

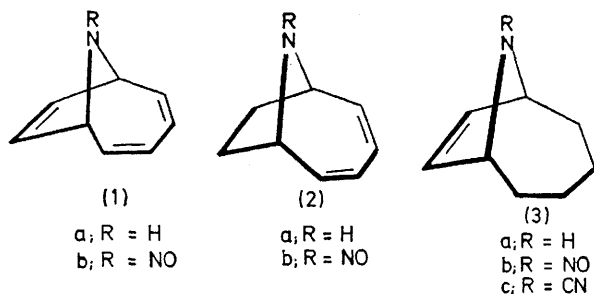
## Thermal Cheletropy in Model Azabicycles; the Question of Linear vs. Non-linear Extrusion

By A. G. ANASTASSIOU\* and H. YAMAMOTO

(Department of Chemistry, Syracuse University, Syracuse, New York 13210)

**Summary** Comparison between *N*-nitroso-9-azabicyclo-[4,2,1]nona-2,4,7-triene (**1b**), *N*-nitroso-9-azabicyclo-[4,2,1]nona-2,4-diene (**2b**) and *N*-nitroso-9-azabicyclo-[4,2,1]non-7-ene (**3b**) in terms of their tendency to undergo bridge extrusion under the influence of basic hydrosulphite, reveals distinct preference for "linear" cheletropy.

In an earlier report<sup>1</sup> we noted that 9-aza[4,2,1]bicycles, *e.g.* (**1**), (**2**), and (**3**), have ideal structures for assessment of the relative merits of 'linear' and 'non-linear' cheletropy<sup>2</sup> within the same molecule. The bicyclic nature of this general skeleton limits its cheletropic potential to the sigma-

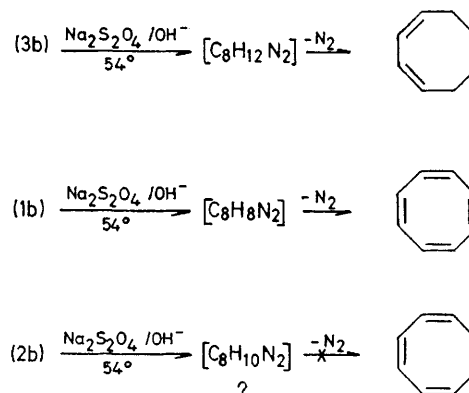


symmetric mode<sup>3</sup> which may materialize either in 'linear' or 'non-linear' fashion depending on the  $\pi$ -electron count of the hydrocarbon segments attached to the 'hetero' bridge.

Thus, for a diazene ( $>N=N$ ) bridge it may be shown<sup>2</sup> that the extrusion process is permitted to proceed linearly under the influence of a ' $4n + 2$ '  $\pi$ -ribbon and non-linearly under the control of a ' $4n$ '  $\pi$ -ribbon. To test this hypothesis experimentally we examined the hydrosulphite-induced fragmentation of *N*-nitroso-compounds into molecular nitrogen and a hydrocarbon fragment, with its obvious implication of a diazene intermediate.<sup>4</sup>

Nitroso-derivatives (**1b**)<sup>5</sup> and (**2b**)<sup>†</sup> (m.p. 62–63°) were prepared, in 72 and 58% yield respectively, on exposure of amines (**1a**) and (**2a**) to sodium nitrate in glacial acetic acid.

The third nitroso-derivative (**3b**)<sup>†</sup>, m.p. 82.5–84°, was prepared similarly from the hitherto unknown amine (**3a**), formed *via* basic hydrolysis of the cyanamide (**3c**),<sup>†</sup> m.p. 41–43°, which, in turn, was prepared by treatment of 1,4-dibromocyclo-octene with disodium cyanamide.



On treatment with basic (alcoholic KOH) sodium hydrosulphite at 54° (**3b**) undergoes rapid ( $t_{\frac{1}{2}}$  ca. 30 min) fragmentation to molecular nitrogen (85% of theory) and cyclo-octa-1,3-diene (71% yield).<sup>‡</sup> Under similar conditions, triene (**1b**) suffers equally rapid nitrogen loss (67% of theory) and yields cyclo-octatetraene (28% yield)<sup>‡</sup> as the sole identifiable product while the corresponding diene (**2b**) evolves very little gas (ca. 10% of theory) and fails to generate a hydrocarbon fragment. The resistance of (**2b**) to undergo bridge cheletropy sharply contrasts the readiness of (**3b**) to do so and since both these bicycles incorporate singly allylic bridges we infer that there exists a distinct preference for 'linear' [only concerted mode possible for (**3b**)] over 'non-linear' [only concerted mode possible for (**2b**)] cheletropy in these model systems.

The behaviour of (**1b**) is interesting since the two formally isolated  $\pi$  segments are predicted to trigger opposing modes of nitrogen loss. The less efficient fragmentation of the

<sup>†</sup> This substance was formulated on the basis of fully consistent spectral properties (n.m.r., u.v., i.r., m.s.) and combustion analysis.

<sup>‡</sup> The amount of hydrocarbon in the mixture was determined spectrophotometrically (u.v.), while its characterization rests on g.c. isolation and direct spectral (n.m.r., i.r.) comparison with authentic samples.

triene (**1b**) to N<sub>2</sub> (67%) and hydrocarbon (28% cyclo-octatetraene), in spite of the diallylic nature of its bridge, might be reasoned in terms of the opposition introduced by the butadiene unit to the linear process.<sup>§</sup>

We are grateful to the National Science Foundation for support of this work.

(Received, 16th July 1973; Com. 1024.)

<sup>§</sup> In order to test the reliability of our measurements we also exposed the fully saturated counterpart of (**1b**) to alkaline hydro-sulphite at 54° and failed to detect any nitrogen evolution (< 0.3%).

<sup>1</sup> A. G. Anastassiou and R. P. Cellura, *J. Org. Chem.*, 1972, **37**, 3126.

<sup>2</sup> R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Academic Press, New York, 1970, ch. 10.

<sup>3</sup> For a definition of this term see: D. M. Lemal and S. D. McGregor, *J. Amer. Chem. Soc.*, 1966, **88**, 1335.

<sup>4</sup> C. G. Overberger, *Rec. Chem. Prog.* 1960, **21**, 21; C. G. Overberger, M. Valentine, and J. P. Anselme, *J. Amer. Chem. Soc.*, 1969, **91**, 687; for an application of this degradative procedure to the photodimer of (**1b**) see: A. G. Anastassiou and R. M. Lazarus, *Chem. Comm.*, 1970, 373.

<sup>5</sup> W. L. Mock and P. A. H. Isaak, *J. Amer. Chem. Soc.*, 1972, **94**, 2749.