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Reactions of TCNE with Isomeric 2,4-Hexadienes

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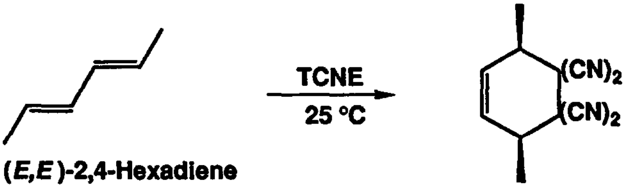
Summary : The reactivities of the isomeric 2,4-hexadienes with tetracyanoethylene (TCNE) differ enormously, in the order *E,E*>>*E,Z*>>*Z,Z*. The inertness of the *Z,Z* isomer allows complete removal of the other isomers by formation of adducts.

Tetracyanoethylene (TCNE) is a very electrophilic dienophile and an important diagnostic reagent for study of the cycloadditions of acyclic and cyclic dienes.[1] TCNE undergoes [2 + 4], [2 + 2] and (to a much lesser extent) ene reactions. With various dienes, concerted reactions, intermediates formed by electron and charge transfer, and biradical and zwitterionic intermediates can be involved. Huisgen[2] and Kataoka[3] have reported that the reaction of TCNE with electron-rich olefins and dienes is non-stereospecific. Although no isomerization of starting materials was observed in the diene reactions, the authors proposed the involvement of zwitterions to explain the solvent effects on the product distributions.

Analogous mechanisms and products from the reactions of TCNE, PTAD (4-phenyl-1,2,4-triazoline-3,5-dione), and singlet oxygen with olefins and dienes have recently been reported.[4,5,6] Results of studies by Jensen and Foote[7] and O'Shea and Foote[8] on the reactivities of PTAD and singlet oxygen with the isomeric 2,4-hexadienes prompted study of the reactions of TCNE with these dienes.[9]

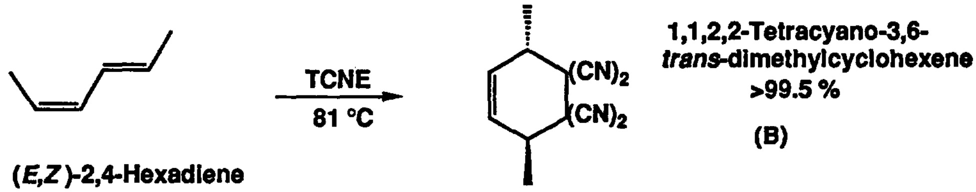
(*E,E*)-2,4-Hexadiene reacted with TCNE in CH_2Cl_2 at 25 °C to yield the Diels-Alder adduct (**A**) quantitatively (>99.5%). On addition of the diene, the solution instantaneously turned brown for 1-2 minutes, and quickly faded to yellow. Evaporation of the solvent yielded only **A**, which was characterized by MS, IR, and NMR.[10] The crude solution was free of isomeric products by NMR. ^{1}H NMR at -78 °C provided no evidence for any [2 + 2] adduct or any other intermediates in the reaction.



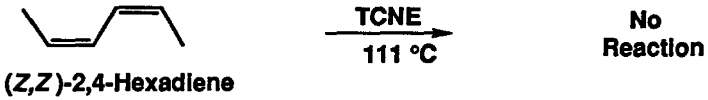
(*E,E*)-2,4-Hexadiene

1,1,2,2-Tetracyano-3,6-*cis*-dimethylcyclohexene
>99.5 %
(A)

In contrast, a solution of the (*E,Z*) isomer in CH_2Cl_2 turned brown after addition of TCNE but did not react after 12 hours at room temperature followed by 3 hours of refluxing. ^{1}H NMR and gas chromatography gave no evidence for product formation or isomerization of the diene. Reaction occurred only after 3 hours of refluxing in benzene, and *trans*-isomer (B), characterized by MS, IR and NMR[11], was the sole product(>99.5%). In contrast to the analogous endoperoxides[8], coalescence of methyl groups because of half-chair-half-chair interconversion of the cyclohexenes was not observed at accessible temperatures (> -78 °C).



The (Z,Z) isomer also formed a brown charge-transfer complex with TCNE. However, even after refluxing in toluene for several days, no detectable reaction products were formed.



In an attempt to determine the effect of solvent polarity, the reactions were run in toluene, tetrahydrofuran, and acetonitrile. Although the observed products were unchanged, the lifetime of the visible charge-transfer complex decreased in more polar solvents, suggesting that a charged intermediate or transition state may be involved in the formation of the products. Similar solvent effects are well known for the reactions of other dienes with TCNE.[1] However, there is no direct evidence for reactive intermediates other than the charge-transfer complex in the reactions of the isomeric dienes with TCNE, and the relative energy of the *s-cis* conformation of the isomeric dienes appears to be the main factor controlling the reactivity toward TCNE, as shown in the Table.

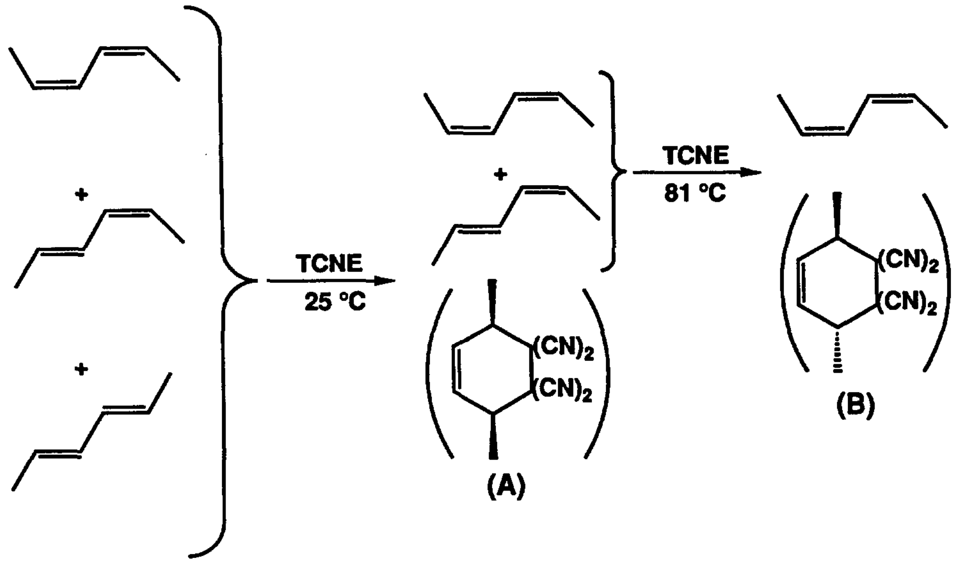
Table: Energy Difference Between Planar *s-trans* and *s-cis* Conformations Calculated by MM2[8] and Reactivity with TCNE

2,4-Hexadiene isomer	ΔE (kcal/mole)	Reaction Conditions
(*E,E*)	2.8	60 sec[a], 25 °C
(*E,Z*)	5.9	3 Hrs[a], 81 °C
(*Z,Z*)	11.5	No Reaction[b], 111 °C

a - Time required for complete reaction.

b - No products were observed after several days of refluxing in toluene.

The dramatic differences in reactivity of the diene isomers are shown by the scheme below. At room temperature, the Diels-Alder adduct from the (*E,E*)-diene is easily formed and can be removed from a mixture, leaving the (*E,Z*) and (*Z,Z*) isomers. Similarly, (*E,Z*)-diene can be removed from the resulting mixture by refluxing with TCNE in benzene, leaving isomerically pure (*Z,Z*)-2,4-hexadiene, which is difficult to obtain by other means.



The fact that the [2 + 2] adduct was not observed from any of the dienes, even the (*Z,Z*)-isomer after several days in refluxing toluene, is particularly surprising in light of the large amount of [2 + 2] adduct formed with many other dienes[1] including 4-methyl-1,3-pentadiene[9,12] and Z-cyclopropyl-1,3-butadiene[3]. In contrast, the [2 + 2] adduct is formed from the (*Z,Z*) diene with PTAD even at -55 °C,[8] and some [2 + 2] adduct is formed from all isomers with $^1O_2$.[8]

The TCNE reactions appear to involve a charge-transfer mechanism which is affected by solvent polarity; whether the complex is with the diene or an isolated double bond is unclear. However, the observed product selectivity suggests that the conjugated acyclic dienes are complexed as dienes, since [2 + 2] product might have been expected if they were complexed as isolated double bonds.

The results of this study emphasize the extraordinary differences in the reactions of these dienes with the three electrophilic dienophiles, PTAD, $^1O_2$, and TCNE. PTAD gives stereospecific but fast reaction with the *E,E* and *E,Z* isomers, and a mixture of both [2 + 4] products (via a [2 + 2] intermediate) from the *Z,Z* isomer via a zwittterion, but with no diene isomerization;[7] singlet oxygen gives rapid isomerization of all three dienes, leading to a mixture of nonstereospecific [2 + 4], [2 + 2], and ene products via zwitterions,[8] but TCNE gives only [2 + 4] adduct formation, rapidly from the *E,E* isomer and slowly from the *E,Z*, and no reaction whatsoever from the *Z,Z*. The reasons for these differences are being explored.

References and Notes

(1) For a review see Fatiadi, A. J. *Synthesis*, **1987**, 749.

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(9) C. A. Stewart, (*J. Org. Chem.*, **1963**, *28* 3320) reported products from the reaction of (*E,E*)- and (*E,Z*)-2,4-hexadiene with TCNE that were identical by ^{1}H NMR. Since this author used diene mixtures in this study, the difference in reactivity of TCNE towards these dienes suggests that he actually obtained only the product from the more reactive (*E,E*) isomer. The reported melting point of both isomers was close to that of **A** [10], although the melting point of the mixture was depressed. In this study, **A** and **B** were found to have different melting points and noticeably different NMR spectra (clearly resolved in mixtures)[10,11], although the NMR differences are small enough that they might not have been resolved in Stewart's study. Significant differences also exist in the fingerprint region of the IR spectrum.[10,11] Attempts to epoxidize **A** and **B** in order to conclusively establish the stereochemistry of the products[7] were unsuccessful.

(10) 1,1,2,2-Tetracyano-3,6-*cis*-dimethylcyclohex-3-ene (**A**) was recrystallized from a mixture of hexanes and benzene. M.P. 124-5 °C; ^{1}H NMR (200 MHz) 5.67 (2H, s, alkene), 3.11 (2H, q, CH), 1.50 (6H, dd, CH_3) ppm; ^{13}C NMR 126.3, 111.4, 110.0, 42.2, 37.0, 17.5 ppm; MS, *m/z* 210.0900 (M^+, Calcd. for $C_{12}H_{10}N_4$, 210.090546), 195, 118 (base), 105, 91, 82. IR (KBr) 3000, 2950, 2340, 1680, 1480, 1115, 1080, 940, 850, 760, 730 cm^{-1}.

(11) 1,1,2,2-Tetracyano-3,6-*trans*-dimethylcyclohex-3-ene (**B**) was recrystallized from a mixture of hexanes and benzene. M.P. 106-8 °C; ^{1}H NMR (200 MHz) 5.53 (2H, s, alkene), 3.14 (2H, q, CH), 1.45 (6H, d, CH_3) ppm; ^{13}C NMR 126.9, 111.1, 108.9, 45.2, 36.8, 16.6 ppm; MS, *m/z* 210.0893 (M^+, Calcd. for $C_{12}H_{10}N_4$, 210.090546), 195, 118 (base), 105, 91, 82. IR (KBr) 3000, 2950, 2340, 1680, 1480, 1230, 1150, 935, 850. 775, 720 cm^{-1}.

(12) C. A. Stewart, *J. Am. Chem. Soc.*, **1962**, *84*, 117.

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