On the Nature of Diradical Intermediates Formed during the Thermal and Photochemical Decomposition of Bicyclic Azo-compounds

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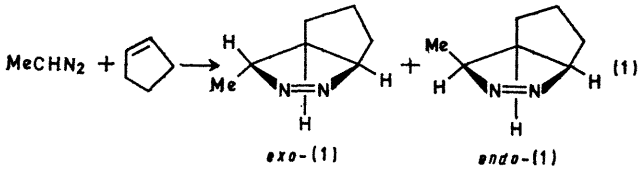
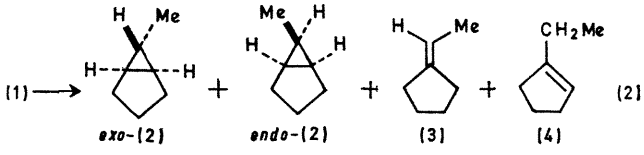
Summary Direct and sensitized photodecomposition of *exo*- and *endo*-2-methyl-3,4-diazabicyclo[3,3,0]oct-3-enes proceeds through singlet and triplet diradical intermediates, but predominant single inversion of configuration in the products formed on thermal decomposition indicates a more complex mechanism.

THERMOLYSIS of cyclopropanes[1] gives rise to "trimethylene diradical" intermediates[2] which undergo stereochemically-random ring closure,[3] while the decomposition of monocyclic pyrazolines,[4] and the reactions of thietanium salts



with alkyl-lithiums[5] proceed with predominant single inversion of stereochemistry. The single-inversion components have been explained on the basis of π-cyclopropane intermediates.[4b,6]

To understand the causes of the different mechanisms in the two types of reactions, we have begun a study of the decomposition of two isomeric azo-compounds *exo*-(**1**) and *endo*-(**1**) whose structures should prevent the easy formation of π-cyclopropanes.



The addition of diazoethane to cyclopentene (reaction 1) produced, in 50% yield, a mixture of compounds *exo*-(**1**) and *endo*-(**1**).[7] We have separated these isomers by preparative g.l.c. and assigned their stereochemistries[8] on the basis of i.r. and n.m.r. data.‡

Thermal decomposition products of *exo*-(**1**) and *endo*-(**1**) at 260° (reaction 2) are shown in Table 1; structures have been assigned by comparison of spectral data[9] with those of authentic samples.

Exo-(**1**) and *endo*-(**1**) decompose with predominant

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‡ In *exo*-(**1**) the H_a–H_b coupling constant J_{ab} is 3·0 Hz, whereas J_{ab} for *endo*-(**1**) is 7·0 Hz. Besides allowing an assignment of stereochemistry, this suggests that the pyrazoline rings are nearly planar (*cf.* ref. 8).

inversion of configuration at the methyl-substituted carbon. In the case of *endo*-(**1**), the stereoselectivity is about the same as that found in the decomposition of *trans*-3,4-dimethylpyrazoline,[4b] while *exo*-(**1**) decomposes with even the rate-determining step of the reaction,§ producing intermediate (**6a**). The postulate that free-radical displacement at the methyl-substituted carbon must take place from the back[11] would require that rotamer (**6a**)

TABLE 1. *Products formed in the thermal and photochemical decomposition of* endo- *and* exo-4-*methyl*-2,3-*diazabicyclo*[3,3,0]*oct*-2-*ene* endo-(**1**) *and* exo-(**1**)

Substrate	Decomposition conditions	Products (%) *exo*-(2)	*endo*-(**2**)	(**3**)	(**4**)
endo-(**1**)	260°[a]	67·2	21·2	6·3	5·3
exo-(**1**)	260°[a]	8·1	72·8	8·1	11·0
endo-(**1**)	260°[b]	65·8	22·2	6·8	5·2
exo-(**1**)	260°[b]	7·5	74·1	8·0	10·4
endo-(**1**)	[c]	29·8	61·0	3·4	5·8
exo-(**1**)	[c]	62·2	21·3	7·5	9·0
endo-(**1**)	[d]	59·4	40·6	trace	trace
exo-(**1**)	[d]	68·9	31·1	trace	trace

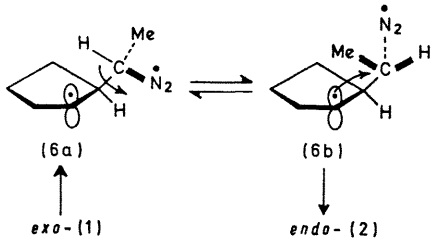
[a] Gas phase, flow system, atmospheric pressure with N_2 carrier gas, contact time 70 s. [b] Same as in footnote a, except tube packed with glass helices. [c] Direct irradiation with an Ultra-Violet Products 305 nm lamp, Pyrex filter, pentane solvent, *c* 0·14M, 25°. [d] Same as in footnote c, except benzophenone sensitizer present in concentration sufficient to absorb > 98% of the incident light, pyrazoline concentration 0·014 M. The use of benzophenone as a sensitizer avoids complications from singlet energy transfer due to its very rapid intersystem crossing rate.[14] [e] All products were stable to the thermolysis and photolysis conditions employed, except in the case of the olefins in the photosensitization experiments. Control experiments under conditions of footnote d, however, showed that no more than 2% olefins could have been formed as kinetic product from either *endo*-(**1**) or *exo*-(**1**) in the presence of benzophenone.

TABLE 2. *Rate constant ratios for the reaction of diradicals* A *and* B *calculated from product ratios formed in the photolysis of* exo-(**1**) *and* endo-(**1**)

Conditions	k_r^A/k_c^A	k_r^B/k_c^B	k_3^A/k_c^A	k_c^B/k_3^B	k_4^A/k_c^A	k_4^B/k_c^B
Direct irradiation 305 nm, pentane	0·68	0·95	0·13	0·03	0·12	<0·01
Irradiation sensitised with Ph_2CO, 305 nm, pentane[a] ..	3·3	6·2	—	—	—	—

[a] The very small percentage of olefin formed in the photosensitization experiment prevented accurate calculation of hydrogen shift–cyclization rate ratios. These numbers must all be > 0·02, however.

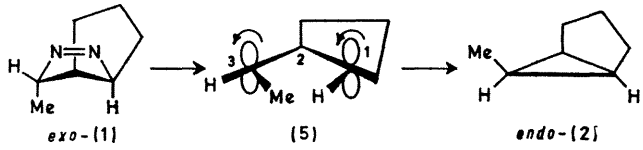
greater inversion than that found in *cis*-3,5-dimethylpyrazoline.[4b] The π-cyclopropane intermediate (**5**), which can be suggested to explain these results, appears to be



highly strained because C-1 and C-2 are connected by a short 3-carbon bridge (Scheme 1). This strain would be expected to decrease the amount of π-cyclopropane which intervenes relative to that observed in the 3,5-dimethylpyrazoline thermolysis,[4b] thus lowering the stereoselectivity. Since this decrease in stereoselectivity is not observed, we considered other causes for the inversion stereochemistry in pyrazoline decompositions.

One such is an extension of a mechanism suggested earlier by Roth and Martin:[10] that only one C–N bond cleaves in undergo rotation to (**6b**) before ring closure, yielding inverted *endo*-(**2**) as a final product.¶

In contrast to the thermal results, photochemical



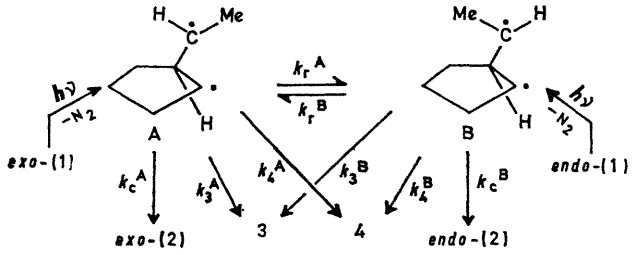
SCHEME 1

decomposition of (**1**) proceeds *via* intermediates which behave more like conventional diradicals, and both isomers produce predominant *retention* of configuration under direct irradiation (Table 1).[13] Assuming a photon provides enough energy to cleave both C–N bonds rapidly, the product data can be fitted to the mechanism illustrated in Scheme 2. Steady-state analysis of this scheme yields a set of six equations which can be solved for the six independent rate-constant ratios reported in Table 2. The behaviour of the diradicals A and B as judged from these parameters parallels that observed in other systems.[3] As might be expected, triplet A and B formed in photosensitized

§ Although concurrent cleavage of both C-N bonds appears to be the accepted mechanism for decomposition of phenyl-substituted, acyclic azo-compounds, the situation in simple alkyl-substituted azo-compounds is less clear. For discussion and references, see ref. 2b, pp. 31—34 and ref. 12.

¶ In an independent study, Schneider and Crawford, [8d] have examined the thermal decomposition of *exo*-4-methyl-2,3-diazabicyclo-[3,3,0]octa-2,7-diene. The possible π-cyclopropane formed from this compound should be even more highly strained than (**5**), and yet the reaction once again proceeds with predominant inversion at C-4.

decomposition[14] apparently undergo ring closure at a slower rate than do the corresponding singlets. The cause of the low percentage of olefin, however, is not yet clear.



SCHEME 2

The sequential C–N cleavage mechanism can also be used to explain the double inversion observed in the decomposition of 2,3-diazabicyclo[2,2,1]hept-2-enes,[10b,15] and the microscopic reverse reaction, the addition of olefins to bicyclo[2,1,0]pentanes.[10a,16] A definitive choice between this and other mechanisms, however, awaits further study.

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