclic lactone **6** [9], while the corresponding 5-but-4-enyl derivative **7** gives mainly the *straight* tricycle **8** [10] (*Scheme 1*).

We have recently reported [11] that the diastereoisomeric *u*- and *l*-dihydropyrroles **9** and **10** photoisomerize selectively to azatetracyclodecanones **11** and **12**, respectively; these conversions represent the first example of a photochemical reaction wherein two diastereoisomeric hexa-1,5-dienes undergo photoisomerization to a *crossed* and a *straight* cycloadduct, respectively (*Scheme 2*). Here, we report the synthesis of **13a**–**13e** and the photochemical behavior of these five novel (open-chain) alkenyl derivatives containing the same dihydropyrrole moiety as **9** and **10**.

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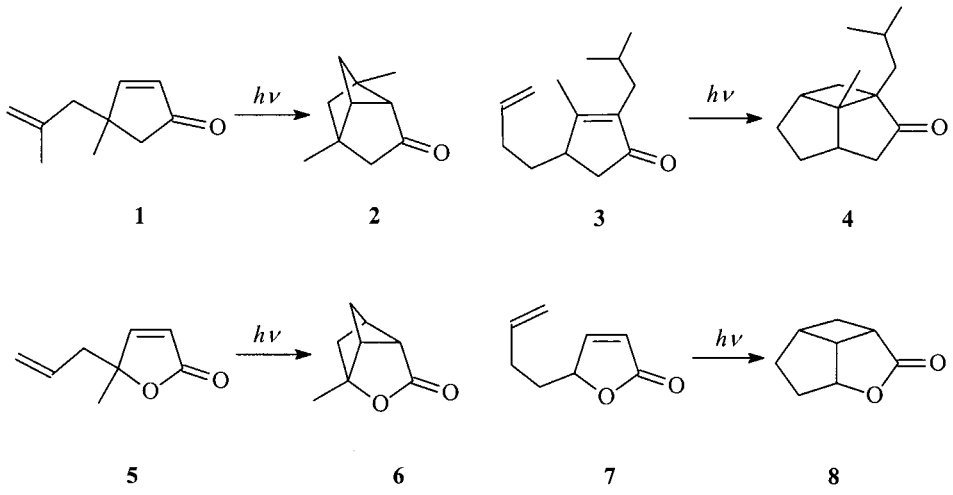
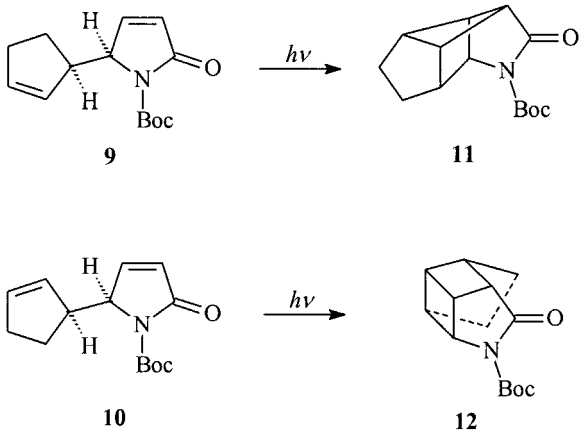
[1]) Part of the Ph.D. thesis of *M. N. W.*, Universität Hamburg, 2002.

Scheme 1

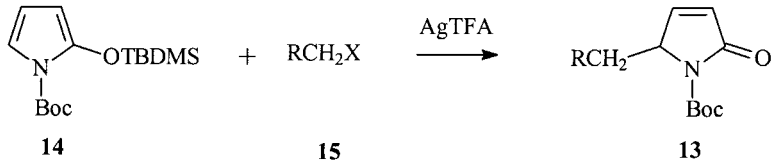


Scheme 2



Results. – Compounds **13** were obtained by alkylation of *tert*-butyl 2-[(*tert*-butyl)dimethylsilyloxy]-1*H*-pyrrole-1-carboxylate (**14**) [12] with the appropriate alkenyl halide **15** (X = Br for **15a**–**15c** and X = I for **15d**,**e**) in the presence of CF_3COOAg (AgTFA) [13] (*Scheme 3*). Irradiations (254 nm) of **13** were performed in MeCN as solvent, and the separation/isolation of products (*Scheme 4*) were achieved by chromatography. The yields given are those of isolated products **16**–**21**. The structural assignment of the methylene-bridged tricycles **16a** and **19** stems from their ^{1}H-NMR spectra wherein the H-atoms of this methylene bridge resonate as an *AB* system with $^2J = -7.1$ and -10.2 Hz, respectively. This finding is in agreement with the general knowledge [14] that the (absolute) value of a geminal coupling constant

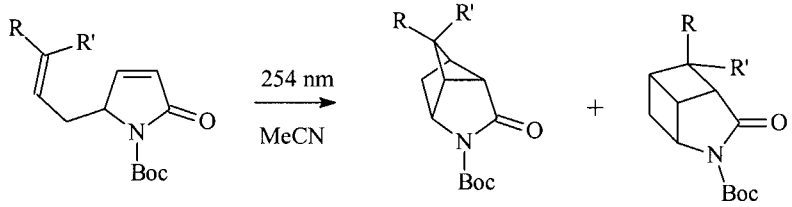
Scheme 3



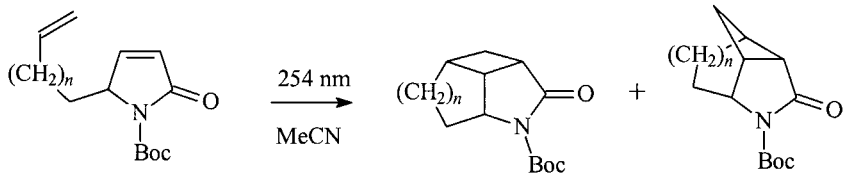
14 **15** **13**

a R = CH_2=CH **d** R = CH_2=$CHCH_2$
b R = (*E*)-CH_3CH=CH **e** R = CH_2=$CH(CH_2)_2$
c R = $(CH_3)_2$C=CH

Scheme 4



13a R, R' = H **16a**: 52% **17a**: 10%
13b R = H, R' = Me **16b**: 54% **17b**: -
13c R, R' = Me **16c**: 34% **17c**: 21%



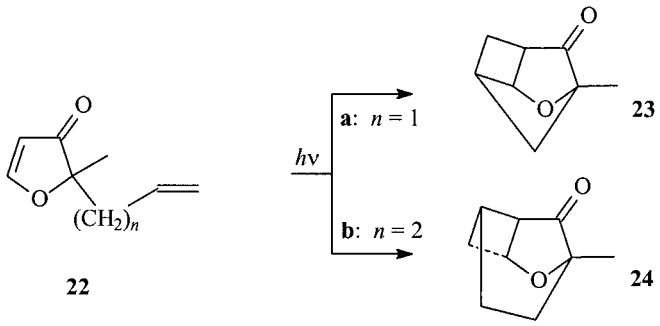
13d *n* = 1 **18**: 62% **19**: 8%
13e *n* = 2 **20**: 61% **21**: -

decreases with increasing sp^2 character of the corresponding C-atom. In the ^{13}C-NMR spectra, the ring carbonyl C-atoms of the *straight* cycloadducts **17**, **18**, and **20** ($\delta \approx 177-179$ ppm) always resonate at lower field than those of the *crossed* cycloadducts **16** and **19** ($\delta \approx 171-173$ ppm), reflecting the higher strain in a bicyclo[2.2.0]hexane as compared to a bicyclo[2.1.1]hexane unit [15]. Finally, the structure of **17a** was established by X-ray analysis.

Discussion. – Reactions at C(5) of silyloxy-pyrrole **14** with formation of a new C–C bond [16] continue to be of interest, as illustrated in a recent enantioselective synthesis of the antiinfluenza compound A-315675 [17]. Moreover the sequence *a*) intermolecular photocycloaddition of a Boc-protected pyrrolone to ethene, and *b*) methanolysis of the lactam ring has been used in the synthesis of a γ-amino acid derivative containing a cyclobutane skeleton [18]. In this connection, pyrrolones **13a**–**13c** represent convenient model compounds for studying the regiochemical control in intramolecular photochemical reactions of 1-acylhexa-1,5-dienes, as they also undergo preferential cyclization by way of 1,5 (*crossed*) closure. The relatively high amount of **17c** formed on irradiation of **13c**, *i.e.*, a shift to 1,6 (*straight*) closure, is of interest, as, for open-chain model compounds, alkyl substitution at C(6) normally does not modify the regiochemistry [19]. The preferential formation of **18** from **13d** proceeds in analogy to the selective conversion of furanone **7** to tricycle **8** [10]. In this context, it should be mentioned that the corresponding S-heterocycles, *i.e.*, 5-alkenyl-2(5*H*)-thiophen-2-ones, undergo efficient S–C(O) homolysis from their excited singlet state and, therefore, do not afford any products resulting from (triplet) interaction between the two C=C bonds [20].

The selective conversion of **13e** to **20**, analogous to that of **13d** to **18**, seems to correspond to the assumption [21] that *straight* cycloadducts are formed in high regioselectivity, whenever the 'enone' is tethered to the 'olefin' by three or four atoms, *i.e.*, for both 1-acylhepta-1,6-dienes and 1-acylocta-1,7-dienes. Nevertheless, such general inferences have to be applied with caution, as quite often subtile conformational factors govern the outcome of such reactions. This has been shown very recently for the allyl- and butenyl-substituted 2*H*-furan-3-ones **22** (*Scheme 5*): while **22a** photoisomerizes selectively to the *straight* cycloadduct **23** [22], a complete reversal in the regioselectivity is observed for **22b**, which affords the *crossed* cycloadduct **24** in 90% yield [23].

Scheme 5



Experimental Part

1. *General.* tert-*Butyl 2-[(*tert-*butyl)dimethylsilyloxy]-1*H-*pyrrole-1-carboxylate* (**14**) was prepared according to the procedure in [12]. *3-Bromoprop-1-ene* (**15a**), *(*E*)-1-bromobut-2-ene* (**15b**), and *1-bromo-3-methylbut-2-ene* (**15c**) were commercially available. *4-Iodobut-1-ene* (**15d**) and *5-iodopent-1-ene* (**15e**) were obtained by

reaction of the (commercially available) bromoalkenes with NaI in acetone. ^{1}H- and ^{13}C-NMR Spectra: 400 and 100.6 MHz, resp.; chemical shifts δ in ppm rel. to Me_4Si (=0 ppm). Photolyses: *Rayonet RPR-100* photoreactor equipped with 254-nm lamps. X-Ray crystal-structure analysis: *Enraf-Nonius CAD-4* four-circle diffractometer at 293 K with CuK_α radiation ($\lambda = 1.54178$ Å).

2. *Synthesis of Unsaturated Lactams* **13a**–**13e**. To a soln. of 1.488 g (5 mmol) **14** and the haloalkene (10 mmol) in 15 ml of CH_2Cl_2 at 0°, 2.21 g (10 mmol) CF_3COOAg was added, and the mixture was stirred for 1 h and allowed to warm up to r.t. After addition of 25 ml of sat. aq. $NaHCO_3$, the org. phase was separated, and the aq. phase was extracted 5 × with Et_2O (15 ml). The combined org. phases were washed with sat. aq. NaCl soln., dried ($MgSO_4$), the solvent was evaporated, and the residue was purified by column chromatography (CC) on SiO_2.

2.1. tert-*Butyl 2,5-Dihydro-2-oxo-5-(prop-2-enyl)-1*H-*pyrrole-1-carboxylate* (**13a**). With **15a**. 606 mg (54.3%). Colorless oil. R_f (Et_2O/hexane 5:3) 0.43. ^{1}H-NMR ($CDCl_3$): 7.14 (*dd*, *J* = 2.0, 6.1); 6.11 (*dd*, *J* = 1.5, 6.1); 5.64 (*dddd*, *J* = 6.3, 8.1, 10.4, 16.8); 5.13 (*m*, 2 H); 4.64 (*dddd*, *J* = 1.5, 2.0, 3.6, 8.1); 2.80 (*m*); 2.50 (*ddd*, *J* = 8.1, 8.1, 13.7); 1.57 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$): 169.2 (*s*); 149.9 (*d*); 149.4 (*s*); 131.1 (*d*); 126.9 (*d*); 119.6 (*t*); 83.0 (*s*); 61.7 (*d*); 35.8 (*t*); 28.1 (*q*).

2.2. tert-*Butyl 2-[(*E*)-But-2-enyl]-2,5-dihydro-5-oxo-1*H-*pyrrole-1-carboxylate* (**13b**). With **15b**. 688 mg (58%). Colorless oil. R_f (AcOEt/hexane 1:1) 0.58. ^{1}H-NMR ($CDCl_3$): 7.13 (*dd*, *J* = 2.0, 6.1); 6.09 (*dd*, *J* = 1.5, 6.1); 5.54 (*m*); 5.26 (*m*); 4.57 (*m*); 2.72 (*m*); 2.41 (*ddd*, *J* = 8.1, 8.1, 13.7); 1.65 (*d*, *J* = 6.4, 3 H); 1.57 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$): 169.4 (*s*); 150.3 (*d*); 149.4 (*s*); 130.4 (*d*); 126.7 (*d*); 123.5 (*d*); 82.9 (*s*); 62.2 (*d*); 34.8 (*t*); 28.1 (*q*); 18.0 (*q*).

2.3. tert-*Butyl 2,5-Dihydro-2-(3-methylbut-2-enyl)-5-oxo-1*H-*pyrrole-1-carboxylate* (**13c**). With **15c**. 543 mg (43.2%). Colorless oil. R_f (AcOEt/hexane 1:2) 0.37. ^{1}H-NMR ($CDCl_3$): 7.12 (*dd*, *J* = 2.0, 6.1); 6.09 (*dd*, *J* = 1.5, 6.1); 4.99 (*m*); 4.58 (*m*); 2.76 (*m*); 2.39 (*m*); 1.70 (*s*, 3 H); 1.62 (*s*, 3 H); 1.57 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$): 169.4 (*s*); 150.6 (*d*); 149.5 (*s*); 136.5 (*s*); 126.6 (*d*); 116.8 (*d*); 82.9 (*s*); 62.4 (*d*); 30.5 (*t*); 28.2 (*q*); 25.8 (*q*); 17.8 (*q*).

2.4. tert-*Butyl 2-(But-3-enyl)-2,5-dihydro-5-oxo-1*H-*pyrrole-1-carboxylate* (**13d**). With **15d**. 347 mg (29.2%). Colorless oil. R_f (Et_2O/hexane 5:2) 0.47. ^{1}H-NMR ($CDCl_3$): 7.17 (*dd*, *J* = 2.0, 6.1); 6.10 (*dd*, *J* = 1.5, 6.1); 5.78 (*dddd*, *J* = 6.6, 6.6, 10.2, 16.8); 5.08–4.99 (*m*, 2 H); 4.63 (*m*); 2.20–1.94 (*m*, 3 H); 1.84 (*m*); 1.56 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$): 169.2 (*s*); 150.0 (*d*); 149.4 (*s*); 137.0 (*d*); 126.8 (*d*); 115.8 (*t*); 83.0 (*s*); 61.9 (*d*); 30.6 (*t*); 28.4 (*t*); 28.2 (*q*).

2.5. tert-*Butyl 2,5-Dihydro-5-oxo-2-(pent-4-enyl)-1*H-*pyrrole-1-carboxylate* (**13e**). With **15e**. 637 mg (50.7%). Colorless oil. R_f (Et_2O/hexane 3:1) 0.54. ^{1}H-NMR ($CDCl_3$): 7.15 (*dd*, *J* = 2.0, 6.1); 6.10 (*dd*, *J* = 1.5, 6.1); 5.75 (*dddd*, *J* = 6.6, 6.6, 10.2, 17.0); 5.01 (*m*); 4.98 (*m*); 4.62 (*m*); 2.04 (*m*, 3 H); 1.78 (*m*); 1.56 (*s*, 9 H); 1.35 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 169.4 (*s*); 150.3 (*d*); 149.4 (*s*); 137.8 (*d*); 126.7 (*d*); 115.3 (*t*); 82.9 (*s*); 62.3 (*d*); 33.4 (*t*); 30.8 (*t*); 28.2 (*q*); 23.2 (*t*).

3. *Photolyses.* Ar-degassed solns. of **13** (1 mmol) in 75 ml of MeCN were irradiated in a quartz vessel for 6 h. After evaporation of the solvent, the residue was separated and purified by CC on SiO_2.

3.1. *Irradiation of* **13a**. Elution with AcOEt/hexane 1:2 afforded first (R_f 0.41) 116 mg (52%) of tert-*butyl 3-oxo-4-azatricyclo[3.3.0.0^{2,7}]octane-4-carboxylate* (**16a**). M.p. 112°. ^{1}H-NMR (C_6D_6): 4.38 (*m*, H–C(5)); 2.33 (*m*, H–C(2)); 2.16 (*m*, H–C(7)); 2.06 (*m*, H–C(1)); 1.48 (*s*, 9 H); 1.37 (*dd*, *J* = 4.6, 11.2, H_{exo}–C(6)); 1.19 (*m*, H_{endo}–C(6), H_{syn}–C(8)); 0.39 (*d*, *J* = 7.1, H_{anti}–C(8)). ^{13}C-NMR (C_6D_6): 170.4 (*s*, C(3)); 150.7 (*s*); 81.2 (*s*); 57.1 (*d*, C(5)); 55.5 (*d*, C(2)); 45.8 (*d*, C(1)); 39.6 (*d*, C(7)); 36.3 (*t*, C(6)); 35.0 (*t*, C(8)); 28.2 (*q*).

The second fraction (R_f 0.34) consisted of 25 mg (10.2%) of tert-*butyl 7-oxo-6-azatricyclo[3.2.1.0^{3,8}]octane-6-carboxylate* (**17a**). M.p. 83°. ^{1}H-NMR ($CDCl_3$): 4.69 (*m*, H–C(5)); 3.28 (*m*, H–C(8)); 3.20 (*m*, H–C(1)); 3.07 (*m*, H_{exo}–C(4)); 2.95 (*m*, H_{exo}–C(2)); 2.81 (*m*, H–C(3)); 2.31 (*m*, H_{endo}–C(2)); 2.12 (*m*, H_{endo}–C(4)); 1.54 (*s*, 9 H). ^{13}C-NMR (C_6D_6): 178.8 (*s*, C(7)); 150.2 (*s*); 82.7 (*s*); 63.2 (*d*, C(5)); 40.7 (*d*, C(1)); 37.3 (*t*, C(4)); 36.7 (*d*, C(8)); 32.9 (*t*, C(2)); 32.0 (*d*, C(3)); 28.1 (*q*).

X-Ray Crystal-Structure Determination of **17a**. Pale colorless transparent blocks (1.2 × 0.5 × 0.5 mm) from hexane, $C_{12}H_{17}NO_3$, M_r 223.27, triclinic, space group $P\bar{1}$, $Z = 4$, $a = 5.878(1)$, $b = 14.148(1)$, $c = 14.422(1)$ Å, $\alpha = 76.31(1)°$, $\beta = 84.89(1)°$, $\gamma = 87.80(1)°$, $V = 1160.5(2)$ Å^3, $D_x = 1.278(1)$ g·cm^{-3}.

3.2. *Irradiation of* **13b**. Elution with Et_2O/hexane 2:1 afforded as main product (R_f 0.49) 128 mg (53.9%) of tert-*butyl* syn-*8-methyl-3-oxo-4-azatricyclo[3.3.0.0^{2,7}]octane-4-carboxylate* (**16b**). M.p. 52°. ^{1}H-NMR (C_6D_6): 4.40 (*m*, H–C(5)); 2.86 (*m*, 2 H); 1.89 (*m*, H–C(1), H–C(7)); 1.49 (*s*, 9 H); 1.46 (*dd*, *J* = 4.6, 11.2, H_{exo}–C(6)); 1.22 (*dd*, *J* = 2.0, 11.2, H_{endo}–C(6)); 0.93 (*q*, *J* = 6.6, H_{anti}–C(8)); 0.68 (*d*, *J* = 6.6, 3 H). ^{13}C-NMR (C_6D_6): 171.1 (*s*, C(3)); 150.6 (*s*); 82.0 (*s*); 57.7 (*d*, C(5)); 52.9 (*d*, C(2)); 50.4 (*d*, C(1)); 43.6 (*d*, C(7)); 43.4 (*d*, C(8)); 37.5 (*t*, C(6)); 28.2 (*q*); 12.6 (*q*, Me).

3.3. *Irradiation of* **13c**. Elution with Et_2O/hexane 3:2 afforded first (R_f 0.40) 86 mg (34.2%) of tert-*butyl 8,8-dimethyl-3-oxo-4-azatricyclo[3.3.0.0^{2,7}]octane-4-carboxylate* (**16c**). M.p. 81°. ^{1}H-NMR ($CDCl_3$): 4.52 (*m*, H–C(5)); 3.12 (*m*, H–C(2)); 2.61 (*m*, H–C(7)); 2.56 (*m*, H–C(1)); 2.40 (*dd*, *J* = 4.4, 12.0, H_{exo}–C(6)); 1.54 (*s*, 9 H); 1.367 (*dd*, *J* = 1.9, 12.0, H_{endo}–C(6)); 1.29 (*s*, 3 H); 0.84 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 173.1 (*s*, C(3)); 149.6 (*s*); 82.7 (*s*); 58.5 (*d*, C(5)); 54.6 (*d*, C(1)); 51.9 (*d*, C(2)); 47.5 (*d*, C(7)); 44.1 (*s*, C(8)); 33.7 (*t*, C(6)); 28.2 (*q*); 21.5, 21.0 (*q*, Me).

The second fraction (R_f 0.33) consisted of 53 mg (21%) of tert-*butyl 2,2-dimethyl-7-oxo-6-azatricyclo[3.2.1.0^{3,8}]octane-6-carboxylate* (**17c**). M.p. 53°. ^{1}H-NMR ($CDCl_3$): 4.63 (*m*, H–C(5)); 3.23 (*m*, H–C(8)); 2.75 (*m*, H–C(1), H_{exo}–C(4)); 2.42 (*m*, H–C(3)); 2.17 (*ddd*, *J* = 1.5, 1.5, 13.9, H_{endo}–C(4)); 1.53 (*s*, 9 H); 1.31, 1.13 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 176.9 (*s*, C(7)); 150.0 (*s*); 82.6 (*s*); 55.6 (*d*, C(5)); 52.3 (*d*, C(1)); 42.6 (*d*, C(3)); 41.8 (*s*, C(2)); 32.5 (*d*, C(8)); 31.6 (*q*, Me); 28.1 (*q*); 20.8 (*q*, Me).

3.4. *Irradiation of* **13d**. Elution with AcOEt/hexane 1:2 afforded first (R_f 0.43) 20 mg (8%) of tert-*butyl 8-oxo-7-azatricyclo[4.3.0.0^{3,9}]nonane-7-carboxylate* (**19**). M.p. *ca.* 30°. ^{1}H-NMR (C_6D_6): 4.32 (*m*, H–C(6)); 2.49 (*m*, H–C(9)); 2.14 (*m*, H–C(3)); 2.06 (*m*, H–C(1)); 1.84 (*m*, H_{endo}–C(5)); 1.73 (*m*, H_{endo}–C(4)); 1.54 (*s*, 9 H); 1.49 (*m*, H_{exo}–C(5)); 1.39–1.28 (*m*, H_{exo}–C(4), H_{anti}–C(2)); 1.06 (*d*, *J* = 10.2, H_{syn}–C(2)). ^{13}C-NMR (C_6D_6): 172.5 (*s*, C(8)); 151.2 (*s*); 81.8 (*s*); 58.5 (*d*, C(6)); 49.8 (*d*, C(9)); 36.6 (*d*, C(1)); 28.2 (*q*); 23.6 (*t*, C(2)); 22.9 (*t*, C(4)); 22.4 (*t*, C(5)).

The second fraction (R_f 0.37) consisted of 147 mg (61.7%) of tert-*butyl 4-oxo-5-azatricyclo[4.2.1.0^{3,9}]nonane-5-carboxylate* (**18**). Colorless oil. ^{1}H-NMR (CD_3COCD_3): 4.52 (*m*, H–C(6)); 3.09 (*m*, H–C(9)); 2.91 (*m*, H–C(3)); 2.77 (*m*, H–C(1), H_{exo}–C(2)); 2.16 (*m*, H_{endo}–C(7)); 2.04 (*m*, H_{endo}–C(8)); 1.86 (*dddd*, *J* = 5.1, 8.1, 10.2, 13.5, H_{exo}–C(7)); 1.64 (*ddd*, *J* = 3.0, 3.0, 11.6, H_{endo}–C(2)); 1.55 (*m*, H_{exo}–C(8)); 1.51 (*s*, 9 H). ^{13}C-NMR (CD_3COCD_3): 176.6 (*s*, C(4)); 151.1 (*s*); 82.1 (*s*); 64.3 (*d*, C(6)); 39.9 (*d*, C(9)); 39.2 (*d*, C(3)); 37.0 (*d*, C(1)); 36.3 (*t*, C(7)); 32.2 (*t*, C(8)); 31.6 (*t*, C(2)); 28.2 (*q*).

3.5. *Irradiation of* **13e**. Elution with Et_2O/hexane 3:2 afforded as main product (R_f 0.38) 153 mg (60.8%) of tert-*butyl 4-oxo-5-azatricyclo[4.3.1.0^{3,10}]decane-5-carboxylate* (**20**). M.p. 69°. ^{1}H-NMR ($CDCl_3$): 4.36 (*m*, H–C(6)); 3.13 (*ddd*, *J* = 6.1, 8.2, 10.2, H–C(3)); 2.86–2.71 (*m*, H–C(1), H_{exo}–C(2)); 2.56 (*dddd*, *J* = 2.2, 10.2, 10.3, 12.7, H–C(10)); 2.26 (*m*, H_{endo}–C(7)); 2.00 (*ddd*, *J* = 5.9, 7.6, 12.7, H_{endo}–C(2)); 1.54 (*s*, 9 H)); 1.70–1.30 (*m*, H_{exo}–C(7), H_{exo}–C(8), H_{endo}–C(8), H_{exo}–C(9), H_{endo}–C(9)). ^{13}C-NMR ($CDCl_3$): 177.7 (*s*, C(4)); 150.4 (*s*); 82.7 (*s*); 55.6 (*d*, C(6)); 38.3 (*d*, C(3)); 28.2 (*t*, C(2)); 28.1 (*q*); 28.0 (*d*, C(10)); 27.8 (*d*, C(1)); 27.3 (*t*, C(7)); 26.9 (*t*, C(9)); 14.3 (*t*, C(8)).

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