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THE CYCLOADDITION OF BICYCLO[2.1.0]PENT-2-ENE WITH TETRACYANOETHYLENE[1]

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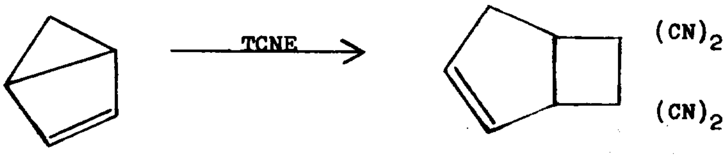
The familiar Diels-Alder reaction giving cyclohexenes[3] and the exceedingly rare homologous combination of a vinylcyclopropane with an olefin to give a cycloheptene[4] both may be, according to the precepts of orbital symmetry theory[5], thermally-allowed $[\pi_s^2 + \pi_s^2 + \pi_s^2]$ or $[\pi_s^2 + \sigma_s^2 + \pi_s^2]$ cycloreactions.

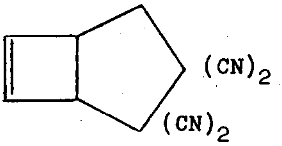
Recent work with vinylcyclopropanes, however, has shown that even with such strongly electrophilic olefins as tetracyanoethylene, cyclobutanes through (2+2) cycloadditions rather than cycloheptenes through the homologous Diels-Alder process are formed.[6,7]

We have found that the somewhat exceptional vinylcyclopropane derivative bicyclo[2.1.0]pent-2-ene[8-10] (I) reacts as a homodiene with tetracyanoethylene, giving 6,6,7,7-tetracyanobicyclo[3.2.0]hept-2-ene(II).

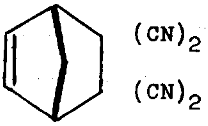


I II

When a solution of bicyclopentene[9] and TCNE in tetrahydrofuran is warmed to 0° for several hours, concentrated, and triturated with methanol, a colorless light-sensitive 1:1 adduct is obtained (50% yield after recrystallization from acetone); mp 196-198° (dec); m/e 194 (M^+, $C_{11}H_6N_4$), 167, 129, 76, and 66 (base peak). The nmr spectrum of the adduct in acetone-d_6 has multiplets at δ 6.34, 5.98, 4.37, 4.17, and 3.02 ppm in a 1:1:1:1:2 ratio. Double irradiation experiments at 100 MHz established the absolute magnitudes of the spin-spin coupling interactions among the various protons; both of the methylene protons were coupled to each vinyl hydrogen to comparable extents (1.8 to 2.2 Hz) and the ^3J-coupling between vinyl protons was 5.9 Hz, thus supporting structure II and excluding the alternative III.[11,12]



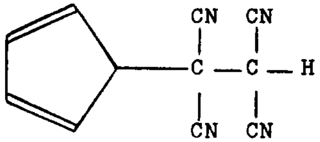
III



IV

A side product in the reaction proved to be adduct IV[13] formed, presumably, either through a two-step addition across the C(1)-C(4) bond of bicyclopentene or through an unexceptional Diels-Alder process utilizing cyclopentadiene[13], a common impurity in bicyclopentene preparations. The first possibility seemed plausible in light of known additions across strained 0-bridge single bonds of bicyclobutanes[14] and bicyclopentane.[15] Additional experiments, though, supported the second explanation. A solution of bicyclopentene in THF was treated with dimsyl anion in DMSO and flash distilled at 10° (50 mm); glpc analysis gave an estimate of the small amount of cyclopentadiene contaminating the bicyclopentene preparation. The product mixture from this preparation and TCNE contained only the amount of adduct IV derivable from the original cyclopentadiene impurity.

If there is a two-step component in the bicyclopentene addition with TCNE, it fails to produce IV in significant yield; other possible products, such as V and the numerous other compounds derivable from V, are not presently excluded.[16]



V

The energetic demands of the thermally allowed $[\pi_s^2 + \sigma_s^2 + \pi_s^2]$ homodiene plus ethylene cycloaddition, though normally prohibitively high, are met by bicyclopentene, thanks to its unusually high ground state energy and favorable geometry. It and other appropriate hydrocarbons with high heats of formation may provide other examples of allowed but energetically expensive and therefore seldomly achieved cycloreaction processes.

NOTES AND REFERENCES

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16. In preliminary experiments, bicyclopentene has not given adducts with N-phenylmaleimide, fumaronitrile, or 1,1-dicyano-2-methylpropene; very complex reaction mixtures are produced from bicyclopentene and triazolinediones.