Intramolecular Charge Transfer Processes in Donor-Acceptor Substituted Vinyltetrahydropyrenes

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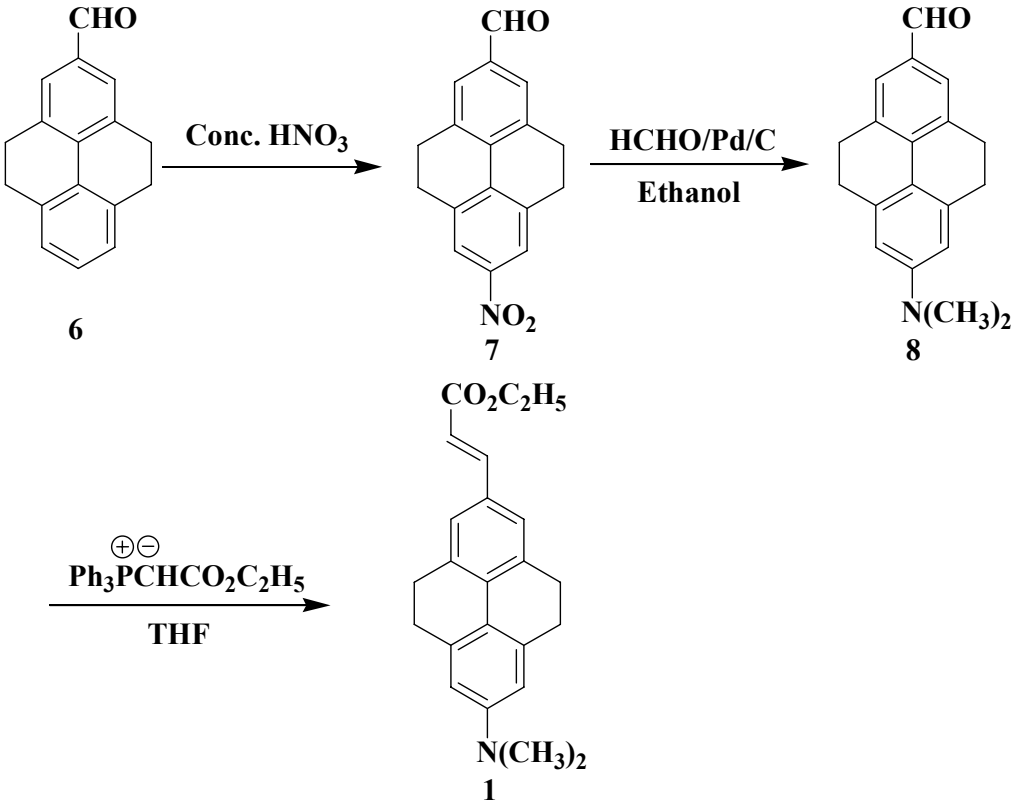
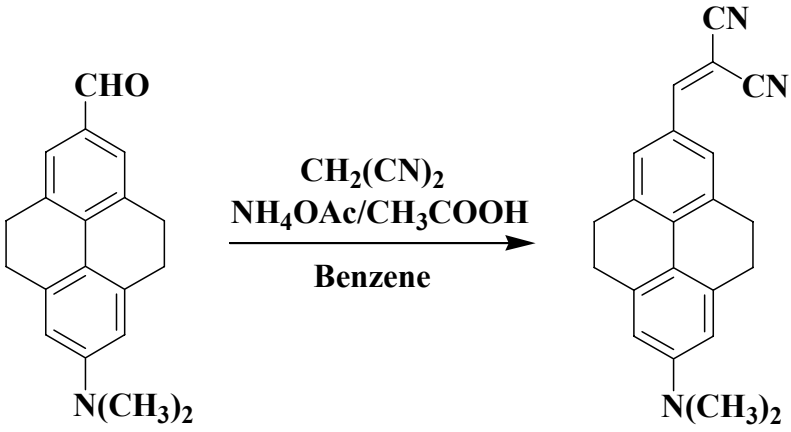
Supplementary Information

Compounds **1**, **2**, **4** and **5** were prepared according to Schemes 1S-4S. The synthesis of **3** and **6** is reported else where.[1]

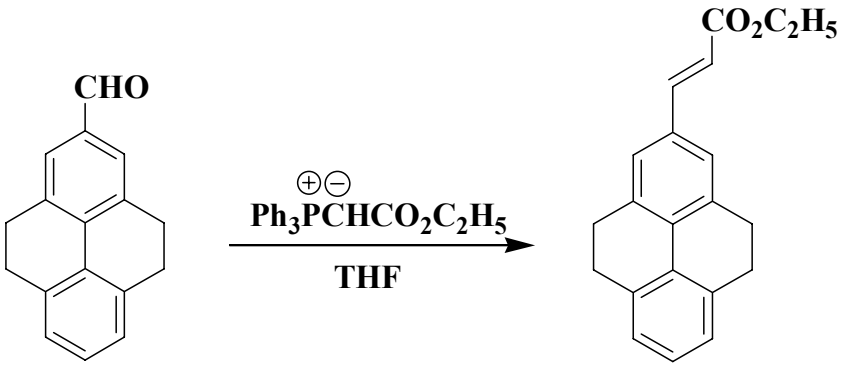


Scheme S1



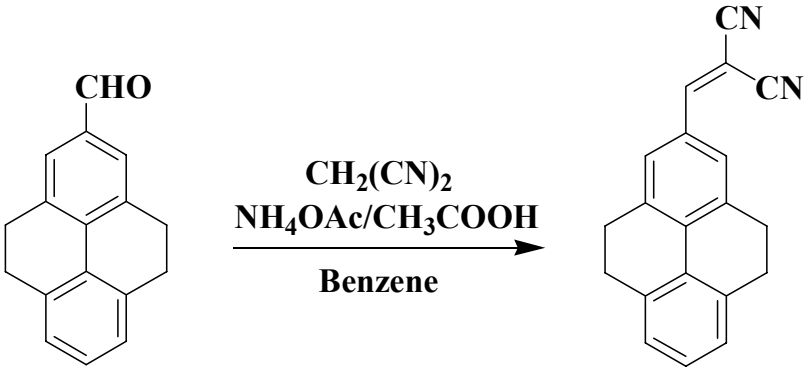
8 **2**

Scheme S2



6 **4**

Scheme S3



6 **5**

Scheme S4

Preparation of 7: Aldehyde **6** (500 mg, 2.1 mmol) was stirred with concentrated nitric acid (15 ml) at room temperature for 2 h. The mixture was then poured into crushed ice and the precipitate was filtered and dried. It was then purified by column chromatography over silica gel using a mixture (1:1) of hexane and chloroform to give 320 mg (60%) of **7**, mp 234-235 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.86 (s, 8H, benzylic), 7.57 (s, 2H ArH), 7.91 (s, 2H, ArH), 9.91 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$): δ 27.62, 27.91, 121.33, 127.63, 134.55, 135.63, 136.28, 136.97, 137.57, 147.17, 191.83. IR (KBr): 2941, 2837, 1688, 1602, 1517, 1438, 1333, 1208, 1133, 898, 740 cm^{-1}.

Preparation of 8: Nitro aldehyde **7** (200 mg, 0.72 mmol) was subjected to reductive methylation, using hydrogen in the presence of Pd/C (10%) and formaldehyde (0.2 mL), in ethanol for 1 h. (Longer reaction times led to the formation of by-products, which considerably reduced the yield). The solvent was removed and the residue chromatographed over silica gel using a mixture (5:95) of ethyl acetate and hexane to give 160 mg (80%) of **8**, mp 141-142 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.9 (s, 8H, benzylic), 2.98 (s, 6H, $N(CH_3)_2$, 6.46 (s, 2H, ArH), 7.98 (s, 2H, ArH), 9.88 (s, 1H, CHO). IR (KBr): 2934, 2882, 2825, 1688, 1584, 1543, 1517, 1481, 1444, 1372, 1341, 1268, 1134, 932, 881 cm^{-1}.

Preparation of 1: The compound **8** (100 mg, 0.36 mmol) was treated with (carbethoxymethyl)triphenyl-phosphonium ylide (189 mg, 0.54 mmol) in THF (10 mL) for 2 h under reflux. (The ylide was prepared by the reaction between triphenyl phosphine (2g, 0.071mol) and ethyl bromoacetate (2.9 gm, 0.011mol) in dry toluene at ice temperature. The precipitated product was washed with toluene, followed by petroleumether and then dissolved in water. To this was added phenolphthalein and the solution was made alkaline with sodium hydroxide. The precipitated product was filtered and dried).[2] The solvent was evaporated and the residue extracted with chloroform and washed with water. The organic layer was separated and the solvent was removed under reduced pressure to get a residue which was chromatographed over silica gel using a mixture (5:95) of ethyl acetate and hexane to give 80 mg (64%) of **1**, which was further crystallized from a mixture (9:1) of benzene and hexane to get analytically pure sample, mp 107-108 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.26 (t, 3H, J = 7.1 Hz, CH_3), 2.85 (s, 8H, benzylic), 3.0 (s, 6H, $N(CH_3)$), 4.26 (q, 2H, J = 7.1 Hz, CH_2), 6.36 (d, 1H, J = 15.3 Hz, CH), 6.79 (s, 2H, ArH), 7.18 (s, 2H, ArH) 7.8 (d, 1H, J = 15.3 Hz, CH). ^{13}C NMR ($CDCl_3$): δ 14.43, 28.14, 28.86, 41.6, 60.2, 96.19, 111.39, 116.41, 121.3, 126.07, 131.87, 134.39, 137.2, 144.9, 167.16, 191.26. IR (KBr): 2940, 1724, 1610, 1383, 1264, 1155, 1041, 876 cm^{-1}. HRMS (m/z) calculated for $C_{23}H_{25}NO_2$: 347.1885, Observed mass: 347.1890)

Preparation of 2: The compound **2** was prepared according to Scheme 2S. A mixture of **8** (100 mg, 0.36 mmol), malononitrile (48 mg, .72 mmol), ammonium acetate (10 mg), acetic acid (5 mL) and benzene (10 mL) was refluxed for 2 h. The solvent was removed under reduced pressure and the residue extracted with dichloromethane. The organic layer was separated and washed with water. The solvent was then removed under reduced pressure and the residue chromatographed over silica gel using a mixture (95:5) of hexane and ethyl acetate to give 85 mg (73%) of **2**, which was further purified by recrystallization from ethanol. mp 212-213 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.8 (s, 8H, benzylic), 2.96 (s, 6H, $N(CH_3)_2$), 6.36 (s, 2H, ArH), 7.47 (s, 1H, CH), 7.49 (s, 2H, ArH).

^{13}C NMR ($CDCl_3$): δ 28.16, 28.57, 40.21, 109.54, 113.79, 114.97, 118.37, 127.62, 128.79, 134.37, 138.39, 138.77, 151.27, 159.11. IR (KBr): 3330-3352, 2360, 1921, 1607, 1438 cm^{-1}. Anal. Calcd. for $C_{22}H_{19}N_3$: C, 81.2; H, 5.89; N, 12.91. Found: C, 80.95; H, 5.89; N, 12.71.

Preparation of 4: Model compound **4** is prepared as shown in Scheme 3S by the reaction between **6** (100 mg, 0.4 mmol) and (carbethoxymethyl)triphenylphosphonium ylide (223 mg, 0.64 mmol) in dry THF (10 mL). The solid obtained was purified by chromatography over silica gel using a mixture (95:5) of hexane and ethyl acetate gave 90 mg (70%) of **4**, mp 91-92 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.36 (t, 3H, *J* = 7 Hz, CH_3), 2.88 (s, 8H, benzylic), 4.26 (q, 2H, *J* = 7 Hz, CH_2), 6.4 (d, 1H, *J* = 15.2 Hz CH), 7.0-7.15 (m, 3H, ArH), 7.24 (s, 2H, ArH), 7.82 (d, 1H, *J* = 15.2 Hz CH). ^{13}C NMR ($CDCl_3$): δ 14.32, 28.13, 28.49, 60.2, 96.1, 117.2, 125.15, 126.0, 127.6, 130.03, 133.03, 135.53, 135.66, 144.7. IR (KBr): 2981, 2929, 2887, 2831, 1703, 1631, 1600, 1429, 1372, 1305, 1243, 1165, 1144, 1031, 934, 840 cm^{-1}.

Preparation of 5: Compound **5** was prepared according to Scheme 4S by the reaction between **6** (100 mg, 0.4 mmol) and malononitrile (53 mg. 0.8 mmol) in the presence of ammonium acetate (10 mg) and acetic acid using benzene as solvent (Scheme 3.3). The residue obtained after the reaction was purified by recrystallization from benzene to give 94 mg (78%) of **5**, mp, 176-177 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.92 (m, 8H, benzylic), 7.65 (s, 1H, CH), 7.63 (s, 2H, ArH), 7.1-7.25 (m, 3H, ArH). ^{13}C NMR ($CDCl_3$): δ 27.8, 28.02, 113.21, 114.36, 126.38, 128.71, 129.24, 129.37, 129.48, 136.49, 136.63, 137.41, 137.412, 159.44. IR (KBr): 2934, 2893, 2831, 2215, 1574, 1543, 1436, 1465, 1424, 1362, 1325, 1263, 1145, 953, 821 cm^{-1}.

References

1. Sumalekshmy, S.; Gopidas, K. R.; *J. Phys. Chem. B* **2004**, *108*, 3705.
2. *Org. Synth., Coll.* Vol. VII. 1990, 232.