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Supplementary Material.

Intramolecular Long-Distance Electron Transfer and Triplet Energy Transfer. Photophysical and Photochemical Studies on a Norbornadiene-Steroid-Benzidine System

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3 β -hydroxy-androst-5-en-17 β -yl-2,2',6,6',N,N',N'-heptamethylbenzidine (HO-S-17 β -B) and 3 β -hydroxy-androst-5-en-17 α -yl-2,2',6,6',N,N',N'-heptamethylbenzidine (HO-S-17 α -B). These compounds were synthesized as described in the literature for reductive amination of ketones with sodium triacetoxymethylborohydride as reducing agent.¹ The mixture of the distereomers HO-S-17 β -B and HO-S-17 α -B were obtained. These isomeric amines were separated by chromatography on silica with methylene chloride/ ethyl acetate/ petroleum ether (3/2/12) as eluant. HO-S-17 β -B : m.p. 138-140 °C; Anal: Calcd for C₃₈H₅₄N₂O: C: 82.31, H: 9.75, N: 5.05, Found: C: 82.24, H:9.67, N:4.98; IR (KBr, cm⁻¹): 3570 (-O-H), 2810 (-CH₃), 1630 (phenyl), 1600 (-C=C), 1350 (C-N), ¹H NMR(CDCl₃, 300 MHz): 7.20 (s, 4H, ArH), 5.40 (dd, 1H, steroid olefinic H), 3.49 (m, 1H, 3 α -H), 3.40 (m, 1H, 17 α -H), 2.90 (s, 6H, N'CH₃), 2.80 (s, 3H, NCH₃), 2.25 (s, 12H, ArCH₃), 2.40-1.10 (m, 19H), 1.05 (s, 3H, 19-CH₃) 0.90 (s, 3H, 18-CH₃) MS: m/e 555 (M⁺+1). HO-S-17 α -B : ¹H NMR (CDCl₃, 300 MHz): 7.20 (s, 4H, ArH), 5.40 (dd, 1H, steroid olefinic H), 3.49 (m, 1H, 3 α -H), 3.10 (m, 1H, 17 β -H) 2.90 (s, 6H, N'CH₃), 2.80(s, 3H, N'CH₃), 2.25 (s, 12H, ArCH₃), 2.40-1.10 (m, 19H), 1.05 (s, 3H, 19 CH₃), 0.90 (s, 3H, 18 CH₃).

3 β -(2-(Methoxycarbonyl)bicyclo-[2.2.1]hepta-2,5-diene-3-yl)-carboxy)-androst-5-en-17 β -yl-2,2',6,6',N,N',N'-heptamethylbenzidine (N-S-B). This compound was prepared by esterification of 2-(methoxycarbonyl)bicyclo[2,2,1]hepta-2,5-diene-3-carboxylyl chloride with HO-S-17 β -B by use of a procedure as described in the previous paper.² A 50 ml round bottom flask equipped with a magnetic stir bar and a condenser with a nitrogen inlet tube. The apparatus was flame dried under dry nitrogen and charged with anhydrous 2-(methoxycarbonyl)bicyclo[2,2,1]hepta-2,5-diene-3-carboxylic acid (0.35g, 1.8 mmol) and thionyl chloride (5 ml). The mixture was refluxed for 3 h and the excess of thionyl chloride was removed under reduced pressure. The resulting 2-(methoxycarbonyl) bicyclo[2,2,1]hepta-2,5-diene-3-carboxylyl chloride was dissolved in anhydrous tetrahydrofuran (5 ml), and to the solution was added first HO-S-17 β -B (1g 1.81 mmol) and then anhydrous triethylamine (0.2 ml). The mixture was refluxed overnight, at which time TLC analysis showed the complete disappearance of the alcohol. Water was then added, and the mixture was extracted with chloroform. The chloroform extract was washed successively with sodium bicarbonate solution (5%) and water. The organic layer was dried over MgSO₄. Evaporation of the solvent afforded a yellow oily product. The product was purified by column chromatography on silica eluted with methylene chloride/ ethyl acetate (2/7 in volume) to give N-S-B as white crystals (32%). m.p. 167-169 °C; Anal. Calcd for C₄₈H₆₂N₂O₄: C: 78.90, H: 8.49, N: 3.84, Found: C: 78.75, H: 8.21, N:3.65. IR(KBr, cm⁻¹) : 2930 (C-H), 2810 (-CH₃), 1720 (-COO), 1700 (-C=O), 1630 (phenyl), 1600 (-C=C), 1350 (C-N), 1240 (-C-O), ¹H NMR (CDCl₃, 300 MHz), 7.20 (s, 4H, ArH), 6.95 (dd, 1H, NBD olefinic H), 6.90 (dd, 1H, NBD olefinic H), 5.40 (dd, 1H, steroid olefinic H), 4.25 (dd, 1H, NBD bridgehead H), 4.15 (m, 1H, NBD bridgehead H), 3.95 (s, 3H, O-CH₃), 3.55 (m, 1H, 3 α -H), 3.40 (m, 1H, 17 α -H), 2.90 (s, 6H, N-CH₃), 2.80 (s, 3H, NCH₃), 2.25 (s, 12H, Ar-CH₃), 2.05-2.55 (m, 2H, NBD bridge H), 2.40-1.10 (m, 19H), 1.05 (s, 3H, 19CH₃), 0.90 (s, 3H, 18CH₃).

3 β -(2-(Methoxycarbonyl)quadriclane-3-yl)-carboxy)androst-5-en-17 β -yl-

2,2',6,6',N,N,'N'-heptamethylbenzidine (Q-S-B). A N₂-saturated solution of N-S-B (2×10^{-4} M) in 200 ml cyclohexane was irradiated at $\lambda > 300$ nm at room temperature. The yield of the product was determined by ¹H NMR spectroscopic analysis of the crude reaction mixture and by HPLC analysis. The product was separated from the photolysed mixture by TLC on silica with methylene chloride/ ethyl acetate/ petroleum ether (2/1/8 in volume) as eluant. MS m/e: 731(M⁺+1); IR (KBr, cm⁻¹): 2930 (C-H), 2810 (-CH₃), 1720 (-COO), 1700 (-C=O), 1640 (phenyl), 1600 (-C=C), 1350 (C-N), 1240 (-C-O), ¹H NMR (CDCl₃): 7.20 (s, 4H, ArH), 5.40 (dd, 4H, steroid clefinic H), 3.75 (s, 3H, OCH₃), 3.55 (m, 1H, 3 α -H), 3.40 (m, 1H, 17 α -H), 2.90 (s, 6H, N-CH₃), 2.80 (s, 3H, NCH₃), 2.75-2.85 (m, 2H, QC bridge lead H), 2.55 (m, 2H, QC cyclobutane H), 2.35 (m, 2H, QC bridge H), 2.40-1.10 (m, 19H), 2.25 (s, 12H, Ar-CH₃), 1.05 (s, 3H, 19-CH₃), 0.90 (s, 3H, 18-CH₃).

References

1. (a) Hutchins, R. O.; Su, W.; Sivakumar, R.; Cistone, F.; Steroho, Y. P. *J. Org. Chem.* **1983**, *86*, 3412. (b) Adel-Magdid, D. F.; Maryanoff, C. A.; Carson, K. G. *Tetrahedron Lett.* **1990**, *31*, 5595.
2. Tung, C.-H.; Zhang, L.-P.; Li, Y.; Cao, H.; Tanimoto, Y. *J. Phys. Chem.* **1996**, *100*, 4480.