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Convenient Synthesis of Some Styrylpyridinium Dyes Containing Methylenebis[benzenamine] Moiety

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Synopsis. Condensation of 4-vinylpyridine with 4, 4′-[(4-bromophenyl) methylene]bis[benzenamine] and its *N*-ethyl analogue adopting Heck's reaction yielded corresponding new styrylpyridines which were converted into their pyridinium bromides. All the compounds reported were characterized by analytical and spectral data.

Of the organic molecules capable of exhibiting high nonlinear optical coefficients, styryl compounds have been found to exhibit in solution some of the highest values.1) Also, styrylpyridinium dyes contain and their analogues are currently used as electrochromic probes for investigation of membrane potentials.2) Therefore, a series of *trans*-(*p*-aminostyryl) pyridines and their derivatives were prepared earlier3) in our laboratory as precursors for polymer synthesis. Various attempts to polymerize these molecules have generated an unforeseen problems. In order to obtain a suitable route to a polymer it became necessary to change the nature of the monomer. This paper describes the synthesis of the monomer **3** and related compounds as precursors for the generation of polymers with potential nonlinear optical properties.

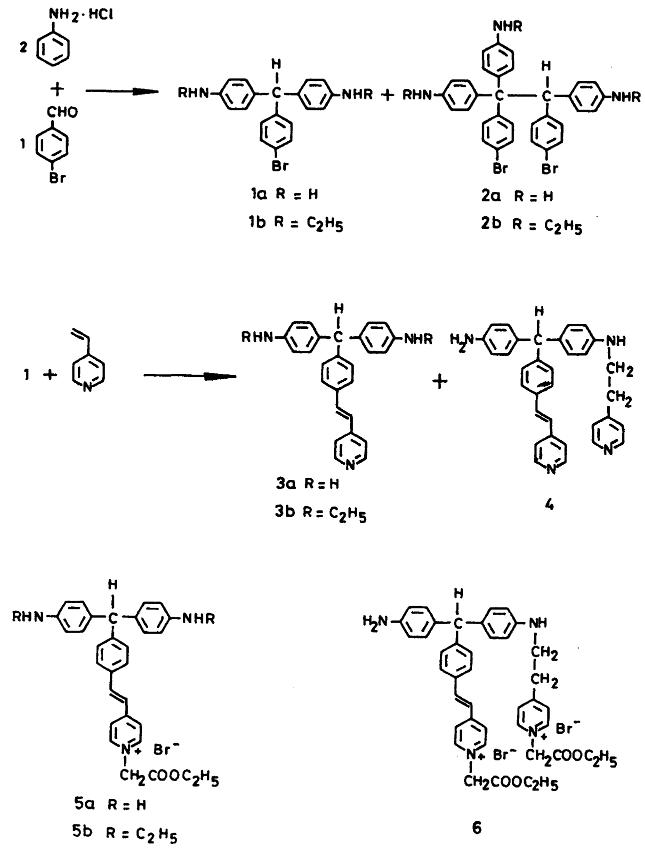
Results and Discussion

The key intermediate **1a** required for the synthesis of title compound was prepared from *p*-bromobenzaldehyde and aniline hydrochloride adopting the method of Ghatge and Khune.4) In addition to **1a** another crystalline compound **2a**, mp 99—101°C, M$^+$ 615, analyzed for $C_{32}H_{27}Br_2N_3$ was also obtained in the reaction. On the basis of analytical and spectral data **2a** was characterized as 1,2-bis(*p*-bromophenyl)-1,1,2-tris-(*p*-aminophenyl)ethane. This is the first report of the isolation and characterization of an ethane derivative **2a** in this type of reaction which was not observed by earlier workers.4) Following above procedure condensation of *p*-bromobenzaldehyde with *N*-ethylaniline hydrochloride gave **1b** and **2b**.

Pd-Catalyzed Coupling. In continuation of our interest in the synthesis of styryl compounds3) as potential precursors for polymers, we have attempted the synthesis of **3a** and **3b**. Thus 4-vinylpyridine was condensed with the key intermediate **1** following the Heck's procedure5) employing 3 : 1 mixture of tri-*O*-tolylphosphine and palladium acetate in dry triethylamine at 105°C for 12 h. The reaction mixture after purification procedure yielded two crystalline compounds designated as compound-A (yield 65%), mp 87—88°C, M$^+$ 377 (100%) analyzed for $C_{26}H_{23}N_3$, and compound-B (yield 25%), mp 98—100°C, M$^+$ 482 (39%) analyzed for $C_{33}H_{30}N_4$. Constitutions of compound-A and B were established as **3a** and **4** on the basis of analytical and spectral data (see Experimental). The presence of strong absorption at 966 cm^{-1} due to trans olefinic bond and two AB doublets at $\delta=6.99$ (1H, $J=15.7$ Hz) and 7.31 (1H, $J=15.7$ Hz) strongly supports the trans configuration of compound-A.

In order to study the nonlinear optical properties **3a**, **3b**, **4** were converted very smoothly into their corresponding pyridinium dyes **5a**, **5b**, and **6** using ethyl bromoacetate in dry benzene. However, none of the compounds synthesized in the present investigation showed the required nonlinear optical properties (Scheme 1).

Therefore, presently attempts are being made to polymerize 4, 4′-[[[2-(4-pyridinyl) ethenyl] phenyl] meth-



Scheme 1.

ylene] bis[benzenamines] (**3**) and the results will be published elsewhere.

Experimental

Melting points obtained using a Gallankamp apparatus and are uncorrected. UV spectra were recorded in methanol. IR spectra were obtained in KBr and mass spectra were taken VG micromass 7070H and Finnigan Melt 1020B mass spectrometer. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Varian FT-80A spectrometer with TMS as an internal standard.

4,4′-[(4-Bromophenyl)methylene]bis[benzenamine] (1a). A mixture of *p*-bromobenzaldehyde (3.7 g, 0.02 mol) and aniline hydrochloride (5.18 g, 0.04 mol) in nitrobenzene using $ZnCl_2$ as a catalyst was heated at 165—170°C for 4 h according to the procedure reported by Gatge and Khune.[4] The product was worked up in the usual way to give a mixture of two products (TLC). These were separated by chromatography over silicagel using benzene–ethyl acetate (4 : 1) as eluant. The first major fraction obtained after concentration of the solvent gave the diamine (**1**) as a brown crystalline solid (4.53 g, 65%), mp 68—70°C; R_f 0.7 (benzene–ethyl acetate 4 : 1). UV 245 nm (ϵ 50651); IR 3340 cm^{-1}; ^{1}H NMR δ=5.25 (1H, s, C–H), 3.45 (4H, b, NH_2), 6.55 (4H, d, J=8.8 Hz), 6.83 (4H, d, J=8.8 Hz), 6.95 (2H, d, J=8.4 Hz), 7.35 (2H, d, J=8.4 Hz); MS *m*/*z* (rel intensity) 353 (32, M^+), 273 (100). Found: C, 64.51; H, 4.68; N, 7.82%. Calcd for $C_{19}H_{17}BrN_2$: C, 64.58; H, 4.80; N, 7.90%.

The second fraction after concentration of the solvent gave **2a** as a pale yellow solid (1 g, 15%), mp 99—101°C, R_f 0.5 (benzene–ethyl acetate 4 : 1). UV 240 nm (ϵ 54240); IR 3350 cm^{-1}; ^{1}H NMR δ=5.25 (1H, s, C–H), 3.45 (6H, b, NH_2), 6.5—6.9 (12H, m), 7.25 (4H, d, J=8.4 Hz), 7.35 (4H, d, J=8.4 Hz); MS *m*/*z* (rel intensity) 615 (28, M^+), 613 (68), 351 (100). Found: C, 62.58; H, 4.37; N, 6.45%. Calcd for $C_{32}H_{27}Br_2N_3$: C, 62.64; H, 4.40; N, 6.80%.

4,4′-[(4-Bromophenyl)methylene]bis[*N*-ethylbenzenamine] (1b). The bis(*N*-ethylamine) **1b** was prepared under conditions to those described for the synthesis of **1a** starting from *N*-ethylaniline hydrochloride (6.28 g 0.04 mol) and *p*-bromobenzaldehyde (3.7 g, 0.02 mol). It was worked up in the usual way to give a mixture of two products (TLC). The first major fraction after concentration of the solvent gave **1b** as a brown solid (5.72 g, 70%), mp 62—64°C, R_f 0.7 ($CHCl_3$). UV 250 nm (ϵ 52523); IR 3340 cm^{-1}; ^{1}H NMR δ=5.30 (1H, s, C–H), 3.45 (2H, b, NH), 3.14 (4H, q, CH_2, J=7.6 Hz), 1.28 (6H, t, CH_3, J=7.6 Hz), 6.55 (4H, d, J=8.8 Hz), 6.90 (4H, d, J=8.8 Hz), 7.90 (2H, d, J=8.6 Hz), 7.40 (2H, d, J=8.6 Hz). Found; C, 67.41; H, 6.01; N, 6.72%. Calcd for $C_{23}H_{25}BrN_2$: C, 67.48; H, 6.11; N, 6.84%.

The second fraction after concentration of the solvent gave the by-product **2b** as brown solid (0.41 g, 5%), mp 73—75°C, R_f 0.5 ($CHCl_3$). UV 246 nm (ϵ 54165); IR 3340 cm^{-1}; ^{1}H NMR δ=5.25 (1H, s, C–H), 3.45 (3H, b, NH), 3.10 (6H, q, CH_2, J=7.6 Hz), 1.23 (9H, t, CH_3, J=7.6 Hz), 6.40—6.80 (12H, m), 7.00 (4H, d, J=8.4 Hz), 7.35 (4H, d, J=8.4 Hz); MS *m*/*z* 699 (M^+). Found: C, 65.15; H, 5.27; N, 6.12%. Calcd for $C_{38}H_{39}Br_2N_3$: C, 65.23; H, 5.58; N, 6.00%.

(*E*)-4,4′-[[[2-(4-Pyridinyl)ethenyl]phenyl]methylene]bis[benzenamine] (3a). A mixture of 3.83 g (0.01 mol) of **1a**, 1.1 g (0.01 mol) of 4-vinylpyridine, 23 mg (0.0001 mol) of palladium diacetate, 60 mg (0.002 mol) of tri-*O*-tolylphosphine and 10 ml of dry triethylamine was heated at 105°C for 12 h under nitrogen atmosphere. To the cooled mixture was added water and $CHCl_3$ (all solids dissolved). The water layer was extracted with chloroform (2×100 ml) and the combined chloroform solutions were washed with water dried over $MgSO_4$ and evaporated. The product shown to contain two compounds by TLC. These were separated by chromatography over alumina using benzene–ethyl acetate (1 : 1) as the eluant. The first fraction was diamine **3a** (2.45 g, 65%) mp 87—88°C, R_f 0.65 (benzene–ethyl acetate 1 : 4). UV 316 nm (ϵ 75539), 234 (56724); IR 3340, 970, 960 cm^{-1}; ^{1}H NMR δ=5.35 (1H, s, C–H), 3.50 (4H, b, NH_2), 6.99 (1H, d, J=15.7 Hz), 7.31 (1H, d, J=15.7 Hz), 8.54 (2H, d, J=6.5 Hz), 7.35 (2H, d, J=6.5 Hz), 6.65 (4H, d, J=8.8 Hz), 6.90 (4H, d, J=8.8 Hz), 7.15 (2H, d, J=8.7 Hz), 7.45 (2H, d, J=8.7 Hz); ^{13}C NMR δ=54.88, 114.86, 120.62, 125.07, 126.68, 129.61, 129.91, 132.97, 133.10, 133.66, 144.47, 144.73, 146.07, 149.73; MS *m*/*z* (rel intensity) 377 (100, M^+), 361 (9), 286 (41), and 197 (70). Found: C, 82.74; H, 6.10; N, 11.13%. Calcd for $C_{26}H_{23}N_3$: C, 82.75; H, 6.10; N, 11.14%.

(*E*)-*N*-[4-[(Aminophenyl)[4-[2-[(4-pyridinyl) ethenyl]phenyl]methyl]phenyl]- 4- pyridineethanamine (4). The second fraction after concentration of the solvent gave the new product **4** as yellow crystalline solid (0.88 g, 25%) mp 98—100°C, R_f 0.4 (benzene–ethyl acetate 1 : 4). UV 317 nm (ϵ 30662), 255 (32575), 240 (72060); IR 3350, 970 cm^{-1}; ^{1}H NMR δ=5.38 (1H, s, C–H), 3.13 (3H, b, NH_2), 3.45 (2H, t, CH_2, J=7.7 Hz), 2.92 (2H, t, CH_2, J=7.7 Hz), 6.95 (1H, d, J=15.7 Hz), 7.30 (1H, d, J=15.7 Hz), 8.56 (4H, d, J=6.5 Hz), 7.35 (4H, d, J=6.5 Hz), 6.60 (4H, d, J=8.8 Hz), 6.90 (4H, d, J=8.8 Hz), 7.15 (2H, d, J=8.7 Hz), 7.45 (2H, d, J=8.7 Hz); MS *m*/*z* (rel intensity) 482 (38, M^+), 390 (59), 377 (100). Found: C, 82.08; H, 6.13; N, 11.50%. Calcd for $C_{33}H_{30}N_4$: C, 82.15; H, 6.20: N, 11.60%.

(*E*)-4,4′-[[[2-(4-Pyridinyl)ethenyl]phenyl]methylene]bis[*N*-ethylbenzenamine] (3b). 4-Styrylpyridine **3b**, was prepared under conditions similar to those described for the synthesis of **3a** starting from **1b** (4.09 g, 0.01 mol) and yielded (3.85 g, 90%), mp 138°C, R_f 0.6 (benzene–ethyl acetate 3 : 2). UV 318 nm (ϵ 77538); IR 3300 cm^{-1}; ^{1}H NMR δ=5.35 (1H, s, C–H), 3.20 (2H, b, NH), 3.14 (4H, q, CH_2, J=6.7 Hz), 1.28 (6H, t, CH_3, J=6.7 Hz), 6.99 (1H, d, J=15.7 Hz), 7.30 (1H, d, J=15.7 Hz), 8.56 (2H, d, J=6.5 Hz), 7.35 (2H, d, J=6.5 Hz), 6.60 (4H, d, J=8.8 Hz), 6.91 (4H, d, J=8.8 Hz), 7.15 (2H, d, J=8.4 Hz), 7.45 (2H, d, J=8.4 Hz); ^{13}C NMR δ=15.17, 38.81, 55.29, 112.81, 120.10, 125.45, 127.05, 130.07, 130.31, 133.24, 133.37, 134.00, 145.07, 146.85, 147.01, 150.35; MS *m*/*z* (rel intensity) 433 (40, M^+), 352 (100). Found: C, 82.56; H, 7.10; N, 9.58%. Calcd for $C_{30}H_{31}N_3$: C, 83.14; H, 7.15; N, 9.70%.

(*E*)- 4- [2- [4- [Bis(4- aminophenyl)methyl]phenyl]-ethenyl]- 1- (2- ethoxy- 2- oxoethyl) pyridinium bromide (5a) was obtained by refluxing 0.75 g (0.002 mol) of **3a** and 0.34 g (0.002 mol) of ethyl bromoacetate in dry benzene for 3 h. Concentration of the solvent under vacuum gave (**5a**) as red solid and was crystallized from ethanol–hexane, 0.76 g (70%); mp 166—168°C, UV 370 nm (ϵ 11350), 250 (35721); IR 3340, 1740 cm^{-1}. Found; C, 66.02; H, 5.30; N, 7.51%. Calcd for $C_{30}H_{30}BrN_3O_2$: C, 66.17; H, 5.51; N, 7.72%.

(*E*)-4-[2-[4-Bis(4-*N*-ethylaminophenyl)methyl]-phenyl]ethenyl]-1-(2-ethoxy-2-oxoethyl)pyridinium Bromide (5b) was prepared from **3b** and ethyl bromoacetate as described **5a**. The product **5b** (72%) was crystallized from ethanol–hexane; mp 158°C; UV 357 nm (ϵ 11890), 254 (35839); IR 3340, 1740 cm^{-1}. Found: C, 68.21; H, 6.24; N, 7.12%. Calcd for $C_{34}H_{38}BrN_3O_2$: C, 68.00; H, 6.33; N, 7.00%.

(*E*)-4-[2-[4-[[4-Aminophenyl-4′-[2-[1-(2-ethoxy-2-oxoethyl)-4-pyridinio]ethylamino]phenyl]methyl]-phenyl]ethenyl]-1-(2-ethoxy-2-oxoethyl)pyridinium Dibromide (6) was obtained in 70% yield by refluxing 1.2 g (0.0025 mol) of **4** and 0.84 g (0.005 mol) of ethyl bromoacetate in dry benzene and crystallization from ethanol–hexane; mp 158—161°C; UV 370 nm (ϵ 11926), 250 (35862); IR 3340, 1740 cm^{-1}. Found: C, 60.20; H, 5.28; N, 6.65%. Calcd for $C_{41}H_{44}Br_2N_4O_4$: C, 60.29; H, 5.39; N, 6.86%.

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