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REACTION OF 2,2-DIPHENYLMETHYLENECYCLOPROPANE WITH ELECTRON-DEFICIENT QUINOID COMPOUNDS. NEW $[_{\sigma}2 + _{\pi}2 + _{\pi}2]$-TYPE CYCLOADDITIONS

R. Noyori, N. Hayashi, and M. Katô

Department of Chemistry, Nagoya University, Chikusa, Nagoya 464, Japan

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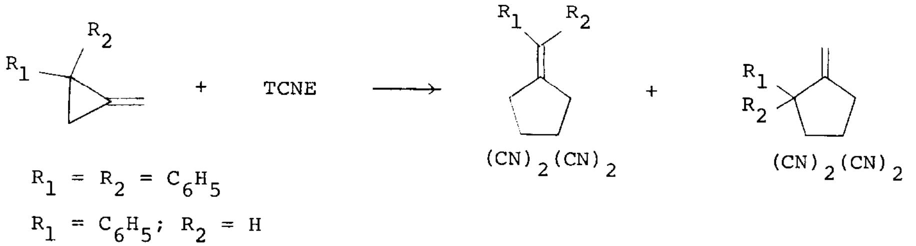
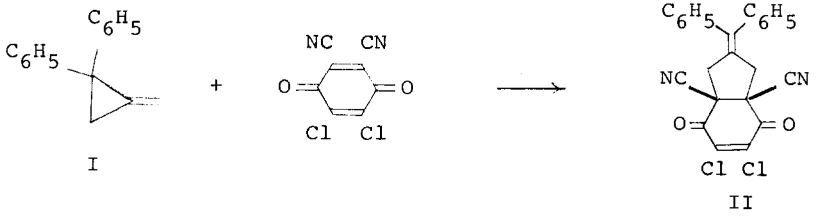
We recently reported a $[_{\sigma}2 + _{\pi}2 + _{\pi}2]$-type cycloaddition of methylenecyclopropanes and tetracyanoethylene (TCNE) affording an isomeric mixture of five-membered adducts (eq 1).[1] This paper describes the achievement of the related, regiospecific reaction.



(1)

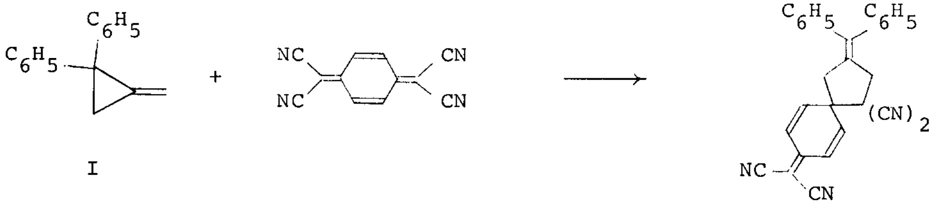
When a dark-red solution of 2,2-diphenylmethylenecyclopropane (I) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (1:1.2 mole ratio) in benzene was heated at 100° for 24 hr (sealed tube, nitrogen atmosphere), a single bicyclic adduct II, mp 167--169°, was obtained in 75% yield (eq 2).[2] The C_s symmetry incorporated in II (cis ring fusion) was verified by the fact that treatment with m-chloroperbenzoic acid in benzene led to a single epoxide [ir ($CHCl_3$) 2240



(2)

(CN), 1715 (C=O), and 1550 cm^{-1} (C=C)] showing in the nmr spectrum only one set of AB quartet ($CDCl_3$, δ 2.51 and 2.59, *J* = 15 Hz) due to the methylene protons.

In a similar manner, heating an equimolar mixture of I and 7,7,8,8-tetracyanoquinodimethane (TCNQ) in benzene at 100° for 48 hr resulted in the formation of the spiro-fused adduct III, mp 219—220°, in 60% yield (eq 3).[3] To our best knowledge, the present reaction provides the first example of cycloaddition of TCNQ.



I III (3)

The cycloaddition is the sole observed path of the reaction between methylenecyclopropanes and electron-deficient olefins (eqs 1—3). The possible concerted $[({}_{\sigma}2_s + {}_{\pi}2_s) + {}_{\pi}2_s]$ or $[({}_{\sigma}2_a + {}_{\pi}2_a) + {}_{\pi}2_s]$ process could explain most reasonably the cleanness of these reactions as well as the previously obtained findings.[1] Rigorously, however, the alternative stepwise mechanism could not be ruled out, since the intriguing molecular structure of methylenecyclopropanes in which the π and C-2—C-3 σ bonds are perpendicular to one another might prohibit the sufficient orbital overlap for the transition states of the concerted cycloaddition. Elucidation of the exact reaction mechanism awaits further theoretical and experimental scrutinies.

REFERENCES AND FOOTNOTES

1. R. Noyori, N. Hayashi, and M. Katô, *J. Amer. Chem. Soc.*, **93**, 4948 (1971).
2. Ir ($CHCl_3$) 2240 (nonconjugated CN), 1714 (C=O), and 1548 cm^{-1} (C=C); nmr ($CDCl_3$) δ 3.36 (s, 4 H, CH_2) and 7.0—7.5 (m, 10 H, C_6H_5); uv ($CHCl_3$) 230 (log ε 4.23), 248 (4.22), and 285 nm (4.18); mass (70 eV) *m/e* 434 and 432 (M^+), and 206 (base peak, M^+ - DDQ).
3. Ir (KBr) 2240 (nonconjugated CN) and 2220 cm^{-1} (conjugated CN); nmr ($CDCl_3$) δ 3.00 (br s, 2 H, CH_2), 3.50 (br s, 2 H, CH_2), 6.73 (A part of AB q, *J* = 10 Hz, 2 H, =CH), and 7.1—7.6 (m, 12 H, =CH and C_6H_5); uv ($CHCl_3$) 257 (log ε 4.00) and 318 nm (4.31); mass (70 eV) *m/e* 410 (M^+) and 206 (base peak, M^+ - TCNQ).