

## Preparation and Chemoselective Thermolysis of Potential Azatricyclic Synthons Containing an Eight-membered Nucleus

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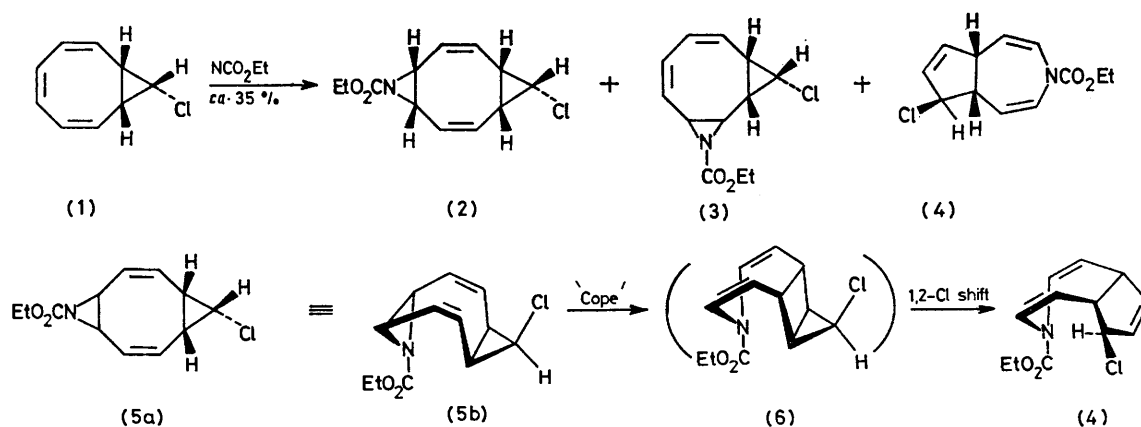
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**Summary** The nitrene-based preparation and epimerically controlled thermolysis of certain synthetically useful azatricyclics are described.

$\pi$ -EXCESSIVE heteroannulenyl ions are rare  $\pi$  entities<sup>1</sup> possessing structures which are well suited for studying the phenomenon of 'heteroaromaticity' in a molecular environment where the development of cyclic conjugation can only be realized through direct interaction between one or more heteroatomic lone pairs and a charged carbon centre. We

report on the preparation and thermal bond relocation of certain potential progenitors to the general aza[10]annulenyl frame.

The procedure involves addition of ethoxycarbonylnitrene† to *syn*-9-chloro-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (1), a compound whose 'bridge' substituent is potentially amenable to anionically as well as cationically assisted removal.‡ This leads to a mixture consisting of three isomers of composition C<sub>12</sub>H<sub>14</sub>NO<sub>2</sub>Cl. Column chromatography at *ca.* -15 °C yields the individual components (2;

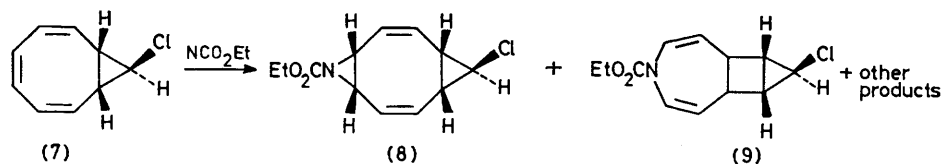


† Generated upon exposure of benzene sulphonyurethane to tetramethylguanidine in CH<sub>2</sub>Cl<sub>2</sub> at *ca.* 8 °C.

‡ In an effort to minimize the formation of undesirable stereoisomeric mixtures we specifically selected the sterically constrained *syn* epimer (1) over the more skeletally flexible *anti* analogue (7) as our substrate.

m.p. 62–64 °C), (3; m.p. 58.5–59.5 °C), and (4; liquid).§ Structural assignments were made primarily on the basis of n.m.r. data which unequivocally establish the respective presence of symmetrically and unsymmetrically disposed aziridine and cyclopropane units in (2) and (3) and the absence of such units (as well as molecular symmetry) in

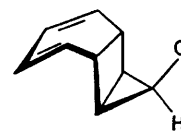
shift and might thus be expected to be thermally stable and readily isolable. In keeping with this reasoning the reaction of (7) with NCOOEt yields (8; liquid, <sup>1</sup>H n.m.r., m.s.) and (9; m.p. 55–57 °C)§ *i.e.*, the epimer of (6). Further, (9) was found to resist any type of bond relocation upon prolonged heating at 100 °C.



(4). The stereochemical assignment depicted in (2), *i.e.*, *cis* disposition of three-membered rings was made primarily on the basis of the known sterically-derived conformational restrictions present in the system<sup>2</sup>¶ compared with the non-primary nature of (4) and its evident formation from the hitherto undetected stereoisomer (5a) which, unlike (2), must exist in the folded–extended conformation (5b) necessary for the activation of the initial ‘Cope’ rearrangement the molecule must undergo to produce (4). Another significant feature of this interpretation is that the proposed key intermediate (6) possesses proper stereochemistry, *i.e.*, *syn*-directed chlorine group, for ready cyclopropane-assisted 1,2-chlorine transfer leading to (4).

In order to test the significance of this structural detail we examined the reaction of ethoxycarbonylnitrene with (7), *i.e.*, the epimer of (1), the rationale being that the intermediate expected to form in this case *via* ‘Cope’ relocation of the ‘epimer’ of (5) would be improperly structured (*anti* disposition of Cl group) for cyclopropane-assisted chlorine

We conclude by noting that the readiness with which (6) rearranges to (4) supports the intermediacy of a carbocyclic analogue of (6), namely (10), recently advanced<sup>3</sup> to account for the thermal isomerization of *syn*-9-chloro-*cis*-bicyclo-[6.1.0]nona-2,4,6-triene to the corresponding *cis*-8,9-dihydroindene.



(10)

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§ These structural assignments were made on the basis of spectroscopic data (<sup>1</sup>H n.m.r., u.v., m.s., i.r.) and elemental (combustion) analysis.

¶ For obvious steric reasons the central ring of the *cis* tricycle (2) must exist in the ‘extended’ (E) form with regard to either three-membered groups (ref. 2), *i.e.*, with respect to conformational detail the molecule ought to be designated as 2 (EE).

<sup>1</sup> For an interesting member of this family, see: T. Sasaki, K. Kanematsu, and K. Hayakawa, *J. Chem. Soc. (C)*, 1971, 2142.

<sup>2</sup> For a description of the situation in related systems, see: A. G. Anastassiou and E. Reichmanis, *J. Org. Chem.*, 1973, **38**, 2421.

<sup>3</sup> J. C. Barborak, T-M. Su, P. v. R. Schleyer, G. Boche, and G. Schneider, *J. Amer. Chem. Soc.*, 1971, **93**, 279.