

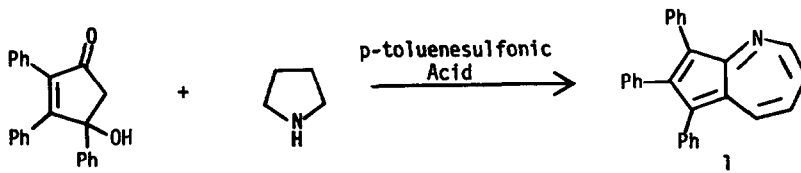
SYNTHESIS OF 1,2,3-TRIPHENYL-4-AZAAZULENE

Mary K. Conner<sup>1</sup> and E. LeGoff<sup>2</sup>

Department of Chemistry, Michigan State University  
East Lansing, Michigan 48823

(Received in USA 21 May 1970; received in UK for publication 8 June 1970)

We wish to report a novel synthesis of the first example of a 4-azaazulene, 1,2,3-triphenyl-4-azaazulene, 1<sup>3</sup>. This compound is formed from the reaction of 4-hydroxy-2,3,4-triphenyl-2-cyclopenten-1-one with pyrrolidine in refluxing toluene containing a catalytic amount of p-toluenesulfonic acid. Azaazulene 1 is a dark green crystalline compound. Its



absorption maxima in the visible region at 610, 654 and 710 nm are similar to those of 1,2,3-triphenylazulene which occur at 606, 656 and 726 nm<sup>4</sup>. In the mass spectrum a parent molecular ion at m/e 357.1507 and an abundance of doubly ionized fragments are consistent with the fused-ring structure of 1. The nmr spectrum of 1 consists of three multiplets at  $\delta$  8.33-8.08 (1H), 8.07-7.82 (1H) and 7.32-6.82 (17H). Computer analysis<sup>5</sup> of the two low field multiplets indicated that they are the H<sub>A</sub> and H<sub>D</sub> part of an ABCD spin system the other two members of which are obscured by the phenyl protons. The calculate chemical shifts and coupling constants of the proton in the seven-membered ring are shown below.

$\nu$	H <sub>1</sub> = 495.8	H <sub>3</sub> = 420.3	
(cps)	H <sub>2</sub> = 425.9	H <sub>4</sub> = 478.4	
J	1,2 = 6.52	2,3 = 9.46	
(cps)	1,3 = 1.11	2,4 = 1.30	
	1,4 = 0.267	3,4 = 8.96	

$\nu$  in cps from Me<sub>4</sub>Si ( $\nu_0$  = 60 MHz)

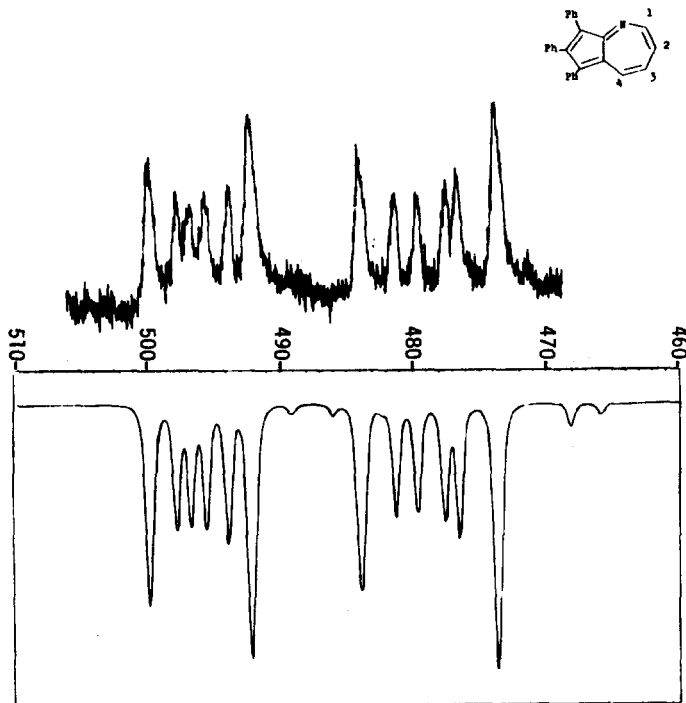


Figure 1. Comparison of Calculated (Bottom) and Observed (Top) Spectrum of  $H_1$  and  $H_4$  of 4-Azazulene **1** at 60 MHz.

In conjunction with the other spectral data the presence of four adjacent interacting hydrogens in the nmr spectrum establishes the structure of this novel 4-azazulene.

Azazulene **1** may have arisen from the pyrrolidine enamine of the starting hydroxy-ketone via the following sequence: (a) acid catalyzed elimination of water from the enamine, (b) Vilsmeier type addition of the pyrrolidine ring to the cyclopentadiene ring, and (c) acid catalyzed ring expansion, followed by (d) air oxidation during chromatography. The final step is supported by isolation of a yellow compound which analyzed for the corresponding tetrahydroazazulene,  $C_{27}H_{23}N$ . The nmr spectrum indicated a mixture of tetrahydro isomers. The ratio of phenyl to aliphatic hydrogens was 15:8. The ease of oxidation reflects the stability of the heteroaromatic azazulene which is formed.

1 dissolves in trifluoroacetic acid forming a yellow solution from which 1 may be recovered. As yet we have been unable to find conditions which would affect the alkylation of 1 (using triethyloxonium fluoroborate) or its conversion to an N-oxide. Presumably, both steric and electronic effects are interfering with these reactions.

1,2,3-Triphenyl-4-azazulene (1): A mixture of 1.7 g (0.0052 mole) of 4-hydroxy-2,3,4-triphenylcyclopent-2-en-1-one, 0.7 g (0.01 mole) of pyrrolidine and 0.1 g of toluene-sulfonic acid in 10 ml of toluene was refluxed overnight with continuous removal of water. The solvent was removed under reduced pressure to give a tarry black residue which was chromatographed on Alcoa F-20 alumina with benzene. Initially a yellow band began to separate but before it could be eluted it had turned green. Upon removal of the solvent from this green fraction a dark green solid remained which was crystallized from heptane giving 80 mg of 1: mp 224-226°; uv max (CH<sub>3</sub>CN) 285 (log ε 4.51), 325 (log ε 4.48), 380 (log ε 3.64), 610 (log ε 2.35), 654 (log ε 2.43), and 710 mμ (log ε 2.35); ir (ClC1<sub>3</sub>) 1535, 1570, 1590 (arom), and (hexachlorobutadiene) 3020 cm<sup>-1</sup> (arom C-H); nmr (CDCl<sub>3</sub>) δ 8.33-8.08 (m, 1H), 8.07-7.82 (m, 1H), and 7.32-6.82 (m, 17H); mass spectrum (70 eV) m/e 357.1507 (Parent). Anal. Calcd. for C<sub>27</sub>H<sub>19</sub>N: C, 90.80; H, 5.33; mol. wt. 357.1517. Found: C, 90.70; H, 5.50.

#### References

1. Taken from part of the Ph.D. thesis of M. K. Conner, 1969.
2. To whom inquiries should be addressed.
3. The compound 5-azaazulene has previously been prepared: K. Hafner and M. Kreuder, Angew. Chem., 73, 657 (1961).
4. S. J. Assony and N. Kharasch, J. Amer. Chem. Soc., 80, 5978 (1958).
5. Calculations were carried using the LAOCOON-III program of A. A. Bothner-By and S. M. Castellano.

Acknowledgement: We are grateful to the donors of the Petroleum Research Fund administered by the American Chemical Society and to the National Science Foundation for the financial support of this research. We also thank Professor A. A. Bothner-By (Carnegie-Mellon University) for providing us with a copy of LAOCOON-III.