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CHEMICAL REACTIONS OF ELECTRON DONOR-ACCEPTOR SYSTEMS: THERMAL [2+2] CYCLOADDITION REACTIONS OF SOME AROMATIC-SUBSTITUTED OLEFINS WITH TETRACYANOETHYLENE

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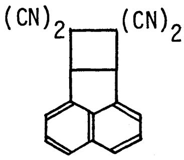
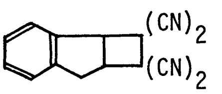
Some aromatic-substituted olefins, e.g., acenaphthylene, indene, and 1-vinylpyrene cycloadded thermally to tetracyanoethylene to give the corresponding cyclobutane derivatives, the reactivity of the olefins increasing with a decrease in their ionization potentials. With 1-vinylnaphthalene Diels-Alder addition of tetracyanoethylene was favored over [2+2] cycloaddition, and with 1,2-dihydronaphthalene, dehydrogenation by tetracyanoethylene occurred to give naphthalene and tetracyanoethane.

The cycloaddition reaction has been the subject of many reports in view of both synthetic and mechanistic interest. The recent finding1) that tetracyanoethylene(TCNE) cycloadds thermally to electron-rich olefins under very mild reaction conditions has received much attention. However, the scope of the thermal [2+2] cycloaddition reaction of TCNE has been limited only to some special 1,3-dienes to which Diels-Alder addition is difficult or impossible2) and such electron-rich olefins as containing a strong electron-donating group, e.g., RO-, RS-, RR'N-, or R(R'CO)N-, attached directly to the double bond or conjugated through a benzene ring, that is, vinyl ethers, vinyl sulfides, vinyl amines, vinyl amides, or styrene derivatives substituted by the above electron-donating groups at the para-position of the benzene ring.3,4) Very recently, cyclopropyl-substituted olefins were also found to undergo ready thermal [2+2] cycloaddition reaction with TCNE.5)

In this communication we wish to report the reactions of some aromatic-substituted olefins with TCNE, in which acenaphthylene, indene, and 1-vinylpyrene were found to cycloadd thermally to TCNE under relatively mild reaction conditions to give the corresponding cyclobutane derivatives, I ~ III. In contrast to 1-vinylpyrene, the Diels-Alder addition of TCNE occurred instead of the [2+2] cycloaddition reaction with respect to 1-vinylnaphthalene.6,7)


I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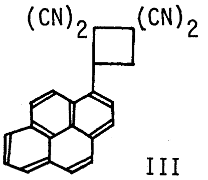
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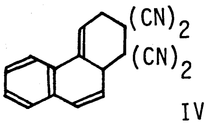
IV

Each reaction system involved the formation of the charge-transfer complex, as evidenced from the electronic absorption spectra. The reactivity of the aromatic-substituted olefins was found to be closely related to the magnitude of their ionization potentials. The reactivity of the olefins increased with a decrease in the ionization potential, namely, with an increase in the electron-donating property of the olefins. A striking solvent effect was observed with respect to the reaction of acenaphthylene and indene which possess relatively high ionization potentials. That is, the cycloaddition reaction proceeded only in a polar solvent like acetonitrile, almost no reaction occurring in less polar 1,2-dichloroethane.[8)] With 1-vinylnaphthalene and 1-vinylpyrene which possess relatively low ionization potentials, the cycloaddition reactions proceeded easily in 1,2-dichloroethane as well as in acetonitrile with the fading of the color due to the charge-transfer complex. The results are summarized in Table 1.

In addition, it was found for the first time that 1,2-dihydronaphthalene is dehydrogenated by TCNE to give naphthalene and tetracyanoethane, instead of undergoing cycloaddition reaction.[9)]

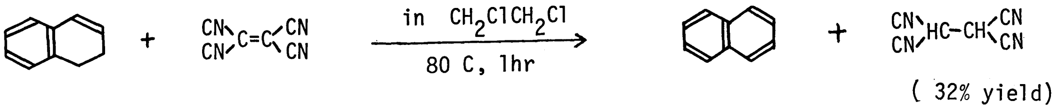

Table 1. Thermal cycloaddition reactions of some aromatic-substituted olefins with TCNE.

Olefin	CT_{max}(nm)[a]	I_p(eV)[b]	Reaction Condition[c] Solvent	 Temp.	 Time(hr)	Cycloadduct[d] Decomp.p.(°C)	 Yield(%)
acenaphthylene	510	8.18	1,2-dichloroethane	reflux	30	I, 186	0
			acetonitrile	reflux	30		16
indene	542, 430[e]	8.01	1,2-dichloroethane	reflux	30	II, 187	0
			acetonitrile	reflux	30		28
1-vinyl-naphthalene	618, 435	7.67	1,2-dichloroethane	room temp.	5	IV, 160	39
			acetonitrile	room temp.	5		41
1-vinyl-pyrene	825, 505	7.05	1,2-dichloroethane	room temp.	1	III, 210	68
			acetonitrile	room temp.	1		69

a Maximum wavelengths of the charge-transfer absorption bands measured in chloroform at room temp.
b The ionization potentials of the olefins were calculated from the charge-transfer absorption bands using the equation[10)]: $h\nu_{CT} = 0.82\ I_p - 4.28$ c Concentrations: [Olefin] = [TCNE] = 0.05 M (0.025 M with 1-vinylpyrene). d The cycloadducts I~IV were identified respectively by the IR, UV, NMR, and mass spectrophotometric data and elementary analyses. The structures of the Diels-Alder adduct and the [2+2] cycloadduct can be differentiated with each other by the NMR and UV spectra.
e See ref. 11.

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3) For examples, see P.D.Bartlett, Quart.Rev., 24, 473 (1970).
4) A suggestive cycloaddition of parent styrene with TCNE is reported to occur in refluxing xylene since seemingly its decomposition product is obtained.[1)]
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6) We are grateful to a referee for his helpful advice concerning the identification of IV. An analogous Diels-Alder addition reaction is reported with respect to 2-vinylnaphthalene.[7)]
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