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CYCL[4.2.2]AZINIUM SALTS

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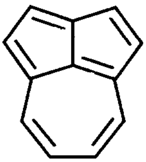
Cycl[4.2.2]azinium salts 3, 9 and 11 have been synthesized and shown to be diatropic.

Butadiene-bridged pentalenes 1 and ethylene-bridged heptalenes 2 have been prepared by Hafner et al. and shown to possess only small differences in their properties1).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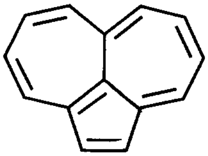
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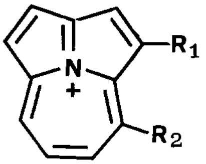
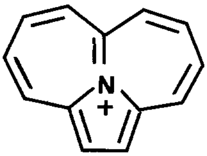


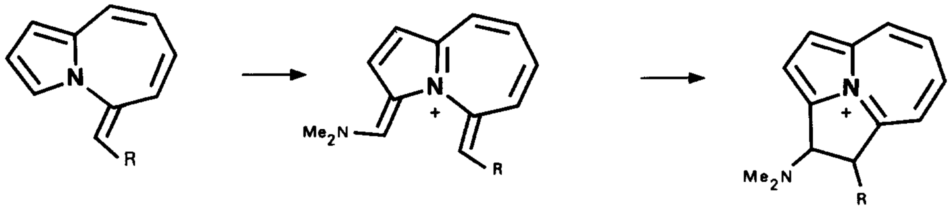
3a $R_1 = R_2 = H$
3b $R_1 = CN, R_2 = H$



4

Following PMO-theory2) a replacement of the central carbon atom by a nitrogen atom of the ammonium type should result in a drastic splitting of the properties of both π-systems yielding stabilized, diatropic cycl[4.2.2]azinium salts 3 and destabilized cycl[4.4.2]azinium salts 4 for which a diradikaloid character is likely3,4).

We have synthesized cycl[4.2.2]azinium salts 3 on two routes and found their properties to be in agreement with the abovementioned expectations5,6). A dihydro derivative of 3 has been obtained previously which could not be dehydrogenated to a cycl[4.2.2]azinium salt7).



5a R = CN
5b R = $CO_2tC_4H_9$

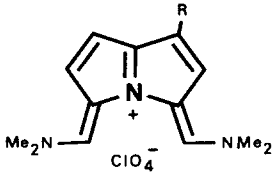
6

7

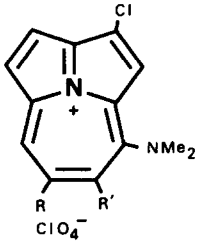
3b8,9a) is formed in 10 % yield from 5a10) under Vilsmeier conditions in ethylendichloride at -10°C. It cristallizes after treatment with methanolic $NaClO_4$.

We propose an attack of the Vilsmeier salt to the α-position of the pyrrole ring of 5a11), an allowed electrocyclic reaction of the ion 6 yielding the stabilized 3a-azaazulenium ion 712) and a final elimination of dimethylamine as a possible route to 3b.

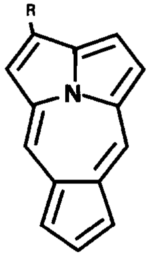
3a8,9b) has been obtained from 5b4,8) using the same route. According to our expectations the t-butoxycarbonyl group has been removed simultaneously by acid catalysed fragmentation.



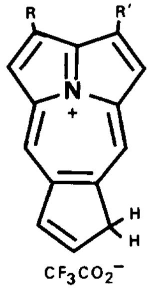
8a R = H
8b R = Cl



9a R = R' = H
9b R/R' = $-(CH_2)_3-$



10a R = H
10b R = Cl



11a R = R' = H
11b R = Cl,R' = H
11c R = H,R' = Cl

Cycl[4.2.2]azinium salts are also accessible from 3,4-bismethylenepyrrolizinium salts 813) via cycloaddition reactions. Treatment of 8b with ethyl-vinylether and N-morpholino-cyclopentene in boiling ethanol yielded 9a8,9c) and 9b8,9d) respectively.

TABLE

^{1}H-NMR spectral data of cycl[4.2.2]azinium salts (solvent: trifluor= acetic acid). Chemical shifts are given in ppm downfield from tetramethyl= silane, coupling constants in Hz; m = multiplet.

	H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-8	J_{12}	J_{34}
3a	8.85	9.21	9.21	8.85	(m, 9.61 - 9.32)				4.65	4.65
3b	-	9.38	9.10	8.92	(m, 9.65 - 9.38)				-	4.98
9a	8.46	-	8.71	8.63	(m, 9.70-9.26)			-	-	4.82
9b	8.41	-	8.75	8.68	9.27	-	-	-	-	4.67

Reaction of 8b with sodium cyclopentadienide under conditions, which have been used earlier for the synthesis of 10a[13] led to the cyclopentano-cycl[4.2.2]azin 10b[8]. Is has been shown earlier, that 10 represents a π-system of its own right the properties pointing at close similarities to azulenes[13].

10b is protonated in trifluoroacetic acid to give a mixture of the cycl[4.2.2]azinium salts 11b and 11c in a ratio of 1:1[14].

A cristalline salt 11b,c[8] separated from the solution after addition of ether the structure of which could not be determined definitely since it forms the abovementioned equilibrium quickly after resolution in trifluoro= acetic acid.

The protonation of 10a[14] and 10b leads to an average downfield shift of 0.8 ppm the shift being greater for the protons of the five-membered rings (1.0 ppm) than for those of the seven-membered ring (0.6 ppm). Taking into consideration the influence of the positive charge in 11 one can state a similar diatropism for the π-system 10 and 11.

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REFERENCES AND NOTES

1) K. Hafner, J. Schneider, *Liebigs Ann. Chem.* **624**, 37 (1959); K. Hafner, K.F. Bangert, *Liebigs Ann. Chem.* **650**, 98 (1961).

2) M.J.S. Dewar, D.C. Dougherty, The PMO-Theory of Organic Chemistry, *Plenum Press N.Y.* 1975.

3) W. Flitsch, U. Krämer, *Adv. Heterocycl. Chem.* **22**, 352 (1978).

4) E.R. Gesing, Dissertation, Universität Munster 1978.

5) A first derivative **11a** has been obtained by D. Leaver and D. Farquhar, who investigated the ^{1}H-NMR-spectra of **10a** in trifluoroacetic acid. This has been brought to our attention after the completion of this work14).

6) Inspite of several attemps we did not succeed in synthesizing even a derivative of **4**. This may be taken as an indirect proof for the proposed properties of the π-system.

7) D. Johnson, G. Jones, *J.C.S. Perkin I*, **1972**, 844.

8) Analytical and spectral data are in agreement with the structure proposed. In case of contamination with $NaClO_4$9) the ratio of the experimental C/H/N-values is in agreement with those calculated. The molecular weight of these compounds has been determined by high-resolution mass spectrometry.

9) Mixture with $NaClO_4$: a) 41 % **3b**, b) 20 % **3a**, c) 35.6 % **9a**, d) 31.8 % **9b**.

10) W. Flitsch, B. Müter, U. Wolf, *Chem. Ber.* **106**, 1993 (1973).

11) For a similar formylation of 3a-azaazulene-4-one see: W. Flitsch, A. Gurke, B. Müter, *Chem. Ber.* **108**, 2969 (1975).

12) 3a-Azaazulenium salts have been prepared previously and found to be diatropic: W. Flitsch, F. Kappenberg, *Chem. Ber.* **111**, 2407 (1978).

13) **8a** has been prepared from 3H-pyrrolizine in a two step synthesis. Reaction with sodium cyclopentadienide gave **10a**: D. Leaver, M.A. Jessep, *J. Chem. Soc., Chem. Commun.* **1970**, 790. **8b** can be obtained from the easier accessible 1-oxo-1,2-dihydropyrrolizine on a slightly different route: W. Flitsch, J. Koszinowski, P. Witthake, *Chem. Ber.*, in press.

14) This follows from an ^{1}H-NMR-spectroscopic study4). The protonation of **10a** to **11a** has been investigated previously: D. Leaver, personal communication

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