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1H-Naphtho[2,1-b]thiete and 2H-Naphtho[2,3-b]thiete - Synthesis and Reactivity

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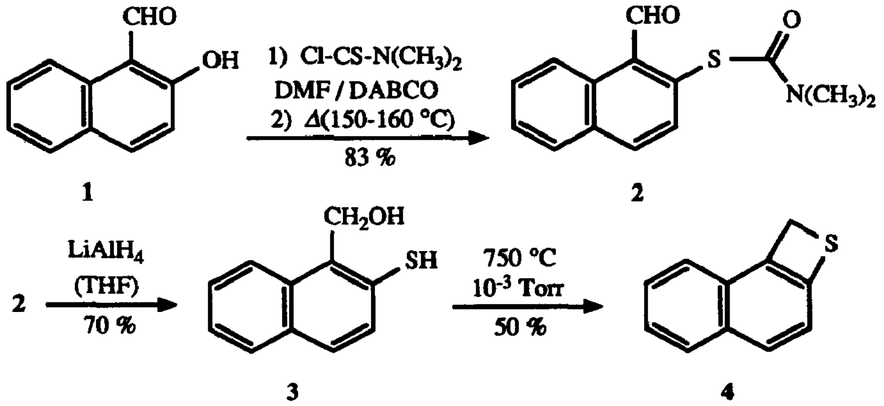
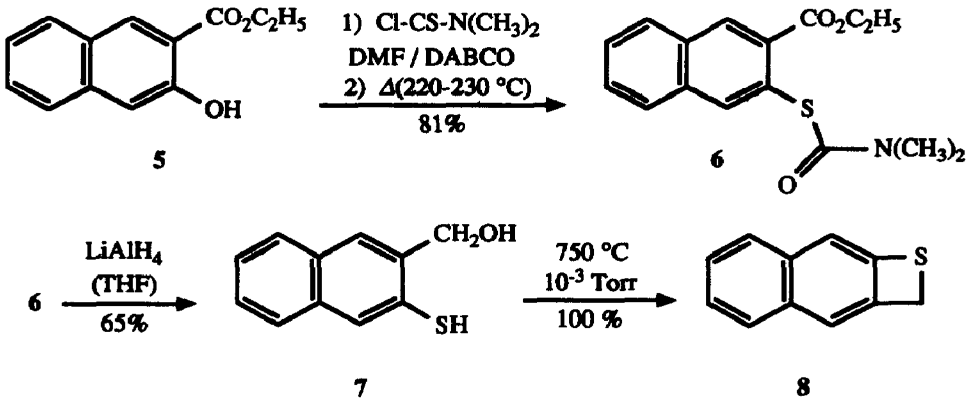
Abstract: The title compounds 4 and 8 are obtained by flash vacuum pyrolysis of the corresponding hydroxymethylthionaphthols 3 and 7. Whereas 4 shows a smooth ring opening on heating, 8 is thermally stable but reacts photochemically. The different behavior is explained on the basis of an MNDO calculation. The valence isomers 4' and 8' represent thioquinonemethides, which are highly reactive components in [12π + 2π]cycloaddition processes (4 → 9, 10, 11; 8 → 12).

2H-Benzo[b]thiete and its derivatives proved to be very useful and versatile reagents for the preparation of heterocyclic ring compounds containing sulfur and possibly further heteroatoms.[1,2] We report here on the synthesis and the cycloaddition reactions of 1H-naphtho[2,1-b]thiete (4) and the isomeric 2H-naphtho[2,3-b]thiete (8). 2-Hydroxynaphthalene-1-carbaldehyde (1) is transformed with N,N-dimethylthiocarbamoyl chloride to an O-ester which rearranges in a Newman-Kwart reaction[3,4] to the S-ester 2. Reduction of both functional groups furnishes the thionaphthol 3 and cyclization by FVP (flash vacuum pyrolysis)[5] finally leads to the target compound 4.



The isomeric compound 8 can be obtained on a principally similar route. Ethyl 3-hydroxynaphthalene-2-carboxylate (5) is transformed to the S-ester 6. Reduction with lithium aluminium hydride yields the thionaphthol 7 and FVP leads to the formation of 8. Compared to 3, 7 is much less sensitive towards self-condensation, thus a quantitative yield can be obtained for the 1,4-elimination 7 → 8. In both pyrolyses H_2O is extruded - and not H_2S, which would result in an oxete system or the corresponding quinonemethide.



4[6] and 8[7] are colourless solid compounds that are melting at 73 and 152 °C, respectively. Their reactivity differs widely - due to the totally different tendency for the thermal ring opening to the thionaphthoquinonemethides 4' and 8'. An MNDO calculation (version MOPAC 6)[8] reveals similar enthalpies of formation of 4 and 8 but considerably differing values for 4' and 8'. (Figure 1). Whereas the opening of the 4-membered ring in 4 can be observed above 80 °C, the activation barrier for the valence isomerization 8 → 8' is too high for a thermolysis in usual solvents. However, 8' can be formed as a highly reactive 12π electron system by irradiation of 8 ($\lambda \geq 300$ nm).

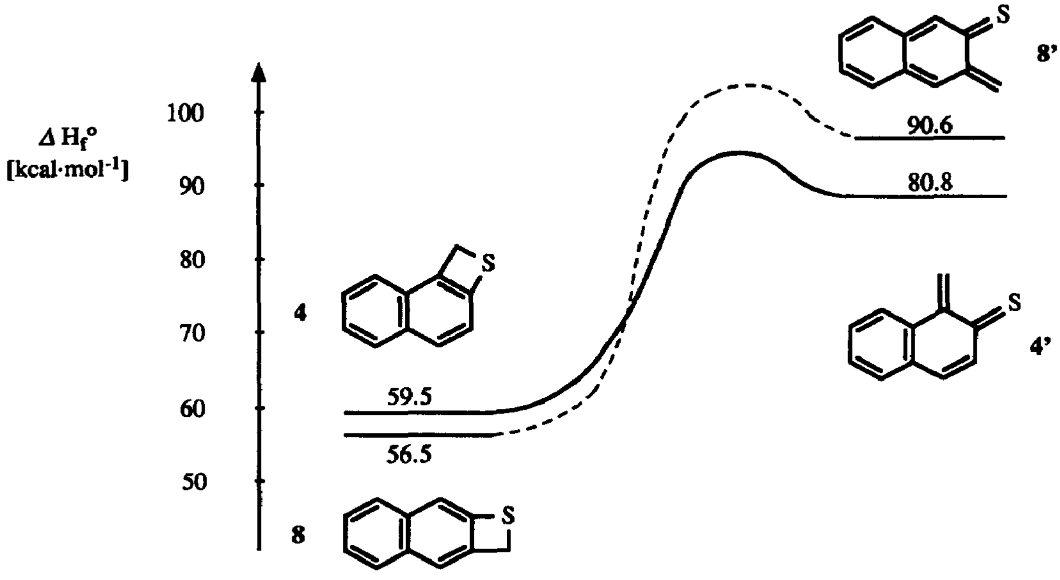
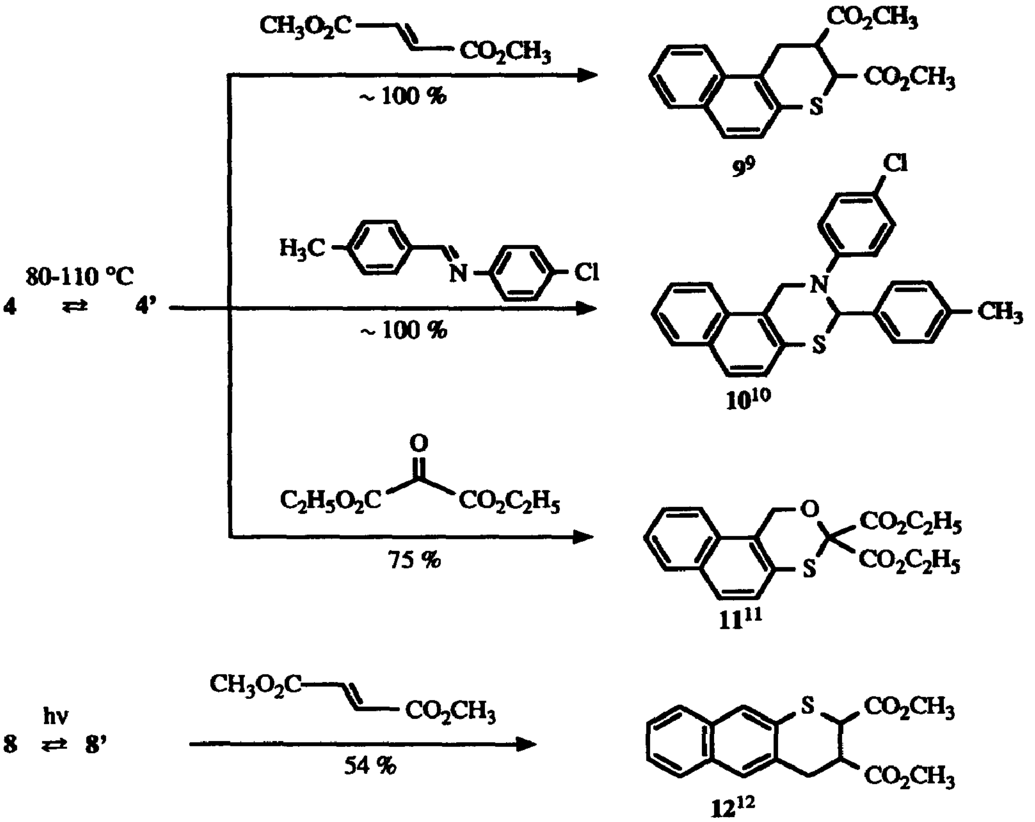


Figure 1. Enthalpies of formation of 4, 4', 8 and 8' calculated by the MNDO method.[8]

The following scheme shows a few cycloaddition reactions which demonstrate the synthetic value of 4/4' and 8/8' as heterodienes. Methyl fumarate adds stereoselectively to 4' and 8' generating the trans configurated compounds 9 and 12. The methoxycarbonyl groups are in pseudoequatorial positions; thus the protons on C-2 and C-3 have pseudoaxial positions with vicinal coupling constants of 8.2 and 8.1 Hz, respectively. Heterodienophiles add in a regioselective manner forming the products 10 and 11.



Until now, only the 2,2-dimethyl-3,8-diphenyl derivative of 8 was synthesized by Paquette.[13] The corresponding naphthocyclobutenes, carbocyclic analogues of 4 and 8 were already prepared by Cava and coworkers in the 60's.[14,15]

Acknowledgments

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References and Notes

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6. ^{1}H NMR ($CDCl_3$): δ = 4.51 (s, 2H, 1-H), 7.23 (d, 1H, 3-H), 7.35 (t, 1H, 6-H), 7.45 (t, 1H, 7-H), 7.56 (d, 1H, 5-H), 7.76 (d, 1H, 4-H), 7.78 (d, 1H, 8-H). ^{13}C NMR ($CDCl_3$): δ = 35.4 (CH_2), 119.8 / 120.2 / 124.1 / 126.9 / 129.5 / 129.6 (CH), 129.2 / 130.8 / 132.9 / 139.8 (C_q). MS (70 eV): m/z = 172 ($M^{+\cdot}$).
7. ^{1}H NMR ($CDCl_3$): δ = 4.40 (s, 2H, 2-H), 7.24 (s, 1H, 8-H), 7.37, m, 3H / 7.71, m, 2H (3-H, 4-H, 5-H, 6-H, 7-H). ^{13}C NMR ($CDCl_3$): δ = 36.4 (C-2), 118.1 / 120.9 / 124.2 / 125.5 / 126.6 / 128.2 (CH), 131.6 / 134.6 / 139.2 / 141.0 (C_q). MS (70 eV): m/z = 172 ($M^{+\cdot}$).
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9. Colourless solid, mp 97 °C. ^{1}H NMR ($CDCl_3$): δ = 3.25 (dd, 1H, 4-H), 3.45 (m, 1H, 3-H), 3.68 (dd, 1H, 4-H), 3.76 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 4.42 (d, $^3J_{trans}$ = 8.2 Hz, 1H, 2-H), 7.18 (d, 1H, 10-H), 7.45, t, 1H / 7.52, t, 1H (6-H, 7-H), 7.60 (d, 1H, 8-H), 7.76 (d, 1H, 9-H), 7.93 (d, 1H, 5-H). ^{13}C NMR ($CDCl_3$): δ = 27.1 (CH_2), 42.3 / 43.5 (CH), 52.5 / 52.9 (OCH_3), 121.8 / 124.9 / 125.1 / 126.8 / 127.2 / 128.8 ($CH_{aromat.}$), 127.1 / 128.4 / 131.7 / 132.1 (C_q), 170.8 / 173.3 (CO). MS (70 eV): m/z = 316 ($M^{+\cdot}$).
10. Colourless solid, mp 170 °C. ^{1}H NMR ($CDCl_3$): δ = 2.33 (s, 3H, CH_3), 4.64 / 4.91 (AB, 2H, 4-H), 6.23 (s, 1H, 2-H), 6.95 / 7.13 (AA'BB', 4H, chlorophenyl), 7.16 / 7.54 (AA'BB', 4H, tolyl), 7.20 (d, 1H, 10-H), 7.44, t, 1H / 7.49, t, 1H (6-H, 7-H), 7.61 (d, 1H, 8-H), 7.77 (d, 1H, 9-H), 7.78 (d, 1H, 5-H). ^{13}C NMR ($CDCl_3$): δ = 21.0 (CH_3), 43.2 (CH_2), 67.7 (CH), 120.1 / 128.2 / 129.1 / 129.4 ($CH_{aromat.}$, double), 120.4 / 124.9 / 126.3 / 126.3 / 126.8 / 127.0 ($CH_{aromat.}$), 123.8 / 126.4 / 130.3 / 130.9 / 131.7 / 136.7 / 138.0 / 147.8 (C_q). MS (70 eV): m/z = 401 ($M^{+\cdot}$).
11. Colourless oil. ^{1}H NMR ($CDCl_3$): δ = 1.24 (t, 6H, CH_3), 4.27 (q, 4H, OCH_2) 5.42 (s, 2H, 4-H), 7.31 (d, 1H, 10-H), 7.40-7.80 (m, 5H, aromat. H). ^{13}C NMR ($CDCl_3$): δ = 13.9 (CH_3), 63.1 (OCH_2), 64.3 (CH_2), 84.9 (C_q), 120.9 / 125.7 / 125.7 / 127.1 / 128.2 / 128.9 ($CH_{aromat.}$), 127.4 / 127.8 / 129.7 / 131.9 (Cq), 166.1 (CO). FD-MS: m/z = 346 ($M^{+\cdot}$).
12. Colourless solid, mp 104 °C. ^{1}H NMR ($CDCl_3$): δ = 3.04 (dd, 1H, 4-H), 3.31 (m, 2H, 4-H, 3-H), 3.74 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 4.42 (d, $^3J_{trans}$ = 8.1 Hz, 1H, 2-H), 7.40, m, 2H / 7.69, m, 4H (aromat. H). ^{13}C NMR ($CDCl_3$): δ = 32.9 (CH_2), 43.1 / 44.0 (CH), 52.6 / 53.0 (OCH_3), 125.8 / 125.9 / 126.1 / 126.8 / 126.9 / 127.4 ($CH_{aromat.}$), 129.7 / 132.0 / 132.8 / 133.8 (C_q), 171.7 / 173.0 (CO). FD-MS: m/z = 316 ($M^{+\cdot}$).
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