

SYNTHESIS OF 4,5-BENZO-3-THIATRICYCLO[4.1.0.0^{2,7}]HEPTENE.

A VALENCE ISOMER OF BENZO[b]THIEPIN

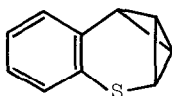
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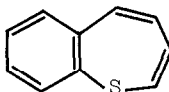
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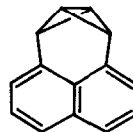
As part of our study on the "valene" type valence isomer of the odd membered cyclic conjugated molecule¹⁾ we report here the synthesis and the characterization of 4,5-benzo-3-thiatricyclo[4.1.0.0^{2,7}]heptene (1) which is regarded as a valence isomer of the unknown heterocyclic 12- π electron system, benzo[b]thiepin (2).²⁾



1



2



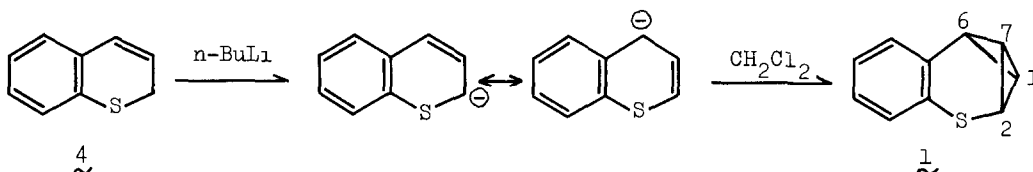
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The most obvious method for the preparation of 1 would be an application of the elegant Katz method for benzvalene and benzobenzvalene synthesis,³⁾ the well established success of preparation of naphtho[1,8]tricyclo[4.1.0.0^{2,7}]heptene (3)⁴⁾ by this method makes this a likely route.

Thus, to a magnetically stirred solution of 1.48 g (10 mmole) of 2H-1-benzothioopyran (4)⁵⁾ and 100 ml of dry ether there was added 10 mmole of a solution of n-butyllithium in n-hexane at -20°. The addition of a solution of 0.66 ml (10 mmole) of methylene chloride in 10 ml of ether to the resulting anion took place over a period of 30 min at about -110~-120°. Stirring under nitrogen was continued for 3 hr, during which time temperature raised to -40°. The reaction mixture was quenched by water and the product was taken up in ether, washed with water and dried over anhydrous sodium sulfate. Removal of the solvent in vacuo and chromatographed on a column of deactivated (with 5% of water) alumina afforded 0.12 g (7.5%) of 1. Recrystallization from n-hexane gave analytically pure 1, colorless prisms, mp 65.5-67.5°C. Anal. Found: C, 74.84; H, 5.23; S, 19.43:

calcd. for $C_{10}H_8S$: C, 74.96; H, 5.03; S, 20.01%.

The structure assigned to 1 follows directly from the spectroscopic data. The uv spectrum shows maxima (in cyclohexane) at 222 nm ($\log \epsilon$ 4.12), 228 (4.08) and 272 (3.89) with shoulders at 290 (3.35) and 300 (2.96). The mass spectrum, m/e 160 (M^+ , 100%), 134 ($M-C_2H_2$, 33%), 128 ($M-S$, 73%), 115 (indenyl cation, 60%), establishes the molecular formula as $C_{10}H_8S$. The pmr spectrum (CCl_4 , 60 MHz), which exhibits four well separated signals at δ 1.90 (t, 2H, H-1 and H-7, $J_{1,2} = J_{1,6} = 2.8$ Hz), 3.04 (dt, 1H, H-6, $J_{6,2} = 4.0$ Hz,⁶) $J_{6,1} = J_{6,7} = 2.8$ Hz), 3.58 (dt, 1H, H-2, $J_{2,6} = 4.0$ Hz,⁶) $J_{2,1} = J_{2,7} = 2.8$ Hz), 6.80 (m, 4H, aryl), is in complete accord with the bicyclobutane formulation.⁷⁾



The bicyclobutane 1 is a stable compound at ambient temperature and no visible change in the nmr spectrum could be observed after standing for a week. Synthesis of 1 provides a first instance of the "valene" type isomer of the heterocyclic conjugated molecule. Detailed study on the chemistry of 1 is currently in progress and the results will be reported elsewhere.

- 1) I. Murata, K. Nakasuji and H. Kume, *Tetrahedron Lett.*, in the press (1973).
- 2) W.E. Parham and D.G. Weetman, *J. Org. Chem.*, 34, 56 (1969) and refs. therein.
- 3) T.J. Katz, E.J. Wang and N. Acton, *J. Amer. Chem. Soc.*, 93, 3782 (1971). see also T.J. Katz and J.J. Cheung, *ibid.*, 91, 7772 (1969); T.J. Katz, J.J. Cheung and N. Acton, *ibid.*, 92, 6643 (1970); K. Hojo, R.T. Seidner and S. Masamune, *ibid.*, 92, 6641 (1970).
- 4) I. Murata and K. Nakasuji, *Tetrahedron Lett.*, 47 (1973); R.M. Pagni and C.R. Watson, *ibid.*, 59 (1973).
- 5) A. Lüttringhaus and M. Engelhard, *Chem. Ber.*, 93, 1525 (1960); W.E. Parham and R. Koncos, *J. Amer. Chem. Soc.*, 83, 4034 (1961).
- 6) Quite substantial long-range interaction, 4.4~10 Hz, between protons attached exo to the bicyclobutane was well recognized: L.M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry" 2nd Ed., Pergamon Press, Oxford, 1969, p. 335.
- 7) A bicyclobutane ring system 1 was quoted as a possible reaction intermediate in the footnote 12 of reference 1).