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Ab Initio Transition Structures for Diels–Alder Reactions of 2-Azabutadiene with Alkenes and Alkynes: Effects of Substituents, the Aza Group, and Catalysis on Reactivity

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Transition structures for the Diels–Alder reactions of 2-azabutadiene with ethylene, acrylonitrile, vinyl chloride, vinyl alcohol, acetylene, cyanoacetylene, and dicyanoacetylene have been located with ab initio molecular orbital calculations and the 3-21G basis set; the activation energies were also evaluated by single-point calculations at the RHF/6-31G* and MP2/6-31G* theory levels on the 3-21G geometries. The activation energies and asynchronicities of these reactions follow the same trends as the corresponding reactions of butadiene with alkenes and alkynes. The effect of the aza group in the diene is very small. The influence of a Lewis acid complexed to the 2-azabutadiene was also studied.

Introduction

The Diels–Alder reaction is the most general method employed for the synthesis of six-membered rings.[1] The hetero-Diels–Alder reaction is also becoming a very useful method for the preparation of six-membered-ring heterocycles.[2] In contrast to all-carbon Diels–Alder reactions, there are few theoretical studies on the mechanism of the hetero-Diels–Alder reactions.[3] We recently undertook a study of several hetero-Diels–Alder reactions, including those of 1-azadienes.[4] In this paper, theoretical studies of transition structures for the Diels–Alder reactions of 2-azabutadiene, 1, with ethylene and acetylene derivatives (Scheme I) are reported.

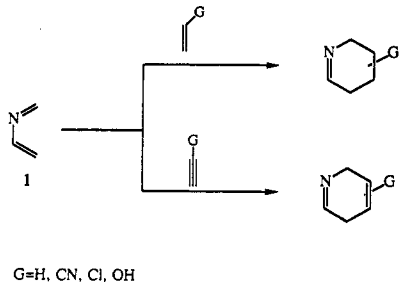
The participation of 2-azabutadiene derivatives in Diels–Alder reactions has been reported frequently in the literature.[5,6] Thus, siloxy-substituted 2-azabutadienes prepared from imides react with typical electron-poor dienophiles like acrylates, maleic anhydride, and acetylenic esters.[6] Thermolysis of substituted 1-azirines[7] or 1-azetines[8] leads to 2-azabutadiene derivatives; these undergo Diels–Alder reactions with olefinic and acetylenic dienophiles. The reactions of unactivated 2-azabutadienes with electron-poor alkenes,[9] heterodienophiles,[9,10] and electron-rich alkenes[11] have also been studied. Some selected examples of these reactions are given in Figure 1.

In this paper we have addressed the following points: (1) How does aza substitution influence the geometries and the activation energies of the transition structures of the Diels–Alder reactions of 2-azabutadienes with alkenes and alkynes? (2) What is the influence of the dienophile substitution on the degree of asynchronicity, activation energy, and in the regio- and stereochemistry of these reactions? (3) What is the role of Lewis acids on the catalysis of the Diels–Alder reactions of 2-azabutadienes?

Computational Methods

The calculations were carried out with the restricted Hartree-Fock method, using the GAUSSIAN 88 program.[12] In the case of the parent Diels–Alder reaction of butadiene with ethylene, RHF, MP2, and MCSCF calculations give similar results, supporting the synchronous mechanism for this reaction.[13-17] The inclusion of polarization functions and electron correlation to fourth order (MP4SDTQ/6-31G*) gives an activation energy very close to the experimental value.[13b] Also, a reaction path involving a diradical intermediate was found at MCSCF/4-31G theory level,[13a] but is disfavored by 2 kcal/mol compared to the synchronous concerted mechanism. In the case of the Diels–Alder reaction of 2-azabutadiene with ethylene, the influence of the aza

Scheme I



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(1) Carruthers, W. *Cycloaddition Reactions in Organic Synthesis*; Pergamon Press: New York, 1990.

(2) Boger, D. L.; Weinreb, S. N. *Hetero Diels–Alder Methodology in Organic Synthesis*; Academic Press: San Diego, 1987.

(3) Tietze, L. F.; Fennen, J.; Ernst, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1371. Ikchoon, L.; Han, E. S.; Choi, J. Y. *J. Comput. Chem.* **1984**, *5*, 606. McCarrick, M. A.; Wu, Y.-D.; Houk, K. N. *J. Am. Chem. Soc.* **1992**, *114*, 1499.

(4) McCarrick, M. A.; Houk, K. N., manuscript in preparation.

(5) (a) Boger, D. L. *Tetrahedron* **1983**, *39*, 2869. (b) Barluenga, J.; Joglar, J.; Gonzalez, F. J.; Fustero, S. *Synlett* **1990**, 129.

(6) Demoulin, A.; Gorissen, H.; Hesbain-Frisque, A.-M.; Ghosez, L. *J. Am. Chem. Soc.* **1975**, *97*, 4409.

(7) Sanite, F.; Serckx-Poncin, B.; Hesbain-Frisque, A.-M.; Ghosez, L. *J. Am. Chem. Soc.* **1982**, *104*, 1428.

(8) Aue, D. H.; Thomas, D. *J. Org. Chem.* **1975**, *40*, 1349.

(9) Barluenga, J.; González, F. J.; Fustero, S.; Foces-Foces, M. C.; Hernández Cano, F.; San Feliciano, A. *J. Chem. Res., Synop.* **1989**, 66.

(10) Barluenga, J.; Joglar, J.; Fustero, S.; Kruger, C.; Romão, M. J. *Chem. Ber.* **1985**, *118*, 3652. Barluenga, J.; González, F. J.; Fustero, S.; Gotor, V. *J. Chem. Soc., Chem. Commun.* **1986**, 1179. Barluenga, J.; González, F. J.; Fustero, S. *Tetrahedron Lett.* **1989**, 2685.

(11) (a) Cheng, Y.-S.; Ho, E.; Mariano, P. S.; Ammon, H. L. *J. Org. Chem.* **1985**, *50*, 5678. (b) Ho, E.; Cheng, Y.-S.; Mariano, P. S. *Tetrahedron Lett.* **1988**, 4799.

(12) GAUSSIAN 88. Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A. Gaussian Inc., Pittsburgh, PA, 1988.

(13) (a) Bernardi, F.; Bottini, A.; Field, M. J.; Guest, M. F.; Hillier, I. H.; Robb, M. A.; Venturini, A. *J. Am. Chem. Soc.* **1988**, *110*, 3050. (b) Bach, R. D.; McDouall, J. J. W.; Schlegel, H. B.; Wolber, G. J. *J. Org. Chem.* **1989**, *54*, 2931.

(14) Houk, K. N.; Lin, Y.-T.; Brown, F. K. *J. Am. Chem. Soc.* **1986**, *108*, 554.

(15) Houk, K. N.; Loncharich, R. J.; Blake, J. F.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 9172.

(16) Birney, D. M.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 4127.

(17) Loncharich, R. J.; Houk, K. N. Unpublished results.

0022-3263/92/1957-3031$03.00/0 © 1992 American Chemical Society

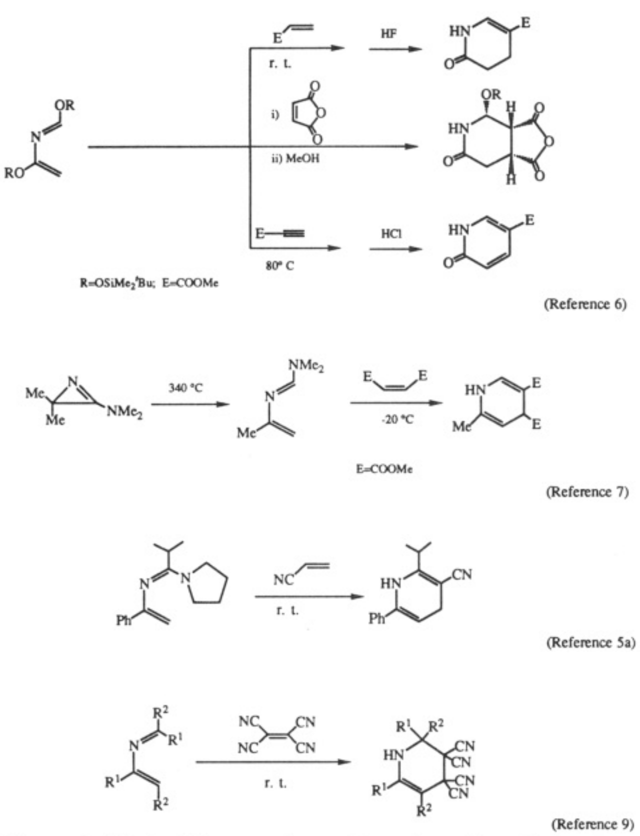


Figure 1. Diels–Alder reactions of 2-azabutadiene derivatives with alkenes and alkynes.

group on the activation energy and asynchronicity was found to be very small at all levels studied (see below), and it can be expected that the concerted reaction mechanism remains favored at higher levels of theory as in the parent reaction of butadiene with ethylene.

All transition structures were fully optimized with the 3-21G basis set;[18] each transition structure has only one imaginary frequency corresponding to the formation of the two new carbon–carbon bonds. In addition, the energies were also evaluated by single-point calculations with the 6-31G* basis set and at the MP2/6-31G* theory level[18] on the 3-21G geometries.

Results and Discussion

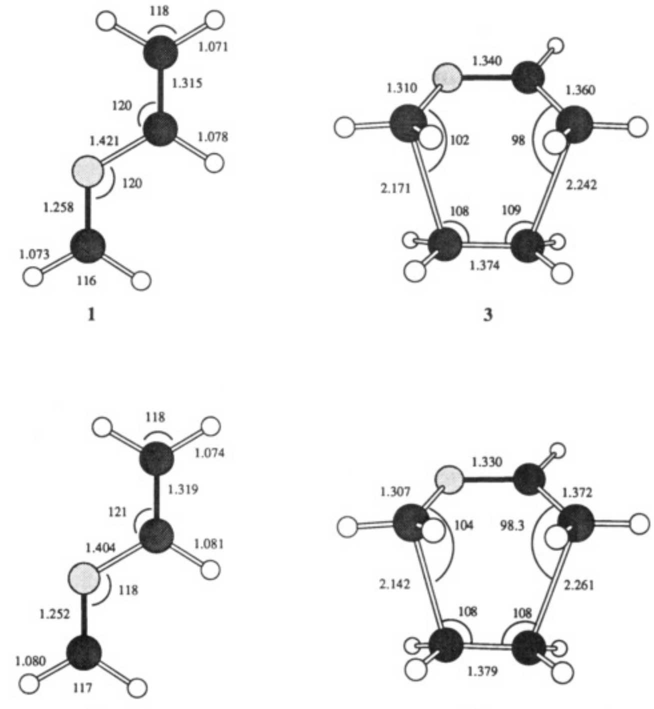
Transition structures were located for the reactions of 2-azabutadiene, **1**, with ethylene, acrylonitrile, vinyl chloride, vinyl alcohol, acetylene, cyanoacetylene, and dicyanoacetylene; in the case of acrylonitrile, vinyl chloride, and vinyl alcohol, four transition structures, leading to the two possible regioisomers and the endo and exo stereoisomers, were considered. The two possible regioisomeric transition states in the reaction with cyanoacetylene were also located.

The effects of the Lewis acid catalyst on the energy and geometry of the transition structures were studied. The transition structures for the H^+- and BH_3-catalyzed reactions of 2-azabutadiene with ethylene were found. The transition structure for the prototype reaction of 2-azabutadiene with ethylene was also fully optimized with the 6-31G* basis set, and only minor changes in the geometry were found as compared to the 3-21G geometries.

Table I. Calculated Activation Energies (kcal/mol) for the Diels–Alder Reactions of 2-Azabutadiene with Ethylene and Acetylene Derivatives

transition structure	E_a (3-21G)	E_a (6-31G*//3-21G)	E_a (MP2/6-31G*//3-21G)
3	32.2	41.3 (40.8)[a]	14.0
4	30.5	39.5	12.1
5	32.7	41.9	13.9
6	32.4	42.1	12.0
7	33.3	42.8	12.4
8	31.9	43.3	15.6
9	35.5	46.0	17.4
10	33.2	44.8	15.0
11	35.1	45.9	16.1
12	34.8	45.8	15.8
13	33.8	44.7	13.9
14	32.8	42.5	13.6
15	34.7	43.3	15.0
16	36.3	43.4	16.3
17	35.4	41.3	14.0
18	36.5	42.7	13.2
19	35.5	39.9	11.2
21	25.8	34.2	8.5
23	9.3	16.0	1.4

[a] 6-31G*//6-31G*.



1 **3**

1A **3A**

Figure 2. 3-21G (**1**) and 6-31G* (**1A**) optimized structures (Å, deg) of 2-azabutadiene and 3-21G (**3**) and 6-31G* (**3A**) optimized transition structures for the Diels–Alder reaction of 2-azabutadiene with ethylene.

The calculated activation energies with respect to the reactants, and the total energies of *s-trans*-2-azabutadiene, transition structures, H^+- and BH_3-complexes of 2-azabutadiene, and the adduct of **1** with ethylene, **2**, are given in Table I and II, respectively. The optimized transition structures are shown in Figures 2–5. The 3-21G and 6-31G* optimized structures of 2-azabutadiene are shown in Figure 2.

Energetics of the Transition Structures and Heat of Reaction. The activation energy calculated for transition structure **3** (Figure 2) for the reaction of 2-azabutadiene and ethylene is lower by 3.7, 1.7, and 3.6 kcal/mol than for the reaction of butadiene and ethylene[14,17] at 3-21G, 6-31G*//3-21G, and MP2/6-31G*//3-21G levels, respectively.

There are no experimental measures of the activation energy for the Diels–Alder reaction of 2-azabutadiene with

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(18) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

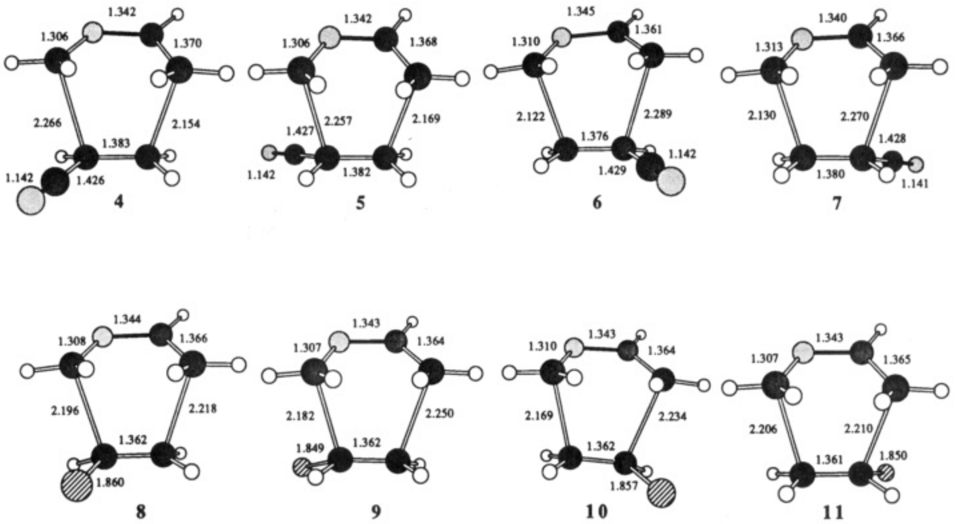


Figure 3. 3-21G optimized transition structures (Å) for the Diels–Alder reaction of 2-azabutadiene with acrylonitrile (**4–7**) and with vinyl chloride (**8–11**).

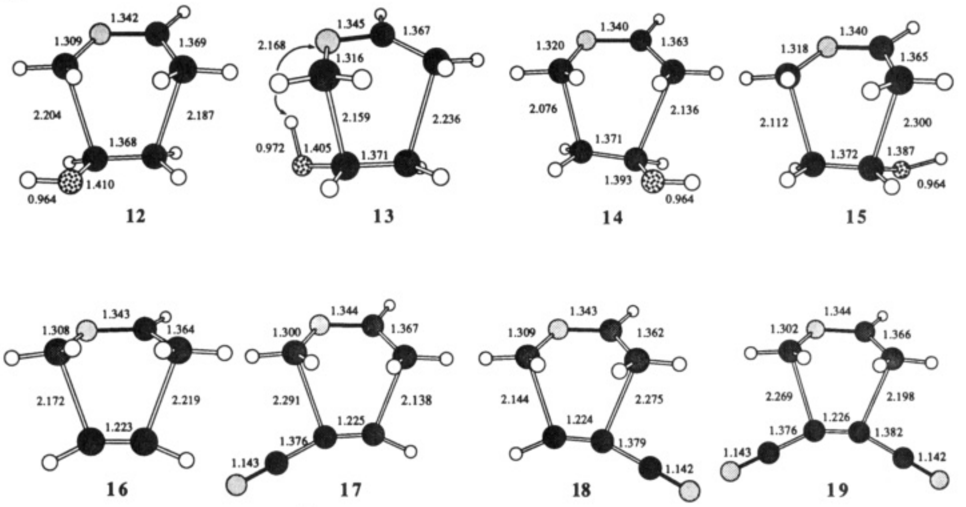


Figure 4. 3-21G optimized transition structures (Å) for the Diels–Alder reaction of 2-azabutadiene with vinyl alcohol (**12–15**), acetylene (**16**), cyanoacetylene (**17, 18**), and dicyanoacetylene (**19**).

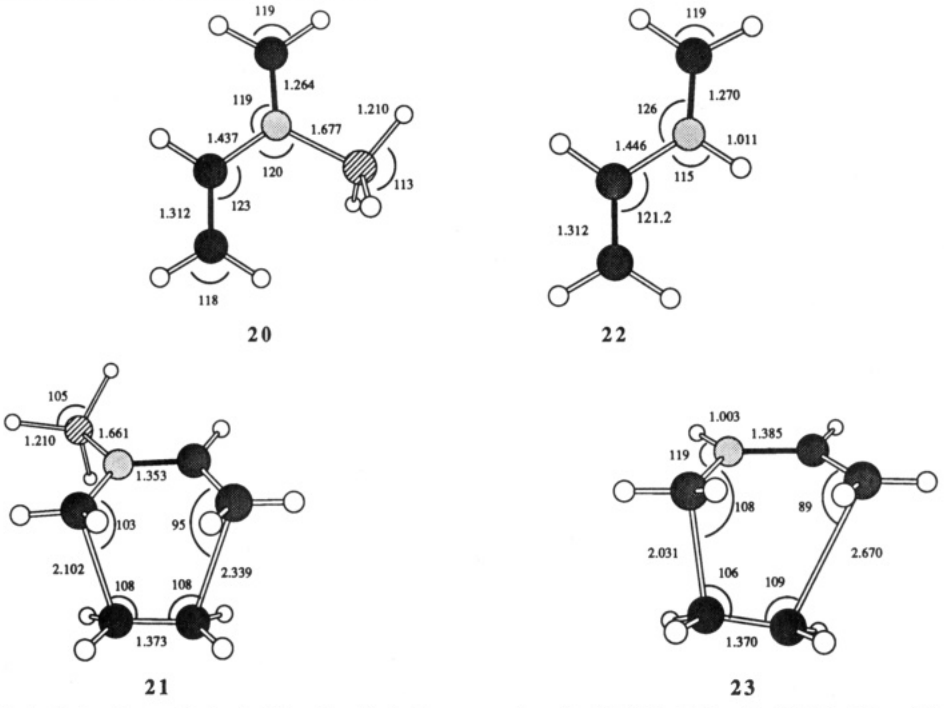


Figure 5. 3-21G optimized structures (Å, deg) of the 2-azabutadiene complexed with BH_3 (**20**) and with H^+ (**22**) and transition structures (Å, deg) for the BH_3- and H^+-catalyzed Diels–Alder reaction of 2-azabutadiene with ethylene (**21–23**).

Table II. Total Energies (in au) of Reactants and Transition Structures for the Diels–Alder Reactions of 2-Azabutadiene with Alkenes and Alkynes

species[a]	3-21G	6-31G*// 3-21G	MP2/6-31G*// 3-21G
1	−169.949 37	−170.911 10	−171.444 65
2	−247.616 36		
3	−247.498 91	−248.877 05	−249.706 49
4	−338.721 23	−340.615 96	−341.718 59
5	−338.717 58	−340.612 14	−341.715 77
6	−338.718 14	−340.611 84	−341.718 76
7	−338.716 62	−340.610 57	−341.718 22
8	−704.213 36	−704.772 37	−708.731 54
9	−704.207 61	−704.768 00	−708.728 58
10	−704.211 38	−707 770 01	−708.732 48
11	−704.208 24	−707.768 17	−708.730 76
12	−321.930 73	−323.722 20	−324.734 17
13	−321.933 21	−323.723 85	−324.737 13
14	−321.933 95	−323.727 36	−324.737 68
15	−321.931 02	−323.726 08	−324.735 51
16	−246.287 51	−247.659 70	−248.483 34
17	−337.506 55	−339.394 12	−340.494 37
18	−337.504 92	−339.391 92	−340.495 58
19	−428.718 09	−431.119 45	−432.501 05
20	−196.235 56	−197.331 78	−197.960 84
21	−273.795 40	−275.309 03	−276.231 40
22	−170.321 58	−171.271 28	−171.796 43
23	−247.907 74	−249.277 40	−250.083 64

[a] The total energy TS **3A** is −248.877 69 au.

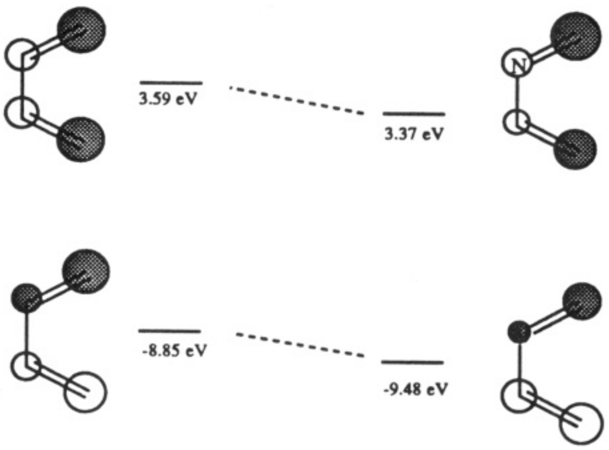
ethylene, but in the case of the reaction of butadiene with ethylene, the activation energy has been measured to be 27.5 kcal/mol[19a] and 24.2–26.7 kcal/mol.[19b–d] These results indicates that the MP2 calculations underestimate the activation energy by 8–12 kcal/mol. It has been shown before that the MP2 calculations often overestimate the effect of electron correlation on activation energies, but the inclusion of more terms in the perturbation expansion, MP3 and MP4, results in oscillations in the value of the activation energy.[20] Bach and co-workers[13b] have found, for the reaction of butadiene with ethylene, a very good agreement between the value of the activation energy calculated at MP4 theory level and the experimental value. In the present study, the MP2 theory level was used to compute the energies, but the effect of the higher-order correlation corrections is expected to be similar for the isomeric transition structures.

The structure of the Diels–Alder adduct of 2-azabutadiene and ethylene, tetrahydropyridine **2**, was optimized with the 3-21G basis set. The heat of reaction is calculated to be −41.4 kcal/mol which is close to the calculated value for the reaction of butadiene with ethylene.[14]

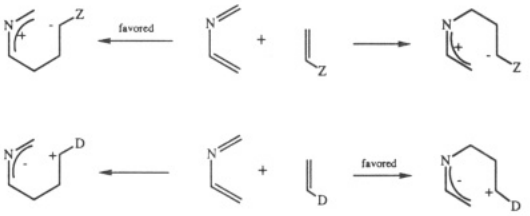
For the reaction with acrylonitrile, a typical electron-deficient alkene (transition structures **4–7** in Figure 3), the activation energy is lower by 1.7 and 1.9 kcal/mol (3-21G and MP2/6-31G*//3-21G) than for the reaction with ethylene. This substituent effect on the activation energy has been also found in the ab initio calculations on the Diels–Alder reaction of butadiene with acrylonitrile.[4]

The calculated 3-21G activation energy for the reaction of 2-azabutadiene with vinyl chloride via **8** (see transition structures **8–11** in Figure 3) is 0.3 kcal/mol lower than in the case of the reaction of 2-azabutadiene with ethylene, but at 6-31G*//3-21G and MP2/6-31G*//3-21G levels, this activation energy is higher by 2.0 and 1.6 kcal/mol, respectively.

Chart I



Scheme II



In the reactions of 2-azabutadiene with both acrylonitrile and vinyl chloride, there is an anomaly in the energies of the transition structures **6** and **10** that will be discussed later.

For the reactions of 2-azabutadiene with vinyl alcohol, four transition structures were located (**12–15** in Figure 4). Transition structure **14** is the most stable. Its activation energy relative to the parent reaction of 2-azabutadiene with ethylene is 0.6, 1.2, and −0.4 kcal/mol at 3-21G, 6-31G*//3-21G, and MP2/6-31G*//3-21G levels. The reaction of 2-azabutadiene and vinyl alcohol appears to be very slightly favored, at the highest level of theory studied, compared to the parent reaction.

The Diels–Alder reaction of 2-azabutadiene with acetylene (Figure 4, TS **16**) is disfavored compared to the reaction between 2-azabutadiene and ethylene, by 4.1 (3-21G), 2.1 (6-31G*//3-21G), and 2.3 (MP2/6-31G*//3-21G) kcal/mol. Cyano substituents lower the activation energy; thus, the MP2/6-31G*//3-21G relative activation energies for the reactions of 2-azabutadiene with acetylene (TS **16**), cyanoacetylene (TS **17** and **18**), and dicyanoacetylene (TS **19**) are 0.0, −2.3, −3.1, and −5.1 kcal/mol, respectively. The 3-21G activation energy for TS **18** is 0.2 kcal/mol higher than for the reaction of 2-azabutadiene with acetylene.

In summary, the Diels–Alder reaction of 2-azabutadiene and ethylene is predicted to be slightly favored relative to the reaction of butadiene with ethylene. The predicted activation energies of both reactions are lowered by cyano substitution in the dienophile.[15] In the case of the 2-azabutadiene, the activation energy is increased by substitution with chlorine, and the OH group has a very small effect. The cycloaddition with acetylene is disfavored relative to ethylene. According with the results of this calculations, the 2-azabutadiene derivatives react preferentially with electron-deficient dienophiles.[2,5]

Regioselectivity and Stereoselectivity. The regioselectivity of reactions can be predicted by various qualitative methods. The 3-21G frontier molecular orbitals of butadiene and 2-azabutadiene are shown schematically in Chart I.

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(19) (a) Rowley, D.; Steiner, H. *Discuss. Faraday Soc.* **1951**, *10*, 198. (b) Uchiyama, M.; Tomioka, T.; Amano, A. *J. Phys. Chem.* **1964**, *68*, 1878. (c) Tsang, W. *J. Chem. Phys.* **1965**, *42*, 1805. (d) Tardy, D. C.; Ireton, R.; Gordon, A. S. *J. Am. Chem. Soc.* **1979**, *101*, 1508.

(20) Jensen, F.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 3139.

The coefficients at C-2 of butadiene are relatively small, and the influence of 2-aza substitution is correspondingly small.

The HOMO is only slightly polarized, and C-1 and C-4 have nearly the same coefficients. The effect on the LUMO coefficients is somewhat larger, and the C-1 coefficient is larger than the C-4 coefficient.

The frontier MO polarizations imply that C-1 is more electrophilic than C-4, while C-4 is slightly more nucleophilic than C-1. These conclusions fit with considerations of relative stabilities of potential intermediates (Scheme II). Some asynchronism in the direction of the formal mode of bond formation is expected even in concerted transition structures.

The frontier MO energies imply that the 2-azadiene should be slightly more electrophilic than butadiene. Most experimentally studied 2-azadienes also have one or more electron-donor substituents, and these make the diene relatively nucleophilic.

In the Diels–Alder reactions of 2-azabutadiene with acrylonitrile, vinyl chloride, vinyl alcohol, and cyanoacetylene, two regioisomers are possible. With acrylonitrile, transition structure 4 (Figure 3) is favored by 1.9 and 2.6 kcal/mol (3-21G and 6-31G*//3-21G, respectively) with respect to the regioisomeric transition structure 6. At the MP2/6-31G*//3-21G level, this preference disappears, and the transition structure 6 is now favored by a small amount (0.1 kcal/mol). The predicted regiochemistry at 3-21G and 6-31G*//3-21G levels agrees with the reported experimental results in the Diels–Alder reactions of 2-azabutadiene derivatives with unsymmetrical electron-poor alkenes.[5a] The general trends in the regioselectivity of the Diels–Alder reactions of 2-azabutadienes[5a] are quite similar to those observed in the case of analogous all-carbon dienes;[21] as in these cases, the regioselectivity in the case of the 2-azabutadienes is mainly controlled by the substituents, and the nitrogen seems to have little influence.

A similar situation occurs in the case of vinyl chloride: at 3-21G and 6-31G*//3-21G levels, the regioisomeric transition structure 8 is favored by 1.2 and 1.5 kcal/mol, respectively, but 10 is preferred by 0.6 kcal/mol at MP2/6-31G*//3-21G level.

In the Diels–Alder reaction of 2-azabutadiene with vinyl alcohol, a model for typical electron-rich dienophiles, the regioisomer corresponding to the transition structure 14 is favored by 1.0 kcal/mol at the 3-21G level, but only by 0.3 kcal/mol at MP2/6-31G*//3-21G level of theory; this is the regioisomer obtained in the Diels–Alder reaction of 2-azabutadienes with electron-rich alkenes like enol ethers[11] and enamines.[5a]

With cyanoacetylene, there are also two different predictions: at 3-21G and 6-31G*//3-21G levels, the regioisomeric transition structure 17 is predicted to be the most stable, by 1.1 and 1.4 kcal/mol, respectively. At the MP2/6-31G*//3-21G level, the prediction is reversed, and the regioisomer corresponding to the transition structure 18 is preferred by 0.8 kcal/mol.

There are no examples of the Diels–Alder reaction of 2-azabutadienes with cyanoacetylene, but in the reactions with other electron-deficient dienophiles like methyl propiolate,[6] the regiochemistry agrees with the predicted one here at 3-21G and 6-31G*/3-21G levels (see Figure 1).

The RHF predictions seem more in accord with expectation and experience on substituted dienes than the MP2 predictions. This may be related to the fact that geometries were not reoptimized at the MP2 level, so the single point calculations may not reflect the true MP2 preferences. It may also be related to the overestimate of correlation energy at the MP2/6-31G* level.[20]

Table III. Calculated Endo–Exo Activation Energy Differences in the Diels–Alder Reactions of 2-Azabutadiene with Acrylonitrile, Vinyl Chloride, and Vinyl Alcohol

	$\Delta E_{\text{endo-exo}}$ (kcal/mol)		
dienophile	3-21G	6-31G*//3-21G	MP2/6-31G*//3-21G
acrylonitrile	2.2	2.4	1.8
vinyl chloride	3.6	2.7	1.4
vinyl alcohol	1.9	0.8	1.4

Stereochemistry. The endo–exo stereoselectivity was studied for the reactions of 2-azabutadiene with acrylonitrile, vinyl chloride, and vinyl alcohol. The results for the preferred regioisomer are summarized in Table III. As can be seen, in all cases the exo transition structure is predicted to be the most stable by about 1.4–1.8 kcal/mol at MP2/6-31G*//3-21G theory level.

How does this result compare with experiments? There is little stereochemical information about the Diels–Alder reactions of 2-azabutadienes because, in most cases, the cycloaddition reaction is followed by aromatization of the Diels–Alder adduct. In the reaction of siloxy-substituted 2-azabutadienes with maleic anhydride[5a,6] (see Figure 1), the stereochemistry of the reaction appears to be endo; on the other hand, the stereochemical preferences reported in the Lewis acid-catalyzed Diels–Alder reaction of 2-azabutadiene derivatives with enol ethers are strongly dependent on the type of substitution in the dienophilic double bond.[11] Thus, the calculations err in the preference for the exo transition structures, and probably higher level calculations will be required to reproduce the experimental observations.

In the case of Diels–Alder reaction of butadiene with acrylonitrile, there is a good agreement with the experiments because almost no selectivity is predicted: the exo transition structure is favored by 0.1 kcal/mol at the MP2/6-31G*//3-21G level), and, experimentally, in the reaction of cyclopentadiene with acrylonitrile, the endo configuration is favored by 0.2 kcal/mol.[15]

Asynchronicity and Geometry of the Transition Structures. The degree of asynchronicity in the formation of the two new carbon–carbon bonds in the Diels–Alder reaction has been debated for some time. The parent reaction is synchronous, but asymmetric substitution causes the transition structures to become asynchronous.[15,16] In the case of the Diels–Alder reaction of 2-azabutadiene with ethylene and acetylene derivatives, the transition structures located show only slight asynchronicity.

The 3-21G transition structure for the reaction of butadiene with ethylene is synchronous, with forming bonds length of 2.210 Å.[14] In the 3-21G transition structure 3 (Figure 1), the lengths of the two forming bonds are 2.242 and 2.171 Å (Δr = 0.071 Å); the forming bond at C-1 of the diene is shorter than for the butadiene reaction, and the forming bond at C-4 is slightly longer. In the 6-31G* transition structure 3A (Figure 1), there are minor changes compared to the 3-21G structure 3: the lengths of the two forming bonds are 2.261 and 2.142 Å. This can be compared to the bond lengths of 2.201 Å in the 6-31G* butadiene–ethylene transition structure.[13b]

In the other transition structures located, the asynchronicity is also small; when the dienophile is acrylonitrile or cyanoacetylene, the longer bond is always at the substituted dienophile terminus. This has been found previously in the transition structures of the reaction of bu-

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[21] Danishefsky, S. *Acc. Chem. Res.* 1981, *14*, 400.

tadiene with several cyanoethylenes.[15] In the case of vinyl chloride, the longer forming bond is always at the C-4 terminus of 2-azabutadiene. The transition structures **12**, **14**, and **15** for the reaction of 2-azabutadiene with vinyl alcohol have the longer bond at the OH-substituted terminus. In the most stable transition structure **13**, the OH-substituted terminus is shorter, a result of the hydrogen bonding involving the nitrogen of the diene. Taken together, these results are consistent with a one-step reaction pathway, with a small difference in forming CC bond lengths, as in all-carbon Diels–Alder reactions.[15]

Other geometrical features of the transition strucures for the Diels–Alder reaciton of 2-azabutadiene with ethylene and acetylene derivatives are similar to the ones previously reported for the parent reaction. The four carbon atoms involved in the formation of the two new bonds are pyramidalized, and C-5, which is not involved in the formation of bonds, is also pyramidalized. The out of plane angle is approximately 8°. The twisting between diene and dienophile moieties in the transition structures ranges between 2° and 10°.

From the preceeding data, we can conclude that the aza substitution does not alter significantly the geometry of the transition structure compared to the butadiene–ethylene Diels–Alder reaction.

Charge Separation in the Transition Structures. In all transition structures located, there is only small charge separation as assessed by Mulliken population analysis. In transition structures **3** (3-21G) and **4** (6-31G*), 0.03 and 0.04 electrons, respectively, are transferred from the ethylene to 2-azabutadiene. When the dienophile is vinyl alcohol, the charge transfer from the dienophile to the diene is 0.09 electrons. The reverse situation is found in the transition structures for the reaction with acrylonitrile and vinyl chloride, where charge transfer (0.05–0.08) from the diene to dienophile occurs. In the case of cyanoacetylene and dicyanoacetylene, 0.10 and 0.20 electrons are transferred from the dienophile to 2-azabutadiene. These values are of the same order of magnitude as those in the case of butadiene reactions: 0.11 electrons are transferred in the transition structure for the butadiene–acrylonitrile cycloaddition and 0.09 in the transition structure of the reaction of butadiene with acrolein.[16]

Transition Structure for the Lewis Acid-Catalyzed Diels–Alder Reaction of 2-Azabutadiene with Ethylene. Lewis acid catalysts have a large influence on the rates and even the mechanistic course of Diels–Alder reactions.[22] For this reason the effect of a Lewis acid on the mechanism of the addition of 2-azabutadiene to ethylene was studied, using BH$_3$ and H$^+$ as Lewis acid models. Several examples of the influence of the Lewis acid on the rates of [4 + 2]-cycloadditions of 2-azabutadienes have been reported.[11] It has been assumed that the Lewis acid catalyst coordinates to the nitrogen atom of the diene.

The optimized structure of the 2-azadiene–BH$_3$ complex **20** (Figure 4) was calculated at 3-21G level, and the energy was also evaluated at the MP2/6-31G*//3-21G level. The geometry of complex **20** is shown in Figure 4. The most remarkable feature in this structure is the polarization of the double CN bond in the 2-azabutadiene moiety, as indicated by the elongation of the C1–N2 and N2–C3 bonds.

The calculations predict that the activation energy of the Diels–Alder reaction of the 2-azadiene–BH$_3$ complex and ethylene (**21**, Figure 4) is lower by 6.4, 7.1, and 5.5 kcal/mol than for the parent reaction of 2-azabutadiene and ethylene, at 3-21G, 6-31G*//3-21G, and MP2/6-31G*//3-21G levels, respectively. The calculated activation energies are 25.8, 34.2, and 8.5 kcal/mol, respectively. A similar trend was found in the Lewis acid-catalyzed reaction of butadiene and acrolein, where BH$_3$ coordination causes a decrease in activation energy by 9 and 7 kcal/mol at 3-21G and 6-31G* levels, respectively.[16,23]

The most characteristic change in the transition structure **21** is an increase of asynchronicity: the forming bond between diene C-1 and an ethylene carbon is shortened by 0.069 Å, and the other forming bond is lengthened by 0.078 Å. Nevertheless, these changes in the geometry of the transition structure for the catalyzed reaction are much less dramatic than those reported in the case of BH$_3$-catalyzed Diels–Alder reaction of butadiene with acrolein.[16]

The charge transfer from the ethylene to the 2-azadiene–BH$_3$ complex in the transition structure is also increased: 0.11 electrons are transferred in the TS **21** compared to 0.03 in the uncatalyzed reaction. Again, this is much less than the 0.3 electrons transferred in the opposite direction for the BH$_3$-catalyzed butadiene–acrolein reaction.[16]

In terms of frontier molecular orbitals, the Diels–Alder reaction of 2-azabutadiene with ethylene appears to be controlled by the HOMO of the dienophile [$\Delta E_{(\mathrm{LUMOazadiene-HOMOethyl})}$ = 13.8 eV, and $\Delta E_{(\mathrm{LUMOethyl-HOMOazadiene})}$ = 14.4 eV]. Thus, the effect of the Lewis acid catalyst is explained by the narrowing of the $\mathrm{LUMO}_{\mathrm{azadiene}} - \mathrm{HOMO}_{\mathrm{ethyl}}$ gap to 12.5 eV.

The effect of a stronger Lewis acid on the activation energy of the Diels–Alder reaction of 2-azabutadiene with ethylene was studied with the protonation of 2-azabutadiene (**22**, Figure 4). A transition structure, **23** (Figure 4), was located with the 3-21G basis set. The most interesting features of this transition structure, compared to TS **21**, are the very low activation energy (9.3 kcal/mol, at 3-21G level) and the high asynchronicity obtained (ΔR = 0.64 Å). The shorter forming bond is at the C-1 terminus. Also, there is an increased charge transfer from the dienophile to the diene: 0.33 electrons. This reaction appears to resemble that for the attack of an iminium cation on an alkene. The stepwise reaction of methyleneiminium cation with ethylene has a forming bond length of 2.042 Å.[24]

Conclusion

The transition structures for the Diels–Alder reactions of 2-azabutadiene with alkenes and alkynes are similar to the ones reported previously for the all-carbon Diels–Alder reactions. The substitution of nitrogen for a CH group in the diene does not exert an important influence on either the asynchronicity or the energies of the transition structures. The reactions with substituted dienophiles were also studied, and the predicted regiochemistry agrees with the experimental findings. The predicted activation energy for the transition structure of the Diels–Alder reactions of 2-azabutadiene with acetylene is higher than that for the corresponding reaction with ethylene, as in the case of all-carbon reactions. In all these cases there is a little increase of the asynchronicity, caused by the substituents in the dienophile. Coordination of the 2-azabutadiene with a Lewis acid causes the transition structure to became more asynchronous and the activation energy to be lowered.

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(22) Inukai, T.; Kojima, T. *J. Org. Chem.* **1966**, *31*, 2032. Inukai, T.; Kojima, T. *J. Org. Chem.* **1971**, *36*, 924. Sauer, J.; Kredel, J. *Tetrahedron Lett.* **1966**, 731.

(23) Loncharich, R. J.; Brown, F. K.; Houk, K. N. *J. Org. Chem.* **1989**, *54*, 1129.

(24) Wu, Y.-D.; Houk, K. N. Unpublished results.

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Registry No. 4, 140438-51-3; 20, 140438-52-4; 22, 62399-28-4; 2-azabutadiene, 38239-27-9; BH_3, 13283-31-3; ethylene, 74-85-1; acrylonitrile, 107-13-1; vinyl chloride, 75-01-4; vinyl alcohol, 557-75-5; acetylene, 74-86-2; cyanoacetylene, 1070-71-9; dicyanoacetylene, 1071-98-3.

Photocyclization of 4-(Dialkylamino)-2-aryl-1-butenes

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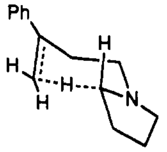
Irradiation of 4-(dialkylamino)-2-aryl-1-butenes gave cyclization products, 3-methyl-3-arylpyrrolidines, in high yields. These styrylamines formed fluorescent intramolecular exciplexes, but studies based on Stern–Volmer quenching for the fluorescence and the photoreaction suggested that the emissive exciplexes did not participate in the photoreaction.

Photochemical hydrogen abstraction by acyclic alkenes is quite rare[1] in contrast to the fact that some cyclic alkenes undergo such reaction[2] as with carbonyl compounds.[3] This fact may be attributed to the presence of competitive processes such as *E*–*Z* isomerization. Hornback et al. reported very inefficient type II analogous reaction of styrenes.[4] On the other hand, some acyclic alkenes undergo efficient hydrogen abstraction from electron donors such as amines. Lewis et al. reported photoaddition of secondary or tertiary amines to singlet-excited stilbene via hydrogen transfer.[5] Intermolecular photoaddition of amines to styrenes has also been reported.[6] These photoreactions of stilbene and styrenes have been reported to proceed via proton transfer from charge transfer exciplexes or ion pairs produced by single-electron transfer. Recently, Lewis et al. reported photocyclization of ω-(styrylamino)alkanes which proceeded via hydrogen transfer from the NH group to the olefinic carbons.[7] This reaction has also been explained in terms of proton transfer of intramolecular exciplexes although emission from the exciplexes was not observed. In relation to our studies on photochemical reactions of styrenes bearing a nitrogen-containing functional group,[8] we report here facile photocyclization of α-[(dialkylamino)ethyl]styrenes **1**.[9] This cyclization proceeds via hydrogen abstraction from the C–H group by the olefinic carbon in distinction from the above-mentioned cyclization of ω-(styrylamino)alkanes. This reaction provides a useful method for the synthesis of some pyrrolidines and is of interest mechanistically since these styrylamines show emission from intramolecular exciplexes.

Chart I

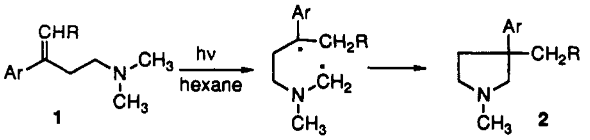


Results and Discussion

The unsaturated amines **1** can be easily prepared by the Wittig reaction of the corresponding Mannich bases.

Photochemical Reactions. When 4-(dimethylamino)-2-phenyl-1-butene (**1a**) in hexane was irradiated with a low-pressure mercury lamp, 1,3-dimethyl-3-phenylpyrrolidine (**2a**) was obtained in 72% yield. The structure of **2a** was determined on the basis of elemental analysis and spectral data. The ^1H- and ^{13}C-NMR spectra showed the presence of a methyl group on a nitrogen atom and that on a quaternary carbon and the absence of olefinic carbons. The formation of **2a** is readily explained in terms of intramolecular hydrogen abstraction by the terminal olefinic carbon and subsequent cyclization of the resulting diradical. Irradiation of 4-methoxyphenyl and 4-biphenylyl derivatives **1b** and **1c** also gave the corresponding cyclization products **2b** and **2c** in high yields, whereas a 4-cyanophenyl derivative **1d** was unreactive toward photolysis and prolonged irradiation resulted in the formation of an intractable mixture. Meanwhile, irradiation of 5-(dimethylamino)-3-phenyl-2-pentene (**1e**), which has a trisubstituted double bond, underwent facile photocyclization.

The reactions of **1a** and **1b** were found to be singlet reactions because they were neither sensitized by xanthone nor quenched by 1,3-pentadiene.



a: R=H, Ar=Ph	78%
b: R=H, Ar=4-MeO-C_6H_4	87%
c: R=H, Ar=4-Ph-C_6H_4	63%
d: R=H, Ar=4-CN-C_6H_4	0%
e: R=Me, Ar=Ph	82%

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[1] Kropp, P. J. *Org. Photochem.* **1979**, *4*, 1–142.

[2] Padwa, A.; Chou, C. S.; Rosenthal, R. J.; Terry, L. W. *J. Org. Chem.* **1988**, *53*, 4193 and references cited therein.

[3] Wagner, P. J.; Park, B.-S. *Org. Photochem.* **1991**, *11*, 227.

[4] Hornback, J. M.; Proehl, G. S. *J. Am. Chem. Soc.* **1979**, *101*, 7367.

[5] Lewis, F. D. *Adv. Photochem.* **1986**, *13*, 203–215.

[6] (a) Cookson, R. C.; Costa, S. M. de B.; Hudec, J. *Chem. Commun.* **1969**, 753. (b) Brentnall, R. L.; Crosby, P. M.; Salisburry, K. *J. Chem. Soc., Perkin Trans. 2* 1977, 2002. (c) Toki, S.; Hida, S.; Takamuku, S.; Sakurai, H. *Nippon Kagaku Kaishi* **1984**, 152.

[7] Lewis, F. D.; Reddy, G. D.; Schneider, S.; Gahr, M. *J. Am. Chem. Soc.* **1991**, *113*, 3498.

[8] (a) Aoyama, H.; Arata, Y.; Omote, Y. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1165. (b) Aoyama, H.; Arata, Y.; Omote, Y. *J. Org. Chem.* **1987**, *52*, 4639. (c) Aoyama, H.; Tomohiro, T.; Arata, Y.; Omote, Y. *J. Phys. Org. Chem.* **1988**, *1*, 123. (d) Aoyama, H.; Arata, Y.; Omote, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 736.

[9] Photoreaction of **3b** has been briefly mentioned in a preliminary report: Aoyama, H.; Arata, Y.; Omote, Y. *J. Chem. Soc., Chem. Commun.* **1985**, 1381. The low yields of the products reported in the paper are apparently due to the secondary decomposition. See the Experimental Section.

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