

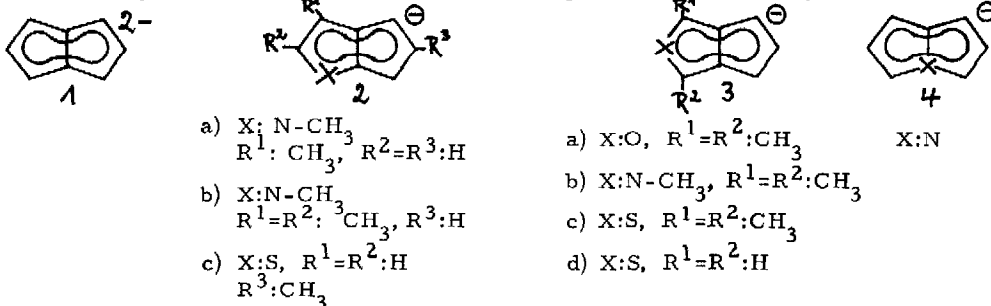
THE 5-METHYL-1-THIAPENTALENYL ANION <sup>1)</sup>

Heinrich Volz <sup>+</sup> and Heinrich Kowarsch

Institut für Organische Chemie der Universität Karlsruhe, D-75 Karlsruhe

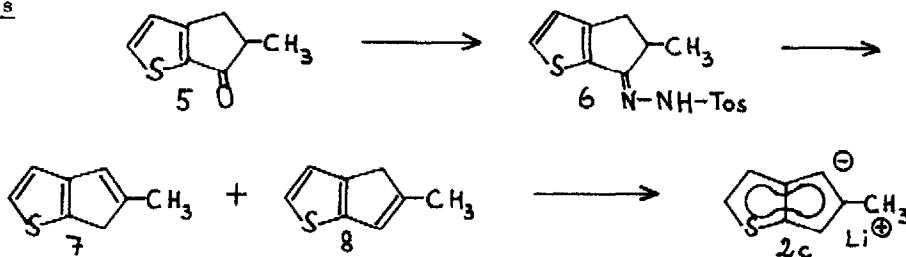
(Received in UK 27 September 1976; accepted for publication 11 October 1976)

Anionic nonbenzenoid aromatic heterocycles with  $10\pi$ -electrons are of considerable interest. They are isoelectronic with the cyclooctatetraene dianion and the pentalene dianion <sup>2)</sup>. The synthesis of 2a, 2b, 3a, 3b, 3c, 3d and 4 was accomplished in the last years <sup>3)</sup>.



In this communication we want to report on the first synthesis of 2c.

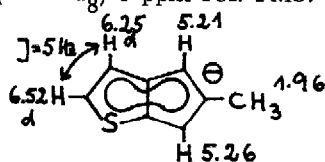
Synthesis



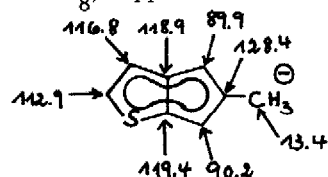
Ketone 5 <sup>4)</sup> reacts with tosylhydrazine in ethanolic HCl to give tosylhydrazone 6 in 93% yield. The ethereal suspension of 6 was treated with 2.5 equivalents of butyllithium (in hexane) and the mixture refluxed for 1 hr. Hydrolysis and workup gave the two olefins 7 and 8 (41%). The olefins are sensitive to air and acids. Addition of 1.17 equivalent of butyllithium (in hexane) to a solution of 7 and 8 in THF at  $-20^{\circ}$ , stirring for 10 min. at this temperature, followed by warming to  $0^{\circ}$  gave the 5-methyl-1-thiapentalenyl anion 2c. At  $-78^{\circ}$  the anion 2c crystallizes in pale yellow crystals. 2c is stable for weeks at  $-78^{\circ}$ C.

### NMR-spectra of 2c

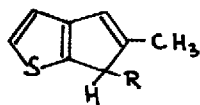
$^1\text{H-NMR}$  (THF- $d_8$ )  $\delta$  ppm rel. TMS:



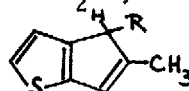
$^{13}\text{C-NMR}$  (THF- $d_8$ )  $\delta$  ppm rel. TMS:



Reaction of 2c with methyl iodide gave the two olefins 9a and 10a (57% ; mass spectrum:  $\text{M}^+$ -peak at  $m/e = 150$  has  $I_{\text{rel}} 72\%$ ). Hydrolysis of 2c with  $\text{D}_2\text{O}$  yielded the olefins 9b and 10b.



9a: R=CH<sub>3</sub>; 9b: R=D



10a: R=CH<sub>3</sub>; 10b: R=D

**Discussion:** Due to the ring current in 2c the nmr-signals for H<sub>4</sub> and H<sub>6</sub> (5.21 resp. 5.26 ppm) appear at relatively low field. The nmr-spectrum of the isoelectronic pentalene dianion shows the signals for the protons H<sub>1</sub>, H<sub>3</sub>, H<sub>4</sub> and H<sub>6</sub> at  $\delta$  4.98. The signals of the thiophene protons of 2c are shifted upfield 0.6-0.7 ppm relative to the thiophene protons of the olefin 8. This indicates that negative charge is delocalized to some extent into the thiophene ring in 2c. This charge delocalization is also documented by the  $^{13}\text{C}$ -nmr-spectrum. The signals for C<sub>2</sub> and C<sub>3</sub> of the anion 2c are shifted upfield 10-12 ppm relative to thiophene (C<sub>a</sub> 125.4; C<sub>B</sub> 127.2 ppm)<sup>5</sup>. The  $^{13}\text{C}$ -nmr-spectrum shows furthermore that the greatest charge density resides at carbon atoms 4 and 6. The  $^{13}\text{C}$ -chemical shifts of C<sub>4</sub> and C<sub>6</sub> in 2c are of the same order as of C<sub>1</sub> and C<sub>3</sub> in the indenyl anion (91.8 ppm).

The authors are grateful to Fonds der Chemischen Industrie for support of this work.

- 1) Heteropentalenes, part 4; part 3 see 3c).
- 2) T. J. Katz, M. Rosenberger and R. K. O' Hara, *J. Amer. Chem. Soc.* **86**, 249 (1964)
- 3) a) H. Volz and B. Meßner, *Tetrahedron Lett.* 4111 (1969)  
 b) H. Volz, U. Zirngibl and B. Meßner, *Tetrahedron Lett.* 3593 (1970)  
 c) H. Volz and R. Draese, *Tetrahedron Lett.* 4917 (1970)  
 d) W. H. Okamura and Th. J. Katz, *Tetrahedron* **23**, 2941 (1967)  
 e) T. S. Cantrell and B. L. Harrison, *Tetrahedron Lett.* 4477 (1967)  
 f) T. S. Cantrell and B. L. Harrison, *Tetrahedron Lett.* 1299 (1969)  
 g) J. Skramstad, *Chimica Scripta* **4**, 81 (1973)
- 4) O. Meth-Cohn and S. Gronowitz, *Acta Chem. Scand.* **20**, 1577 (1966)
- 5) G. C. Levy and G. L. Nelson, *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*, p. 97. Wiley-Interscience, New York 1972
- 6) J. B. Stothers, *Carbon-13 NMR Spectroscopy*. p. 269, Academic Press, New York 1972