

Effect of Substituents on the Stereochemical Course of Diels–Alder Reaction between β -Nitrostyrenes and *trans,trans*-1,4-Diphenylbutadiene

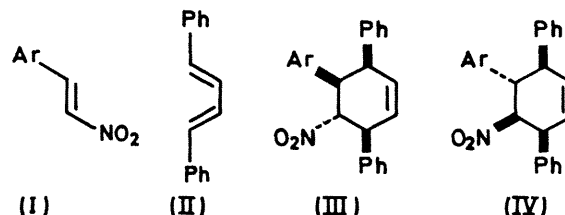
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Summary In a study of the Diels–Alder reaction of *trans,trans*-1,4-diphenylbutadiene with β -nitrostyrenes a marked stereoselectivity to phenyl "endo" adducts has been observed on introduction of electron-withdrawing substituents in the *para*-position of the phenyl ring of the β -nitrostyrenes.

A SYMMETRY-ALLOWED, *supra, supra* $4 + 2$ ($4\pi_s + 2\pi_s$), cycloaddition of *trans,trans*-1,4-diphenylbutadiene (I) and β -nitrostyrenes (II) would involve transition states which are stabilized by secondary bonding interactions¹ between the highest occupied molecular orbitals (HOMO) of the diene and the lowest vacant molecular orbitals (LVMO) of the dienophile. In the present case the phenyl or the nitro-group would be involved in the secondary interaction, thus leading to the product with the aryl "endo" (III) or the NO₂ "endo" (IV). We found earlier² that both these adducts are formed in equal proportion when Ar = Ph. In order to clarify the nature³ of these secondary MO interactions, the condensation of variously substituted β -nitrostyrenes and *trans,trans*-1,4-diphenylbutadiene has been carried out.

in the crude mixture could thus be very conveniently used to monitor the ratio of the two adducts and the results are summarised in the Table. It has been found that the ratio of (III) and (IV) is independent of the time and temperature of the reaction, although the total yield of the adducts is affected.



The results show that most of the substituents introduce a certain amount of steric control in the reaction, but the most striking effect is that of electron-withdrawing substituents in the *para*-position of the β -nitrostyrene, when

Condensation of β -nitrostyrene with *trans,trans*-1,4-diphenylbutadiene

| | Ar | Total yield (III)+(IV) | (III) | | (IV) | |
|------|--|------------------------|----------|-----|----------|----|
| | | | M.p. | % | M.p. | % |
| (1) | Ph | 70 | 159° | 50 | 169° | 50 |
| (2) | <i>p</i> -OMe-C ₆ H ₄ | 65 | — | 75 | — | 25 |
| (3) | <i>m</i> -OMe-C ₆ H ₄ | 70 | — | 68 | — | 32 |
| (4) | 3,4-(OMe) ₂ -C ₆ H ₃ | 74 | 149° | 65 | 159° | 35 |
| (5) | 3,4,5-(OMe) ₃ -C ₆ H ₂ | 65 | — | 68 | — | 32 |
| (6) | <i>m</i> -HO-C ₆ H ₄ | 70 | 129° | 45 | 154° | 55 |
| (7) | <i>p</i> -F-C ₆ H ₄ | 72 | 154–155° | 60 | — | 40 |
| (8) | <i>p</i> -HO-C ₆ H ₄ | 71 | 194–195° | 89 | 110° | 11 |
| (9) | α -C ₁₀ H ₇ | 50 | 187° | 75 | 182° | 25 |
| (10) | <i>m</i> -NO ₂ -C ₆ H ₄ | 50 | 205° | 65 | 124–125° | 35 |
| (11) | <i>p</i> -NO ₂ -C ₆ H ₄ | 87 | 180° | 100 | — | 0 |
| (12) | <i>p</i> -CN-C ₆ H ₄ | 73 | 177° | 100 | — | 0 |
| (13) | <i>p</i> -MeSO ₂ -C ₆ H ₄ | 85 | 202° | 100 | — | 0 |

The cycloadditions were carried in *o*-dichlorobenzene at reflux temperature for 5 h. The unreacted starting materials were removed by chromatography, and the products (III) and (IV) were then separated by fractional crystallisation or by chromatography. However, for calculating the ratio of (III) and (IV) the crude reaction mixture obtained after removal of the reactants was used for n.m.r. spectroscopy.† In the n.m.r. spectra³ of (III; Ar = Ph) having Ph "endo", NO₂-CH appeared as a pair of doublets centred at 4.9 ($J_{4,5}$ 12, and $J_{3,4}$ 10.5, two *a,a* couplings) and in (IV; Ar = Ph) with NO₂ "endo", NO₂-CH appeared as a quartet centred at 4.35 ($J_{4,5}$ 12 and $J_{3,4}$ 6, one *a,a* and one *a,e* coupling), and are of diagnostic value in identifying (III) and (IV). The integration for NO₂-CH

in all the cases studied (11,12,13) there is absolute stereospecificity and (III) is formed exclusively.

It is known that an electron-deficient dienophile favours cycloaddition.⁴ The role of charge-transfer complex formation (CT) in Diels–Alder reactions has been emphasised recently.⁵ It is likely that an electron-deficient dienophile would act as a better acceptor in CT-complex formation, thus favouring the reaction. In the present case the *para*-electron-withdrawing substituent in the phenyl ring of the β -nitrostyrene would thus favour the reaction. Also, the electron-deficient phenyl ring may itself be able to act as a good acceptor and take part in CT-complex formation in secondary bonding interaction, and thus favour the formation of phenyl "endo" product (III). The

† The n.m.r. spectra were recorded on a Varian A-60D instrument using Me₄Si as internal reference. Chemical shifts are expressed in τ values, and J values in Hz. All the compounds analysed within ± 0.4 per cent of theoretical values for C, H, and N.

lack of stereospecificity in the case of *m*, β -dinitrostyrene (10) would indicate that the stereoselectivity in (11, 12, and 13) is a result of the overall electron withdrawal from the aryl group and the π -bond of the dienophile.

The case of *p*-hydroxy- β -nitrostyrene (8) is rather anomalous; its steric control is like that of an electron-withdrawing

substituent. This stereoselectivity in (8) does not appear to be due to proton catalysis since addition of acetic acid in case (1) did not affect the ratio of (III) and (IV).

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