

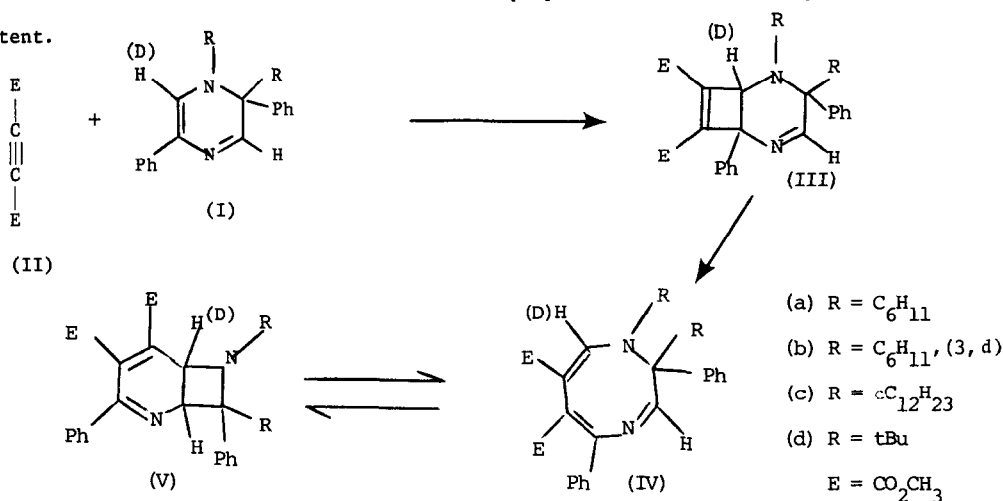
SEQUENTIAL VALENCE TAUTOMERISM, 1,3-SIGMATROPIC ( $C \rightarrow N$ ) ALKYL SHIFT AND CYCLOREVERSION TO  
 PYRROLE AND KETENIMINE IN THE REACTION OF SOME 1,2-DIHYDROPYRAZINES WITH DIMETHYL ACETYLENE-  
 DICARBOXYLATE

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(Received in USA 5 July 1973; received in UK for publication 7 August 1973)

Considerable interest attaches to heterocycles containing  $(4n+2)$   $\pi$  systems of electrons. We report that reaction of certain 1,2-dihydropyrazines (I) with dimethyl acetylenedicarboxylate (II) leads to a novel series of pericyclic reactions plausibly implicating the elusive 10 electron 1,4-diazocine and which serve to delineate the properties of this heterocyclic system to some extent.



SCHEME 1

Treatment of 1,2-dicyclohexyl-1,2-dihydro-2,5-diphenylpyrazine (1a)<sup>1</sup> with an equivalent of (II) at room temperature for 3 days in THF affords a 1:1 adduct (Va) (see table) formulated as the 1,2-dicyclohexyl-6,7-dicarbomethoxy-2,5-diphenyl-3,8-dihydroazetidino[3,2-b]pyridine. A parallel experiment with 6-deutero-(1b) (>95% d) gave (Vb) in which the vicinal proton at  $\delta$  4.64 was absent.<sup>2</sup>

The valence tautomerism of (IV) to (V) is represented as reversible to account for thermolysis products of (V).<sup>2</sup> (q.v.). New heterocycles similarly prepared are listed in table 1.

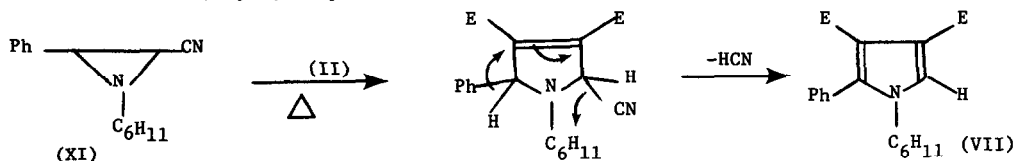
Table 1

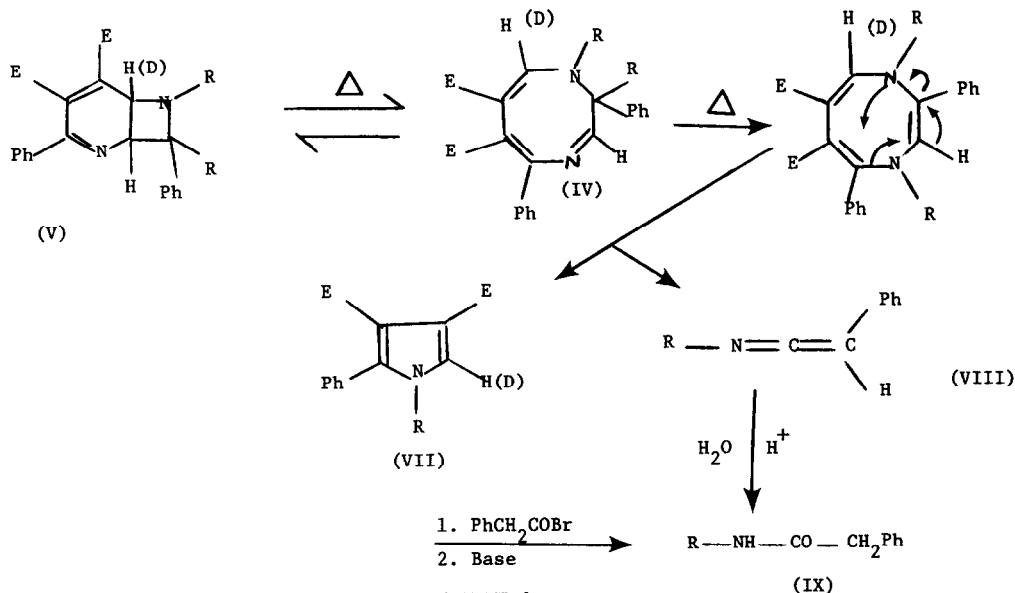
## 1,2-Dialkyl-6,7-dicarbomethoxy-2,5-diphenyl-3,8-dihydroazetidino[3,2-b]pyrazines (V)\*

(V)	m.p.	Yield (%)	N.m.r. spectra data
a	144-145.5	(87)	0.51-1.95 (m, 20H, cyclohexyl), 2.05-2.49 (b, 1H, methine), 2.67-3.17 (b, 1H, methine), 3.27 (s, 3H, ester) 3.86 (s, 3H, ester), 4.18(d,1H, J=4.0 Hz, C <sub>3</sub> H), 4.64 (d, 1H, J=4.0 Hz, C <sub>8</sub> H) 7.11-7.77 (m, 10H, aromatic).
b	144-145.5	(87)	0.50-1.96 (m, 20H, cyclohexyl), 2.05-2.48 (b, 1H, methine), 2.67-3.15 (b, 1H, methine), 3.27 (s, 3H, ester), 3.86 (s, 3H, ester), 4.18 (t, 1H, J=2.0 Hz, C <sub>3</sub> H), 7.11-7.78 (m, 10H, aromatic).
c	122-3.5	(73)	0.77-2.01 (m, 44H, dodecyl), 2.17-2.72 (b, 1H, methine), 2.89-3.41 (b, 1H, methine), 3.40 (s, 3H, ester), 3.90 (s, 3H, ester), 3.98 (d, 1H, J=4.2 Hz, C <sub>3</sub> H), 4.60 (d, 1H, J=4.2 Hz, C <sub>8</sub> H) and 7.04-7.71 (m, 10H, aromatic).
d	135-7	(91)	0.82 (s, 3H, -C(CH <sub>3</sub> ) <sub>3</sub> ), 1.03 (s, 3H, -C(CH <sub>3</sub> ) <sub>3</sub> ), 3.25 (s, 3H, ester), 3.90 (s, 3H, ester) 4.17 (d, 1H, J=4.5 Hz, C <sub>3</sub> H) 4.76 (d, 1H, J=4.5 Hz, C <sub>8</sub> H) 7.08-7.71 (m, 10H, aromatic).

Heating (V) briefly in benzene gave pyrroles (VII) and the ketenimines (VIII)<sup>4</sup> in approximately equal amounts. For the thermolysis of (Vd) the progress of the reaction was conveniently followed by n.m.r. and is rationalized as a valence tautomerism of (V) to (IV),<sup>5</sup> selective [1,3] sigma-tropic<sup>6</sup> (C→N) alkyl shift to (VI) followed by cycloreversion<sup>7</sup> with an accompanying 1,2-hydride shift to give (VII) and (VIII) (see Scheme 2 and table 2).

Exposure of ketenimines (VIII) to water (e.g. chromatography on Al<sub>2</sub>O<sub>3</sub>) afforded the amides (IX) the structure of which were proven by synthesis. The structure of the pyrrole (VII) was proven (in the case of Va+VIIa) by 1,3-dipolar addition of (II) to the aziridine (X)<sup>8</sup>





SCHEME 2

TABLE 2

PRODUCTS OF THERMOLYSIS OF 3,8-DIHYDROAZETIDINO[3,2-b]PYRAZINES

Substrate	Pyrrole(VII) <sup>A</sup>	Amide(IX) <sup>A</sup>	Ketenimine(VIII) <sup>B</sup>
Va	oil (89%) <sup>A</sup>	m.p. 131-2.5 (93%)	$\delta_{\text{TMS}}$ ( $\text{CDCl}_3$ ) 4.72 (d, $J = 1.5$ Hz) ir( $\text{CHCl}_3$ ) 2050 $\text{cm}^{-1}$
Vc	m.p. 106-7.5 (87%)	m.p. 142-3.5(82%)	$\delta_{\text{TMS}}$ ( $\text{CDCl}_3$ ) 4.73 (d, $J = 1.5$ Hz) ir( $\text{CHCl}_3$ ) 2045 $\text{cm}^{-1}$
Vd	m.p. 92-93 (92%)	m.p. 135-6.5(89%)	$\delta_{\text{TMS}}$ ( $\text{CDCl}_3$ ) 4.85(s) } ir( $\text{CHCl}_3$ ) 2050 $\text{cm}^{-1}$ } C

A. Identical with authentic samples. B. Characterized spectroscopically, readily hydrated to amides (IX). C. Treatment with  $\text{D}_2\text{O}$  gave  $\text{PhCHDCONDtBu}$

Additional evidence in support of the proposed mode of cleavage of (V) in scheme 2 is provided by a parallel experiment with 8-deutero - (Vb) which gave (VII) in which the 5-position was deuterated and (VIII) in which the allenic proton was clearly visible at  $\delta 4.72$ . The stereochemistry of the transformations given in Scheme 2 are currently under investigation.

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- \* Satisfactory analyses and accurate mass spectral peak measurements were obtained on all new compounds reported.
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6. R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry", Academic Press, New York, 1970 p.119.
7. The cleavage of (VI) to (VII) and (VIII) may be a two-step process, experiments are in hand with other models to elucidate this.
8. J. W. Lown, T. W. Maloney and G. Dallas, Can. J. Chem., **48**, 584 (1970).