## Synthesis of Cycl[3,2,2]azines, 6-Azacycl[3,2,2]azines, and Cyclopenta[h]cycl[4,2,2]azines from 3*H*-Pyrrolizine

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Summary 3H-Pyrrolizine has been converted into dimethyl cycl[3,2,2]azine-5,6-dicarboxylate, 6-azacycl-[3,2,2]azine, 6-nitrocycl[3,2,2]azine, and cyclopenta[h]cycl[4,2,2]azine: the last compound is a  $14\pi$ -analogue of azulene.

PREVIOUS approaches to the synthesis of cyclazines have started from indolizines<sup>1</sup> or quinolizines;<sup>2</sup> routes starting from pyrrolizines, while clearly possible in principle, seemed less attractive because the synthesis and chemistry of pyrrolizine remained unexplored. Recently, however, 3H-pyrrolizine (1) has become available by two different routes<sup>3</sup> and its conjugate base has been shown<sup>4</sup> to react with carbonyl compounds at C-3. Our present investigations were inspired by the work of Hafner<sup>5</sup> and of Jutz<sup>6</sup> on the synthesis of conjugated cyclic systems from cyclopentadiene, a compound that resembles pyrrolizine in many ways.

3H-Pyrrolizine reacted with NN-dimethylformamidephosphoryl chloride, at low temperature, to give a salt (isolated as the perchlorate) which was assumed to be the 5-dimethylaminomethylene compound (2). The conjugate base of this compound was unstable but treatment of the salt with sodium hydride, in the presence of dimethyl acetylenedicarboxylate, gave the cycl[3,2,2]azine derivative (3) which was converted, by standard procedures, into cycl[3,2,2]azine (4) (m.p. and n.m.r. and u.v. spectra identical with those reported previously <sup>1a,7</sup>). This result confirmed our initial assumption that the reaction of the Vilsmeier reagent with 3H-pyrrolizine had taken place at the 5-position.



ιH	N.m.r.	absorptions <sup>a</sup>	$(\tau$ -values)	l of	compounds	(5),	(7),	and (	8)	
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	(5)	(7)	(8)
H-1, 4 <sup>b</sup> H-2, 3 <sup>b</sup> H-5, 7	$\left. \begin{array}{c} 2\cdot 56{ m d} \\ 2\cdot 36{ m d} \\ 0\cdot 79{ m s} \end{array} \right\} { m AB} \; (J \; 4\cdot 5 \; { m Hz})$	$\left. \begin{array}{c} 2 \cdot 45 \mathrm{d} \\ 2 \cdot 25 \mathrm{d} \\ 1 \cdot 14 \mathrm{s} \end{array} \right\} \mathrm{AB} \; (J \; 4 \cdot 5 \; \mathrm{Hz})$	$ \begin{array}{ccc} \text{H-1, 4}^{\text{c}} & 2 \cdot 56\text{d} \\ \text{H-2, 3}^{\text{c}} & 2 \cdot 33\text{d} \\ \text{H-5, 9} & 1 \cdot 24\text{s} \end{array} \right\} \text{AB} (J \ 4 \cdot 6 \ \text{Hz}) $
			$ \begin{array}{c} \text{H-6, 8} & 2 \cdot 18 \\ \text{H-7} & 2 \cdot 06 \end{array} \right\} \text{AB}_{2} (J \ 3 \cdot 8 \text{ Hz}) $

a In CDCl<sub>2</sub>. b The higher-field doublet is assigned to H-1 and H-4 by analogy with cycl[3,2,2]azine. c These assignments should possibly be reversed.

The salt (2) reacted with NN-dimethylthioformamide in acetic anhydride<sup>8</sup><sup>†</sup> to give a bis(dimethylaminomethylene)-pyrrolizinium salt, the n.m.r. spectrum of which suggested

the presence of more than one isomer. In view of the success of subsequent reactions, however, the mixture must have contained a substantial proportion of the 3,5-isomer

† The more classical Vilsmeier procedures, using NN-dimethylformamide, failed to give more than a trace of disubstituted material.

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(5). Thus treatment of the salt (Scheme) gave 6-azacycl-[3,2,2]azine (6), 6-nitrocycl[3,2,2]azine (7), and cyclopenta-[h]cycl[4,2,2]azine (8), the structures of which follow from their n.m.r. spectra (Table). Compound (8) was also synthesised (lower yield) from the fulvene derivative (9)<sup>9</sup> and pyrrolizine.

Compound (8), green plates, m.p. 193-194°, has 14 peripheral  $\pi$ -electrons and incorporates the previously unknown cycl[4,2,2]azine ring-system which might be expected to form an aromatic cation (10) with 10 peripheral

 $\pi$ -electrons. The ion (10) is related to cycl[3,2,2]azine as the tropylium ion is related to benzene and, consequently, compound (8) is an analogue of azulene. Its electronic absorption spectrum is similar to that of azulene and electrophilic substitutions (deuteriation, nitration, nitrosation, acylation, bromination, Mannich reaction) occur very readily in the 6- and 8- positions.

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