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SYNTHESIS OF THE BENZOTHIOPHEN ANALOGUE OF BIPHENYLENE BY FVP

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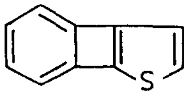
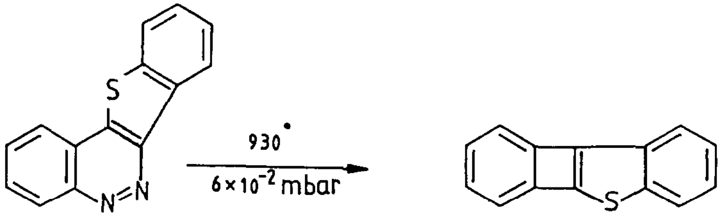
Extrusion of dinitrogen from the cinnoline (2) by flash vacuum pyrolysis (FVP) gave the benzothiophen analogue of biphenylene (3), which is more stable than the corresponding thiophen derivative.

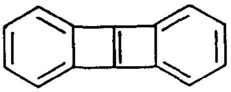
The thiophene analogue (1) of biphenylene isolated by Barton and Lapham[1] as an unstable oil is of particular interest because interaction of the aromatic π-electron systems across the four-membered ring, which reduces the π-electron density in the ring-junction bonds and increases it at the alternative positions of biphenylenes[2], is expected to cause exceptional perturbation of the thiophene π-electron system which normally has a high π-bond order at this face. We set out to prepare the benzo-derivative in the hope of obtaining a more stable example for further study, and to investigate the possibility that the heterocyclic system (2) might provide a route to the hitherto unknown dibenzobutalene (DBB) (4); our studies of the latter will be described in a subsequent paper.



(1)



(2) (3)



(4)

Following the general route[3] to heterocyclic biphenylenes, also used[1] for compound (1), flash vacuum pyrolysis (FVP) of the known[4] cinnoline (2) (which showed remarkable thermal stability) at 930 ° C, $6x10^{-2}$ mbar gave the required benzothiophen (3)[+]in 23% yield after t.l.c. as a light yellow powder (from methanol, 5% water) m.p. 104-108°C without apparent decomposition. The i.r. spectrum (KBr) of (3) is similar to that of benzothiophen with an additional strong multiplet at $1440cm^{-1}$ (similar to that of biphenylene) and very strong bands at 765 and $740cm^{-1}$ corresponding with the o.o.p. bend of two dissimilar sets of four adjacent H-atoms. The u.v. spectrum (MeOH; λ_{max} 221 nm (log 4.50), 246 (4.47), 264 (4.33), 269 (4.32), 274 (4.54), 294 (3.70), 307 (3.77), 332 (3.71), 347(3.69), 373(2.79) is strikingly similar to that of benzo[b]biphenylene[5] but shifted about 20 nm to shorter wavelength.

The proton n.m.r. spectrum of (3) ($CDCl_3$, 60MHz) shows unsymmetric multiplets of equal intensity δ 7.5-8.0 and 7.0-7.5 which we assign to the benzothiophen and o-phenylene protons respectively. Like the parent-compound (1)[1], the upfield shift characteristic of biphenylene protons is absent.

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[+] Correct micro-analyses and spectra were obtained for new compounds.

REFERENCES

1. J.W. Barton and D.J. Lapham, Tetrahedron letters, 1979, 3571.
2. For x-ray measurements of bond lengths see: S.H. Banes, C.F. Wilcox and A. Yakozeki, J. Amer. Chem. Soc., 1974, 96, 1026; S. Kanoktanaporn, T.J.King and J.A.H. MacBride, J. Chem. Research, (S), 1980, 204-205; (M) 1980, 2911-2940. For a chemical consequence of bond alternation see R. Hull, J.A.H. MacBride, M. Wardleworth and P.M. Wright, J. Chem. Soc. Chem. Commun., 1983, 74.
3. For further examples of this route to nitrogen heterocyclic biphenylenes see J.A.H. MacBride and P.M. Wright, Tetrahedron Letters, 1981, 4545, and references therein.
4. K.E. Chippendale, B. Iddon and H. Suschitzky, J. Chem. Soc. Perkin 1, 1972, 2023.
5. W. Baker, J.W. Barton, J.F.W. McOmie and R.J.G. Searle, J. Chem. Soc. 1962, 2633.

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