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Novel Intermolecular Heterocycle Exchange Reaction of Cyclohepta[b][1,4]benzoxazines and Their S-Analogs with 1,2-Bifunctional Reagents[1)]

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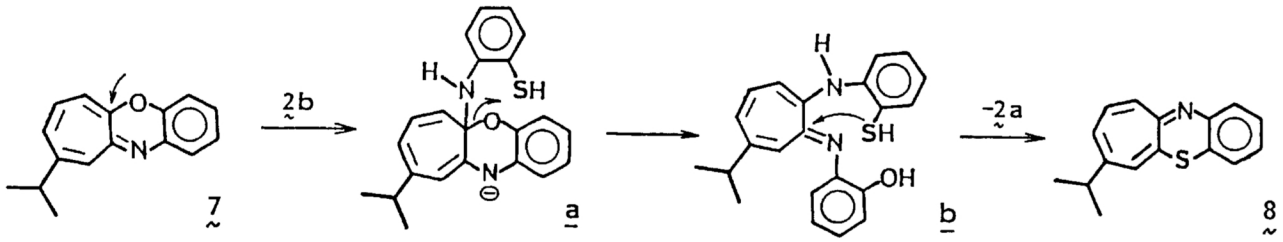
The benzoxazine and the benzothiazine moieties of cyclohepta-[b][1,4]benzoxazines and their S-analogs were easily exchanged with

When 1 was treated with an excess of 2b, cyclohepta[b][1,4]benzothiazine 3[3] was formed in a high yield. Similarly, both 1 and 3 were converted into the diazine analog 4 of the quinoxalo form[4,5] by the reaction with 2c. The reverse reaction of 3 or 4 to 1 did not take place apparently because of the less favorable nucleophilicity of 2a. Conversion of 1 to N-methyl derivative 5[6] and N,N'-dimethyl cation 6[7] was also achieved by the heterocycle exchange reaction



7 a b 8

with 2d and 2e. 9-Isopropylcyclohepta[b][1,4]benzoxazine 7[8] and 2b gave a thiazine analog 8[9] which did not isomerize anymore with 2b.

7.24 (2H, dd, J=11 and 9.5 Hz, H-7,9).

8) T. Nozoe and T. Someya, Bull. Chem. Soc. Jpn., 51, 3316 (1978).

9) 8: ^{1}H NMR(270 MHz in $CDCl_3$) δ =1.09 (6H, d, J=6.6 Hz, Me), 2.42 (1H, m, J=6.6 Hz, CH), 6.05 (1H, d, J=8.1 Hz, H-8), 6.08 (1H, s, H-6), 6.14 (1H, d, J=11.7 Hz, H-10), 6.34 (1H, dd, J=11.7 and 8.1 Hz, H-9), 6.85 (1H, dd, J=8.1 and 1.1 Hz, H-4), 6.93 (1H, td, J=8.1 and 1.1 Hz, H-3), 7.04 (1H, td, J=8.1 and 1.1 Hz, H-2), and 7.10 (1H, dd, J=8.1 and 1.5 Hz, H-1).

10) 9a: Pale yellow needles, mp 134 °C; UV (MeOH) 254, 366, and 424 nm (log ε 4.37, 3.88, and 3.80); ^{1}H NMR (100 MHz in $CDCl_3$) δ =3.53(4H, s, CH_2), 6.08 (1H, t, J= 9 Hz, H-7), 6.20 (2H, d, J=10 Hz, H-5,9), and 6.51 (2H, dd, J= 10 and 9 Hz, H-6,8); MS, m/z 146(M^+).

9b: Yellow solid, ; UV (MeOH) 243, 268, and 377 nm (log ε 4.07, 3.99, and 3.75); ^{1}H NMR (270 MHz in CD_3CN) δ =2.94 (2H, t, J=5 Hz, CH_2), 3.80 (2H, t, J=5 Hz,