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Synthesis of new merocyanine dyes of thiophene series

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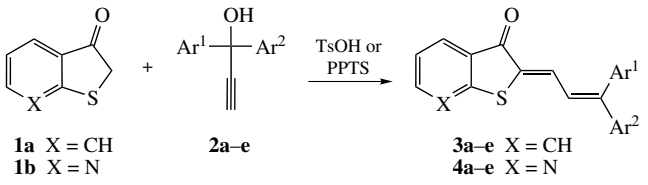
Reaction of benzo[*b*]thiophen-3(2*H*)-one or thieno[2,3-*b*]pyridin-3(2*H*)-one with diarylpropargylic alcohols gives new merocyanine dyes.

Merocyanine dyes[1–4] are used in solar[5,6] and hydrogen[7] energetics, as pigments for dyeing of synthetic fibers[4,8] and nonlinear optics.[9,10] Their ability to aggregate in solution and at the interface has been extensively studied.[11] Such dyes are of interest as photosensitizers for the fluorescence diagnosis and photodynamic therapy of early stages of leukemia.[12–15] The majority of merocyanine dyes were synthesized based on nitrogen heterocycles where a nitrogen atom is part of a donor and a carbonyl group as the electron-withdrawing moiety. Merocyanines containing diarylmethane fragment as a donor substituent and thiophenones as an electron acceptor moiety are practically unknown.[16,17] Isosteres of open form of photochromic naphthopyrans are of independent interest.

In continuation of our research,[18,19] herein a new type of merocyanine dyes based on thiophene derivatives was prepared (Scheme 1).

To access compounds **3a–e** and **4a–e**, various methodologies that are generally used for the preparation of benzene and indole analogues have been examined.[20–23] The most suitable procedure for these thiophene substrates proved to be a reaction of propargylic alcohols **2a–e** with naphthol under acidic conditions.[24] Various solvents such as dichloroethane, dichloromethane, acetonitrile and toluene were tested. *p*-Toluenesulfonic acid or its pyridine salt (PPTS – pyridinium *p*-toluenesulfonate) were examined as acid catalyst.



1a X = CH
1b X = N

2a–e

3a–e X = CH
4a–e X = N

Scheme 1 For Ar^1 and Ar^2, see Table 2.

Table 1 Reaction conditions and yields of merocyanine **3a**.

Medium	Catalyst	Reaction time/h	Yield (%)
Toluene	0.1 equiv. TsOH	11	41
	0.1 equiv. PPTS	50	55
MeCN	0.1 equiv. TsOH	1	73
	0.1 equiv. PPTS	10	55
CH_2Cl_2	1.0 equiv. TsOH	11	51
	1.0 equiv. PPTS	15	60
$ClCH_2CH_2Cl$	1.0 equiv. TsOH[a]	3	63
	1.0 equiv. PPTS[a]	8	65
Silica gel	0.1 equiv. TsOH	120	49
	0.1 equiv. PPTS	120	0

[a] With 0.1 equiv. TsOH or PPTS the reaction proceeds very slowly.

To optimize the reaction conditions, we used diphenylpropargyl alcohol and benzothienone **1a** as the model substrates (Table 1). The product yield was strongly effected by both the solvent and the catalyst. In 1,2-dichloroethane with both TsOH or PPTS, the yields were almost comparable. In acetonitrile in the presence of PPTS the reaction proceeded too slowly (40 h) and yields did not exceed 40–45%, whereas in the presence of 0.1 equiv. TsOH it was completed within 1 h in good yields. In case of dichloroethane or dichloromethane the reaction was slowed down on using 0.1 equiv. TsOH or PPTS.

Previously[19] in analogous reactions between propargylic alcohol and naphthol the use of trimethyl orthoformate as a dehydrating agent in combination with PPTS significantly increased the naphthopyranes yields. However, in our study the effect of orthoformate turned to be negligible. In addition, 'solid-state' method in the presence of TsOH (0.1 equiv.) on silica gel has also been investigated (*cf.* ref. 25). However, under these conditions we succeeded only in obtaining merocyanines **3a** and **4a** in yields of 49 and 57%, respectively. With other substrates the reaction either did not proceed (the starting compounds were returned) or the resinification of propargylic alcohol occurred.

As a result, for the model compound **3a** the better yields were achieved when acetonitrile was used as the solvent and TsOH as the catalyst (see Table 1).

The optimized conditions (MeCN, TsOH) were applied to the preparation of other merocyanines (Table 2).‡ However, in the case of propargylic alcohols bearing donor substituents a strong resinification occurred. Therefore, TsOH was replaced by PPTS. Similar findings were observed for thieno[3,2-*b*]pyridin-3(2*H*)-one **1b**. In case of diphenylpropargyl alcohol **2a** better results were achieved when TsOH was used as a catalyst, while PPTS was suitable for the other propargylic alcohols. However, unlike benzothienone **1a**, for the reaction of thienopyridinone **1b** the amount of PPTS had to be increased to 1.1 equiv.

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‡ *Synthesis of merocyanines* **3a–e** *and* **4a–e** *(general procedure).* To a stirred mixture of ketone **1a** or **1b** (3 mmol) and diarylpropargylic alcohols **2a–e** (3 ml) in acetonitrile (3 ml) the corresponding catalyst (Table 1) was added and the reaction mixture was refluxed under argon for 1 h. After cooling, the solvent was distilled off *in vacuo*. The residue was purified by recrystallization from the corresponding solvent or by chromatography on silica gel using the light petroleum/ethyl acetate (8:1) system as an eluent.

Table 2 Synthesis of merocyanines **3a–e** and **4a–e**.

Compound	Ar^1	Ar^2	Catalyst	Yield (%)
3a	Ph	Ph	0.1 equiv. TsOH	73
3b	2,4-$(MeO)_2C_6H_3$	2-FC_6H_4	0.1 equiv. PPTS	68
3c	2,4-$(MeO)_2C_6H_3$	4-FC_6H_4	0.1 equiv. PPTS	55
3d	5-methylthiophen-2-yl	4-FC_6H_4	0.1 equiv. PPTS	54
3e	2,4-$(MeO)_2C_6H_3$	3,4,5-$(MeO)_3C_6H_2$	0.1 equiv. PPTS	82
4a	Ph	Ph	1.1 equiv. TsOH	98
4b	2,4-$(MeO)_2C_6H_3$	2-FC_6H_4	1.1 equiv. PPTS	64
4c	2,4-$(MeO)_2C_6H_3$	4-FC_6H_4	1.1 equiv. PPTS	90
4d	5-methylthiophen-2-yl	4-FC_6H_4	1.1 equiv. PPTS	74
4e	2,4-$(MeO)_2C_6H_3$	3,4,5-$(MeO)_3C_6H_2$	1.1 equiv. PPTS	73

The optimization of the reaction conditions has not only improved the yield of the target product, but also significantly reduced the reaction time. Another important achievement of the study is the formation of the target product without impurities, which allows one to avoid the chromatographic purification.

In summary, we have developed an easy access to novel merocyanine dyes of thiophene series from available reactants. The compounds obtained can possess photocontrolled properties which might be of practical value.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2015.07.009.

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(2Z)-2-(3,3-Diphenylprop-2-en-1-ylidene)-1-benzothiophen-3(2H)-one **3a**: mp 141–143 °C (MeOH). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.9 (d, 1H, *J* 12.6 Hz), 7.3 (m, 2H, H_{arom}), 7.38 (m, 5H, H_{arom}), 7.45 (m, 3H, H_{arom}), 7.49 (m, 2H, H_{arom}), 7.55 (d, 1H, H_{arom}), 7.61 (d, 1H, *J* 12.8 Hz), 7.87 (d, 1H, H_{arom}, *J* 8.09 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 124.0, 125.3, 125.9, 126.7, 127.3, 129.8, 130.0, 130.2, 130.3, 131.1, 131.2, 131.4, 131.5, 131.7, 132.0, 132.4, 134.5, 136.5, 138.4, 141.4, 145.0, 154.2, 187.9 (C=O). MS, *m*/*z* (%): 340 $[M]^+$. IR (KBr, ν/cm^{-1}): 1668 (C=O), 2924, 3020, 3060 (=CH). UV [MeCN, λ_{max}/nm (ε)]: 460 (22400). Found (%): C, 80.10; H, 4.79; S, 9.24. Calc. for $C_{23}H_{16}OS$ (%): C, 81.15; H, 4.74; S, 9.42.

2-(3,3-Diphenylprop-2-en-1-ylidene)thieno[2,3-b]pyridin-3(2H)-one **4a**: mp 194–195 °C (EtOH). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.94 (d, 1H, *J* 12.2 Hz), 7.29 (m, 2H, H_{arom}), 7.4 (m, 6H, H_{arom}), 7.47 (m, 3H, H_{arom}), 7.69 (d, 1H, *J* 12.2 Hz), 8.07 (d, 1H, H_{arom}, *J* 6.83 Hz), 8.68 (m, 1H, H_{arom}). MS, *m*/*z* (%): 341 $[M]^+$. IR (KBr, ν/cm^{-1}): 760 (CH_{Py}), 1668 (C=O). UV [MeCN, λ_{max}/nm (ε)]: 456 (17400). Found (%): C, 77.16; H, 4.39; N, 3.98. Calc. for $C_{22}H_{15}NOS$ (%): C, 77.39; H, 4.43; N, 4.10.

For characteristics of compounds **3b–e** and **4b–e**, see Online Supplementary Materials.

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