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5H-1,4-DITHIEPIN AND ITS ANION. A LACK OF AROMATICITY IN THE 1,4-DITHIEPINIDE ION

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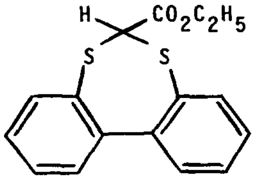
Since sulfur is isoelectronic with carbon-carbon double bond and can participate in π-electron delocalization, the anions derived from 1,2-, 1,3- and 1,4-dithiepins may be regarded as potential 10 π-electron monocyclic aromatic systems.$^{1)}$ From a detailed examination of the deuterium exchange behavior of ethyl dibenzo[*b*,*d*][1,3]dithiepin-6-carboxylate (*1*), Breslow and Mohacsi$^{2)}$ concluded that no aromaticity associated with the cyclic 10 π-electron system could be observed.



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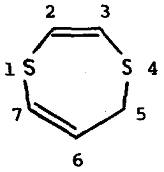

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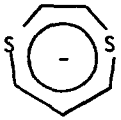
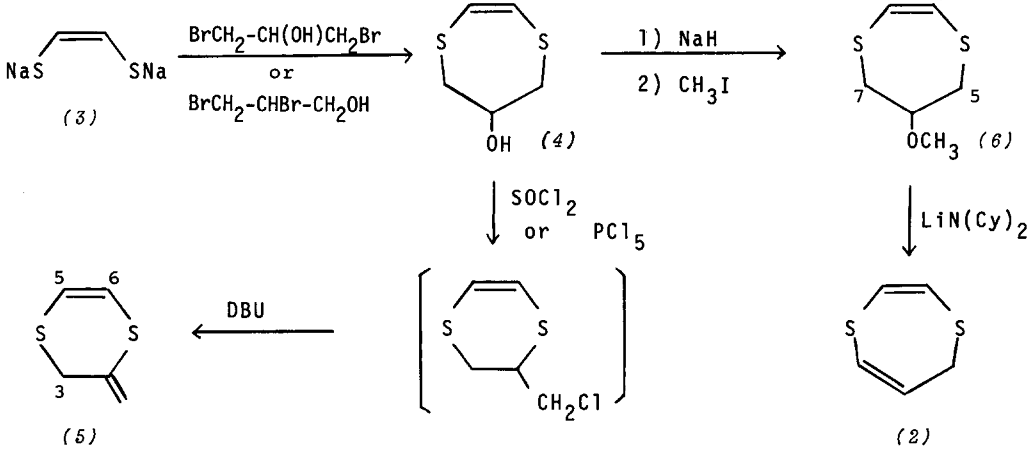


(2a)

According to predictions based upon Hückel molecular orbital calculations by Zahradnik and Parkanyi,$^{3)}$ the 1,4-dithiepinide ion (*2a*), a formal conjugate base of the parent 5*H*-1,4-dithiepin (*2*), should be unstable and difficult to prepare. In order to gain insight into the validity of this theoretical prediction we have synthesized *2* and have examined its behavior towards lithiation.

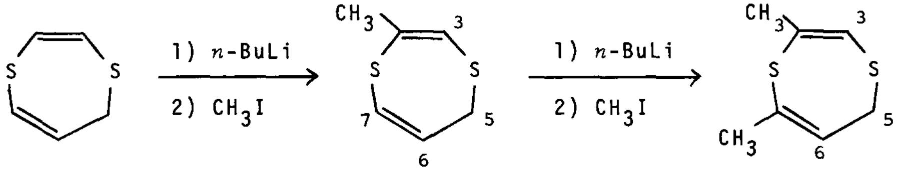
The preparation of 5*H*-1,4-dithiepin (*2*) was achieved *via* the route depicted in Scheme-1. Reaction of disodium *cis*-dimercaptoethylene (*3*)[4] with either 1,2-dibromo-3-propanol or 1,3-dibromo-2-propanol in ethanol at 20°C under nitrogen for 6 hr yielded 6,7-dihydro-5*H*-1,4-dithiepin-6-ol (*4*) in 40% yield. Treatment of *4* with thionyl chloride or phosphorous pentachloride yielded a chloride which was subjected to dehydrochlorination with 1,8-diazabicyclo[5.4.0]undecene-7 in dioxane. A smooth reaction took place leading to a diene (*5*), the nmr spectrum of which however, *viz*. δ 6.28 and 6.12 (1H each, AB-quartet, H-5,6, $J_{5,6}$=9.5 Hz), δ 5.27 and 5.03 (1H each, s and bs, $>C=CH_2$) and 3.47 (2H, s, H-3,3'), was suggestive 2-methylene-2,3-dihydro-1,4-dithiin (*5*).[5]

[Scheme-1]



The desired 5*H*-1,4-dithiepin was obtained as follows. The alcohol (*4*) was reacted with sodium hydride in tetrahydrofuran followed by methylation with methyl iodide at 0°C to yield 6-methoxy-6,7-dihydro-5*H*-1,4-dithiepin (*6*) in 83% yield as a colorless liquid; ms, m/e 162 (M^+, 74%), 103 (100%); nmr (60 MHz, CCl_4) δ 5.88 (2H, s, H-2,3), 3.6-3.9 (1H, m, H-6), 3.3-3.5 (4H, m, H-5,5' and 7,7') and 3.32 (3H, s, OCH_3). While other method failed to produce *2*, treatment of an ethereal solution of *6* with two equivalents of lithium dicyclohexylamide[6] in ether at -70∼-55°C for 6 hr resulted in the effective elimination to give 5*H*-1,4-dithiepin (*2*); a colorless liquid, obtained in 60% yield after chromatography on silica gel [elution with pet. ether]. The structure of *2* was assigned on the basis of its elemental analysis [Anal. Calcd. for $C_5H_6S_2$: C, 46.11; H, 4.64; S, 49.25 %. Found: C, 46.04; H, 4.81; S, 48.74 %] and nmr spectrum (100 MHz, $CDCl_3$) which showed two aliphatic hydrogens as a doublet at δ 3.72 ($J_{5,6}$=7.0 Hz), vinyl hydrogen (H-2) as a double doublet at δ 5.92 ($J_{2,3}$=10.0, $J_{2,7}$=2.0 Hz), vinyl hydrogen (H-3) as a doublet at δ 6.38 ($J_{3,2}$=10.0 Hz), vinyl hydrogen on the allyl moiety adjacent to the sulfur (H-7) as a double doublet at δ 6.08 ($J_{7,6}$=9.5, $J_{7,2}$=2.0 Hz) and the remaining vinyl hydrogen (H-6) as a double triplet at δ6.48 ($J_{6,7}$=9.5, $J_{6,5}$=7.0 Hz). These assignments were confirmed by double resonance experiments. Compound (*2*) is reasonably stable under nitrogen upon refrigeration but it decomposes gradually in contact with air at room temperature.

Quite unexpectedly, lithiation of *2* with *n*-butyllithium in tetrahydrofuran at -70°C during 2 hr followed by quenching with methyl iodide gives a vinyl methylated product (*7*) in 70% yield. The site of the introduced methyl group was easily deduced from a comparison of its nmr spectrum (100 MHz, $CDCl_3$), δ 1.97 (3H, d, CH_3, $J_{CH_3,3}$=1.4 Hz), 3.58 (2H, d, H-5,5', $J_{5,6}$=7.0 Hz), 5.96 (1H, d, H-7, $J_{7,6}$=10.0 Hz), 6.24 (1H, q, H-3, J_{3,CH_3}=1.4 Hz), and 6.36 (1H, dt, H-6, $J_{6,7}$= 10.0, $J_{6,5}$=7.0 Hz), with that of *2*.

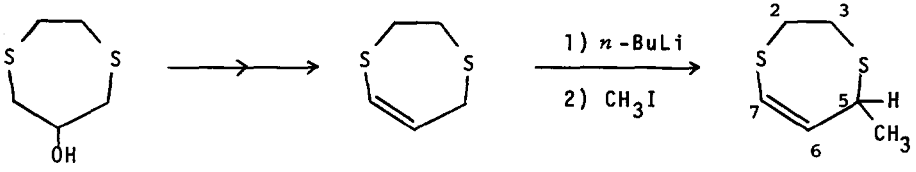


(*2*) (*7*) (*8*)

When *7* was allowed to react successively with *n*-butyllithium and methyl iodide, a second methylation smoothly took place, as evinced by decoloration of the anion to give a solution of dimethyl derivative, isolated in ca. 50% yield as a colorless liquid. The nmr spectrum with a vinyl proton of H-3 at δ 6.05 (bs), a vinyl proton of H-6 at δ 6.28 (tq, $J_{6,5}$=7.5, J_{6,CH_3}=1.5 Hz), methylene protons of H-5,5' at δ3.75 (bd, $J_{5,6}$=7.5 Hz), together with 2-methyl and 7-methyl protons at 1.93 (d, J=1.0 Hz) and at 1.99 (dt, J=1.5 and 0.8 Hz), respectively, suggested again that vinyl methylation had occurred.

Finally, we chose 2,3-dihydro-5*H*-1,4-dithiepin (*9*) as a model compound to elucidate the site of lithiation since the lack of a double bond between C-2 and

C-3 in *9* would prohibit cyclic delocalization of the anionic charge. Compound *9* was obtained as a colorless liquid, nmr (100 MHz, $CDCl_3$), AA'BB'-system of H-2,2',3,3' centered at δ 3.04, δ 6.3-6.6 (2H, m, H-6,7) and δ 3.3-3.6 (2H, m, H-5,5'), from 1,4-dithiepan-6-ol (10)[5a)] by the same procedure used for the synthesis of *2*. In striking contrast to the behavior of *2*, when *9* was allowed to react successively with *n*-butyllithium and methyl iodide a methylated product (*11*) was obtained. Allylic methylation in *11* may be adduced from its nmr spectrum since the methyl doublet at δ 1.37 with J=7.0 Hz, a methine proton (H-5) at δ 4.08 (J=7.0 and 5.0 Hz), vinyl protons (H-6,7) multiplet at δ 6.32-6.08 ($J_{6,7}$=10.0 Hz), clearly attests to the presence of an allylic methyl group.



(*10*) (*9*) (*11*)

These results provide conclusive evidence for the instability of *2a* and for the lack of aromaticity associated 10 π-electron delocalization through sulfur atoms in the 1,4-dithiepinide ion.

REFERENCES AND FOOTNOTES

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