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3-Phenyl-5-[1-(phenylsulphonyl)-pent-4-yn]-1,2,4-triazine and 3-Phenyl-5-[1-(phenylsulphonyl)-hex-5-yn]-1,2,4-triazine

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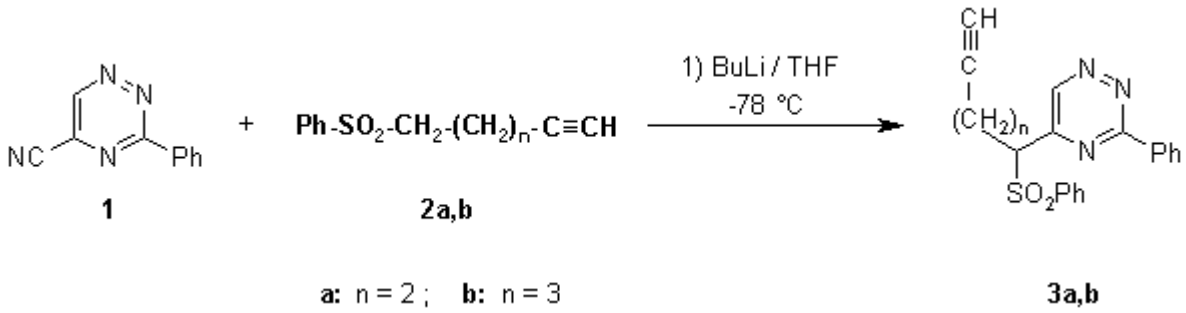
As part of ongoing research programme we synthesised the title compounds as valuable intermediates for intramolecular cycloaddition reactions, leading to biologically active heterocycles.



In a three-necked round-bottom flask (50 mL), equipped with a thermometer, a solution of 4-pentyn phenyl sulphone (**2a**) or 5-hexyn phenyl sulphone (**2b**) (1.0 mmole) [1] in dry THF (6 mL) is cooled to -78°C. To the stirred solution, BuLi (1.5 mmole, 0.94 mL of 1.6 N solution in hexane) was added gradually *via* syringe in such a rate to keep the temperature below -35°C. The mixture was cooled again to -78°C and a solution of 3-phenyl-1,2,4-triazine-5-carbonitrile [2] (**1**, 182 mg, 1.0 mmole) in dry THF (10 mL) was added dropwise *via* syringe during a period *ca* 10 min. It was stirred for *ca* 2 h and then allowed to warm to room temperature. To this mixture saturated aqueous NH_4Cl solution (20 mL) was added and it was extracted with CH_2Cl_2 (2 x 20 mL), dried over $MgSO_4$, and evaporated to dryness. Column chromatography purification (silica gel 200-300 mesh, eluent: $CHCl_3$) yielded 190 mg (52.5%) of pure 3-phenyl-5-[1-(phenylsulphonyl)-pent-4-yn]-1,2,4-triazine (**3a**) as a yellow solid (or 140 mg of 3-phenyl-5-[1-(phenylsulphonyl)-hex-5-yn]-1,2,4-triazine (**3b**), 37%).

3-Phenyl-5-[1-(phenylsulphonyl)-pent-4-yn]-1,2,4-triazine (3a):

M.p. 86-87ºC.

IR (KBr, cm^{-1}): 3280 (C≡C-H), 1325 & 1165 (SO_2).

^{1}H NMR ($CDCl_3$, 200 MHz): 1.97 (t, J = 2.6 Hz, 1 H, C≡CH), 2.00-2.20 (m, 1 H), 2.34-2.52 (m, 1 H), and 2.55-2.68 (m, 2 H) [2 x CH_2], 4.65 (dd, J_1 = 9.0 Hz, J_2 = 5.5 Hz, 1 H, CH(SO_2Ph)), 7.41-7.67 (m, 8 H, H-Ar), 8.21-8.27 (m, 2 H, H-Ar), 9.23 (s, 1 H, H-triazine).

MS (EI), m/z (% rel. int.): 363 (2, $M^{+\bullet}$), 362 (2), 311 (28), 222 (28), 194 (48), 184 (23), 169 (11), 167 (13), 141 (12), 125 (11), 104 (35), 91 (100), 77 (45), 65 (35), 51 (13).

HR-MS (EI) Calcd for $C_{20}H_{17}N_3SO_2$: 363.1042; Found: 363.1044.

3-Phenyl-5-[1-(phenylsulphonyl)-hex-5-yn]-1,2,4-triazine (3b):

M.p. 102-103°C.

IR (KBr, cm^{-1}): 3295 (C≡C-H), 1370 & 1170 (SO_2).

^1H NMR ($CDCl_3$, 200 MHz) 1.40-1.62 (m, 2 H, CH_2), 1.95 (t, J = 2.6 Hz, 1 H, C≡CH), 2.23 (td, J_1 = 6.8 Hz, J_2 = 2.6 Hz, 2 H, CH_2), 2.47-2.61 (m, 2 H, CH_2), 4.43 (dd, J_1 = 9.9 Hz, J_2 = 5.3 Hz, 1 H, $CH(SO_2Ph)$), 7.40-7.66 (m, 8 H, H-Ar), 8.20-8.28 (m, 2 H, H-Ar), 9.26 (s, 1 H, H-triazine).

MS (EI), m/z (% rel. int.): 377 (2, $M^{+\bullet}$), 376 (4), 311 (11), 208 (40), 105 (100), 104 (34), 103 (29), 79 (33), 77 (48), 65 (11), 51 (9).

HR-MS (EI) Calcd for $C_{21}H_{19}N_3SO_2$: 377.1198; Found: 377.1192.

References

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