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A REPLY TO: "BIS-PERICYCLIC RETROCYCLOADDITION AND THE IMPORTANCE OF AVOIDING PIECEWISE ANALYSIS"

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Summary: Recent criticism of a tentative interpretation of the cheletropic response of the azabicyclo[4.2.1]nona-2,4,7-triene frame is shown to be invalid.

Approximately half a decade ago we reported[1] on the question of *linear vs non-linear* cheletropy based on observations relating to the thermally induced extrusion of molecular nitrogen from the three skeletally related azines shown in 1b-3b and generated *in situ* on thermal (54°) exposure of the corresponding N-nitroso derivatives 1a-3a to ethanolic sodium hydrosulfite. Having determined that under these conditions 1b readily extrudes molecular nitrogen (85%) with attendant formation of substantial quantities of 1,3-cyclooctadiene (COD; 71%) and that 2b entirely fails to do so, we were able to safely conclude that the "linear" (4n + 2)-electron cheletropic process available to 1b is significantly favored over its "nonlinear" (4n)-electron counterpart, *i.e.*, the pathway open to the corresponding diene 2b. Moreover, having discovered that exposure of the triply unsaturated member of the series 3 to identical reaction conditions results in significantly reduced N_2 evolution (~67%) and the formation of only small quantities of cyclooctatetraene (COT; 28%) and this despite the presence in 3 of a basically weaker "diallylic" bridge, we *tentatively* concluded that 3b probably experiences some symmetry-controlled opposition to "linear" cheletropy because of the presence of the butadiene unit.

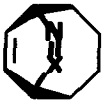
1

2

3

a, X=NO

b, X= N



4

5

6

Very recently[2] our *tentative* explication of the phenomenon was critized by Snyder and Olsen on the basis of findings concerning the relative ease of thermally-induced diheteroatomic bridge extrusion from the [4.2.2] systems shown in **4**-**6**. We have carefully examined the Snyder-Olsen criticism and have found it to be seriously lacking.

Experimentally, what these workers find[2] is that N-oxides **4a** and **6a** quantitatively yield COD and COT, respectively, upon multiple-hour exposure to hexachlorodisilane in $CDCl_3$ at -30° to -40°. Further, they report that the presumed intermediates **4b** and **6b** could not be detected by NMR during the course of the fragmentation and correctly interpreted this observation to mean that the formation of the key diazo compound from the N-oxide counterpart, i.e., **4a**→**4b** and **6a**→**6b**, is in each instance rate limiting. In obvious disregard of this rather critical observation Snyder and Olsen then proceed to conclude that "within the experimental limits, the results suggest that the bispericyclic process (*i.e.*, that originating from **6b**) occurs unretarded relative to the simple pericyclic reaction (*i.e.*, that available to **4b**)". We submit that this conclusion, which our critics extended to encompass the response of our diazenes (**1b**, **3b**) as well, has no valid basis since it was evidently conceived *on the tenuous assumption that the relative rates of nitrogen loss from* **4b** *and* **6b** *closely parallel those pertaining to the formation of these substances from the respective N-oxides* **4a** *and* **6a**! Clearly there is no compelling reason to believe this to be the case. Consequently, the viability of the Snyder-Olsen criticism must rest entirely on the strength of their theoretical analysis which though based on a widely utilized method (CNDO) may well be lacking in crucial detail of the early stages of bridge extrusion which are expected to be kinetically significant, since what one has in **3b** is a relatively unstable substance fragmenting into two stable units (N_2 + COT). Also, given the diallylic nature of the hetero bridge in **3** and **6** one must, for obvious reasons, give serious consideration to the possibility of stepwise bridge extrusion; such a process does not appear to have been seriously considered in the Snyder-Olsen CNDO analysis.

We conclude by stressing the fact that the Snyder-Olsen finding of a faster fragmentation of **4b** compared to **5b** simply confirms the conclusions arrived at several years ago from our work with azines **1b** and **2b**.

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References

(1) A. G. Anastassiou and H. Yamamoto, *J. Chem. Soc. Chem. Commun.*, 840 (1973).

(2) J. P. Snyder and H. Olsen, *J. Am. Chem. Soc.*, **100**, 2566 (1978).

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