Synthesis and Electronic Absorption Spectra of Some Five-membered Bisheterocyclic Polymethine Cyanine Dyes

J. Chem. Research (S), 1997, 128–129
J. Chem. Research (M), 1997, 0850–0865

Reda Mahmoud Abd El-Aal

Chemistry Department, Aswan-Faculty of Science, Aswan, Egypt

3,5-Dimethyl-1-phenyl-1*H*-pyrazolo[4,3-*d*]oxazole **5** was prepared and used as starting material in the synthesis of some new polymethine cyanine dyes incorporating a bisheterocyclic system.

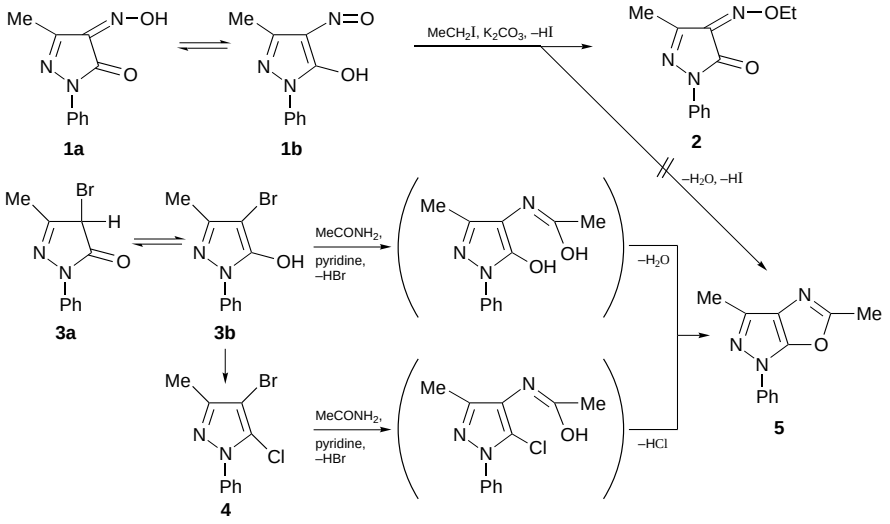
Polymethine cyanine dyes[1] including mono-, di- and trimethine types have found various applications as photographic sensitisers for both colour and black and white films[2] and textile dyes.[3] They are also useful as photosensitisers in blue green light[4–6] and as analytical reagents.[7]

In the present paper, a new synthesis of 3,5-dimethyl-1-phenyl-1*H*-pyrazolo[4,3-*d*]oxazole **5** is developed and confirmed by the interaction between 4-bromo-3-methyl-1-phenyl-1,4-dihydropyrazol-5-one (**3a**↔**3b**)[8] and/or 4-bromo-5-chloro-3-methyl-1-phenylpyrazole **4** with pyridine as catalyst and ethanol as solvents, Scheme 1.

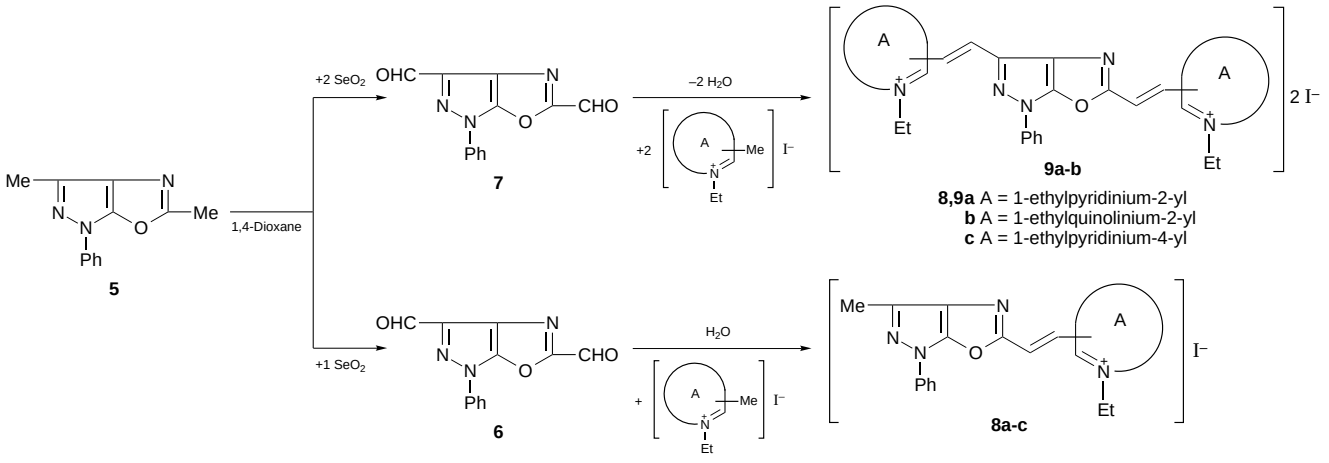
Selective oxidation of **5** with an equi- or bi-molar ratio of SeO_2[17] in boiling 1,4-dioxane afforded the corresponding 3-methyl-1-phenyl-1*H*-pyrazolo[4,3-*d*]oxazole-5-carbaldehyde **6** or its 3,5-dicarbaldehyde **7**, respectively. The ^{1}H NMR spectra of the aldehydes **6** and **7** show characteristic absorptions at δ 10.2 and 10.0, respectively, for the CHO groups and other signals which, along with the IR spectra, are presented in Table 4 (full text).

The condensation of compounds **6** and **7** with 2(4)-methyl-substituted heterocyclic quaternary salts (equi- or bi-molar) in refluxing ethanol in the presence of piperidine as catalyst afforded the corresponding asymmetric 3-methyl-1-phenyl-1*H*-pyrazolo[4,3-*d*]oxazol-5-yl [2(4)]-dimethine (**8a–c**) and symmetric 1-phenyl-1*H*-pyrazolo[4,3-*d*]oxazole-3,5-diyl [2(4)]-bis(dimethine) cyanine dyes (**9a–c**), Scheme 3.

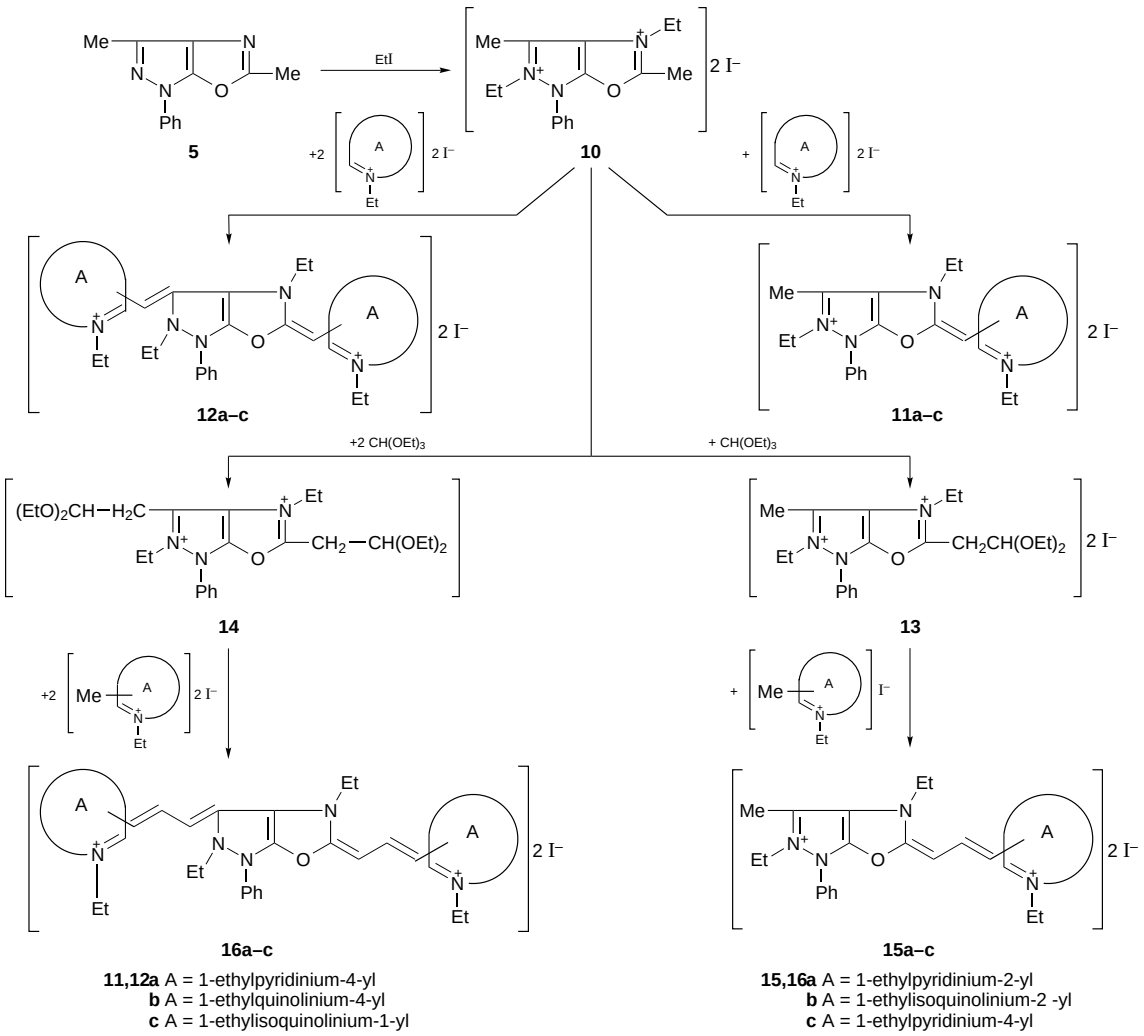
Quaternisation of 3,5-dimethyl-1-phenyl-1*H*-pyrazolo[4,3-*d*]oxazole **5** using iodoethane afforded the corresponding bisquaternary-2,4-diethyl-3,5-dimethyl-1-phenyl-1*H*-pyrazolo[4,3-*d*]oxazole-2,4-diium bis(iodide) **10**. Interaction of **10** with 1-methyl-pyridinium (-quinolinium or -isoquinolinium) iodide (equi- or bi-molar) afforded the corresponding asym-



Scheme 1



Scheme 3



Scheme 4

metric and symmetric monomethine cyanines **11a–c** and **12a–c**, Scheme 4.

Treatment of **10** with ethyl orthoformate (equi- or bi-molar) in the presence of piperidine afforded compounds **13** and **14** respectively. These compounds are key intermediates in the synthesis of asymmetric and symmetric trimethine cyanine dyes **15a–c** and **16a–c** *via* condensation with 2(4)-methyl-substituted heterocyclic quaternary salts (equi- or bi-molar).

The electronic absorption spectra of the asymmetric and symmetric dimethine (**8a–c**, **9a–c**), monomethine (**11a–c**, **12a–c**) and trimethine (**15a–c**, **16a–c**) cyanine dyes in 95% ethanol were dependent on the nature of the heterocyclic quaternary salts (A) and on the type of cyanine molecules, *i.e.* whether asymmetric or symmetric. The structures of all new compounds were confirmed by elemental analysis as well as by IR and ^{1}H NMR spectral data.

I am grateful to Professor Dr A. I. M. Koraiem, Professor of organic chemistry, Aswan-Faculty of Science, for his help and guidance in the preparation of the manuscript.

Techniques used: IR, ^{1}H NMR, GCMS, UV–VIS

References: 17

Schemes: 4

Table 1: Characterisation data for **6**, **7**, **8a–c** and **9a–c**

Table 2: Characterisation data for **10**, **11a–c** and **12a–c**

Table 3: Characterisation data for **13**, **14**, **15a–c** and **16a–c**

Table 4: IR and ^{1}H NMR data of selected cyanine dyes

Received, 13th June 1996; Accepted, 3rd January 1997
Paper E/6/04155H

References cited in this synopsis

1 N. Tyutyuikov, J. Fabian, A. Mehlhorm, F. Dietz and A. Tadjer, *Polymethine Dyes – Structure and Properties*, St. Kliment Ohridski University Press, Sofia, Bulgaria, 1991.
2 A. M. Osman and Z. H. Kalil, *J. Appl. Chem. Biotechnol*., 1975, **25**, 633.
3 G. D. Kandel and G. F. Duffin, *Br. Pat*., 797 144, 1930.
4 L. G. S. Brooker and G. H. Keyes, *J. Am. Chem. Soc*., 1935, **57**, 2488.
5 M. S. Fujiravara, T. K. Masukawe and M. Kawasaki, *Ger. Offen*., 2 734 335, 1978 (*Chem. Abstr*., 1978, **88**, 161 442c).
6 S. Baba, B. Okubo and E. Sakamato, *Ger. Offen*., 260 968, 1976 (*Chem. Abstr*., 1977, **86**, 49 175a).
7 A. S. Fakhonov, A. A. Anisimova, K. N. Bagdasarov and M. S. Chernovyant, *Zh. Anal. Khim*., 1984, **39**, 1040.
13 L. Smith, *Kgl. Fysiograf. Sallskab*, Lond., Forh., 18 No. 1, 3, 1948 (*Chem. Abstr*., 1950, **44**, 490.
17 Z. H. Khalil, A. I. M. Koraiem, M. A. El-Maghraby and R. M. Abu El-Hamd, *J. Chem. Tech. Biotechnol*., 1986, **36**, 379.