Thermal and Photochemical Decompositions of 5-*exo*- and 5-*endo*-Methyl-2-cyano-3,4-diazapentacyclo[6,4,0,$0^{2,6}$,$0^{7,11}$,$0^{10,12}$]dodec-3-ene: A Lowered Stereoselectivity by the Steric Inhibitions of the Rotation of an Intermediate Nitrogen-containing Diradical

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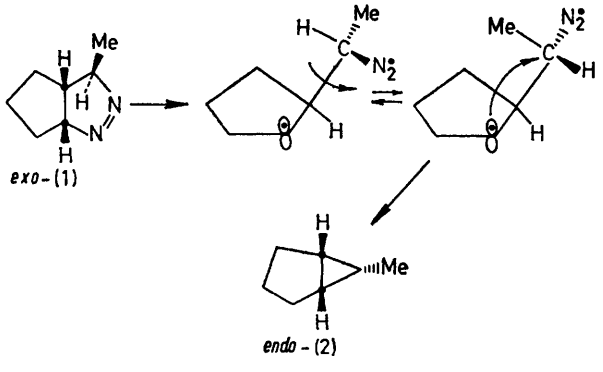
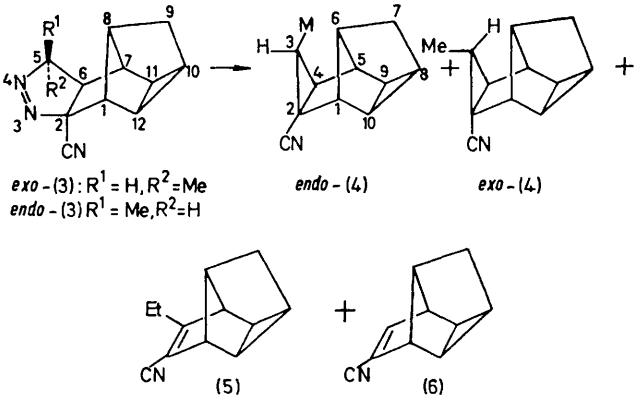
Summary Considerably lower stereoselective formation of the single inversion product was observed for 5-*endo*-methyl 2-cyano-3,4-diazapentacyclo[6,4,0,$0^{2,6}$,$0^{7,11}$,$0^{10,12}$]dodec-3-ene [*endo*-(3)] compared to its *exo*-isomer in their thermal and direct photodecompositions.

RECENTLY Condit and Bergman[1] have postulated that bicyclic pyrazolines [for example, *exo*-(**1**)] decompose *via* only one C–N bond cleavage in the rate-determining step, followed by the rotation of the C–C(N_2·) bond and loss of nitrogen by a rear-side attack with the C-radical to afford predominantly the single inversion product (Scheme 1). We have therefore studied the decomposition of a pyrazoline which was constructed so that it suffered steric inhibition of rotation in the intermediate nitrogen-containing diradical, in view of this possible lowering of the stereoselectivity. We prepared the *exo*- and *endo*-isomers of compound (**3**) by addition of diazoethane to 8-cyanodeltacyclene.[2]†



SCHEME 1



SCHEME 2

The thermal and photochemical decomposition products are shown in Scheme 2 and the Table; these products were

† In the cycloaddition, a 86 : 14 mixture of *exo*- and *endo*-(**3**) was obtained in 76% yield, from which *exo*-(**3**), m.p. 83—84° was separated. For the decomposition of *endo*-(**3**), a 65 : 35 *endo*–*exo*-mixture was used. In *exo*-(**3**) $J_{5,6}$ is 3·0 Hz, while $J_{5,6}$ in *endo*-(**3**) is 8·7 Hz.

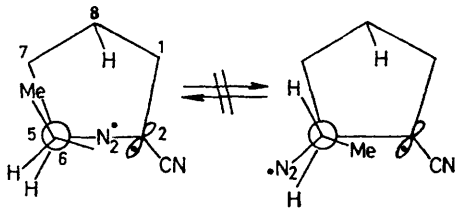
isolated by preparative g.l.c. and their structures were assigned on the basis of analytical and spectral data.‡§

TABLE Products formed in the thermal and photochemical decompositions of *exo*- and *endo*-(3)

Decomposition conditions	Substrate	Products (%)[a] *endo*-(4)	*exo*-(4)	(5)	(6)
180° (30—200 Torr in N_2)	*exo*-(3)	69·4	8·8	21·8	0
	endo-(3)	28·9	51·6	19·5	0
Direct irradiation[b]	*exo*-(3)	60·5	6·7	14·8	18·0
	endo-(3)	22·4	50·7	12·3	14·6
Sensitised irradiation[c]	*exo*-(3)	93·3	6·7	0	0
	endo-(3)	62·5	37·5	0	0

[a] G.l.c. analysis. [b] Irradiated with a 100-W high-pressure mercury lamp through Pyrex filter in $2·51 \times 10^{-3}$ M ether solution at 25°. [c] Same as direct irradiation except presence of benzophenone sensitizer (40 mol. equiv.),

Both *exo*- and *endo*-(3) decompose with predominant inversion of configuration at the methyl substituted carbon. However, the stereoselectivity for *endo*-(3) is considerably lower than that for *exo*-(3) in the thermal and direct photodecompositions. The observed stereoselectivity for *exo*-(3) is approximately the same as those reported in the decompositions of 4-*exo*-methyl-2,3-diazabicyclo[3,3,1]oct-2-ene [*exo*-(1)][1] and *cis*-3,5-dimethylpyrazoline,[3,4] while a similar pattern of stereoselectivity is also reported for *endo*-(1)[1] and *trans*-3,4-dimethylpyrazoline.[5,6] Hence, the decreased stereoselectivity found for *endo*-(3) should have a characteristic steric origin; one of the most plausible rationalizations is the steric inhibition of rotation of the nitrogen-containing diradical intermediate (7) to (8) by the presence of 8-H, assuming that an initial N–C(CN) bond cleavage occurs.¶



(7) (8)

In the sensitized photodecomposition, both *exo*- and *endo*-(3) gave predominantly *endo*-(4), in contrast to the results of the direct photodecomposition, although similar results have been reported for other systems;[1,4] this could be rationalized by a slow ring closure of the triplet diradical.[5]

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‡ All new compounds reported here had satisfactory analyses.

§ Although the n.m.r. spectra of *exo*- and *endo*- (4) were very similar, characteristic signals were observed at δ 1·84 and 1·11 for 4-H of *exo*-(4) and 3-H of *endo*-(4), respectively; comparison with data for 2-*endo*-cyanopentacyclo[4,4,0,$0^{2,4}$,$0^{5,9}$,$0^{8,10}$]nonane, m.p. 50—51°, shows that $J_{3,4}$ for *exo*-(4) is *ca.* 4·5 Hz, and $J_{3,4}$ for *endo*-(4) is 7·5 Hz.

¶ A π-cyclopropane intermediate is not reasonable in the present system for the same reason as postulated in ref. 1.

[1] P. B. Condit and R. G. Bergman, *Chem. Comm.*, 1971, 4. See also W. R. Roth and M. Martin, *Annalen*, 1967, **702**, 1; D. H. White, P. B. Condit, and R. G. Bergman, *J. Amer. Chem. Soc.*, 1972, **94**, 7931.
[2] T. Sasaki, S. Eguchi, M. Sugimoto, and F. Hibi, *J. Org. Chem.*, 1972, **37**, 2317.
[3] R. J. Crawford and A. Mishra, *J. Amer. Chem. Soc.*, 1966, **88**, 3963. See also M. P. Schneider and R. J. Crawford, *Canad. J. Chem.*, 1970, **48**, 628.
[4] R. Moore, A. Mishra, and R. J. Crawford, *Canad. J. Chem.*, 1968, **46**, 3305.
[5] *Cf.* S. D. Nowacki, P. B. Do, and F. H. Dorer, *J.C.S. Chem. Comm.*, 1972, 273.