Pergamon

Tetrahedron Letters, Vol. 37, No. 8, pp. 1191-1194, 1996
Copyright © 1996 Published by Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0040-4039/96 \$15.00 + 0.00

0040-4039(95)02414-2

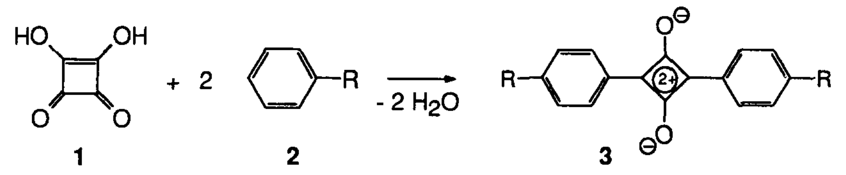
Bis(stilbenyl)squaraines - Novel Pigments with Extended Conjugation

Herbert Meier* and Uta Dullweber
Institute of Organic Chemistry, University of Mainz
J.-J.-Becherweg 18-22, D-55099 Mainz, Germany

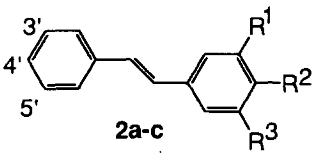
Abstract: We report on the synthesis of a novel type of squaraines (**11a-f**, **17c**) in which the conjugation of the chromophore is extended by stilbene units. These pigments exhibit absorption bands which have their maxima at the end on the Vis region and reach partly into the NIR.

Stilbenes constitute an important class of photochemically well examined compounds - not least owing to their applications in materials science as optical brighteners, laser dyes, optical recording media, photoresists, photoconductors, light emitting diodes, materials for nonlinear optics (NLO) etc.[1] The optical characteristics of squaraines (1,3-disubstituted squaric acid derivatives) have made these organic dyes also very attractive for technological applications like electrophotography,[2] solar energy conversion,[3] optical data storage,[4] and NLO.[5] A combination of these two building blocks - stilbene and squaraine - should create very interesting new materials. The extension of the conjugated system in comparison to the phenylsquaraines should produce a bathochromic shift in the UV/Vis absorption spectra and this would be extremely useful for the absorption of GaAs diode laser light with its emission in the NIR.[6] Squaraines are traditionally[7] prepared by condensation reactions of squaric acid with arenes or hetarenes bearing electron-donating groups (R = Alkoxy, Dialkylamino). Usually an azeotropic removal of water is performed.

Scheme 1



1 **2** **3**



2a-c

2	R^1	R^2	R^3
a	H	OC_6H_{13}	H
b	H	$N(CH_3)_2$	H
c	$OC_{12}H_{25}$	$OC_{12}H_{25}$	$OC_{12}H_{25}$

It turned out, that none of the stilbenes **2a-c** was nucleophilic enough in position 4' to condense with squaric acid. To enhance the required nucleophilicity a hydroxy group was introduced in position 3', but that phenol did not give a reaction with squaric acid, either. Finally the twofold condensation to the symmetrical squaraines **11a-f** succeeded with the 3',5'-dihydroxystilbenes **10a-f**. The synthetic sequence was started with the convenient steps **4** → **5** → **6**. The stilbenes **9a-f** were obtained by a Wittig-Horner olefination. The PO-activated component **7** reacted with the benzaldehydes **8a-f** giving high yields of **9a-f**. A selective cleavage of the methyl ethers was achieved by the action of (diphenylphosphino)lithium; nevertheless this is a critical reaction step. Byproducts of the deprotection are mainly monodemethylated stilbenes and some trihydroxy compounds. The exposure of 3,4,5-tris(hexyloxy)-3',5'-dimethoxystilbene (**9f**) to $LiPPh_2$ generated hydroxy groups in 3'-,5'-, and 4-position; that means the most activated hexyloxy group was cleaved, too. Since the electron-releasing properties between a methoxy group and a hydroxy group are very similar, it is noteworthy that only the dihydroxystilbenes undergo the condensation reaction. H-bonding between the hydroxy groups and the CO groups of the four-membered ring is certainly the reason for this behaviour. The low yields of the condensation with squaric acid (**10a-f** → **11a-f**) are probably due to the still low nucleophilicity of **10a-f**.

Scheme 2

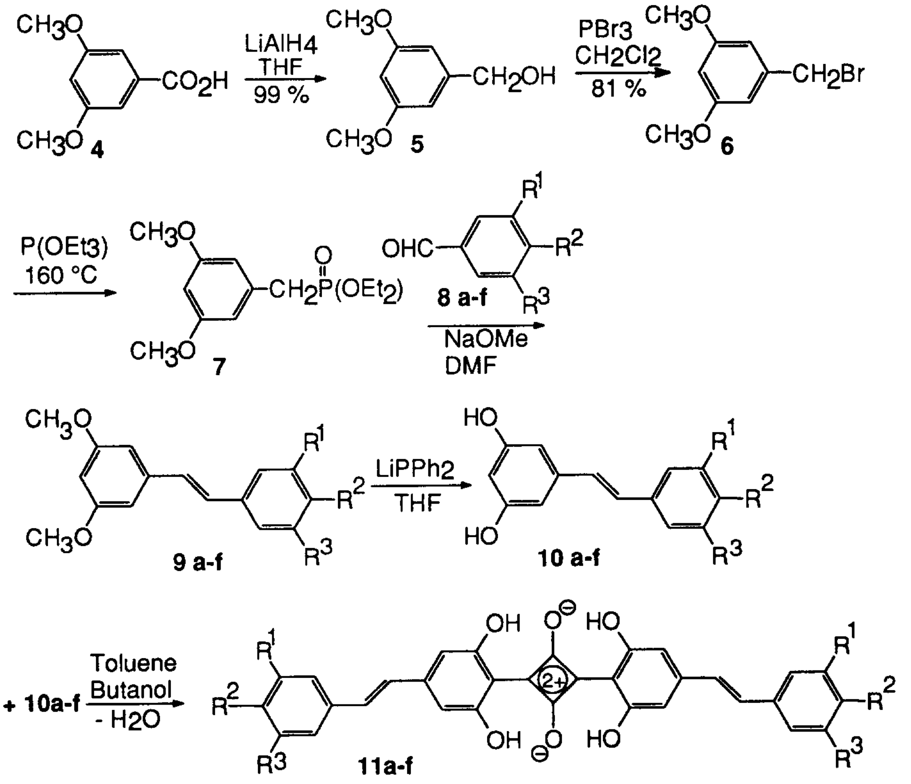


Table 1. Preparation of the squaraines **11 a-f**

	R^1	R^2	R^3	**6 → 9** Yield (%)	**9 → 10** Yield (%)	**10 → 11** Yield (%)	**11** m.p. (°C)	**11** λ_{max} (nm)
a	H	OC_6H_{13}	H	87	50	33	303a)	714
b	H	OC_8H_{17}	H	81	47	23	289a)	721
c	H	$OC_{10}H_{21}$	H	95	11	9	284a)	717
d	H	$OC_{12}H_{25}$	H	86	58	8	283a)	719
e	OC_6H_{13}	OC_6H_{13}	H	76	48	28	295a)	730
f	OC_6H_{13}	OH	OC_6H_{13}	73	8	21	138	735

a) decomposition

The yields of the final steps, the maximum absorption wavelengths, and the melting points of **11a-f** are summarized in Table 1. The squaraines precipitated from the reaction mixture as analytically pure, green "metallic", almost insoluble crystals. Variation of the number and length of the

Scheme 3

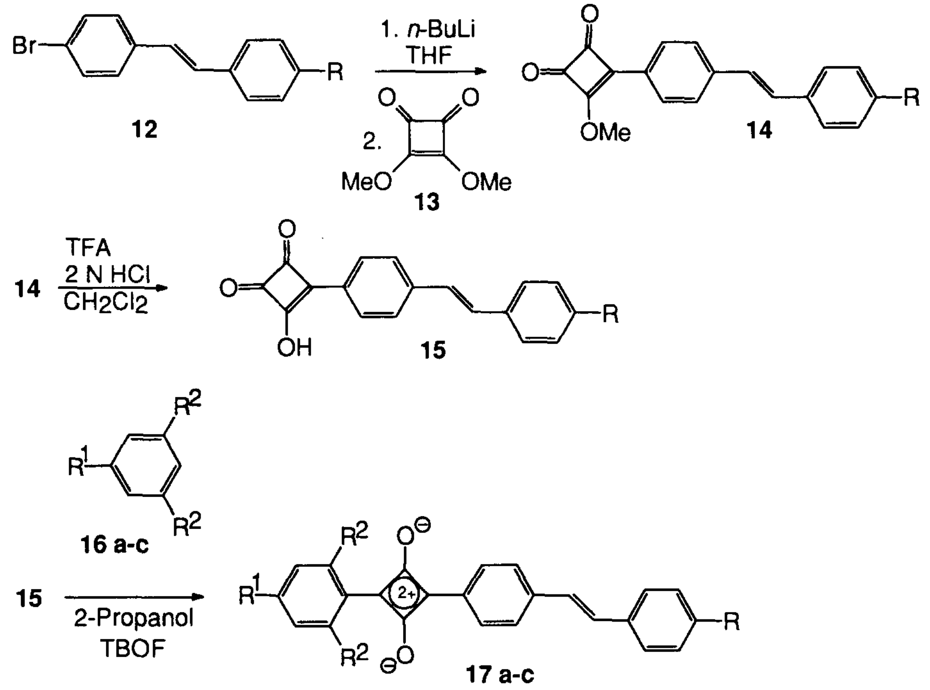


Table 2. Preparation of the squaraines **17 a-c**

	R	R^1	R^2	**12 → 14** Yield (%)	**14 → 15** Yield (%)	**15 → 17** Yield (%)	**17** m.p. (°C)	**17** λ_{max}(nm)
a	OCH_3	$N(CH_3)_2$	H	57	89	69	247a)	627
b	OC_6H_{13}	$N(CH_3)_2$	H	18	91	64	243a)	624
c	OC_6H_{13}	$CH{=}CH{-}C_6H_4{-}OC_{10}H_{21}$	OH	57	89	13	232a)	683

a) decomposition

side-chains did not affect the solubility in conventional organic solvents. The structural assignment was accomplished by elementary analysis, IR and mass spectroscopy (FD, FAB or Laser-FTMS techniques).[8] Due to the bond delocalization in the 4-membered ring the CO stretching vibration is shifted to 1620 cm^{-1}. An intense absorption typical for such 1,3-diarylsquaraines is observed at 1400 cm^{-1}. The (*E*)-configuration of the olefinic double bonds is provided by the vibration at 960 cm^{-1}. All squaraines **11** exhibit intense bands for the electronic absorption in the visible region. Their maxima are located between 714 and 735 nm. The foot of the bands reaches into the NIR region. Normal diarylsquaraines have absorption maxima around 570 nm.[2]

The dihydroxystilbenes were also used to synthesize non-symmetrical squaraines (Scheme 3). Exposure of a lithiated stilbene (generated by transmetallation of 4-bromostilbene (**12**) with n-butyllithium) to 3,4-dimethoxycyclobutenedione (**13**)[9] gave the semisquaric ester **14**. After hydrolysis the resulting semisquaric acid **15** was condensed either with the above mentioned dihydroxystilbene **10c** or with other suitable aromatic compounds such as N,N-dimethylaniline in refluxing 2-propanol in the presence of tributylorthoformate (TBOF).[10] Related, Chen et al. recently developed a squaraine with only one stilbene moiety.[11] Table 2 summarizes the yields, the melting points and the absorption maxima of the squaraines **17a-c**. The good yields of the green dyes **17a,b** are due to the higher nucleophilicity of dimethylaniline. These derivatives are somewhat better soluble than the symmetrical bis(stilbenyl)-squaraines. The characterization was accomplished analogously to the previously described pigments **11a-f** by elementary analyses, UV/Vis, IR and MS spectroscopy.

Acknowledgment: This work was supported by the Fonds der Chemischen Industrie.

References and Notes

1. Meier, H. *Angew. Chem.* **1992**, *104*, 1425; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1309.
2. Law, K. Y. *Chem. Rev.* **1993**, *93*, 449.
3. Loutfy, R. O.; Hsiao, C. K.; Kazmaier, P. M. *Photogr. Sci. Eng.* **1983**, *27*, 5.
4. Emmelius, M.; Pawlowski, G.; Vollmann, H. W. *Angew. Chem.* **1989**, *101*, 1475; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1445.
5. (a) Chen, C.-T.; Marder, S. R.; Cheng, L.-T. *J. Chem. Soc., Chem. Commun.* **1994**, 259. (b) Andrews, J. H.; Khaydarov, J. D. V.; Singer, K. D., Hull, D. L.; Chuang, K. C. *Nonlinear Optics* **1995**, *10*, 227. (c) Ashwell, G. J.; Jefferies G.; Hamilton, D. G.; Lynch, D. E.; Roberts, M. P. S.; Bahra, G. S.; Brown, C. R. *Nature* **1995**, *375*, 385.
6. G. S., Keil, D.; Hartmann, H.; Moschny T. *Dyes Pigm.* **1991**, *17*, 19.
7. (a) Schmidt, A. H. *Synthesis* **1980**, 961. (b) Ziegenbein, W.; Sprenger, H.E. *Angew. Chem.* **1966**, *78*, 937; *Angew. Chem. Int. Ed. Engl.*, **1966**, *5*, 893.
8. Solid state NMR measurements will be published elsewhere.
9. (a) Reed, M. W.; Pollart, D. J.; Perri, S. T.; Foland, L. D.; Moore, H. W. *J. Org. Chem.* **1988**, *53*, 2477. (b) Liebeskind, L. S.; Fengl, R. W.; Wirtz, K. R.; Shawe, T. T. *J. Org. Chem.* **1988**, *53*, 2482.
10. Law, K. Y.; Bailey, F. C. *J. Org. Chem.* **1992**, *57*, 3278.
11. Chen, C. T.; Marder, S. R.; Cheng, L. T. *J. Am. Chem. Soc.* **1994**, *116*, 3117.

(*Received in Germany* 6 *November* 1995; *accepted* 18 *December* 1995)