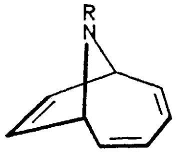
Thermal Cheletropy in Model Azabicycles; the Question of Linear *vs.* Non-linear Extrusion

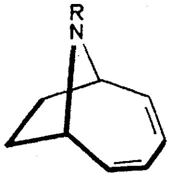
By A. G. ANASTASSIOU* and H. YAMAMOTO
(*Department of Chemistry, Syracuse University, Syracuse, New York* 13210)

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.

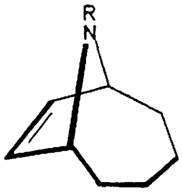
IN an earlier report[1] we noted that 9-aza[4,2,1]bicycles, *e.g.* (**1**), (**2**), and (**3**), have ideal structures for assessment of the relative merits of 'linear' and 'non-linear' cheletropy[2] within the same molecule. The bicyclic nature of this general skeleton limits its cheletropic potential to the sigma-symmetric mode[3] which may materialize either in 'linear' or 'non-linear' fashion depending on the π-electron count of the hydrocarbon segments attached to the 'hetero' bridge. Thus, for a diazene $(>\overset{+}{N}=\overset{-}{N})$ bridge it may be shown[2] that the extrusion process is permitted to proceed linearly under the influence of a '$4n + 2$' π-ribbon and non-linearly under the control of a '$4n$' π-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.[4]



(**1**)
a; R = H
b; R = NO



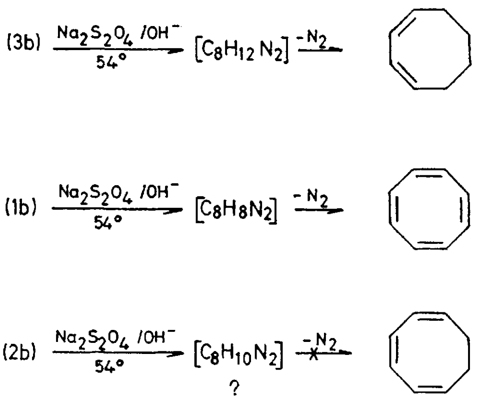
(**2**)
a; R = H
b; R = NO



(**3**)
a; R = H
b; R = NO
c; R = CN

Nitroso-derivatives (**1b**)[5] and (**2b**)† (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**)†, m.p. 82·5—84°, was prepared similarly from the hitherto unknown amine (**3a**), formed *via* basic hydrolysis of the cyanamide (**3c**),† 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).‡ Under similar conditions, triene (**1b**) suffers equally rapid nitrogen loss (67% of theory) and yields cyclo-octatetraene (28% yield)‡ 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 π segments are predicted to trigger opposing modes of nitrogen loss. The less efficient fragmentation of the

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

‡ 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_2 (67%) and hydrocarbon (28% cyclooctatetraene), 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.§

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

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

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§ In order to test the reliability of our measurements we also exposed the fully saturated counterpart of (**1b**) to alkaline hydrosulphite at 54° and failed to detect any nitrogen evolution ($< 0{\cdot}3\%$).

[1] A. G. Anastassiou and R. P. Cellura, *J. Org. Chem.*, 1972, **37**, 3126.
[2] R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Academic Press, New York, 1970, ch. 10.
[3] For a definition of this term see: D. M. Lemal and S. D. McGregor, *J. Amer. Chem. Soc.*, 1966, **88**, 1335.
[4] 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**.
[5] W. L. Mock and P. A. H. Isaak, *J. Amer. Chem. Soc.*, 1972, **94**, 2749.