

## Transannular Cyclisations of Cyclo-olefinic *N*-Chloro-amines

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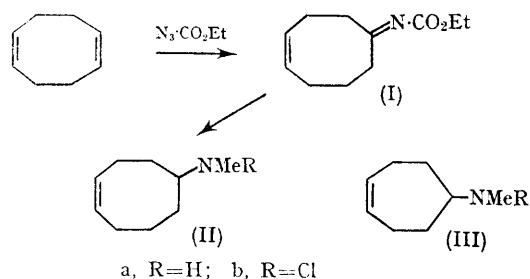
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RECENT communications concerning silver ion-catalysed reactions of alicyclic *N*-chloro-amines have provided examples of intramolecular hydrogen abstraction from saturated carbon,<sup>1</sup> Wagner-Meerwein type rearrangement in bicyclic systems,<sup>2</sup> and intramolecular addition to an olefinic bond.<sup>3</sup> The intervention of nitrenium ion intermediates,  $R_2N^+$ , has generally been presumed, but conclusive evidence for the existence of the free cations is lacking. In particular, the possible role in some of these reactions of radical intermediates, known to be accessible from *N*-chloro-amines under a variety of conditions<sup>4,5</sup> and capable of giving some of the observed products, remains to be clarified. The recent report by Gassman and his colleagues<sup>3</sup> of a silver ion-catalysed cyclisation of a monocyclic olefinic *N*-chloro-amine prompts us to outline here our experience with similar reactions.

*N*-Methylcyclo-oct-4-enamine (IIa) was prepared by reduction (lithium aluminium hydride) of 5-ethoxycarbonyliminocyclo-octene (I), itself readily obtained by reaction of cyclo-octa-1,5-diene with ethyl azidoformate. The lower homologue (IIIa) was obtained *via* Curtius rearrangement of cyclohept-4-enecarboxylic acid<sup>6</sup> azide in ethanol, followed by reduction ( $LiAlH_4$ ) of the carbamate; *N*-chlorosuccinimide in dichloromethane converted the secondary amines (IIa) and (IIIa) into the required starting materials (IIb) and (IIIb).

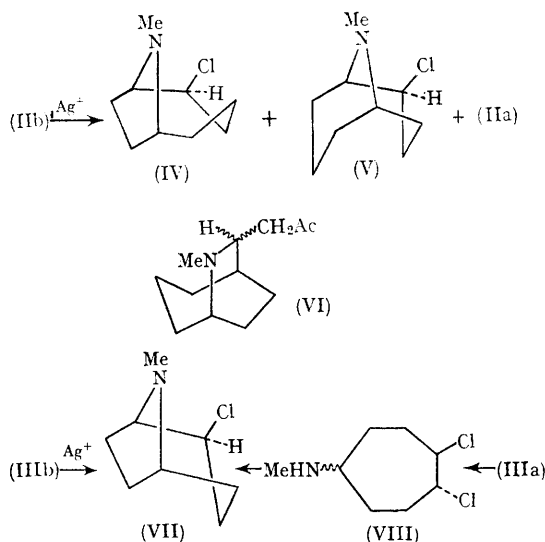
The *N*-chloro-amines were treated with silver perchlorate in homogeneous solution in acetone. The products were partitioned with mineral acid into neutral (largely the corresponding ketone, *e.g.* cyclo-oct-4-enone, presumably formed by hydrolysis of the imine) and basic fractions, the latter being separated and analysed by column chromatography

and g.l.c. Data for reactions of (IIb) are tabulated below; apart from regenerated secondary base (IIa), the bicyclic chlorides (IV) and (V) were the only basic products formed in significant amounts, except in the presence of an excess of silver perchlorate. In this case a fourth component, identified as the rearrangement product (VI), was obtained but was subsequently shown to be generated from both (IV) and (V) by solvolysis in aqueous acetone, with, or without electrophilic catalysis by silver ions.<sup>7</sup>



The skeletons of the chlorides (IV) and (V) were established by reduction with sodium and *t*-butyl alcohol to the corresponding 9-methyl-9-azabicyclonanes, identified by comparison with synthetic materials. The *exo*-configuration of the chlorine atom in each is assigned on the basis of their n.m.r. spectra, their solvolytic behaviour,<sup>7</sup> and by analogy with the course of reaction definitely established for the lower homologue (III)a. With an equivalent amount of silver perchlorate in hot acetone IIIb afforded a single bicyclic compound (VII), found to be identical with the sole product from base-induced cyclisation of the presumed<sup>8</sup> *trans*-dichloride (VIII), prepared by addition of chlorine to the hydrochloride of (IIIa). The n.m.r. spectra of (V) and (VII) showed signals for the protons adjacent to chlorine as broad multiplets centred at  $\tau$  5.7 and 6.0 respectively, both

having  $W_{1/2}$  8 Hz, consistent only with an equatorial configuration.<sup>9</sup>



The data for the cyclisation of (IIb) include the following features:

- (i) In the absence of catalyst no bicyclic compounds are formed, and slow thermolysis to secondary amine occurs, probably *via* intermolecular hydrogen abstraction by neutral amino-radicals, which show little disposition to add to double bonds.<sup>5</sup>
- (ii) In spite of the catalytic role of silver ions in the cyclisations, chlorine is retained in the products, being introduced stereospecifically *cis* to the nitrogen bridge.
- (iii) The same products (IV) and (V) are formed, under comparatively mild conditions, in reactions in methanol in the presence of ferrous ions, or in acid solution. Such conditions are known to

TABLE

Cyclisations of *N*-chloro-*N*-methylcyclo-oct-4-enamine (IIb)

Reagent Moles/mole (IIb)	Solvent/Temp.	Reaction time (min.) <sup>a</sup>	<i>s</i> -Base (IIa)	Basic products (%) <sup>b</sup> Chlorides		Other
				(IV)	(V)	
AgClO <sub>4</sub> (0.1)	Me <sub>2</sub> CO/reflux	720	64			
AgClO <sub>4</sub> (1.0)	Me <sub>2</sub> CO/reflux	90	71	11	4	tr <sup>c</sup> (VI)
AgClO <sub>4</sub> (2.0)	Me <sub>2</sub> CO/reflux	25	tr	25	11	tr (VI)
FeSO <sub>4</sub> (1.0)	Me <sub>2</sub> CO/reflux	25	5	2	4	20 (VI)
	MeOH/20° <sup>d</sup>	120	33	16	5	
	4M-H <sub>2</sub> SO <sub>4</sub> in AcOH/10° <sup>d</sup>	120	tr	6	26	

<sup>a</sup> Approx. time after which an aliquot gave no instantaneous starch-iodide reaction. <sup>b</sup> Yields based on *N*-chloro-amine; polymeric material removed by column chromatography prior to g.l.c. analysis. <sup>c</sup> tr = trace, *i.e.* < 2%.

<sup>d</sup> Kept under N<sub>2</sub>.

facilitate homolysis to aminium radicals, which, in the presence of olefins, take part in radical-chain addition to give  $\beta$ -chlorodialkylamines.<sup>5</sup>

These observations are difficult to reconcile with a mechanism involving free nitrenium ions in the case of the silver-ion promoted cyclisations, in view of the stereospecific *cis*-addition and the incomplete precipitation of the available chlorine. An alternative possibility, that may also deserve consideration in certain other silver ion-*N*-chloro-amine

reactions,<sup>1,3</sup> is that the role of the catalyst may be analogous to that attributed to protons in the Hoffman-Löffler-Freytag reaction,<sup>4</sup> and to protons and metal ions in the radical-addition reactions,<sup>5</sup> *i.e.*, co-ordination with the nitrogen atom of the *N*-chloro-amine. Intramolecular addition, following homolysis of the N-Cl bond, or possibly heterolysis leading to the electrophilic addition of chlorine,<sup>5</sup> could then account for the observed products.

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<sup>4</sup> *Inter alia*, M. E. Wolff, *Chem. Rev.*, 1963, **63**, 55; F. Minisci and R. Galli, *Tetrahedron Letters*, 1967, 2207, and previous papers quoted therein; R. S. Neale and M. R. Walsh, *J. Amer. Chem. Soc.*, 1965, **87**, 1255; R. S. Neale, M. R. Walsh and N. L. Marcus, *J. Org. Chem.*, 1965, **30**, 3863.

<sup>5</sup> R. S. Neale, *J. Org. Chem.*, 1967, **32**, 3253; R. S. Neale and N. L. Marcus, *ibid.*, p. 3273.

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<sup>7</sup> J. D. Hobson and W. D. Riddell, following Communication.

<sup>8</sup> *E.g.* N. L. Allinger and L. A. Tushaus, *Tetrahedron*, 1967, **23**, 2051.

<sup>9</sup> *E.g.* K. H. Baggeley, J. R. Dixon, J. M. Evans, and S. H. Graham, *Tetrahedron*, 1967, **23**, 299.