An Improved Synthesis of the Solvatochromic Dye ET-30

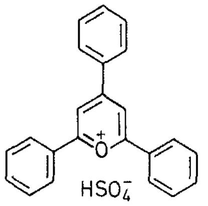
Manfred A. Kessler, Otto S. Wolfbeis*

Analytical Division, Institute of Organic Chemistry, Karl-Franzens University, A-8010 Graz, Austria

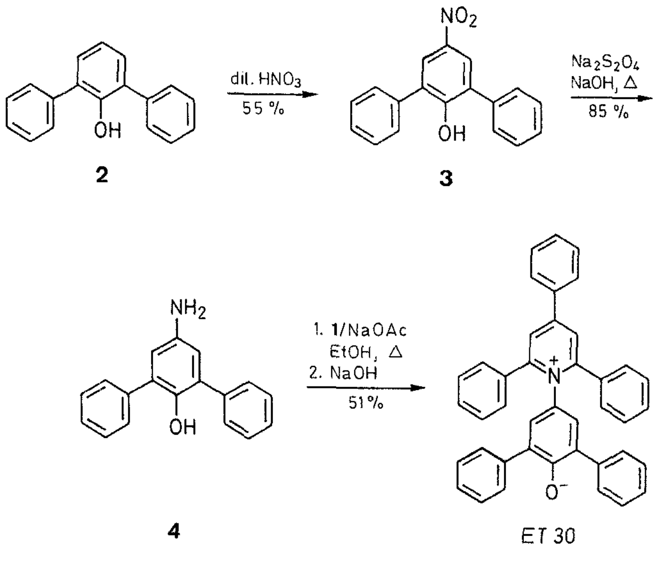
An improved synthesis of the well-known dye ET-30, which is used as a standard for the characterization of solvent polarity, using easily available starting materials is described.

The solvatochromic dye 2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridinio)-phenolate is popularly known as ET-30. This molecule undergoes one of the largest known solvent-induced shifts in absorbance, amounting to some 357 nm in going from water (λ_{max} = 453 nm) to diphenyl ether (λ_{max} = 810 nm).[1] Since ET-30 absorbs practically over the whole visible region, it is possible to visually estimate the polarity of a solvent. From the absorption data of ET-30, the so-called ET-30 values can be calculated, which have been reported for over 200 solvents.[2,3] A review on the varied applications of ET-30 has appeared.[4]

In connection with our work on the lipophilic polarity probes, we looked for an easy access to ET-30, but no convenient synthesis could be located. The major drawback of the existing method is the difficulty in obtaining 4-amino-2,6-diphenylphenol (**4**) needed in the last step of synthesis.[4] A reported synthesis for **4** starts from mucobromic acid, but appropriate care should be exercised in the preparation of sodium nitromalonaldehyde monohydrate due to its explosive nature and the evolution of hydrogen cyanide gas during the reaction.[4,5] Similary, the reduction of 4-nitro-2,6-diphenyl-phenol (**3**) is performed with tin and hydrochloric acid, which in our hands led to a tin complex difficult to work up. Moreover, one could avoid the synthesis of 2,4,6-triphenylpyrylium tetrafluoroborate used in this method, since this compound can easily be replaced by the readily accessible 2,4,6-triphenylpyrylium hydrogen sulfate (**1**).



1



We report here a new and convenient method for the synthesis of ET-30 starting from commercially available 2,6-diphenylphenol (**2**) and **1**. Thus, phenol **2** is treated with dilute nitric acid to yield **3**, which is reduced by sodium dithionite in alkaline solution to give **4**. Compound **1** is commercially available or alternatively may be synthesized.[6] In the final step, **4** is reacted with **1** to yield protonated ET-30, which is transferred into ET-30 by addition of aqueous sodium hydroxide.

The method presented here provides a significant improvement over former synthetic approaches as it avoids working with potentially hazardous chemicals, and less reaction steps are involved.

All reagents were of commercial quality from freshly opened containers. 2,4,6-Triphenylpyrylium hydrogen sulfate (**1**) was prepared according to the literature procedure.[6] Reagent quality 95% EtOH was used without further purification. Melting points were taken using a Tottoli apparatus and are uncorrected. Microanalyses were obtained using a Carlo Erba Elemental Analyser Mod. 1106.

4-Nitro-2,6-diphenylphenol (3):
2,6-Diphenylphenol (**2**; 10.0 g, 40.6 mol) is slowly added at room temperature to a well stirred mixture containing 65% HNO_3 (30 mL) and distilled water (30 mL). After a few minutes the suspension becomes yellowish. The suspension is stirred overnight and finally is of orange color. The crude product is filtered off and carefully washed with distilled water. The solid is dissolved in hot EtOH, treated with a small amount of charcoal and filtered. Crystallization from EtOH gives large yellow crystals; yield: 6.5 g (55%); mp 135 °C (Lit.[4] mp 134–135 °C).

$C_{18}H_{13}NO_3$	calc.	C 74.22	H 4.50	N 4.81
(291.3)	found	74.27	4.44	4.67

4-Amino-2,6-diphenylphenol (4):
4-Nitro-2,6-diphenylphenol (**3**; 5.9 g, 20.3 mmol) is dissolved in boiling 5% aq. NaOH (250 mL). The deep red solution is well stirred, and solid $Na_2S_2O_4$ is added in small portions, until the color has changed to pale yellow. After addition of a small excess of $Na_2S_2O_4$, the solution is kept at boiling temperature for another 15 min. Then, the hot mixture is adjusted to pH 5 with glacial AcOH, whereupon a precipitate forms. The solution is allowed to cool, and the product is filtered off and washed with ice-cold water to give a colorless solid, which acquires a tan color upon standing for several days; yield: 4.5 g (85%); mp 147–148 °C (benzene) (Lit.[4] mp 144–148 °C).

$C_{18}H_{15}NO$	calc.	C 82.73	H 5.79	N 5.36
(261.3)	found	82.51	5.67	5.31

2,6-Diphenyl-4-(2,4,6-triphenyl-*N*-pyridinio)phenolate (ET-30):
4-Amino-2,6-diphenylphenol (**4**; 2.8 g, 10.7 mmol) and 2,4,6-triphenylpyrylium hydrogen sulphate (**1**; 4.1 g, 10.1 mmol) are dissolved in hot 95% EtOH (50 mL). After addition of anhydrous NaOAc (4.0 g), the mixture is refluxed for 3 h. Then, 5% aq. NaOH solution (25 mL) is added to the hot solution. The major part of EtOH is removed *in vacuo* and the deep blue crystals formed are filtered from the hot mixture and washed well with water. During the drying process (in an desiccator over P_4O_{10}, 20 °C, 20 mbar), the color changes from deep blue to dark green as a result of partial loss of water of crystallization. Two molecules of water of crystallization remain in the product dried in this way; yield: 3.2 g (51%); mp 200–275 °C (under loss of crystal water) (Lit.[1] mp 205–276 °C, Lit.[4] mp 200–275 °C).

$C_{41}H_{29}NO \cdot 2H_2O$	calc.	C 83.79	H 5.66	N 2.38
(587.7)	found	83.87	5.38	2.43

The product is identical in its spectral properties with the product obtained by the literature methods.[1,4]

This work was supported by the Fonds zur Förderung der wissenschaftlichen Forschung, Project P 5977C.

Received: 29 January 1988

(1) Dimroth, K., Reichardt, C., Siepmann, T., Bohlmann, F. *Liebigs Ann. Chem.* **1963**, *661*, 1.

(2) Reichardt, C., Harbusch-Görnert, E. *Liebigs Ann. Chem.* **1983**, 721.

(3) Reichardt, C. *Angew. Chem.* **1979**, *91*, 119; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 98.

(4) Johnson, B.P., Gabrielsen, B., Matulenko, M., Dorsey, J.G., Reichardt, C. *Anal. Lett.* **1986**, *19*, 939.

(5) Baumgarten, H.E. *Org. Synth. Coll. Vol. 5*, **1973**, 1004.

(6) Chadwick, T.C. *Anal. Chem.* **1974**, *46*, 1326.