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## Synthesis, Isolation, and Characterization of Naphtho[2,3-c]thiophen

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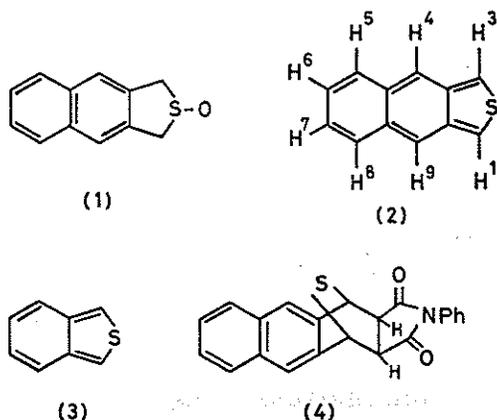
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naphtho[2,3-*c*]thiophen (2). Hitherto, (2) has not been isolated; it has, however, been prepared in solution by thermal dehydration of 1,3-dihydro-naphtho[2,3-*c*]thiophen 2-oxide (1) in the presence of either alumina or acetic anhydride,<sup>4,5</sup> followed by trapping the polycyclic heterocycle with *N*-phenylmaleimide. Mass spectral examination in our laboratory of the sulphoxide (1) revealed a fragment ion corresponding to naphtho[2,3-*c*]thiophen (2), which suggested that flash vacuum thermolysis, a technique which we had used previously for the synthesis and isolation of a host of high-energy *o*-quinonoidal nitrogen and oxygen heterocycles,<sup>1,6</sup> might be successfully applied to the preparation of (2). We now report that (1), when subjected to flash vacuum thermolysis, does undergo dehydration to yield (2) in excellent yield.

Sublimation of the sulphoxide (1) (200 mg per 30–40 min) from a glass reservoir† through a vertically-aligned, unpacked quartz tube (305 mm; 29 mm diam.) at 800 °C

and 0.3 mmHg afforded naphtho[2,3-*c*]thiophen (2) as a bright yellow solid, which was collected in the usual manner<sup>8</sup> in a trap cooled with liquid nitrogen. The assignment of the structure of the product (2) is supported by adduct formation and spectrometric data. The reactivity of naphtho[2,3-*c*]thiophen (2), which is considerably greater than that of the parent benzo[*c*]thiophen (3),<sup>7</sup> precluded determining its m.p. or recording its i.r. spectrum. However, compound (2) was sufficiently stable in dilute solution at room temperature and also in more concentrated solution at low temperature to allow its u.v.-visible and n.m.r. spectra to be measured: u.v.-visible spectra  $\lambda_{\text{max}}$  (heptane) 225, 250, 350 sh, 434, 454, and 462 nm; <sup>1</sup>H n.m.r.,  $\delta$  (CDCl<sub>3</sub>, –30 °C) 7.14 (2H, q, H-6, H-7), 7.70 (2H, q, H-5, H-8), 7.95 (2H, s, H-4, H-9), and 8.21 (2H, s, H-1, H-3).

Treatment of cold crystals of naphtho[2,3-*c*]thiophen (2) in a helium atmosphere with an excess of *N*-phenylmaleimide in ether followed by refrigeration at –10 °C for 48 h afforded, after recrystallization from acetonitrile, the previously described *exo*-adduct (4),<sup>4,5</sup> m.p. 280–281 °C (7%). The adduct (4) was shown by t.l.c., mixed m.p., i.r., and n.m.r. spectroscopy to be identical with an authentic specimen prepared by the method of Cava and co-workers.<sup>4</sup>

Until now, naphtho[2,3-*c*]thiophen (2) was the sole non-isolable member of the family of compounds derived by annelation of one or two benzenoid rings to the parent benzo[*c*]thiophen (3).<sup>4,8</sup> The resistance of (2) to isolation is not surprising in light of its extended *o*-quinonoidal structure.<sup>4</sup>

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† Preheating of the sulphoxide (1) was conveniently accomplished by positioning the reservoir as close as possible to the furnace; this arrangement provided a satisfactory rate of volatilization of the sample without resort to an additional source of heat.

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