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Synthesis of 4-Amino-1,7,8,9-tetramethyl-4-aza-tricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione

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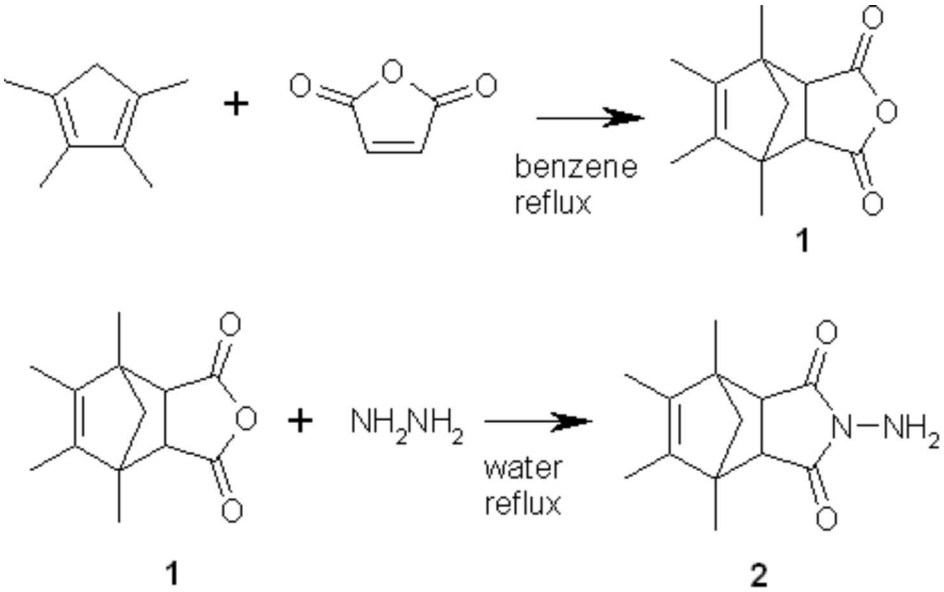
Various imide derivatives of 1,7,8,9-tetramethyl-4-aza-tricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (2) have been reported and shown to exhibit an anxiolytic activities [1].
Starting materials e.g. 1,2,3,4-tetramethyl-1,3-cyclopentadiene, and furan-2,5-dione were commercially available reagents.



1,7,8,9-Tetramethyl-4-oxa-tricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (1).
The synthesis of (1) was performed from 1,2,3,4-tetramethyl-1,3-cyclopentadiene and furan-2,5-dione according to the method described previously [2]. (Lit. m.p. 108-109^{0}C. Yield 68 %.)

White crystals, yield 76 %.

Melting point: 110ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.35 (s, 2H, CH-C=O); 3.29 (s, 12H, CH_3); 2.72 (s, 2H, CH_2).

^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 171.3, 138.4, 137.6, 63.9, 56.3, 54.4, 16.6, 11.0.

ESI MS: m/z = 243.3 $[M + Na]^+$ (100%).

Elemental Analysis: Calculated for C13H16O3 (220.26): C, 70.89 %; H, 7.32 %. Found: C, 70.92 %; H, 7.23 %.

4-Amino-1,7,8,9-tetramethyl-4-aza-tricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (2).
A mixture of anhydride 1 (0.01 mole) and hydrazine hydrate (80% water solution) (10 ml) was refluxed for 5 h. The solvents were evaporated. The residue was purified by a column chromatography (silica gel, chloroform/methanol 19:1) to give compound 2.

White crystals, yield 89 %.

Melting point: 161ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.52 (s, 2H, NH_2); 3.02 (s, 2H, CH-C=O); 1.53 (s, 6H, CH_3); 1.47 (s, 6H, CH_3); 1.33 (dd, 2H, CH_2).

^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 174.4, 137.6, 63.6, 55.2, 51.9, 17.1, 10.9.

ESI MS: m/z = 257.2 $[M + Na]^+$ (100%).

Elemental Analysis: Calculated for C13H18O2N2 (234.3): C, 66.07 %; H, 8.53 %; N, 11.85 %. Found: C, 66.32 %; H, 8.32 %; N, 11.89 %.

References:

1. Kossakowski, J.; Kuśmierczyk, J. *Acta Pol. Pharm.* **1999**, *56*, 94.
2. Mironov, V.A.; Sobolev, E.V.; Elizarova, A.N. *Tetrahedron* **1963**, *19*, 1939.