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BASE-INDUCED ELECTROCYCLIC OPENING OF DIHYDROBENZOTHIOPHENES

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The base-induced electrocyclic opening of dihydrothiophene is known[1] to give thiapentadienylanion (buta-1,3-diene-1-thiolate). Two dihydrobenzothiophenes have now been found to behave in an analogous way.

2,3-Dihydrobenzo[b]thiophene (1), upon reaction with KNH_2 (as described previously[1]) yields, via 2 by loss of a proton from C(3) and electrocyclic ring opening between S and C(2), the *o*-vinylthiophenolate anion 3. Structure 3 follows from the coupling pattern (J_{12} = 11.0, J_{13} = 18.0 and J_{23} = 2.1 c/s) and the formation in high yield of *o*-vinylthioanisole upon addition of methyl iodide. The δ-values of 3 (as well as the vicinal J values for the ring protons of 3: 7-7.5 c/s) show that 3 is the best valence-bond representation. The given configuration 3-implying rotation about the C(aryl)-C(1) bond after opening of 2-is based upon comparison of the δ-values of 3 and styrene[2].

1,3-Dihydrobenzo[c]thiophene (4) likewise gives an anion (seven protons). Although benzylmethyl sulfide is completely converted[3] to the corresponding anion 7, the species observed here cannot be 5 for various reasons. The four "benzo" protons are recognized from their coupling pattern (J = 6-9 c/s). The low-field position of the one-proton singlet at δ = 8.34 cannot, by comparison with 7, be ascribed to 5, but is consistent with a "thioaldehydic" proton[1]. Moreover, the remaining two protons, most likely (magnetically) equivalent in 5, appear at δ = 4.87 and 7.60 with J = 3.5 c/s, a typical methylenic coupling. These data are consistent with a thiophene-ring-opened structure 6. Of the two possible configurations the one drawn is slightly preferred[4].

As to the best valence-bond representation of 6, the data for the ring protons are decisive. Two protons appear, accidentally, as one doublet at δ = 6.36 with J = 8.5-9.0 c/s. Each of the other two protons gives a four-line signal at δ = 5.56 and 5.91 with respective splittings of 8.6 (J_{12}) and 8.9 c/s (J_{34}) and a mutual one of 6.0 c/s (J_{23}). The alternating J values show that the anion should be regarded rather as dimethylenecyclohexa-1,3-dien-7-thiolate anion 6 than as *o*-thiocarboxybenzyl anion (for which one[5] would expect $J_{12} > J_{23} \simeq J_{34}$). It is interesting to note that the electrocyclic isomeric bicyclo[4.2.0]octa-1,3,5-trien-7-thiolate structure can obviously be excluded.

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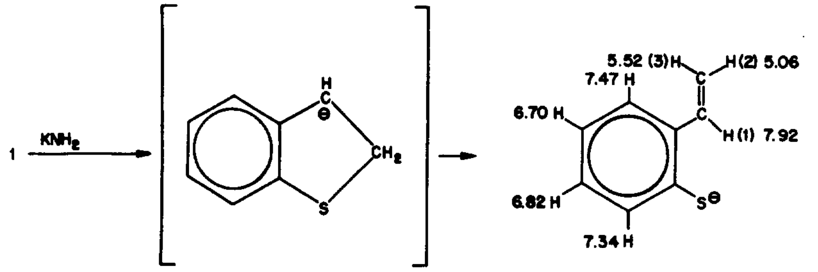
Reaction with methyl iodide yields only polymeric material, the possible initial products being a thiobenzaldehyde, a dimethylenecyclohexadiene or other polyenic compounds.

Anions **3** and **6** are related to the *o*-vinylbenzyl anion by replacing benzylic and vinylic methylene by sulphur.



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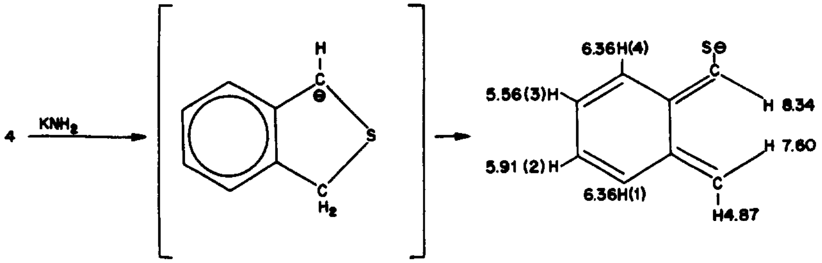

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