Pergamon

Tetrahedron Letters 39 (1998) 8641–8642

TETRAHEDRON
LETTERS

# Synthesis and Enhanced Regioselectivity in the Photodimerization of 9-Aminoacridizinium Perchlorate

Heiko Ihmels*

*Institut für Organische Chemie der Universität Würzburg, Am Hubland, D-97072 Würzburg, Germany*

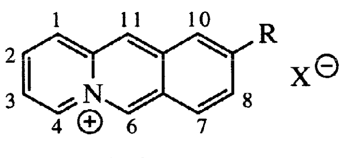
Received 11 August 1998; accepted 23 September 1998

## Abstract

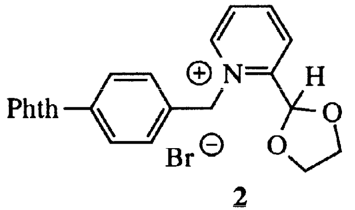
A donor-substituted acridizinium salt was synthesized, and an enhanced regioselectivity in the [4+4] photocycloaddition to give exclusively the head-to-tail products was observed.

*Keywords: photochemistry; cycloadditions; quinolizinium ions*

Photoinduced [4+4] cycloadditions are useful transformations in organic synthesis [1]; and for the general investigation of this reaction the photodimerization of acridizinium salts is an ideal model system [2]. In early reports it was postulated that only one of the four possible regioisomers is formed upon photolysis of chromophore **1a** [2a]; however, Wolff *et al.* showed, that all possible dimers are formed in this reaction [3]. A new strategy to achieve a higher regioselectivity in the dimerization of acridizinium salts may be the integration of a conjugated donor-acceptor system within **1a** by substitution with a donor functionality in the 9 position. The modified electronic structure of such an acridizinium salt is assumed to affect the interaction between ground and excited state molecules and, thus, should influence the regioselectivity of the photoreaction [4]. Presently, first experiments to realize this concept with the acridizinium chromophore are described, which include the synthesis of the amino-substituted acridizinium perchlorate **1b** and the investigation of its photochemical properties.



**1a,b**



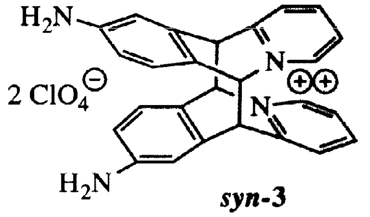
**2**

**1a**: R = H; X = Br; **1b**: R = $NH_2$; X = $ClO_4$; **2**: Phth = *N*-phthalimidyl

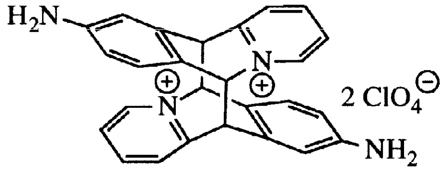
Acridizinium salt **1b**[1] was synthesized by cyclodehydration of the pyridinium derivative **2**[2] [2a], which was obtained by quarternization of 2-(1,3-dioxolan-2-yl)pyridine with *N*-(4-bromomethylphenyl)phthalimide. Irradiation of compound **1b** for 6 h in deoxygenated methanol or acetonitrile in a Pyrex vessel at room temperature gave two photoproducts ***syn*-3** and ***anti*-3** in a 1:1 ratio without any byproduct as was shown by $^1$H-NMR-spectroscopic investigation of the reaction mixture. This is in contrast to the photodimerization of the

0040-4039/98/$ - see front matter
*PII:* S0040-4039(98)02040-1

unsubstituted acridizinium salt **1a in solution, which** yields all four regioisomers [3]; however, a similar regioselectivity was reported recently for the photodimerization of 1,3-diazaanthracenes [5].



***syn*-3**



***anti*-3**

The assignment of the head-to-tail structure (ht) of the dimers is based on symmetry considerations.[3] Whereas each bridgehead proton of the head-to-head (hh) isomers is expected to give a singlet in the $^{1}$H-NMR spectrum, the corresponding protons of the ht dimers give doublets at lower field, as was shown for the dimers of acridizinium salt **1a** [3]. Since $^{1}$H-NMR spectroscopic investigation of the product mixture showed only two sets of two doublets for the bridgehead protons, the formation of hh dimers can be excluded. The ht dimer ***anti*-3** was isolated in low yield (10%) by slow precipitation in methanol. The structures of the *syn* and *anti* isomers were assigned by comparison with the data for the corresponding dimers of **1a** [3]. Moreover, a small nuclear Overhauser effect was observed for the signal of 4-H in ***anti*-3** and for 7-H in ***syn*-3**, respectively, when the proton on C-10 was irradiated.

In summary, a new concept is presented which allows the control of the regioselectivity in the [4+4] photocycloaddition of acridizinium salts by the incorporation of a donor-acceptor functionality within the chromophore.[4] This novel methodology should be extendable to other photocycloaddition reactions.

**Acknowledgement**: This work was financed by the *Fonds der Chemischen Industrie* and the ***Bundesministerium für Bildung und Forschung*** and generously supported by Prof. Waldemar Adam.

## References:

[1] (a) McN. Sieburth S, Cunard NT. Tetrahedron 1996; 52: 6251. (b) Kaupp G. Angew. Chem., Int. Ed. Engl. 1992; 31: 422.

[2] (a) Bradsher CK. The Quinolizinium Ion and Aza Analogs. In Boultier AJ, McKillop A., editors. Comprehensive Heterocyclic Chemistry. Oxford: Pergamon Press, 1985; Vol. 2, 525; for topochemical dimerizations in the solid state see: (b) Wang WN, Jones W. Tetrahedron 1987; 43: 1273; (c) Wang WN, Jones W. Mol. Cryst. Liq. Cryst. 1994; 242: 227.

[3] Lehnberger, C, Scheller, D, Wolff, T. Heterocycles 1997; 10: 2033.

[4] For selective photocycloadditions of donor-acceptor-substituted olefins see: (a) Tscherny I, Döpp D, Henkel G. J. Inf. Recording 1998: in press; (b) Döpp D, Hassan AA, Henkel G. Liebigs Ann. Chem. 1996: 697.

[5] Warner RW, Golic M, Butler DN. Tetrahedron Lett. 1998; 39: 4717.

---

1) Selected analytical data: **1b**: mp 232–233 °C (dec.); UV (MeOH): $\lambda$ 392 (br), 450 (br); $^{1}$H-NMR (DMSO-$d_6$): $\delta$ 7.01 (d, 1 H), 7.46–7.54 (m, 2 H) , 7.75 (dd, 1 H), 8.12 (d, 1 H), 8.21 (d, 1 H), 8.40 (s, 1 H), 8.85 (d, 1 H), 9.83 (s, 1 H); $^{13}$C-NMR (DMSO-$d_6$): $\delta$ 99.9, 116.6, 118.2, 120.2, 124.9, 125.2, 129.4, 130.5, 133.3, 137.3, 138.2, 138.5, 154.8; MS (FAB (+), glycerol): *m/z* (rel. Int.) 195 (M$^+$, 8); correct El. Anal..

2) Selected analytical data: **2**: mp 182–183 °C (dec.); $^{1}$H-NMR (CD$_3$OD): $\delta$ 4.22 (s, 4 H), 6.13 (s, 2 H), 6.47 (s, 1 H); $^{13}$C-NMR (CD$_3$OD) $\delta$ 61.6, 67.4, 99.0; MS (FAB (+), glycerol): *m/z* (rel. Int.) 387 (M$^+$, 83); correct El. Anal..

3) Selected analytical data: ***anti*-3**: $^{1}$H-NMR (DMSO-$d_6$): $\delta$ 5.85 (d, $^{3}J$ = 11 Hz, 2 H), 6.80 (d, $^{3}J$ = 11 Hz, 2 H); $^{13}$C-NMR (DMSO-$d_6$): $\delta$ 50.5, 71.5. – ***syn*-3** : $^{1}$H-NMR (DMSO-$d_6$): $\delta$ 5.83 (d, $^{3}J$ = 10 Hz, 2 H), 6.83 (d, $^{3}J$ = 11 Hz, 2 H).

4) The regioselectivity could be rationalized on the basis of PM3 calculations. These results will be presented in the corresponding Full Paper.