

AN IMPROVED PREPARATION OF THE $E_T(30)$ BETAININE

Marcos Caroli Rezende and Claudemir Marcos Radetski

Departamento de Química
Universidade Federal de S. Catarina
Florianópolis, SC 88049, Brasil

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Abstract: An improved method for the preparation of the solvatochromic dye (3), basis of Dimroth-Reichardt's $E_T(30)$ polarity scale, is described.

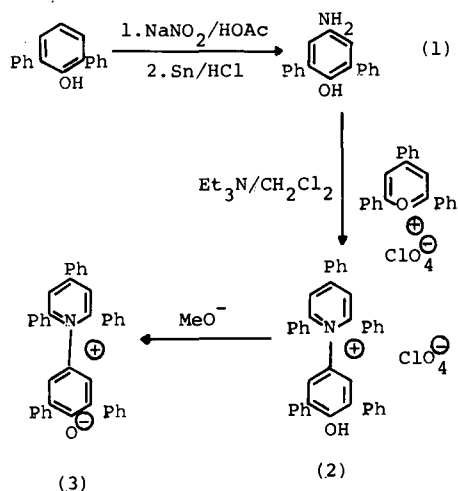
Since it was first proposed¹ as a basis for an empirical polarity scale, the $E_T(30)$ solvatochromic dye 2,6-diphenyl-4-(2,4,6-triphenyl-N-pyridinio)phenolate (3) has found wide application in the study of solvent effects in chemistry². This remarkable compound exhibits one of the largest known solvent-induced shifts of λ_{max} in the visible region, spanning a range of nearly 360 nm, from water (435 nm) to diphenyl ether (810 nm). This unique sensibility to the polarity of the medium has been exploited in the tabulation of polarity values for over 200 solvents³ and nearly 50 binary solvent mixtures⁴. It has been useful in the examination of micellar interfaces in surfactant solutions⁵, in the determination of the water content in organic solvents⁶, in the studies of mobile or stationary phases of chromatographic systems⁷, to mention just a few examples of its use.

In spite of its wide applicability, the access to compound (3) is not straightforward. It was originally prepared by reaction of a 2,4,6-triphenylpyrylium salt⁸ and the phenol (1) in EtOH/NaOAc, in 31% yield¹.

The 4-amino-2,6-diphenylphenol (1) is not a commercial product. More recently, with a view to overcoming the lack of a commercial source for compound (1), a detailed procedure for the preparation of (1) and (3) was published⁹. It did not differ from the original route to the phenol (1)^{1,10} nor was the yield of preparation of the 2,4,6-triphenyl-N-(4-hydroxy-3,5-diphenyl)phenylpyridinium precursor (2) improved. Thus the aminophenol (1) was obtained from the commercially available mucobromic acid in three steps and an overall yield of 28%, after a time-consuming (48 h stirring) condensation of sodium nitromalon-aldehyde and dibenzyl ketone⁹.

As part of our studies on the polarity of electrolyte solutions¹¹ we needed to

prepare betaine (3). This was achieved by a more convenient route, starting from commercially available 2,6-diphenylphenol.



Nitrosation ($\text{NaNO}_2/\text{HOAc}$) of this product followed by reduction (Sn/HCl) gave (1) in 55% yield, without the need of isolating the intermediate nitrosophenol. The crude 4-amino-2,6-diphenylphenol (1) was then reacted with 2,4,6-triphenylpyrylium perchlorate¹² in CH_2Cl_2 in the presence of triethylamine to give the pyridinium precursor (2) in 75% yield, which was converted into the betaine (3) by the published procedure¹.

This preparation, besides being shorter and less time-consuming than the previously published synthesis of (3)^{1,9}, has also the advantage of a better overall yield (41% instead of 10%) from a commercially available starting material.

EXPERIMENTAL:

IR spectra were recorded on a Perkin-Elmer 781 spectrometer. Melting points were taken with a Koffler hot-stage apparatus and were not corrected.

The 2,4,6-triphenylpyrylium perchlorate was prepared by acid condensation of acetophenone and chalcone, following a reported procedure¹².

4-Amino-2,6-diphenylphenol (1)- To a cooled (0-5°C), stirred solution of 2,6-diphenylphenol (Aldrich Chemical Co.) (1.0 g, 4 mmol) in acetic acid (30 ml) and water (3 ml) was added sodium nitrite (1.0 g, 14.4 mmol), portionwise over a period of 20 minutes. The resulting dark brown suspension was stirred for further 30 minutes. It was then poured into ice-cold water (150 ml) and

the brick-red precipitate triturated and filtered. The product was then redissolved in boiling ethanol (40 ml) and filtered hot. To the red filtrate was added granular tin (0.8 g, 6.8 mmol) and concentrated hydrochloric acid (3 ml), and the whole refluxed gently until the solution decolourized to a pale yellow (5-10 minutes). It was then decanted and concentrated to 10 ml in a rotary evaporator. The residue was poured into ice water and the crude, precipitated 4-amino-2,6-diphenylphenol filtered and dried. The product thus obtained weighed 0.58 g (55 % yield) and was pure enough for the subsequent reaction, m.p. 135-138°C, lit. ⁹ 144-148°C.

2,4,6-Triphenyl-N-(4-hydroxy-3,5-diphenyl)phenylpyridinium perchlorate (2) - To a stirred suspension of 2,4,6-triphenylpyrylium perchlorate ¹² (0.5 g, 1.2 mmol) and 4-amino-2,6-diphenylphenol (0.5 g, 1.9 mmol) in dichloromethane (40 ml) was added dropwise triethylamine (0.4 g, 4 mmol). The resulting deep red solution was left standing overnight. It was then washed with a 10% HCl solution and with water, dried over calcium chloride and evaporated. To the residue was added diethyl ether (50 ml) and the precipitate filtered and dried to give 0.59 g (75% yield) of the pyridinium perchlorate (2) as a pale yellow solid, recrystallized from ethanol, m.p. 270-272°C, lit. ¹ 273-274°C, $\bar{\nu}_{\text{max}}$ (KBr) 3500, 1610 and 1050 cm^{-1} .

The pyridinium perchlorate (2) was converted into the betaine (3) by the previously reported procedure ¹.

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