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A convenient synthesis of 1,2-diphenyl-9*H*-[1]benzopyrano [3,2-*b*] pyrrol-9-ones utilizing hypervalent iodine reagent

Surya K De & Asok K Mallik*
Department of Chemistry, Jadavpur University, Calcutta 700 032, India

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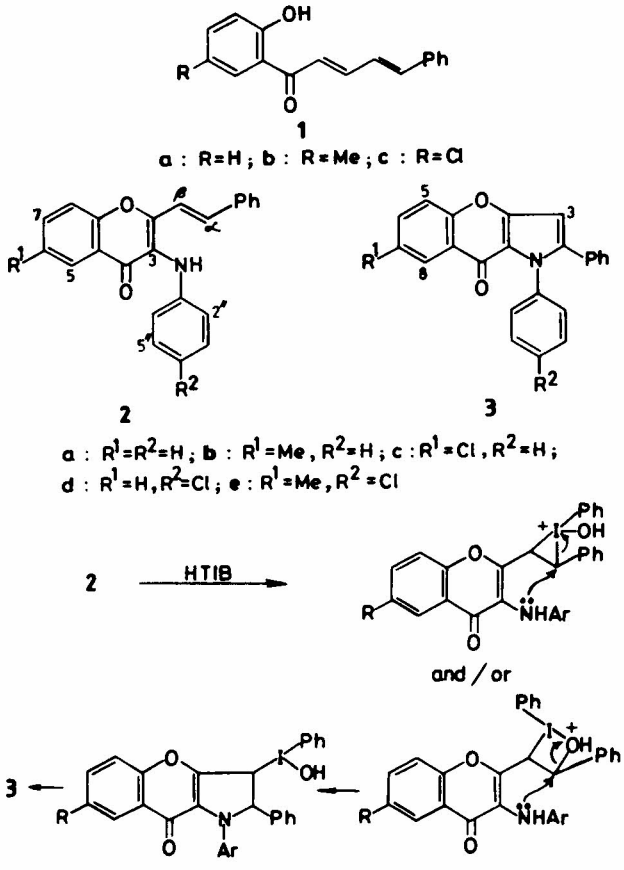
3-(Phenylamino)-2-styryl-4*H*-[1]benzopyran-4-ones **2**, readily obtainable from *o*-hydroxy-ω-cinnamylidene-acetophenones **1**, yield 1,2-diphenyl-9*H*-[1]benzopyrano-[3,2-*b*]pyrrol-9-ones **3** on oxidation with [hydroxy(tosyloxy)iodo]benezene in acetonitrile.

During the last two decades, hypervalent iodine reagents are being used for effecting a variety of transformations of organic molecules[1,2]. Among them, [hydroxy(tosyloxy)iodo]benzene[HTIB] is significantly active on olefinic compounds[2]. With this reagent, olefinic compounds containing nucleophilic functional groups are transformed into cyclic compounds through intramolecular participation. A few heterocyclic systems could thus be synthesised[2]. In continuation of our recent studies on the applicability of hypervalent iodine reagents in organic synthesis[3] we could develop a simple synthesis of 1, 2-diphenyl-9*H*-[1]benzopyrano[3, 2-*b*]-pyrrole-9-ones **3**, a rare class of heterocycles having potential biological activities[4], utilizing HTIB in the final step, which is reported herein.

Recently, for synthesis of *trans*-2, 3-dimethoxy-3-(phenylamino)flavanones, we studied the reactions of a number of 2′-hydroxychalcones with nitrosobenzenes[5]. As an extension of that study we carried out reactions of *o*-hydroxy-.ω-cinnamylidene acetophenones **1** with nitrosobenzenes when 3-(phenylamino)-2-styryl-4*H*-[1]benzopyran-4-ones **2** were obtained in moderate yields. An examination of the structures of these easily available new compounds revealed that they contain the styryl double bond and the amino nitrogen in proper position for construction of a pyrrole moiety at the 2, 3-position of 4*H*-[1]benzopyran-4-one. Thus, **2** was treated with HTIB in acetonitrile at room temperature. The reaction proceeded smoothly and was found to be complete within 8 hr furnishing 1, 2-diphenyl-9*H*-[1]benzopyrano-[3, 2-*b*]pyrrol -9-ones **3** in good yields (60-70%). A plausible mechanism for this conversion is given in Scheme I.

In fine, it may be mentioned that this is the first report of utilization of a hypervalent iodine reagent for construction of pyrrole moiety on a 4*H*-[1]-benzopyran-4-one. The reaction may be extended to other systems also.



Scheme I

Experimental Section

All melting points are uncorrected. IR spectra were recorded in nujol on a Perkin-Elmer 297 spectrophotometer, ^{1}H NMR spectra in $CDCl_3$ on a Varian EM 360 (60 MHz) and a Bruker AC-

200 (200 MHz) spectrometers and mass spectrum on a JEOL D-300 spectrometer.

Preparation of 3-(phenylamino)-2-stryryl-4*H*-[1]benzopyran-4-ones 2: General procedure. To a stirred solution of *o*-hydroxy-ω-cinnamylideneacetophenone (0.002 mole) in 1:9 aq. methanolic KOH (30 mL, 10%) nitrosobenzene (0.005 mole) was added in small portions during 6 hr and the reaction mixture was left overnight at room temperature. It was then diluted with water (200 mL) and extracted with ether (4 × 40 mL). The ether extract was concentrated and the residue was chromatographed over neutral alumina. The yields and melting points of the pure products (yellow needle from $CHCl_3$-petrol) were: **2a**, 48%, 175°; **2b**, 47%, 201°; **2c**, 42%, 191-192°; **2d**, 47%, 211°; **2e**, 51%, 239°. All gave satisfactory IR and ^1H NMR spectral data. The spectral data of **2a** and **2b** were as follows:

2a: IR: 3365 (N−H) and 1660 cm^{-1} (C=O); ^1H NMR (60 MHz): δ 6.10 (1H, br.s, N−H), 6.72-7.80 (15H, Ar−H and olefinic H) and 8.25 (1H, dd, J=8 and 2 Hz, H-5).

2b: IR: 3335 and 1640 cm^{-1}; ^1H NMR (200 MHz): δ 2.48 (3H, s, CH_3), 6.01 (1H, s, N−H), 6.81-6.88 (3H, m, H-2″, 4″, 6″), 7.05 (1H, d, J=16 Hz, H−β), 7.09-7.49 (9H, m, Ar−H), 7.57 (1H, d, J=16 Hz, H−α) and 8.0 (1H, m, H-5).

HTIB Oxidation of 3-(Phenylamino)-2-styryl-4*H*-[1]benzopyran-4-ones 2. To a stirred solution of **2** (0.001 mole) in dry acetonitrile (30 mL), HTIB (0.0011 mole) was added at room temperature and the stirring was continued for 8 hr. Acetonitrile was removed *in vacuo* and methylene chloride (50 mL) was added to the concentrate. The resulting solution was washed with water (2 × 50 mL), dried and concentrated. Chromatography of the residue thus obtained over silica gel (100-200 mesh) gave pure 1, 2-diphenyl-9*H*-[1]benzopyrano[3, 2-*b*]pyrrole-9-ones **3** which crystallized from $CHCl_3$-petrol in colourless needles. Their melting points and spectral data were as follows:

3a: M.p. 205° (Found: C, 81.2; H, 4.6; N, 4.0. $C_{23}H_{15}NO_2$ requires C, 81.9; H, 4.5; N, 4.1%); IR: 1650 cm^{-1} (C=O); ^1H NMR (200 MHz): δ 6.45 (1H, s, H-3), 7.10-.7.61 (13H, m, Ar−H) and 8.22 (1H, dd, J=7.8 and 1.7 Hz, H-8); EIMS: m/z 337 (M^+ 100%), 307 (13.4), 280 (6.5), 260 (M^+ − Ph, 12.8), 203(15), 178 (13.5), 176 (18.1), 151 (10.9), 102 (24.7) and 77 (52.5).

3b: M.p. 238°; IR: 1650 cm^{-1}; ^1H NMR (200 MHz): δ 2.44 (3H, s, CH_3), 6.51 (1H, s, H-3), 7.19-7.43 (12H, m, Ar−H) and 8.06 (1H, d, J=1 Hz, H-8).

3c: M.p. 211-212°; IR: 1650 cm^{-1}; ^1H NMR (200 MHz): δ 6.53 (1H, s, H-3), 7.20-7.61 (12H, m, Ar−H) and 8.23 (1H, d, J=2.3 Hz, H-8).

3d: M.p. 216-217°; IR: 1655 cm^{-1}; ^1H NMR (200 MHz): δ 6.53 (1H, s, H-3), 7.18-7.40 (10H, m, Ar−H), 7.53 (1H, dd, J=8 and 1.8 Hz, H-5), 7.65 (1H, ddd, J=8, 7 and 1.7 Hz, H-6) and 8.29 (1H, dd, J=8 and 1.7 Hz, H-8).

3e: M.p. 227°; IR: 1648 cm^{-1}; ^1H NMR (200 MHz): δ 2.44 (3H, s, CH_3), 6.51 (1H, s, H-3), 7.15-7.44 (11H, m, Ar−H) and 8.05 (1H, br.s, H-8).

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