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DISTINCTIVE STRUCTURE-REACTIVITY SEQUENCES IN THE TYPE I AND TYPE II CYCLOADDITIONS OF CYCLOPROPYL-SUBSTITUTED ETHYLENE WITH TETRACYANOETHYLENE 1)

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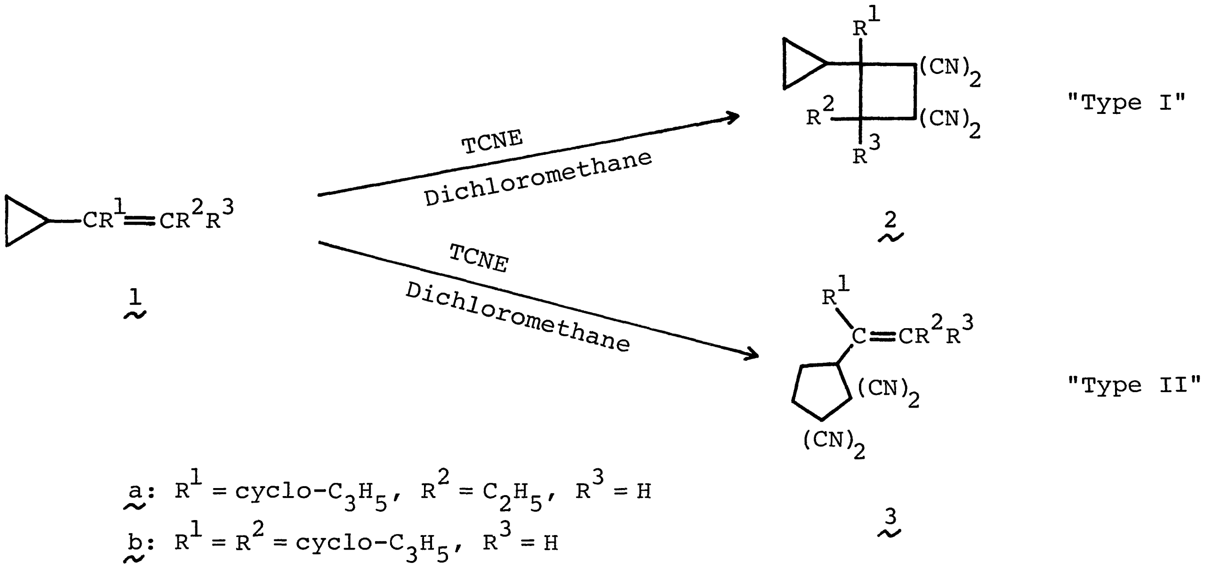
Structure-reactivity sequences of two cycloadditions, distinctive in pattern, between cyclopropylethylene and tetracyanoethylene were totally different. In the type I, a bulky group at C2 decreased the rate of the reaction, whereas, in the type II, bulky alkyls at C2 enhanced the reactivity. The results accommodate to a proposed scheme involving an electron transfer step.

In the study of the reactions between cyclopropylethylenes (1) and tetracyanoethylene (TCNE), we have uncovered the fact that the reaction may take two distinctive courses depending mainly upon the structure of 1.2,3,4) The first course is a $[_{\pi}2+_{\pi}2]$ cycloaddition to give a cyclobutane derivative 2 (the type I reaction).2) The second course is realized in the reactions of certain heavily substituted 1.3) The cycloaddition takes place at a C-C bond of the cyclopropyl group in 1 and a vinylcyclopentane derivative 3 is produced (the type II reaction). Since the type II reaction proceeds smoothly at an ambient temperature, it has been of our great interest to rationalize the necessity of forming such an adduct as 3. Recently, we found that the structure-reactivity sequence of the type II reaction is totally different from that of the type I reaction. The results may accomodate to a previously proposed scheme for the type II reaction.3,5)

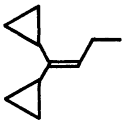
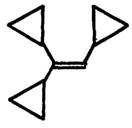
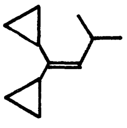
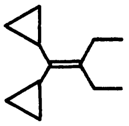
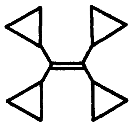
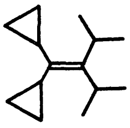
Olefins 1a, 1b, and 1c produced 2 exclusively in dichloromethane at 25 °C, whereas 1d, 1e, and 1f yielded 3 as a sole product under the same conditions.6) Thus, the kinetic studies on the reaction of 1a-1f with TCNE were carried out in order to evaluate the effect of the substituent on the reactivity both in the type I and in the type II reaction. The rates of the reaction were followed in dichloromethane at 25 °C by observing the amount of 1 by GC at appropriate time intervals.7) In all



a: R^1 = cyclo-C_3H_5, R^2 = C_2H_5, R^3 = H
b: R^1 = R^2 = cyclo-C_3H_5, R^3 = H
c: R^1 = cyclo-C_3H_5, R^2 = $CH(CH_3)_2$, R^3 = H
d: R^1 = cyclo-C_3H_5, R^2 = R^3 = C_2H_5
e: R^1 = R^2 = R^3 = cyclo-C_3H_5
f: R^1 = cyclo-C_3H_5, R^2 = R^3 = $CH(CH_3)_2$

Table I

Rate Data for the Reaction of 1 with TCNE at 25 °C in Dichloromethane

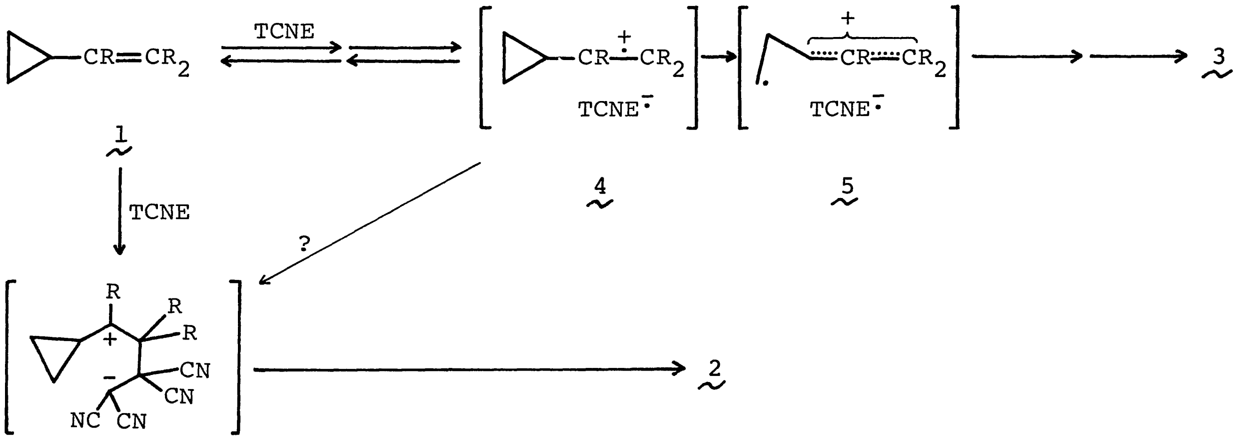
Type I	Olefin	 1a	 1b	 1c
	10^3k_2 (L, mol^{-1} sec^{-1})	330	56	0.76
	Rel. Rate (25 °C)	430	74	1.0*
Type II	Olefin	 1d	 1e	 1f
	10^5k_2 (L, mol^{-1} sec^{-1})	2.4	49	5.7
	Rel. Rate	0.43	8.7	1.0*

runs, a good second order rate plot was obtained up to at least 50% reaction. The results are summarized in Table I.

The type I reaction is evidently influenced by steric bulk of the substituent at C2. Tricyclopropylethylene (1b) reacted faster than 1,1-dicyclopropyl-3-methyl-1-butene (1c), but 1,1-dicyclopropyl-1-butene (1a) did still faster than 1b. In a contradictory manner, olefins substituted by bulky groups at C2 exhibited rather high reactivity in the type II reaction. Thus, diisopropyl-substituted 1f reacted faster than diethyl-substituted 1d. Tetracyclopropylethylene (1e) was the most reactive olefin among them.

A further point to be noted is that symmetrical 1e exhibited the highest reactivity in the type II reaction. This is totally opposite to that observed in the type I reaction. Namely, *cis*- and *trans*-1,2-dicyclopropylethylenes are the least reactive, whereas unsymmetrical 1,1-dicyclopropylethylene is the most reactive.[2)] Vinylcyclopropane shows intermediate reactivity.

The reactivity sequence observed in the type II process suggests that the groups at C2 exert electronic effects in such a way as they increase the pi electron density of 1. Thus, as postulated previously,[3)] an electron transfer from 1 to TCNE will be an important step involved in the reaction scheme.[5)] The rearrangement of a radical ion pair 4 to 5 will most probably the rate-determining step. In support of the involvement of the electron transfer step, it should be mentioned that 1e is now known to have a low ionization potential ($IP_a = 7.25$ eV),[8)] which accounts for the high reactivity of 1e.



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REFERENCES AND NOTES

1) A partial fulfillment for the PhD degree of F. K.
2) S. Nishida, I. Moritani, and T. Teraji, J. Chem. Soc. Chem. Commun., 1970, 501; J. Org. Chem., 38, 1878 (1973). See also F. Effenberger and W. Podszun, Angew. Chem. Int. Ed. Engl., 8, 976 (1969).
3) S. Nishida, I. Moritani, and T. Teraji, J. Chem. Soc. Chem. Commun., 1971, 36.
4) The reaction course depends also upon the solvent polarity and reaction temperature. We recently found that 1d, and 1,1-dicyclopropyl-2-methylpropene produced a mixture of 2 and 3 under certain conditions. Thus, 1d gave exclusively 3d in dichloromethane at 25 °C, but it yielded a 1.4 : 1 mixture of 2d and 3d in acetonitrile. At 80-85 °C, however, 1d produced only 3d even in acetonitrile. Clearly, usage of a less polar solvent and application of a high reaction temperature favor the type II process.
5) In the previous communication,[3)] we reported that oxygen interfered the formation of 3e, but later we found that it did not. The erroneous observation was caused by the difficulty of crystallizing 3e obtained under non-degassed conditions. After these observations, the scheme should be modified in such a way as the radical ion pairs (4 and 5) would remain in a solvent cage.
6) The reactions of 1b, 1c, and 1e with TCNE have been described previously.[2,3)] Preparations of 1d and 1f are reported (S. Nishida and F. Kataoka, J. Org. Chem., 43, 1612 (1978)). The adducts 2a, 3d, and 3f gave satisfactory elemental analyses and spectroscopic data. Details will be published elsewhere.
7) Concentrations of both 1 and TCNE were set equal to 0.025 or 0.050 mol/L. Before GC analysis, the reaction was quenched by adding 4-5 fold excess of 1,1-dicyclopropylethylene, which was known to react with TCNE almost instantly.
8) For ionization potentials of related ethylenes, see S. Nishida, I. Moritani, and T. Teraji, J. Chem. Soc. Chem. Commun., 1972, 114.

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