THE JOURNAL OF
PHYSICAL CHEMISTRY
J. Phys. Chem., 1996, 100(11), 4480-4484, DOI:10.1021/jp952833v

Supplementary material.

Benzophenone-Initiated Photoisomerization of Norbornadiene Group in a Benzophenone-Steroid-Norbornadiene System via Long-Distance Intramolecular Triplet Energy Transfer

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3β-NBD-androst-5-en-17-one (NBD-S-One). Bicyclo[2,2,1]hepta-2,5-diene-2-methylcarboxylate-3-carboxylic acid was prepared by literature method.[1] NBD-S-One was synthesized by esterification of bicyclo[2,2,1]hepta-2,5-diene-2-methylcarboxylate-3-carboxylyl chloride with 3β-hydroxy-androst-5-en-17-one. A 50 ml round bottom flask was 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 bicyclo[2,2,1]hepta-2,5-diene-2-methylcarboxylate-3-carboxylic acid (0.9 g, 4.64 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 bicyclo[2,2,1]hepta-2,5-diene-2-methylcarboxylate-3-carboxylyl chloride was dissolved in anhydrous tetrahydrofuran (5 ml), and to the solution was added first 3β-hydroxy-androst-5-en-17-one (1.3 g, 4.5 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 ether. The ether extract was washed successively with sodium bicarbonate solution (5%) and water. The organic layer was dried over $MgSO_4$. Evaporation of the solvent afforded a yellow oily product. The product was purified by column chromatograhy on silica eluted with petroleum ether/diethyl ether (60/30, in volume) to give NBD-S-One as white crystals (0.2 g, 10%), mp 155-158 °C. Anal. Caled for $C_{29}H_{36}O_5$: C, 75.00; H, 7.75, Found: C, 75.48; H, 7.55. MS m/e 465(M^++1); IR (KBr) 2920 (C–H), 1720 (–COO), 1690 (–C=O), 1600 (–C=C), 1270 (–C–O); ^{1}HNMR ($CDCl_3$, 300 MHz) 6.95 (dd, 1H, NBD olefinic H), 6.90 (dd, 1H, NBD olefinic H), 5.40 (dd, 1H, steroid olefinic H), 4.25 (m, 1H, NBD bridgehead H), 4.15 (m, 1H, NBD bridgehead H), 3.95 (s, 3H, O-CH_3), 3.55 (m, 1H, 3α-H), 2.55-2.05 (m, 2H, NBD bridge H) 2.4-1.1 (m, 19H), 1.05 (s, 3H, 19-CH_3), 0.90 (s, 3H, 18-CH_3).

H-4484-2

3β-NBD-androst-5-en-17β-ol (NBD-S-17β-Ol) and 3β-NBD-androst-5-en-17α-ol (NBD-S-17α-Ol). These compounds were prepared by reduction of NBD-S-One with sodium borohydride. [2] To a stirred solution of NBD-S-One (0.5 g, 1.08 mmol) in 10 ml of tetrahydrofuran at room temperature was added sodium borohydride (0.5 g, 13 mmol). The mixture was refluxed for 3 h, then was cooled and poured into 20 ml of 0.6 N HCl with ice. The mixture was extracted with diethyl ether. The organic layer was washed with water and dried over $MgSO_4$. Evaporation of the solvent afforded the crude alcohols as yellow solid. These products were purified by silica gel chromatography (1:2 diethyl ether/petroleum ether as the eluant) to give a mixture of NBD-S-17β-Ol and NBD-S-17α-Ol with a total yield of 0.35 g (70%). They were separated by TLC on silica with diethyl ether/petroleum ether (30:70) as the eluant. The ratio of NBD-S-17β-Ol to NBD-S-17α-Ol was ca. 3:1. NBD-S-17β-Ol: mp 159-161 °C; Anal. Calcd for $C_{29}H_{38}O_5$: C, 74.48; H, 8.20. Found: C, 74.20; H, 8.00. IR (KBr) 3570 (–O–H), 1720 (–COO), 1600 (–C=C), 1270 (–C–O); ^{1}HNMR ($CDCl_3$, 300 MHz) 6.95 (dd, 1H, NBD olefinic H), 6.90 (dd, 1H, NBD olefinic H), 5.40 (dd, 1H, steroid olefinic H), 4.25 (m, 1H, NBD bridgehead H), 4.15 (m, 1H, NBD bridgehead H), 3.95 (s, 1H, O-CH_3), 3.55 (m, 1H, 3α-H), 3.32 (t, 1H, 17α-H), 2.55-2.05 (m, 2H, NBD bridge H), 2.4-1.1 (m, 19H), 1.05 (s, 3H, 19-CH_3), 0.90 (s, 3H, 18-CH_3); NBD-S-17α-Ol: ^{1}HNMR ($CDCl_3$, 300 MHz) 6.95 (dd, 1H, NBD olefinic H), 6.90 (dd, 1H, NBD olefinic H), 5.40 (dd, 1H, steroid olefinic H), 4.25 (m, 1H, NBD bridgehead H), 4.15 (m, 1H, NBD bridgehead H), 3.95 (s, 3H, O-CH_3), 3.68 (t, 1H, 17β-H), 3.55 (m, 1H, 3α-H), 2.55-2.05(m, 2H, NBD bridge H), 2.4-1.1 (m, 19H), 1.05 (s, 3H, 19-CH_3), 0.90 (s, 3H, 18-CH_3).

3β-NBD-androst-5-en-BP (NBD-S-BP). This compound was prepared by esterification of benzophenone-4-carboxylyl chloride with NBD-S-17β-Ol using a procedure similar to that utilized for NBD-S-One. The product was purified by chromatography on silica with ethyl acetate/petroleum ether (1:2) as eluant to give 12.5% yield of NBD-S-BP as a solid, mp 178-180 °C, Anal. Caled for $C_{43}H_{46}O_7$: C, 76.55 ; H, 6.82; Found: C, 76.24; H, 6.55; MS m/e 675 (M^++1); IR (KBr) 2930 (C–H), 1720 (–COO), 1700 (–C=O), 1640 (phenyl), 1600 (–C=C), 1240 (–C–O); ^{1}HNMR ($CDCl_3$, 300 Hz): 8.25-7.50 (m, 8H, arom.), 6.95 (dd, 1H, NBD olefinic H), 6.90 (dd, 1H, NBD olefinic H), 5.40 (dd, 1H, steroid olefinic H), 4.25 (m, 1H, NBD bridgehead H), 4.15 (m, 1H, NBD bridgehead H), 3.95 (s, 3H, O-CH_3), 3.55 (m, 1H, 3α-H), 3.35 (t, 1H, 17α-H), 2.55-2.05 (m, 2H, NBD bridge H), 2.4-1.1 (m, 19H), 1.05 (s, 3H, 19-CH_3), 0.90 (s, 3H, 18-CH_3).

3β-QC-androst-5-en-17β-BP (QC-S-BP). A N_2-saturated solution of NBD-S-BP (2.5×10^{-4} M) in 200 ml acetonitrile was irradiated at $\lambda > 350$ nm at room temperature. The yield of the product was determined by ^{1}HNMR spectroscopic analysis of the crude reaction mixture and by HPLC analysis. The product was separated from the photolysed mixture by TLC with ethyl acetate/petroleum ether

H-4484-3

(1:2) as eluant. MS m/e 675 (M^++1); IR (KBr), 2930 (C–H), 1720 (–COO), 1700 (–C=O), 1640 (phenyl), 1600 (–C=C), 1240 (–C–O); ^{1}HNMR ($CDCl_3$, 300 MHz), 8.25-7.50 (m, 8H, arom.), 5.40 (dd, 1H, steroid olefinic H), 3.75 (s, 3H, O-CH_3), 3.55 (m, 1H, 3α-H), 3.35 (t, 1H, 17α-H), 2.75-2.85 (m, 2H, QC bridgehead H), 2.55 (m, 2H, QC cyclobutane H), 2.35 (m, 2H, QC bridge H), 2.4-1.1 (m, 19H), 1.05 (s,3H, 19-CH_3), 0.90 (s, 3H, 18-CH_3).

3β-acetoxy-androst-5-en-17β-BP (A-S-BP). This compound was synthesized by a method analogous to that of NBD-S-BP by using acetyl chloride as the starting material and was identified by element analysis, MS, IR and ^{1}HNMR spectroscopies.

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