176. Photochemistry of 2-Allyl-3-oxo-2,3-dihydro-1*H*-pyrrole-2-carboxylates

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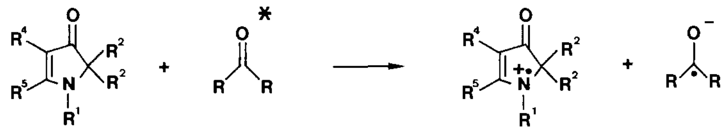
Summary

On acetone-sensitized irradiation the title compounds **3a–c** are converted to 2-allyl-3-hydroxy-1*H*-pyrrole-2-carboxylates **4** in reasonable yields.

In contrast to 4-oxa- and 4-thia-2-cyclopentenones, the corresponding aza-analogues, 1,2-dihydro-3*H*-pyrrol-3-ones **1**, do not undergo the typical intermolecular photochemical enone reactions, *e.g.* cyclodimerization or cycloaddition to olefins. Electron transfer from the amine to an excited carbonyl molecule is observed when trying to use ketones as sensitizers for such reactions *(Scheme 1)* [1] [2].

Scheme 1



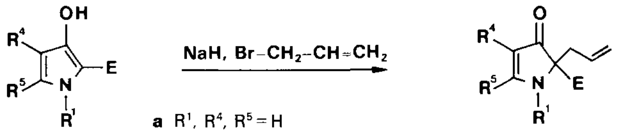
1

a R^1, $R^2 = H$; R^4, $R^5 = CH_3$

b $R^1 = (CH_3)_2CH$; $R^2 = CH_3$; R^4, $R^5 = H$

We have synthesized several such aza-enones **3** bearing an allyl group at position 2 by alkylation of the easily accessible 3-hydroxy-1*H*-pyrrole-2-carboxylates **2** with allyl bromide in the presence of NaH *(Scheme 2)* to investigate intramolecular light-induced interactions between the enone system and the additional C=C bond.

Scheme 2



2 **3**

a R^1, R^4, $R^5 = H$

b $R^1 = CH_3$; R^4, $R^5 = H$

c $R^1 = CH_2{=}CHCH_2$; R^4, $R^5 = H$

d $R^1 = H$; R^4, $R^5 = CH_3$

e R^1, R^4, $R^5 = CH_3$

f $R^1 = H$; R^4, $R^5 = (CH_2)_4$

g $R^1 = CH_3$; R^4, $R^5 = (CH_2)_4$

E = COOEt

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[1]) Taken in part from the Ph. D. Thesis of *R. G.-T.*, University of Hamburg, 1984.

Table. *Spectroscopic Data of* **2c**, **2e**, **3** *and* **4**

Compound[a])	UV [nm (log ε)] (CH$_3$CN)	IR [cm^{-1}] (CCl$_4$)	^{1}H-NMR [ppm] (400 MHz, CDCl$_3$)	^{13}C-NMR [ppm] (100.83 MHz)	MS (70 eV)
2c	263 (4.18)	3450, 1690, 1630, 1540	6.58 and 5.76 (*AB*, *J* = 3.0, 2H); 5.92 (*m*, 1H); 5.03 (*m*, 2H); 4.69 (*d*, 2H); 4.33 (*q*, 2H); 1.31 (*t*, 3H)	–	195 (M^+), *149*
2e	277 (4.11)	3300, 1690, 1630, 1570	4.32 (*q*, 2H); 3.62 (*s*, 3H); 2.07 (*s*, 3H); 1.87 (*s*, 3H); 1.33 (*t*, 3H)	163 (*s*); 153 (*s*); 134 (*s*); 105 (*s*); 103 (*s*); 60 (*t*); 32, 15, 10, 7 (*q*)	197 (M^+), *151*
3a	309 (3.95)	1720, 1650[b])	8.07 and 5.64 (*AB*, *J* = 3.5, 2H); 5.72 (*m*, 1H); 5.22 (*m*, 2H); 4.27 (*q*, 2H); 2.75 (*m*, 2H); 1.28 (*t*, 3H)	–	*195* (M^+)
3b[c])	327 (3.99)	1730, 1670	7.85 and 5.06 (*AB*, *J* = 3.5, 2H); 5.63 (*m*, 1H); 5.13 (*m*, 2H); 4.23 (*q*, 2H); 3.07 (*s*, 3H); 2.94 (*m*, 2H); 1.24 (*t*, 3H)	–	209 (M^+), *28*
3c	328 (4.02)	1740, 1680	7.93 and 5.11 (*AB*, *J* = 3.5, 2H); 5.88 (*m*, 1H); 5.53 (*m*, 1H); 5.35 (*m*, 2H); 5.14 (*m*, 2H); 4.21 (*q*, 2H); 3.89 (*m*, 2H); 2.95 (*m*, 2H); 1.26 (*t*, 3H)	–	235 (M^+), *41*
3d	320 (4.13)	1720, 1680	5.70 (*m*, 1H); 5.16 (*m*, 2H); 4.23 (*q*, 2H); 2.70 (*m*, 2H); 2.15 (*s*, 3H); 1.63 (*s*, 3H); 1.26 (*t*, 3H)	195 (*s*); 175 (*s*); 168 (*s*); 132 (*d*); 119 (*t*); 107 (*s*); 73 (*s*); 62 (*t*); 40 (*t*); 15, 14, 6 (*q*)	223 (M^+), *43*

3e	336 (4.15)	1730, 1670	5.44 (*m*, 1H); 5.07 (*m*, 2H); 4.22 (*q*, 2H); 3.00 (*s*, 3H); 2.90 (*m*, 2H); 2.17 (*s*, 3H); 1.69 (*s*, 3H); 1.26 (*t*, 3H)	193 (*s*); 175 (*s*); 167 (*s*); 132 (*d*); 119 (*t*); 104 (*s*); 76 (*s*); 62 (*t*); 37 (*t*); 30, 14, 12, 7 (*q*)	237 (M^+), *164*
3f	320 (3.96)	1710, 1680	5.71 (*m*, 1H); 5.14 (*m*, 2H); 4.20 (*q*, 2H); 2.92 (*m*, 2H); 2.42 (*m*, 2H); 2.14 (*m*, 2H); 1.69 (*m*, 4H); 1.26 (*t*, 3H)	–	249 (M^+), *176*
3g	336 (4.02)	1730, 1670	5.47 (*m*, 1H); 5.07 (*m*, 2H); 4.23 (*q*, 2H); 2.96 (*s*, 3H); 2.91 (*m*, 2H); 2.46–2.21 (*m*, 4H); 1.72 (*m*, 4H); 1.29 (*t*, 3H)	–	263 (M^+), *190*
4a	265 (4.13)	1700, 1640, 1580	6.38 (*s*, 1H); 5.95 (*m*, 1H); 5.05 (*m*, 2H); 4.37 (*q*, 2H); 3.16 (*d*, 2H); 1.38 (*t*, 3H)	–	195 (M^+), *122*
4b	266 (4.11)	1700, 1650, 1590	6.37 (*s*, 1H); 5.95 (*m*, 1H); 5.07 (*m*, 2H); 4.37 (*q*, 2H); 3.71 (*s*, 3H); 3.14 (*d*, 2H); 1.36 (*t*, 3H)	–	209 (M^+), *163*
4c	265 (4.08)	1700, 1650, 1590	6.46 (*s*, 1H); 5.95 (*m*, 2H); 5.10 (*m*, 4H); 4.68 (*d*, 2H); 4.38 (*q*, 2H); 3.18 (*d*, 2H); 1.38 (*t*, 3H)	–	235 (M^+), *189*

[a] All new compounds gave satisfactory elemental analyses.

[b] In KBr.

[c] *cf.* [8].

Direct ($\lambda > 280$ nm) irradiation of compounds **3** leads only to slow decomposition of starting material. Herein, the photochemical behaviour of **3** parallels that of aza-enones **1**. Acetone-sensitized irradiation of **3a–c** gives one new photoproduct, **4a–c**, respectively. Enones **3d–g** are photostable under these conditions. This divergent reactivity of excited acetone towards **1** (electron transfer from the amine) and **3** (energy transfer for the amine) is apparently due to the difference in ease of oxidation of **1** and **3** (it can be assumed that the oxidation potentials of the aza-enones differ by a similar value as ethyl amine and ethyl aminoacetate, *i.e.* by approx. 0.4–0.5 V [3]). Obviously the oxidation of **3** by triplet acetone is less favourable than the observed energy transfer.

From the spectroscopic data summarized in the *Table*, photoproducts **4** are easily identified as 3-hydroxy-4-allyl-1*H*-pyrrole-2-carboxylates. The formation of **4** from **3** can be explained by the reaction sequence given in *Scheme 3*. Herein triplet **3** – formed *via* energy transfer from triplet acetone – undergoes the first step of an intramolecular [2 + 2] cycloaddition to afford the biradical **5**. Cleavage of a C—C bond gives the biradical **7** which then tautomerizes to product **4**. Although 5-allyl-2-cyclopentenones are known to photoisomerize to tricyclooctanones [4] the diradical **5** does not undergo a ring closure to the corresponding azatricyclooctanone **6**. This is probably due to the ethoxycarbonyl group which facilitates the formation of **7** from **5** by stabilizing the new biradical. For a better understanding of such reactions, it is thus necessary to investigate the photochemical behaviour of carbocyclic-, 4-oxa- and 4-thia-2-cyclopentenones exhibiting the same structural features as compounds **3**, *i.e.* bearing an ethoxycarbonyl and an allyl group on C(5). This work is now in progress.

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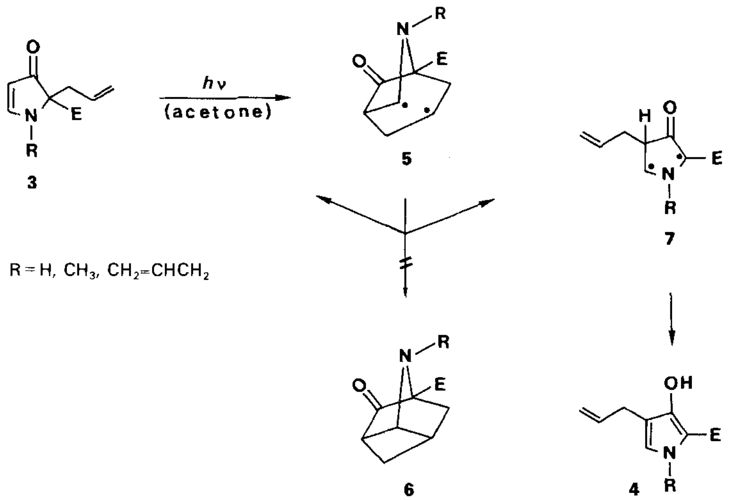
Scheme 3



Experimental Part

Starting Materials. Carboxylates **2a** [5], **2b** [5], **2d** [6], **2f** [6], and **2g** [7] were synthesized according to the references indicated; **2c** (oil, 40%) and **2e** (m.p. 35°, 20%) were prepared in analogy to [5] and [7], respectively.

*Ethyl 2-Allyl-3-oxo-2,3-dihydro-1*H*-pyrrole-2-carboxylates* (**3**). A solution of 3 mmol **2** in 10 ml benzene was added to a stirred suspension of 3 mmol NaH in 20 ml benzene under N_2. After warming to 60° for 1 h, a solution of 9 mmol allylbromide in 20 ml benzene was added dropwise. The mixture was then refluxed for 4 h, cooled, filtered and the solvent evaporated. Chromatography (SiO_2, AcOEt/hexane 2:1) afforded: **3a** (m.p. 106°, 65%), **3b** (oil, [8]), **3c** (oil, 44%), **3d** (oil, 75%), **3e** (oil, 85%), **3f** (m.p. 78°, 85%) and **3g** (oil, 80%).

Photolyses. These were performed using a 250-W Hg-lamp and a *Pyrex* filter. The degree of conversion was monitored by TLC (SiO_2, CH_2Cl_2).

*Ethyl 2-Allyl-3-hydroxy-4-1*H*-pyrrole-2-carboxylates* **4**. Thoroughly degassed 10^{-1} M solutions of **3** in 10 ml acetone were irradiated for 6 h. Evaporation of the solvent and chromatography (SiO_2, CH_2Cl_2) afforded: **4a** (oil, 50%), **4b** (oil, 43%) and **4c** (oil, 39%).

REFERENCES

[1] *R. Ghaffari-Tabrizi & P. Margaretha*, Helv. Chim. Acta *65*, 1029 (1982).
[2] *E. Anklam, R. Ghaffari-Tabrizi, H. Hombrecher, S. Lau & P. Margaretha*, Helv. Chim. Acta *67*, 1402 (1984).
[3] *C.K. Mann*, Analyt. Chem. *36*, 2424 (1964).
[4] *G. Gowda & T.B.H. McMurry*, J. Chem. Soc., Perkin Trans. 1 *1980*, 1516.
[5] *T. Momose, T. Tanaka, T. Yokota, N. Nagamoto & K. Yamada*, Chem. Pharm. Bull. *26*, 2224 (1978).
[6] *H. Bauer & G. Pfeiffer*, Liebigs Ann. Chem. *1976*, 383.
[7] *H. Bauer & G. Pfeiffer*, Liebigs Ann. Chem. *1980*, 564.
[8] *T. Momose, T. Tanaka, T. Yokota, N. Nagamoto & K. Yamada*, Chem. Pharm. Bull. *26*, 3521 (1978).