A New Simple Approach to Aza-azulene Synthesis

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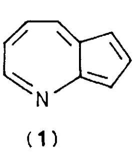
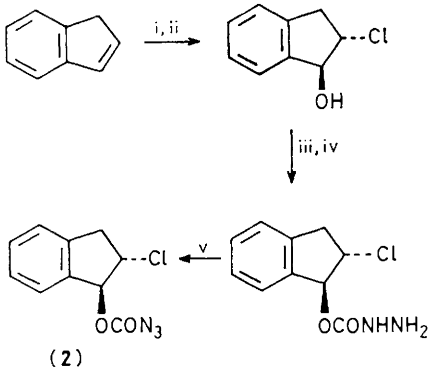
The spray pyrolysis or solution thermolysis of *trans*-2-chlorohydrinden-1-yl azidoformate yields 4-aza-azulene with concomitant elimination of nitrogen, carbon dioxide, and hydrochloric acid.

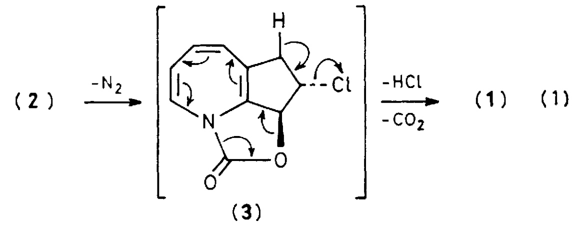
Of the mono-aza-azulenes,[1] all but the 2-aza-isomer are known as derivatives and only the parent 1-,[2] 5-,[3] and (possibly) 6-aza-azulenes[4] have been prepared. 4-Aza-azulene (**1**) is only known as its 1,2,3-triphenyl derivative.[5] Almost all

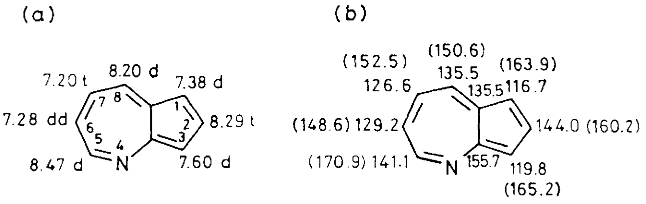


(1)



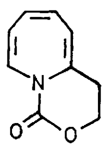
Scheme 1. i, Cl_2, CCl_4, 0.5 °C; ii, aqueous EtOH, heat, recrystallisation; iii, PhOCOCl, pyridine, 20 °C, overnight; iv, $NH_2NH_2 \cdot H_2O$, EtOH, 40 °C; v, aqueous $NaNO_2$, AcOH, 0—5 °C.





J	1,2	2,3	5,6	6,7	7,8
Hz	4.25	4.0	6.75	10.5	8.75

Figure 1. (a) ^1H N.m.r. chemical shifts (δ) and coupling constants; (b) ^{13}C n.m.r. chemical shifts (δ/p.p.m.) and (coupling constants) ($^1J_{CH}$/Hz) for 4-aza-azulene.



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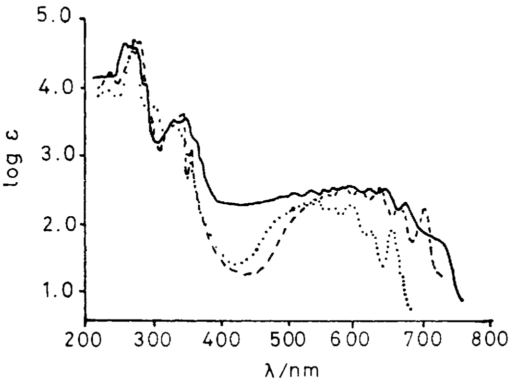

Figure 2. Ultra-violet spectra of azulene (- - - -), 4-aza-azulene (——), and 5-aza-azulene (· · · · · ·).

syntheses of aza-azulenes involve the use of troponoids, pyrroles, or fulvenes and are thus difficult of access or lengthy to prepare.[1] We herein describe a simple, one-step synthesis of 4-aza-azulene (**1**) by the decomposition of a cheap, readily available precursor which can be rapidly made in large quantities.

We have noted elsewhere that azidoformates undergo efficient intramolecular reactions either in the vapour phase, preferably using our 'spray pyrolysis' conditions,[6] or occasionally on solution thermolysis in refluxing 1,1,2,2-tetrachloroethane[7] (a solvent inert to nitrene attack). *trans*-2-Chlorohydrinden-1-yl azidoformate [(**2**), m.p. 39—40.5 °C; i.r. ν_{max} (liquid film): 2120, 2170 (N_3), 1720 (CO), 1220 br. (OCO), 745 cm^{-1} (o-C_6H_4); ^1H n.m.r. δ ($CDCl_3$) 3.20 (3a-H), 3.65 (dd, 3b-H), 4.57 (quint., 2-H), 6.21 (d, 1-H), 7.2—7.6 (m, aromatic H's), $J_{3a,3b}$ 17, $J_{3a,2}$ 4.5, $J_{3b,2}$ 7, $J_{2,1}$ 3 Hz] is readily made from indene as shown in Scheme 1 in an overall 56% yield from the known[8] chlorohydrin. On spray pyrolysis at 300 °C, a dark turquoise product collects on the cold finger which is possibly a mixture of the intermediate (**3**) (which would be expected to be yellow to orange from our previous experience) and the aza-azulene (**1**) [equation (1)]. Albeit on addition of methylene chloride at low temperature the solution instantly becomes intensely blue. Elution of this solution through silica gel yields firstly a small amount of unchanged azide followed by the deep blue aza-azulene (**1**) in 60% yield.†‡ Similarly, rapid addition of the azide (**2**) in a little tetrachloroethane to refluxing tetrachloroethane (2% solution) under nitrogen followed by a brief further reflux and rapid cooling of the solution, yields a deep blue solution from which the same azulene (**1**) may be won on elution through silica gel as before.

The azulene (**1**) is liquid at ambient temperature and is moderately stable in the free state under nitrogen atmosphere but rapidly decomposes in air. When pure, it appears to be indefinitely stable in solution (in air) in organic solvents and is soluble and stable in mineral acids. Similar properties were

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† We have found that the yield and purity of the product is improved by packing the pyrolysis tube with either calcium oxide (3—8 mesh) or copper turnings to absorb HCl. Work-up is thereby less problematic.

‡ The case of this elimination is the more surprising in that the azepine (**4**) is unchanged even on pyrolysis at 900 °C (!) (ref. 9).

noted for the 5-aza-isomer.[3] The decomposition even in solution appears to be autocatalytic, necessitating rapid purification. It reveals a first-order ^1H n.m.r. spectrum at 500 MHz ($CDCl_3$) assigned by selective decoupling and the ^{13}C n.m.r. data ($CDCl_3$) was assigned graphically based on the proton assignment (see Figure 1).[10] The mass spectrum shows the molecular ion as the base peak with successive losses of HCN and acetylene. The u.v. spectrum (Figure 2) is closely comparable with that of azulene and its 5- and 6-aza-analogues.

It would thus appear that aza-azulenes bearing nitrogen in the 5-membered ring are stable species whereas those with the nitrogen in the 7-membered ring are rather sensitive systems.

Received, 3rd August 1983; Com. 1046

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