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CHEMICAL REACTIONS OF ELECTRON DONOR-ACCEPTOR SYSTEMS: THERMAL [2+2] CYCLOADDITION REACTION OF VINYLFERROCENE WITH TETRACYANOETHYLENE

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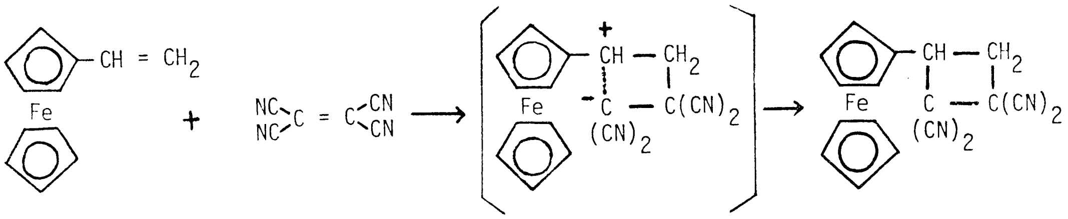
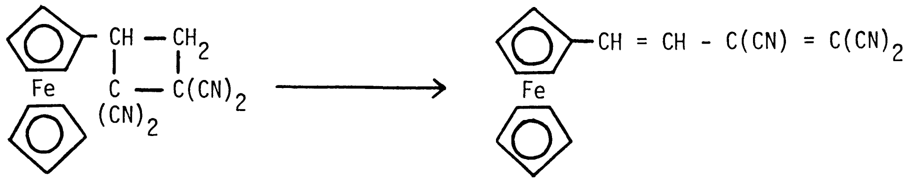
The thermal [2+2] cycloaddition reaction of vinylferrocene with tetracyanoethylene was found to occur under very mild reaction conditions in a non-polar solvent or even in solid states. Stabilization of the α-ferrocenyl carbonium ion in the zwitterionic intermediate or the transition state of that character is suggested to contribute to the facilitation of the reaction.

Olefins which have been reported to undergo thermal [2+2] cycloaddition reaction with tetracyanoethylene(TCNE) under mild reaction conditions are limited to some special 1,3-dienes to which Diels-Alder addition is difficult or impossible and to such electron-rich olefins bearing a strong electron-donating substituent such as RO-, RS-, RR'N-, R(R'CO)N- or cyclopropyl group attached directly to the double bond or conjugated through a benzene ring, e.g., para-substituted styrene derivatives.[1-4] Very recently, we have found that a few aromatic-substituted olefins, e.g., acenaphthylene, indene or 1-vinylpyrene, can undergo thermal [2+2] cycloaddition reaction with TCNE under relatively mild reaction conditions.[5] In this communication we wish to report the very facile [2+2] cycloaddition reaction of vinylferrocene with TCNE.



III I

The cycloaddition reaction of vinylferrocene with TCNE to give the corresponding cyclobutane derivative occurred readily under very mild reaction conditions. The yield of the cycloadduct(I) formed in a benzene solution ([vinylferrocene] = [TCNE] = 2×10^{-2}M) at 30°C after the reaction time of 1, 2 and 5 hr were 37, 55, and 75%, respectively.[6] Interestingly, the cycloaddition reaction occurred even in solid states. That is, when an equimolar mixture of vinylferrocene and TCNE was ground to a fine powder in a mortar with a pestle, the reaction occurred to form the yellow cycloadduct(I), whereas ferrocene and TCNE form the green solid charge-transfer complex by a similar treatment.[7] The cycloadduct(I), yellow needles, decomp.p. 162°C (recrys. from benzene), was identified by the infrared, n.m.r., and electronic absorption spectra, measurement of the molecular weight and the elementary analyses. When refluxed in methanol, I decomposed with elimination of hydrogen cyanide into the tricyanobutadiene derivative(II), decomp.p. 205°C.[8]



I II

That the olefin should possess a rather low ionization potential, that is, the olefin should possess a rather strong electron-donating property, seems to be an important factor for the thermal [2+2] cycloaddition reaction with TCNE to occur under mild reaction conditions, as is evident from the examples of 1-vinylpyrene[5] or vinylferrocene.[9] The detailed mechanism for the thermal [2+2] cycloaddition reaction of the electron-rich olefin with TCNE has not been made clear, but an ionic process involving charge-separation in the rate-determining step has been proposed for the reaction from the effect of the solvent polarity.[2] The electron-donating property of the olefin may be reflected in the stabilization of the intermediate or the transition state involving charge-separation as well as in the charge-transfer interaction at the initial stage.

It is suggested that the stabilization of the α-ferrocenyl carbonium ion in the zwitterionic intermediate or the transition state of that character such as III either by the direct participation of the iron d-orbital[10] or by the σ-π carbon-metal conjugation[11] contributes to the facilitation of the reaction between vinylferrocene and TCNE.[9,12] Indeed, the highly stable character of the α-ferrocenyl carbonium ion has been well established in many studies, and e.g., the facile addition reactions of acetic acid or hydrogen azide to vinylferrocene have been explained as due to the stabilization of the α-ferrocenyl carbonium ion.[13] The present finding of the facile cycloaddition reaction of vinylferrocene with TCNE may be in support of the mechanism proposed for the thermal [2+2] cycloaddition reactions of TCNE with the electron-rich olefin.

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6) The rate of the reaction of vinylferrocene is much faster than that of 1-vinylpyrene in benzene.
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8) The transformation into the tricyanobutadiene derivative has also been reported with respect to other cycloadducts formed from the electron-rich olefins and TCNE.[2]
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