Thermal 2+2 Cycloaddition Reactions of Some Cyclopropyl-substituted Ethylenes with Tetracyanoethylene[1]

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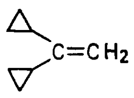
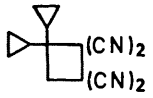
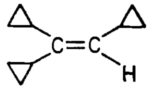
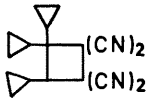
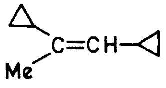
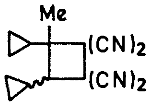
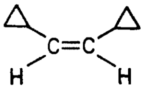
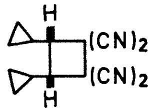
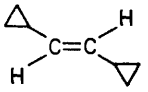
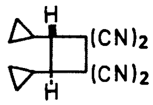
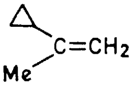
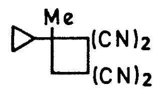
Summary Thermal 2 + 2 cycloadditions of cyclopropylethylenes with tetracyanoethylene to give cyclobutane derivatives are influenced strongly by structural changes in the olefin, but only moderately by the polarity of solvent; the addition is more than 90% stereospecific.

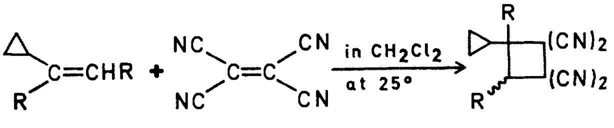
CYCLOPROPYL-SUBSTITUTED ethylenes (**1**—**6**)[2] undergo ready thermal 2 + 2 cycloadditions with tetracyanoethylene in methylene dichloride.[1] A recent communication of Effenberger and Podszun[3] on the cycloadditions of 1,1-dicyclopropylethylene with toluene-*p*-sulphonyl isocyanate and tetracyanoethylene prompts us to report some of our results on these cycloadditions.

2 + 2 *Cycloaddition reactions of cyclopropylethylenes with tetracyanoethylene in methylene chloride at* 25°

					Cycloadduct	
Olefin		C.t. max (nm)	Reaction time (sec.)[a]		M.p.[b]	Yield (%)
	(**1**)	——	1—2		167—168°	57
	(**2**)	635	600		161—162·5°	76
	(**3**)[c]	602	1700		97—98·5°	58
	(**4**)	549	$>6 \times 10^6$		165—167°	(15)[d]
	(**5**)	549	$>6 \times 10^6$		159—160·5°	(10)[d]
	(**6**)	448	1400		108—109·5°	35

[a] Time required to produce a colourless solution. [b] Uncorrected. [c] A mixture of *cis*- and *trans*-isomers. [d] 2 hr. in nitromethane at 100°.

When various cyclopropylethylenes were mixed with tetracyanoethylene in methylene dichloride, coloured solutions resulted, due to the formation of charge-transfer complexes between two ethylenes (Table). A notable observation was that the intensities of the charge-transfer band decreased with time. This was most striking in 1,1-dicyclopropylethylene (**1**); the solution faded almost instantly and the spectroscopic measurement of its charge-transfer maximum could not be performed. The reaction was somewhat slower in the case of tricyclopropylethylene and very much slower for 1,2-dicyclopropylethylenes (**4**) and (**5**) than in the case of (**1**). In all cases, evaporation of the solvent from the colourless solution resulted in the formation of a 1 : 1 cycloadduct of the two components in considerable yields (Table). All the cycloadducts gave satisfactory elemental analyses, molecular weights, and i.r. and n.m.r. patterns as cyclopropyl-substituted cyclobutane derivatives. The presence of the same number of cyclopropyl groups in the cycloadduct as in the starting olefin was most clearly established by inspection of the n.m.r. spectra.



R = H, Me, or cyclo-C_3H_5

This 2 + 2 cycloaddition was affected only moderately by the polarity of the solvent, which was examined in the reaction of tricyclopropylethylene with tetracyanoethylene. The cycloaddition in acetonitrile or in nitromethane proceeded *ca.* 20 times as fast as that in methylene dichloride. The reaction was inhibited strongly by the addition of mesitylene to the reaction mixture This observation indicates that the cycloaddition may proceed *via* the cyclopropylethylene–tetracyanoethylene charge-transfer complex

The cycloadditions of (**4**) and (**5**) with tetracyanoethylene were very slow in methylene chloride at room temperature, so the reaction was studied in nitromethane at 100° A cycloadduct, m p 165—167°, from *cis*-1,2-dicyclopropylethylene and another adduct, m p 159—160 5°, from the *trans*-isomer were obtained, the mixed m p of the two isomers showed a 40° depression The two adducts are clearly stereoisomers, they differ only in the fingerprint region of their i r spectra but differ appreciably in the n m r spectra By careful examination of the n m r spectra it was possible to detect the presence of at least 10% of the one isomeric adduct in the other The crude reaction mixtures were examined by n m r spectroscopy, but in neither case did the cycloadduct contain a detectable amount of its stereoisomer Consequently, it is concluded that the cycloaddition is more than 90% stereospecific

The 2 + 2 cycloadditions of some electron-rich olefins with strongly electron-demanding olefins, *e g* *p*-methoxystyrene with tetracyanoethylene,[4] t-butyl vinyl sulphide or ethyl vinyl ether with 1,2-dicyano-1,2-bis(trifluoromethyl)-ethylene,[5] tetramethoxyethylene with 1,2-dicyanoethylenes,[6] and several others,[7] have been reported and explained as two-step ionic cycloaddition processes [7] The present results, particularly the effects of structural changes on the rates of reaction, might be in accordance with an ionic process However, the stereochemical results favour a polarized cyclic transition state [8] There was no indication of the formation of a 1,4-dipole charge-transfer intermediate reported by Gompper,[7,9] even at lower temperatures

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[1] I Moritani, S Nishida T Tsuji, K Ito T Sato and E Tsuda presented in part at the XIXth Conference on Organic Reaction Mechanism, Chemical Society of Japan, Yamagata Japan, October, 1968, T Teraji, S Nishida, I Moritani, and E Tsuda presented in part at the XXIIth Annual Meeting of the Chemical Society of Japan Tokyo Japan, April, 1969

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[5] S Proskov H E Simmons and T L Cairns, *J Amer Chem Soc* , 1966 **88**, 5254

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