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Dyes and Pigments 64 (2005) 91–92

DYES and PIGMENTS

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Short communication

One step synthesis of dibenzoxanthenes

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Received 12 November 2003; received in revised form 21 January 2004; accepted 9 March 2004
Available online 4 June 2004

Abstract

One pot synthesis of dibenzoxanthene leuco-dye from the reaction of aromatic aldehydes such as C_6H_5CHO, p-$CH_3C_6H_4CHO$, p-$NO_2C_6H_4CHO$, p-BrC_6H_4CHO with 2-naphthol in acidic condition is described.

Keywords: Leuco-dye; Dibenzoxanthenes; 2-Naphthol; Aromatic aldehydes; Acid-catalysis

1. Introduction

The reaction between an aldehyde and phenol is generally catalysed by acid or base to give cyclic or open-chain oligomers [1]. Depending on the reaction conditions such as pH, bis-phenols [2], calix-arenes [3] and open-chain oligomers are synthesised [4]. The condensation of 2-naphthols with compounds containing carbonyl groups is of special interest as it can lead to calix-arenes possessing deeper cavity [6]. Although there are several reports on the synthesis of calix-arenes from the naphthols, the 2-naphthol is also known to give spirodienone derivative [5]. These spirodienones on reduction followed by acid treatment give dibenzoxanthenes [7]. The xanthenes themselves are very important class of compounds widely used as leuco-dye [8]; thus structural analogues and mild synthetic methods are essential for further studies [9]. The conventional synthesis of dibenzoxanthene involves three steps with involvement of different reagents [5]. Another available method that was originally used also involved condensation of 1,3-dihydroxybenzene with phthalic anhydride to give specific kind of xanthene molecules [10], so newer methodology for synthesis of xanthene derivative is very essential. Although there is an acid catalysed synthesis of a similar derivative it is not extended to aromatic aldehydes [11]. The present manuscript describes a one step environmentally benign method for synthesis of various dibenzoxanthenes.

2. Experimental

In a typical procedure, 2-naphthol (2.9 g, 0.02 mol) and benzaldehyde (1.1 g, 0.01 mol) were dissolved in glacial acetic acid (10 ml). The solution was stirred to dissolve the compounds and then cooled in ice. To this stirred solution acetic acid and sulphuric acid (4:1 mixture, 15 ml) were added dropwise over 30 min. The reaction mixture was kept in an ice bath for 72 h and then warmed slowly on a water bath (to 70–80 °C) for about 1 h. The solid precipitate that appeared was filtered and washed free of the acid with warm water. The compound was dried and obtained as colourless solid (3.4 g) after recrystallisation from warm toluene. ^{1}H NMR ($CDCl_3$, 400 MHz) 8.41 (2H, d, $J = 8.5$ Hz), 7.84–7.78 (4H, m), 7.60–7.48 (6H, m), 7.43–7.39 (2H, t, $J = 7.5$ Hz), 7.17–7.13 (2H, t, $J = 7.5$ Hz) 7.01–6.97 (1H, t, $J = 7.5$ Hz) 6.49 (1H, s); ^{13}C NMR ($CDCl_3$) 148.8, 145.0, 131.5, 131.1, 128.5, 126.5, 126.8, 126.4, 124.2, 122.7, 118.0, 117.4, 38.1; m/e 358; IR (KBr, cm^{-1}) 3073 (m), 1593 (s), 1460 (s), 1255 (s), 1081 (s), 968 (s); mass (m/e) 358.

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0143-7208/$ - see front matter
doi:10.1016/j.dyepig.2004.03.010

2.1. Analytical data for *Ib–Ie*

Ib: Yield 60%; ^{1}H NMR (DMSO-d^6) 8.71 (2H, d, $J = 8.46$ Hz), 8.03–7.91 (8H, m), 7.67-7.59 (4H, m) 7.50–7.46 (2H, m), 6.93 (1H, s); ^{13}C NMR (DMSO-d^6) 152.6, 148.1, 145.9, 130.8, 130.7, 129.6, 128.7, 127.2, 124.7, 123.6, 123.1, 117.7, 116.2, 36.4; IR (KBr): 2930 (w), 1594 (m), 1517 (s) 1343 (s), 1241 (s), 828 (s); mass (*m*/*e*) 403.

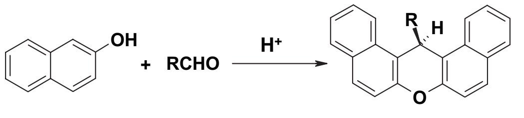
Ic: Yield 77%; ^{1}H NMR (CDCl$_3$) 8.45 (2H, d, $J = 8.46$ Hz), 7.85–7.75 (4H, m), 7.6 (2H, t, $J = 8.5$ Hz) 7.55 (2H,d, $J = 8.5$), 7.4 (4H, m), 7.0 (2H, d, $J = 8.5$ Hz), 6.5 (1H, s) 2.15 (3H, s); IR (KBr): 3421 (w), 3077 (m), 2918 (m), 1594 (m), 1506 (s) 1459 (s), 1239 (s), 964 (s); mass (*m*/*e*) 372.

Id: Yield 90%; ^{1}H NMR (DMSO-d^6) 8.32 (2H, d, $J = 8.45$), 7.79 (4H, m), 7.6–7.56 (2H, dd $J = 7.6$, 1.2) 7.49–7.38 (6H, m), 7.26 (2H, m), 6.45 (1H, s); ^{13}C NMR (DMSO-d^6) 144.8, 144.0, 131.6, 131.1, 129.9, 129.1, 128.9, 126.9, 124.4, 122.4, 120.3, 118.0, 116.7, 37.5; IR (KBr): 2924 (w), 1594 (s), 1462 (s), 1402 (s), 1240 (s), 1075 (s), 1010 (s); mass (*m*/*e*) 437.

Ie: Yield 68%; ^{1} H NMR (DMSO-d^6) 9.77 (1H, s), 8.48 (2H, d, $J = 8.48$ Hz), 7.98–7.80 (6H, m); 7.71–7.46 (8H, m), 6.86 (1H, s); ^{13}C NMR (DMSO-d^6) 197, 179, 157, 153, 139, 136, 135, 134, 130, 128, 122, 121, 30; IR (KBr): 3073 (w), 1691 (m), 1591 (s) 1397 (s), 1240 (s), 1160 (s), 960 (s); mass (*m*/*e*) 386.

3. Results and discussion

We have observed that the reaction of 2-naphthol with an aromatic aldehyde in acidic media containing AcOH–H$_2$SO$_4$ gives dibenzoxanthenes selectively in quantitative yield without side product (Eq. (1)). The reaction is applicable to aldehyde containing electron withdrawing as well as electron donating groups attached to an aromatic aldehyde. In an earlier report it was shown that the synthesis of dibenzoxanthenes involves the reduction of the corresponding spironaphthalone with a reducing agent such as KBH$_4$ and followed by rearrangement in the presence of an acid [7]. In our study we could prepare dibenzoxanthenes in a single step. In addition to this, the reaction leads to the selective functionalisation of 2-naphthol at C1 rather than both at C1 and C3.



R = C_6H_5 (Ia) p-$NO_2C_6H_4$ (Ib) p-$CH_3C_6H_4$ (Ic), p-BrC_6H_4 (Id), p-$CHOC_6H_4$ (Ie)

In conclusion, a mild, efficient and selective environmentally benign method for synthesis of dibenzoxanthenes is described.

Acknowledgements

The authors thank the Council of Scientific and Industrial Research, New Delhi, for financial assistance.

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