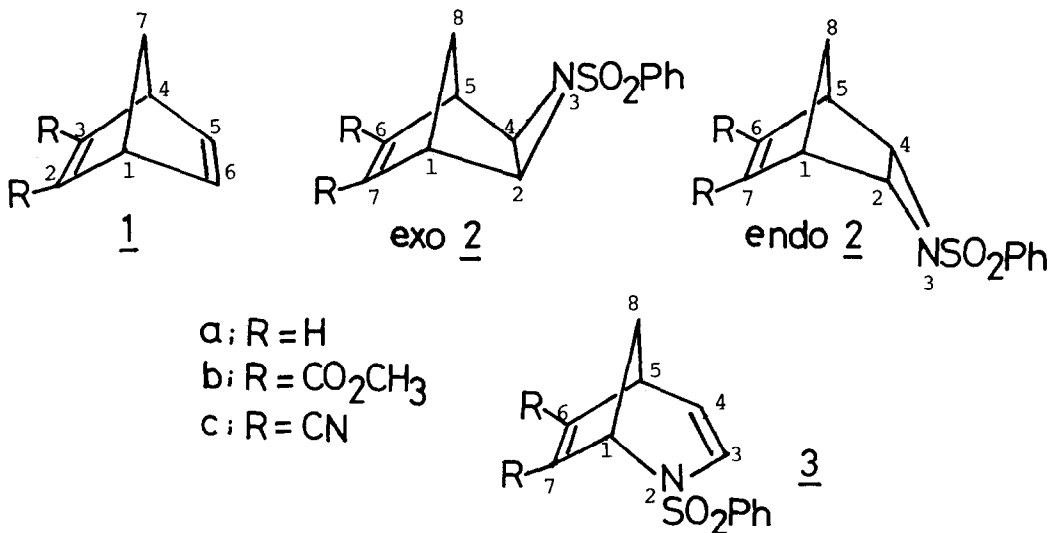


THE THERMAL REARRANGEMENTS OF THE 6,7-DISUBSTITUTED  
3-BENZENESULFONYL-3-AZATRICYCLO[3.2.1.0<sup>2,4</sup><sub>exo</sub>]OCT-6-ENES

Katsumi Umamo\*, Hisaji Taniguchi, Hiroo Inoue, and Eiji Imoto  
Department of Applied Chemistry, College of Engineering, University  
of Osaka Prefecture, Mozu-Umemachi, Sakai, Osaka 591, Japan

Previously it has been reported that norbornadiene (1a) reacts with benzenesulfonyl azide to give 3-benzenesulfonyl-3-azatricyclo[3.2.1.0<sup>2,4</sup><sub>exo</sub>]oct-6-ene (exo 2a) via 1,3-dipolar cycloaddition.<sup>1</sup> In this reaction, the formation of exo 2a was followed by NMR spectroscopy, but not by isolation, since the exo 2a undergoes readily rearrangement to 2-benzenesulfonyl-2-azabicyclo[3.2.1]-oct-3,6-diene (3a).<sup>1</sup> Owing to this difficulty of isolation, detailed descriptions in reactivity of exo 2a and the related aziridines are lacking.

We found that exo 2a, 3-benzenesulfonyl-6,7-bis(methoxycarbonyl)-3-azatricyclo[3.2.1.0<sup>2,4</sup><sub>exo</sub>]oct-6-ene (exo 2b), 3-benzenesulfonyl-6,7-dicyano-3-azatricyclo[3.2.1.0<sup>2,4</sup><sub>exo</sub>]oct-6-ene (exo 2c) and their endo isomers (endo 2b and 2c) are isolated successfully in the reactions of benzenesulfonyl azide with 1a, 2,3-bis(methoxycarbonyl)-norbornadiene (1b), and 2,3-dicyano-norbornadiene (1c)



respectively.<sup>2</sup> We now wish to report our findings on the rearrangements of these aziridines and discuss the mechanism of the rearrangement on the basis of the cyclic three-system interaction theory.

The thermal rearrangements of the unsaturated aziridines (exo 2a-c and endo 2b,c) produced were carried out using benzene, xylene, and o-dichlorobenzene as the reaction solvent. These data are collected in Table 1.

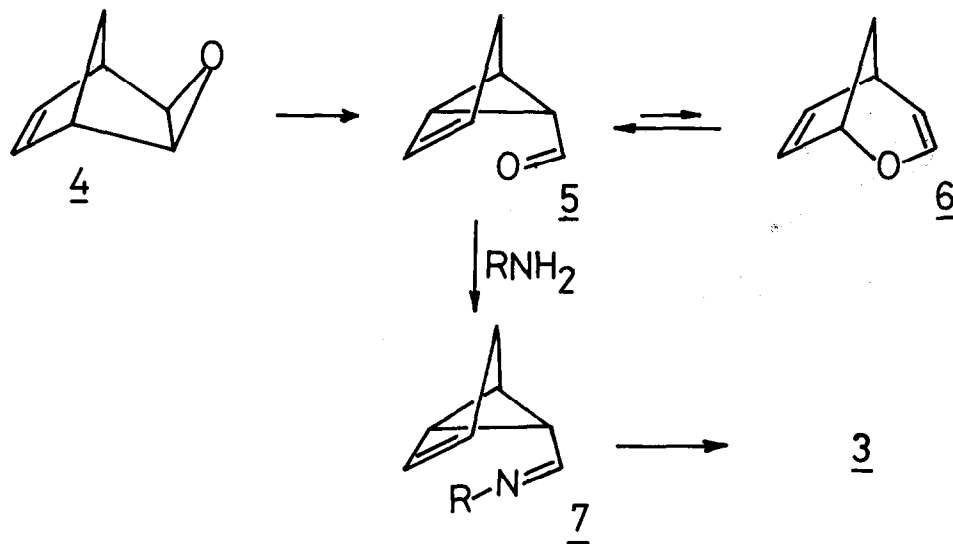
Table 1 The thermal rearrangements of the unsaturated aziridines

Entry	Aziridine	Solvent <sup>a</sup>	Temp (°C)	Time (hr)	Yield of <u>3</u> (%)	Recovered aziridine (%)	T <sub>1/2</sub> <sup>b</sup> (min)
1	exo <u>2a</u>	A	80	5	98	0	51
2	exo <u>2b</u>	A	80	20	0	100	
3	exo <u>2b</u>	B	80	20	0	100	
4	exo <u>2b</u>	B	139	11	99	0	72
5	exo <u>2b</u>	C	139	6	100	0	42
6	exo <u>2b</u>	C	179	0.2	100	0	<4
7	exo <u>2c</u>	A	80	20	0	100	
8	exo <u>2c</u>	B	139	20	<5	>95	
9	exo <u>2c</u>	C	139	20	19	81	>4500
10	exo <u>2c</u>	C	179	7	100	0	63
11	endo <u>2b</u>	C	179	20	0	100	
12	endo <u>2c</u>	C	179	20	0	100	

a) The symbols A, B, and C represent benzene, xylene, and o-dichlorobenzene respectively. b) The symbol T<sub>1/2</sub> represents a half-life.

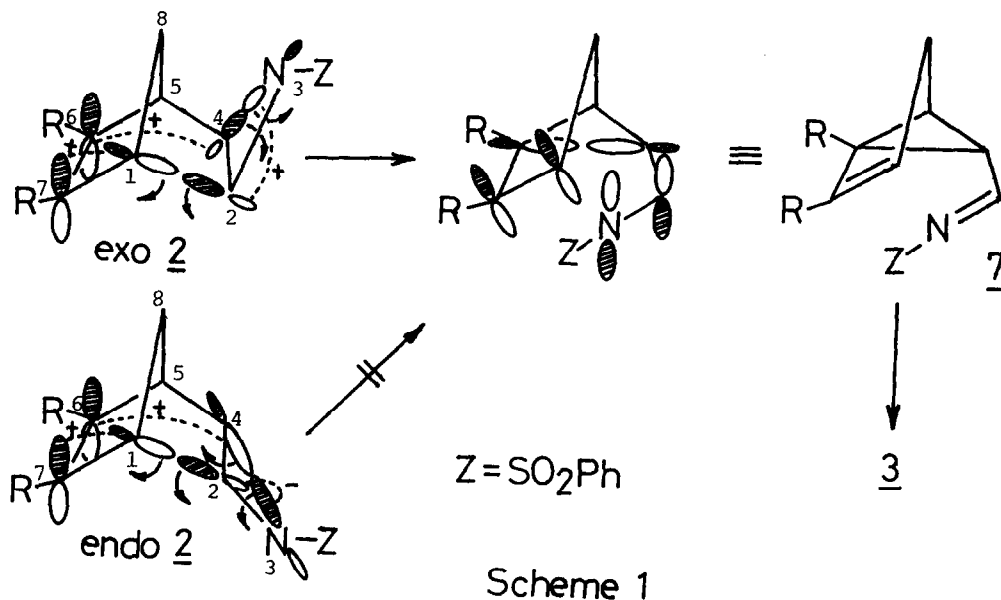
The results are summarized as follows. 1) All of exo 2a-c underwent rearrangement to the corresponding bicyclic dienes (3a-c)<sup>2</sup> quantitatively (Entries 1, 4-6, and 10), but endo 2b and 2c did not do it under similar conditions (Entries 11 and 12).<sup>3</sup> Previously it has been reported that endo 2a is prepared by the decarboxylation of 3-benzenesulfonyl-3-azatricyclo-[3.2.1.0<sup>2,4</sup>endo]octane-exo-cis-6,7-dicarboxylic acid with Pb(OAc)<sub>4</sub> in dry pyridine at 80 °C.<sup>4</sup> This fact also supports that endo 2a does not undergo rearrangement under the conditions described in Table 1. Thus, it was proved that only exo 2 undergoes rearrangement to 3. 2) The half-lives of the rearrangements of exo 2 indicate that the reactions depend remarkably on the temperature rather than the solvent (Entries 4-6 and 8-10). 3) The introduction of the electron-withdrawing substituent such as the methoxycarbonyl or cyano group in the double bond made it difficult to undergo rearrangement (Entries 1, 4, and 10).

Since it has been demonstrated that 3-oxatricyclo[3.2.1.0<sup>2,4</sup>]exooct-6-ene (4) undergoes rearrangement to 2-oxabicyclo[3.2.1]oct-3,6-diene (6) via syn-bicyclo[3.1.0]hex-2-ene-6-carbaldehyde (5)<sup>5</sup> and that 5 reacts with primary amines to give 3 via the imines (7),<sup>6</sup> the thermal rearrangement of exo 2 is rationalized by assuming an intermediary formation of 7, followed by the Cope rearrangement giving 3. The remarkable difference in reactivity between exo and endo 2 can



be reasonably explained by the cyclic three-system interaction theory.<sup>7</sup> As is shown in Scheme 1, the HOMO of the C<sub>6</sub>=C<sub>7</sub> π bond (C<sub>6</sub>=C<sub>7</sub> HOMO), the LUMO of the C<sub>4</sub>-N<sub>3</sub> σ bond (C<sub>4</sub>-N<sub>3</sub> LUMO), and the LUMO of the C<sub>1</sub>-C<sub>2</sub> σ bond (C<sub>1</sub>-C<sub>2</sub> LUMO) are used as three orbitals of exo and endo 2. In the case of exo 2, the sign relation among three orbitals is an in-phase combination, while, in the case of endo 2, that between C<sub>1</sub>-C<sub>2</sub> LUMO and C<sub>4</sub>-N<sub>3</sub> LUMO is an out-of-phase combination. This fact means that endo 2 can not undergo rearrangement.

The methoxycarbonyl and cyano groups in the C<sub>6</sub>=C<sub>7</sub> bond contribute to weakening the interaction between the C<sub>6</sub>=C<sub>7</sub> HOMO and the C<sub>4</sub>-N<sub>3</sub> LUMO or C<sub>1</sub>-C<sub>2</sub> LUMO, since the energy level of the C<sub>6</sub>=C<sub>7</sub> HOMO becomes lower by the substituents.<sup>8</sup> Consequently, the rearrangements of exo 2b and 2c to 3b and 3c are explained to become more difficult than that of exo 2a.



## References and Notes

- 1) A. C. Oehlschlager and L. H. Zalkow, *J. Org. Chem.*, **30**, 4205 (1965).
- 2) The detailed procedures and the structure proof will be reported elsewhere.
- 3) Even when endo 2c was heated 250 °C without solvent, 3c was not obtained at all.
- 4) A. C. Oehlschlager and L. H. Zalkow, *Can. J. Chem.*, **47**, 461 (1969).
- 5) M. Rey and A. S. Dreiding, *Helv. Chim. Acta.*, **48**, 1985 (1965).
- 6) P. Barraclough and D. W. Young, *J. Chem. Soc., Perkin Trans. 1*, 2354 (1975).
- 7) S. Inagaki, H. Fujimoto, and K. Fukui, *J. Am. Chem. Soc.*, **98**, 4693 (1976).
- 8) (a) I. Fleming, "Frontier orbitals and Organic Chemical Reactions", Wiley-Interscience, New York, N. Y. 1976, p. 114; (b) K. N. Houk, *J. Am. Chem. Soc.*, **95**, 4092 (1973).

(Received in Japan 30 September 1978)