

exciplex, is involved. If so, the apparent difference between the present result and other triplet arene [2 + 2] photocycloadditions for which exciplexes have been postulated, e.g., indene dimerization,^{4d} in which exo orientation of the aryl moieties occurs,¹³ remains obscure and merits close scrutiny.

Finally, both our observation of quenching of exciplexes by solute molecules and that of others⁴¹ offer good prospects for the detection of nonemitting exciplexes (by the demonstration of quenching by a molecule which does not quench the initially excited chromophore) plus an obvious *caueat* regarding the incautious interpretation of quenching experiments where long-lived exciplexes may be involved.

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(13) A. G. Anastassiou and G. W. Griffin, *J. Org. Chem.*, **33**, 3441 (1968).

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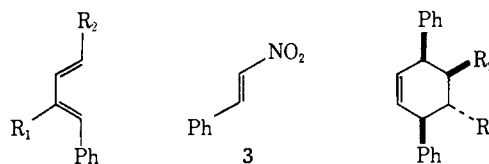
Some Novel Aspects of the Diels–Alder Reaction with 1,4- and 1,2-Diphenylbutadienes under Thermal and Lewis Acid Catalyzed Conditions¹

Sir:

A great deal of attention has been paid by theoretical chemists to explain the experimental facts of regio- and stereoselectivity of the Diels–Alder reaction ever since the propounding of the empirical rules by Alder and Stein,² and two of the recent and more successful such treatments are those of Herndon³ and Houk.⁴ It was reported earlier by us⁵ that in the addition of β -nitrostyrenes to 1,4-diphenylbutadiene electron withdrawing substituents in the 4'-position of the dienophile introduce striking stereoselectivity and lead to the formation of only the phenyl endo adducts (4). The work presented now shows some novel aspects of the stereoselectivity introduced by the Lewis acids and the steric control exerted by the 2-phenyl moiety in the addition of 1,2-diphenylbutadiene to β -nitrostyrene and cinnamic acid. These effects have been explained on the basis of the preferred geometry of the transition state. Any unified theoretical treatment will have to encompass these facts.

The addition reaction of 1 and 3 in benzene at 0° in presence of 1 molar equiv of SnCl₄ or AlCl₃ gave exclusively the nitro endo adduct 5, in contrast to the formation of equal proportions of both the phenyl endo

(4) and nitro endo (5) adducts under thermal conditions.^{5a} Treatment of the adducts formed under thermal conditions with Lewis acids did not change their stereochemistry.



- 1, R₁ = H; R₂ = Ph
2, R₁ = Ph; R₂ = H
10, R₁ = CH₃; R₂ = H
4, R₁ = NO₂; R₂ = Ph
5, R₁ = Ph; R₂ = NO₂
15, R₁ = CO₂H; R₂ = Ph



- 6, R₁ = Ph; R₂ = Ph; R₃ = NO₂
7, R₁ = R₂ = Ph; R₃ = NO₂
11, R₁ = CH₃; R₂ = Ph; R₃ = NO₂
14, R₁ = Ph; R₂ = Ph; R₃ = CO₂H
8, R₁ = R₂ = Ph; R₃ = NO₂
9, R₁ = R₂ = Ph; R₃ = NO₂
12, R₁ = CH₃; R₂ = Ph; R₃ = NO₂
13, R₁ = CH₃; R₂ = NO₂; R₃ = Ph

Reaction of 2 and 3 by heating in *o*-dichlorobenzene gave, of the four possible adducts 6–9, only 6 and 7, in a ratio of 72:25. 6 mp 159–160°; nmr (CCl₄)⁶ 4.88 (m, 5-H), 5.45 (dd, 4-H), 5.8 (d, 3-H); $J_{6e,5} = 6$, $J_{6a,5} = 10.5$, $J_{4,5} = 12$, $J_{3,4} = 10.5$ Hz. 7 mp 162–163°; nmr (CCl₄) 5.0 (dd, 4-H), 5.37 (d, 3-H), 6.38 (m, 5-H); $J_{3,4} = 10.5$, $J_{4,5} = 12.5$, $J_{5,6a} = 10.5$, $J_{5,6e} = 5$ Hz. These assignments were confirmed by introducing deuterium at 4 and 5 positions of the adducts by using α - and β -deuterio- β -nitrostyrenes as dienophiles in this condensation. The formation of 6 and 7 having 3,4 trans geometry is unusual; according to the usually accepted mode of Diels–Alder reaction, an ortho-cis product should be formed.⁷ When the addition of 2 to 3 was carried out in the presence of 1 molar equiv of SnCl₄ or AlCl₃, isomer 8 was the exclusive adduct: mp 162–163°; nmr (CCl₄) 4.55 (q, 4-H), 5.3 (d, 3-H), 6.5 (m, 5-H); $J_{3,4} = 5.5$, $J_{4,5} = 12$, $J_{5,6a} = 11$, $J_{5,6e} = 5$ Hz.

Lewis acids are known to cause rate acceleration⁸ of Diels–Alder reactions and markedly alter the isomer ratio,⁹ forming in some cases a larger ratio of the isomer not expected on steric considerations.¹⁰ A striking reversal of usual orientation in Diels–Alder reaction by Lewis acids has recently been reported by Dickinson, *et al.*¹¹ The formation of 8 under Lewis acid catalysis, having stereochemistry different from that of either of the adducts formed under thermal conditions, is thus novel and noteworthy.

(6) Nmr spectra were recorded at 60 and 220 MHz using Me₄Si as standard. Chemical shift is expressed in τ and J in Hz. Only relevant signals have been given.

(7) A. S. Onischenko, "Diene Synthesis," Israel Programme for Scientific Translations, Daniel Davy and Co., New York, N. Y., 1964, p 63; J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 547 (1961).

(8) P. Yates and P. Eaton, *J. Amer. Chem. Soc.*, **82**, 4436 (1960).

(9) (a) J. Sauer and J. Kredel, *Angew. Chem., Int. Ed. Engl.*, **4**, 989 (1965); (b) *Tetrahedron Lett.*, 731 (1966); (c) R. F. Farmer and J. Hamer, *J. Org. Chem.*, **31**, 2418 (1966); (d) T. Inukai and T. Kojima, *ibid.*, **31**, 2032 (1966); (e) Y. Kishi, F. Nakatsubo, M. Aratani, T. Goto, S. Inoue, H. Kakoi, and S. Sugiura, *Tetrahedron Lett.*, 5127 (1970); (f) J. S. Meek, J. S. Fowler, and J. R. Dann, *J. Org. Chem.*, **35**, 3587 (1970).

(10) (a) K. L. Williamson and Y. F. LiHsu, *J. Amer. Chem. Soc.*, **92**, 7385 (1970); (b) E. F. Lutz and G. M. Bailey, *ibid.*, **86**, 3899 (1964); (c) T. Kojima and T. Inukai, *J. Org. Chem.*, **35**, 1342 (1970).

(11) R. A. Dickinson, R. Kubella, G. A. MacAlpine, Z. Stojanac, and Z. Valenta, *Can. J. Chem.*, **50**, 2377 (1972).

(1) Communication No. 1928 from Central Drug Research Institute, Lucknow, India.

(2) K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

(3) W. C. Herndon, *Chem. Rev.*, **72**, 157 (1972).

(4) (a) K. N. Houk, *J. Amer. Chem. Soc.*, **95**, 4092 (1973); (b) K. N. Houk and R. W. Strozier, *ibid.*, **95**, 4094 (1973).

(5) (a) J. S. Bindra, P. C. Jain, and N. Anand, *Indian J. Chem.*, **9**, 388 (1971); (b) P. C. Jain, Y. N. Mukerjee, and N. Anand, *Chem. Commun.*, 303 (1971).

Addition of 1-phenyl-2-methylbutadiene (**10**) to **3** in the presence of SnCl_4 also gave exclusively the nitro endo adduct **13**, while under thermal conditions the adducts **11** and **12** were formed in almost equal proportion. **13** mp 121–122°; nmr (CDCl_3); 4.62 (q, 4-H), 6 (d, 3-H), 6.55 (sextet, 5-H); $J_{3,4} = 5.5$, $J_{4,5} = 12$, $J_{5,6a} = 10.5$, $J_{5,6e} = 4.5$ Hz. **11** mp 146–147°; nmr (CDCl_3) 4.8 (m, 5-H), 6.5 (d, 3-H), 6.65 (t, 4-H); $J_{4,5} = 12$ Hz. **12** mp 159°; nmr (CDCl_3) 4.7 (m, 5-H), 6.15 (q, 4-H), 6.55 (d, 3-H); $J_{3,4} = 6$, $J_{4,5} = 12$ Hz.

The two common features of the above reactions are: (i) the formation of "ortho"-trans adducts in thermal reactions when 1,2-diphenylbutadiene is the diene; (ii) the exclusive formation of "ortho"-nitro-cis adducts in the presence of Lewis acids. These facts can be explained as follows. In the condensation of 1,2-diphenylbutadiene (**2**) with β -nitrostyrene, the presence of two phenyl rings on adjacent carbons would not allow both the rings to conjugate with the diene and would very likely force the 2-phenyl ring to take a position orthogonal to the plane of the diene. In the transition complex formed for cycloaddition reaction (Figure 1), by 1,3 interaction the 2-phenyl ring would offer steric hindrance to the terminal group of the nitrostyrene assuming an "ortho"-cis orientation, and the adducts formed would thus have an "ortho"-trans stereochemistry (**6** and **7**). In the case of 1-phenyl-2-methylbutadiene, when the steric effect at 2 position is less, both "ortho"-cis (**12**) and ortho-trans (**11**) adducts are formed.

In the presence of Lewis acids the complexing¹² of the nitro group would induce a strong dipole and favor its dipole-dipole or induced dipole^{10a, 14} and C-T bonding with the diene and its two phenyl rings and form a transition state having an "ortho"-nitro-cis stereochemistry leading to the formation of the adducts **5**, **8**, and **13**.

When **1** and cinnamic acid were treated in *o*-dichlorobenzene, **15** was exclusively obtained: mp 245°; methyl ester mp 150–151°; nmr (CDCl_3) 6.05 (d, 3-H), 6.22 (d, 6-H), 6.3 (q, 5-H), 7.0 (t, 4-H); $J_{3,4} = 10.5$, $J_{4,5} = 12$, $J_{5,6} = 6$ Hz. Condensation of **2** with cinnamic acid gave the adduct **14**: mp 235; methyl ester mp 134–135°; nmr (CDCl_3) 6.0 (d, 3-H), 6.8 (dd, 4-H), 6.95 (sextet, 5-H); $J_{3,4} = 10$, $J_{4,5} = 12$, $J_{5,6a} = 12$, $J_{5,6e} = 5$, $J_{6a,6e} = 15$ Hz. These assignments were confirmed by nmr of the adducts obtained from **1** and **2** with *trans*- α -*d*-cinnamic acid. The formation of "ortho"-trans adduct **14** in the case of **2** again points to the important role of the bulk of 2-substituent of the diene to stereoselectivity in the Diels-Alder reaction.

Thus in the Diels-Alder reaction a number of competing factors operate, and their relative dominance determines the stereo- and regioselectivity of the reaction. Under thermal conditions, other factors being equal, steric factors¹⁵ seem to determine the nature of the products. However, when one of the substituents of the dienophile, a Lewis acid complexed nitro group in

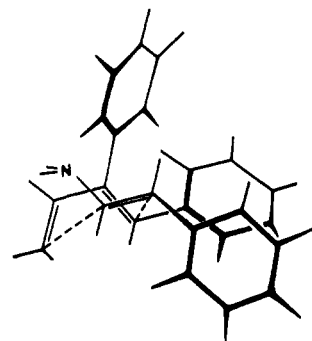


Figure 1.

the present case, can associate strongly with the diene by dipole and C-T bonding,^{5b} this can outweigh the steric constraints and form the thermodynamically less favored¹⁶ products. By a proper choice of the various parameters related to these factors, one can preselect the stereochemistry of the adducts.

(16) I. G. Dinulescu, Gh. D. Mateeseu, and C. D. Nenitescu, *Rev. Roum. Chim.*, **13**, 505 (1968).

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Substituent Effects in the Ring Enlargement of *N*-Arylidene-2,2-diphenylcyclopropylamines

Sir:

Frey, *et al.*, measured the rearrangement rate of vinylcyclopropane to give cyclopentene at 340–390° and suggested a concerted pathway.¹ Later the same group preferred a trimethylene diradical, stabilized by allyl resonance, as an intermediate.² The problem has not been settled yet. Willcott and Cargle's finding, that *cis*,*trans* isomerization of *cis*-2-deuteriovinylcyclopropane is at least five times faster than conversion to cyclopentene,³ is compatible with either mechanism. Neither of the two orbital symmetry allowed 1,3-sigmatropic processes⁴ accounts for the steric course observed in the thermal isomerization of a trisubstituted vinylcyclopropane,⁵ but a combination of concerted and diradical processes cannot be ruled out. We present kinetic evidence for the occurrence of a trimethylene intermediate in the ring expansion of a heteroanalog of the vinylcyclopropane system.

The rearrangement of the *N*-arylidene-2,2-diphenylcyclopropylamines (**1**) of Table I produces at 150° virtually quantitatively the 1-pyrrolines (**3**) which were

(1) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 3547 (1961); R. J. Ellis and H. M. Frey, *ibid.*, 4188 (1964); C. S. Elliott and H. M. Frey, *ibid.*, 345 (1965).

(2) H. M. Frey and D. C. Marshall, *J. Chem. Soc.*, 3981 (1962); R. J. Ellis and H. M. Frey, *ibid.*, 959 (1964); H. M. Frey, *Advan. Phys. Org. Chem.*, **4**, 147, 155 (1966).

(3) M. R. Willcott and V. H. Cargle, *J. Amer. Chem. Soc.*, **89**, 723 (1967).

(4) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(5) P. H. Mazzocchi and H. J. Tamburin, *J. Amer. Chem. Soc.*, **92**, 7220 (1970).

(12) With ethyl acrylate it has been shown that the CO group complexes^{9a, b} with AlCl_3 and the complex has been isolated¹⁰ and studied by ir.¹³

(13) J. F. Norris and P. Arthus, *J. Amer. Chem. Soc.*, **62**, 874 (1940); M. F. Lappert, *J. Chem. Soc.*, 817 (1961).

(14) K. L. Williamson, Y. F. LiHsu, R. Lacko, and C. H. Youn, *J. Amer. Chem. Soc.*, **91**, 6129 (1969).

(15) M. J. Goldstein and A. H. Gevirtz, *Tetrahedron Lett.*, 4417 (1965).