

THE 2-THIAPENTALENYL ANION

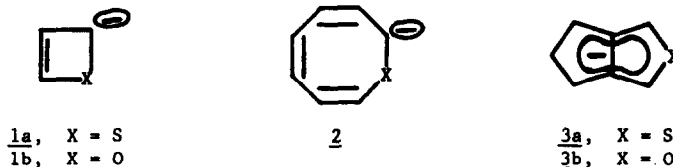
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(Received in U.S.A. 12 July 1967)

Anionic nonbenzenoid aromatic species are of considerable interest with respect to their stability and chemistry.<sup>1</sup> Little is known, however, concerning sulfur- or oxygen-containing cyclic anions with  $(4n + 2)$   $\pi$  electrons, such as 1 and 2.<sup>2</sup>

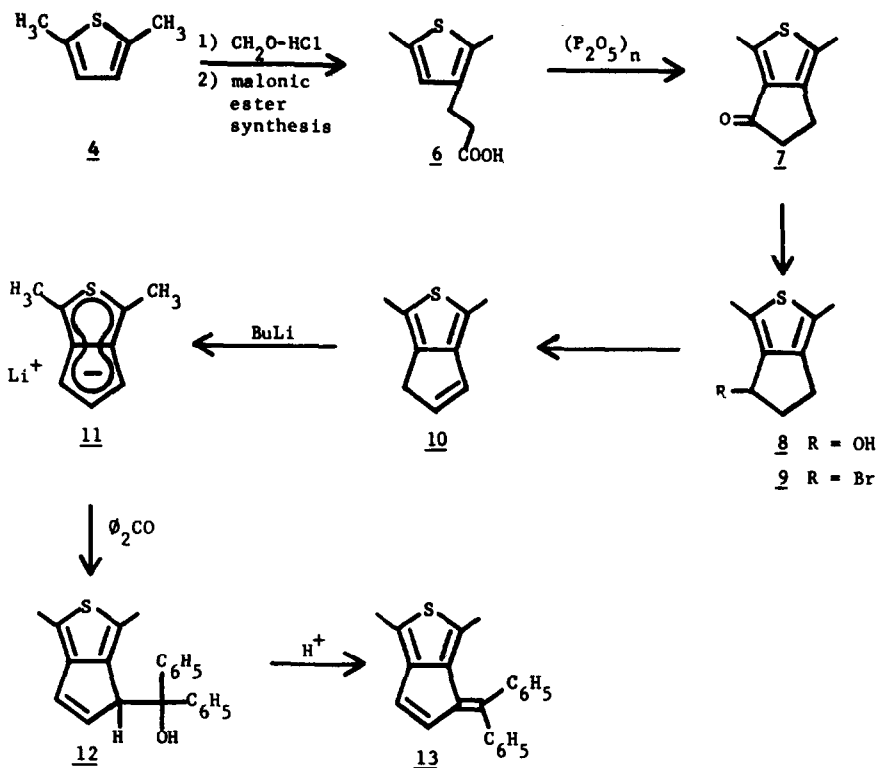


We report here the synthesis and properties of a derivative of 3a, the bicyclic analog of 2a; namely, the 1,3-dimethyl-2-thiapentalenyl anion (11).

Olefin 10, the precursor of 11, was prepared by the route shown in Chart I. Chloromethylation of 2,5-dimethylthiophene (4) with formalin and concentrated HCl at  $-10^\circ$  gave 55% of 3-chloromethyl-2,5-dimethylthiophene (5); this represents a considerable improvement over the previously reported yield<sup>3</sup> of the monochloromethylation product. Compound 5 was converted via a standard malonic ester synthesis to 2,5-dimethylthiophene-3-propionic acid (6), m.p.  $60-61^\circ$  (lit.<sup>4</sup> m.p.  $60^\circ$ ) in 36% overall yield.

Brief warming of 6 with polyphosphoric acid effected cyclization to the ketone 7<sup>5</sup> (b.p.  $110-114^\circ / 0.2$  mm,  $\nu_{\max} 1695 \text{ cm}^{-1}$ ) in 80-90% yield. This ketone was quantitatively reduced to the alcohol 8<sup>5</sup> (m.p.  $71-72^\circ$ ;  $\nu_{\max} \sim 3320 \text{ cm}^{-1}$ ) by addition of sodium borohydride in methanol to a methanolic solution of 7. Replacement of the hydroxyl group of 8 with bromine was effected by phosphorous tribromide in ether at  $0^\circ$ . The bromide (9; n.m.r.: multiplet for

## CHART I



$\text{-CH-Br}$  at  $\tau$  4.92) was an unstable oil which rapidly decomposed in the pure state; consequently 9 was usually not distilled but was directly dehydrohalogenated to 10. Addition of an ethereal solution of crude 9 to potassium *t*-butoxide in *t*-butanol at room temperature gave the olefin 10<sup>5</sup> (b.p.  $65^\circ / 0.2 \text{ mm}$ ; 65% from 8). Compound 10 showed  $\nu_{\text{max}}$   $1660 \text{ cm}^{-1}$  and n.m.r. signals at  $\tau$  2.66 (multiplet, 2H, vinyl hydrogens), 7.17 (doublet,  $J \sim 1 \text{ cps}$ , 2H, methylene H's), and 7.84 and 7.78 (singlets, 3H each, methyls). The ultraviolet spectrum showed a maximum at

241  $m\mu$  ( $\epsilon = 8200$ ).

Treatment of 10 in tetrahydrofuran with excess butyllithium in hexane at  $-20^\circ$  gave the lithium salt of 11 as a cream-colored precipitate which dissolved on warming the solution to room temperature. Solutions of 11 in THF displayed n.m.r. signals at  $\tau$  3.52 (1H, triplet,  $J \sim 3$  cps, H on C-5), 5.25 (2H, doublet,  $J \sim 3$ , H's on C-4 and C-6), and 7.80 (6H, singlet, methyls). The ultraviolet spectrum of 11 displayed a shoulder at  $\sim 315$ -320  $m\mu$  ( $\epsilon \sim 2000$ ) and  $\lambda_{\max} 256 m\mu$  ( $\epsilon \sim 30,000$ ). Addition of water to solutions of 11 regenerated the olefin 10; use of  $D_2O$  gave a monodeuterated olefin, whose methylene and vinyl hydrogen n.m.r. signal intensities indicated that the compound contained ca. 0.95 atom of deuterium.

The simplicity of the n.m.r. spectrum of 11 indicates that it is indeed the symmetrical anion shown, rather than a covalent lithium compound. The high field position of the hydrogens on C-4 and C-6 shows that a high charge density exists at these positions and that structure 11a



makes the chief contribution to the total resonance structure. The charge density at C-1 and C-3 is uncertain; the methyl hydrogen signals in the n.m.r. spectrum of 11 appear at essentially the same field as the methyls of the olefin 10. However, the absence of an appreciable upfield shift for the methyls in the anion does necessarily rule out an appreciable contribution of structure 11b. An upfield shift of the methyls due to increased electron density at C-1 and C-3 could be counterbalanced by a downfield shift caused by a large ring current. A case in point is cyclooctatetraene dianion, whose protons exhibit the same chemical shift as those of the parent olefin.<sup>6</sup> The charge densities in 11 calculated by the HMO method will be reported in the full paper.

Treatment of solutions of 11 with benzophenone in tetrahydrofuran gave ca. 30% of the carbinol 12<sup>5</sup> (m.p. 157-158°;  $\lambda_{\max}^{CCl_4} 3592$  and  $1597 \text{ cm}^{-1}$ ; n.m.r. signals at  $\tau$  2.4 and 2.7 [10H, multiplets, phenyls], 3.44 and 3.90 [AB portion of ABX,  $J_{AB} = 6$ ,  $J_{AX} = J_{BX} \sim 2$ , vinyl hydrogens], 5.38 [OH], 7.70 and 8.72 [3H each, singlets, methyls]). Toluenesulfonic acid-catalyzed dehydration of 12 gave the fulvene 13<sup>5</sup> as yellow needles, m.p. 100-101° (71%;  $\lambda_{\max}^{EtOH} 370$  and  $244 m\mu$ ;  $\epsilon = 9600$  and  $26,000$ ).

Further studies of the properties of 11 and of its oxygen analog 3b are in progress and will be described in a forthcoming publication.

## REFERENCES

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