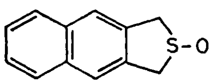
Synthesis, Isolation, and Characterization of Naphtho[2,3-c]thiophen

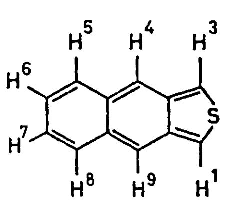
By Joseph Bornstein* and Ricky P. Hardy
(*Department of Chemistry, Boston College, Chestnut Hill, Massachusetts* 02167)
and David E. Remy
(*United States Army, Natick Research and Development Command, Natick, Massachusetts* 01760)

Summary 1,3-Dihydronaphtho[2,3-*c*]thiophen 2-oxide (**1**) undergoes dehydration when subjected to flash vacuum thermolysis to afford the heretofore elusive naphtho-[2,3-*c*]thiophen (**2**) as a highly reactive yellow solid.

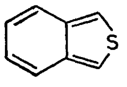
Our continuing interest in the chemistry of *o*-quinonoidal heteroaromatic compounds coupled with our efforts to reconcile the aromatic character of these substances with their high reactivity[1–3] prompted us to turn our attention to



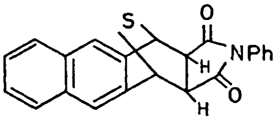
(1)



(2)



(3)



(4)

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-dihydronaphtho[2,3-*c*]thiophen 2-oxide (**1**) in the presence of either alumina or acetic anhydride,[4,5] 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,[1,6] 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[6] 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**),[7] 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 λ_{max} (heptane) 225, 250, 350 sh, 434, 454, and 462 nm; ^1H n.m.r., δ ($CDCl_3$, −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**),[4,5] 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.[4]

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**).[4,8] The resistance of (**2**) to isolation is not surprising in light of its extended *o*-quinonoidal structure.[4]

We thank Dr. Elsamma Chacko for the n.m.r. spectrum of (**2**), and Professor G. Vogel for the mass spectrum of (**1**).

(*Received, 24th March* 1980; *Com.* 312.)

---

† 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.

[1] J. Bornstein, S. E. Hunt, J. D. Mineck, and D. E. Remy, *J. Org. Chem.*, 1979, **44**, 805, and references therein.
[2] E. Chacko, J. Bornstein, and D. J. Sardella, *J. Am. Chem. Soc.*, 1977, **99**, 8248.
[3] E. Chacko, D. J. Sardella, and J. Bornstein, *Tetrahedron Lett.*, 1976, 2507.
[4] M. P. Cava, N. M. Pollack, O. A. Mamer, and M. J. Mitchell, *J. Org. Chem.*, 1971, **36**, 3932.
[5] D. W. H. MacDowell, A. T. Jeffries, and M. B. Meyers, *J. Org. Chem.*, 1971, **36**, 1416.
[6] D. E. Remy, F. H. Bissett, and J. Bornstein, *J. Org. Chem.*, 1978, **43**, 4469.
[7] R. Mayer, H. Kleinert, S. Richter, and K. Gewald, *J. Prakt. Chem.*, 1963, **20**, 244.
[8] J. E. Shields and J. Bornstein, *J. Org. Chem.*, 1975, **40**, 477.