

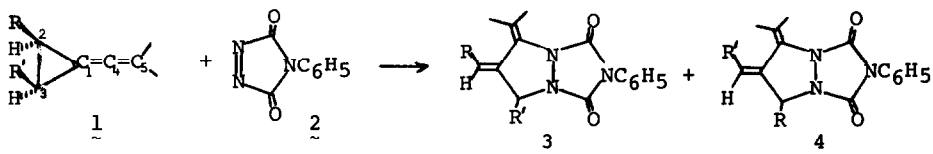
CYCLOADDITION REACTIONS OF ALKENYLIDENE- AND METHYLENOCYCLOPROPANES.
COMPARISON OF REACTIVITY AND MODE OF REACTION WITH
4-PHENYL-1,2,4-TRIAZOLINE-3,5-DIONE

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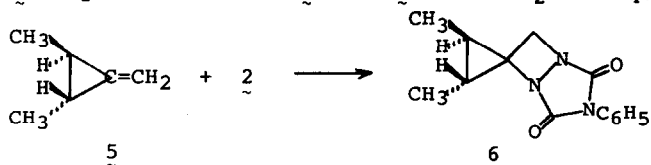
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(Received in USA 14 February 1972; received in UK for publication 16 June 1972)

We recently reported that alkenylidenecyclopropanes (1) undergo very rapid cycloaddition (<2 min. at 0° in dichloromethane) with 4-phenyl-1,2,4-triazoline-3,5-dione (2) to produce adducts of structure 3 and 4 (1). It was suggested that the formation of 3 and 4 occurs via concerted cycloaddition pathways, and could involve either six- or eight-electron processes. We have investigated the reactivity and mode of reaction of some methylenecyclopropanes with 2 in which cycloaddition can occur only via a six-electron process.

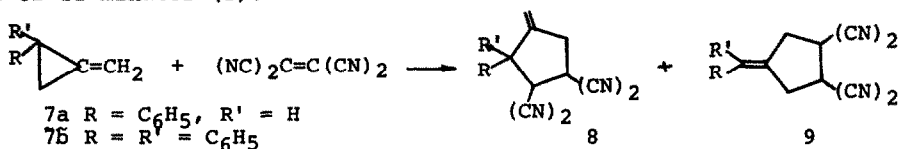


trans-2,3-Dimethylmethylene cyclopropane (5) reacts very slowly (36 hr at 25° in dichloromethane) with 2 to produce a 1:1 adduct (mass spectrum m/e calcd for $C_{14}H_{15}N_3O_2$: 257,114. Found: 257,120). The ir spectrum displayed bands at 1765 and 1710 cm^{-1} characteristic of the urazole ring. No N-H absorption band was present in the 4000-3200 cm^{-1} region. The nmr spectrum of the adduct displayed two doublets at δ 1.10 and 1.28 ($J = 7.0$ and 7.0 Hz, 3 H each) characteristic of methyls attached to a saturated carbon, along with multiplets at δ 1.97 (2 H, cyclopropyl hydrogens), 2.80 (2 H, $-CH_2-N$ split by geminal and long-range coupling to the cyclopropyl hydrogens), and 7.3 (5 H, aromatic hydrogens). The ir and nmr data are consistent only with a $\pi_2 + \pi_2$ cycloaddition product of structure 6. Cycloaddition of 2 with 5 across C_2 and C_4 , or C_2 and C_3 , does

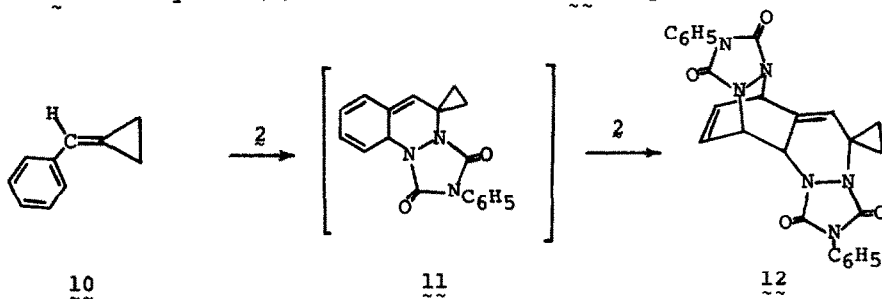


not produce adducts whose structures are consistent with the physical data.

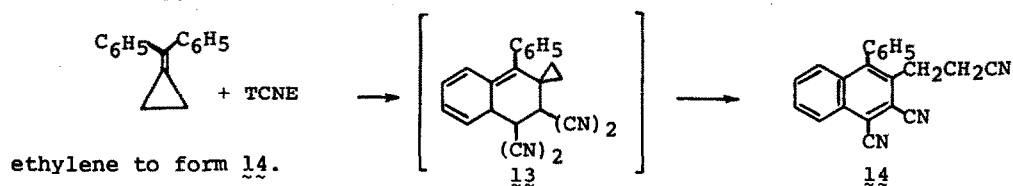
The $\pi 2 + \pi 2$ reaction observed between 5 and 2 is in contrast to the reaction of 2-phenyl- (7a) and 2,2-diphenylmethylenecyclopropane (7b) with tetracyanoethylene (2) which is reported to produce the adducts 8 and 9. The reaction conditions, however, are rather strenuous (5 days at 100° in benzene), conditions under which optically active 7a undergoes racemization with a half-life of 22 minutes (2)!



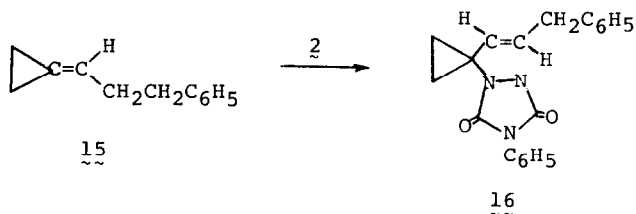
Benzylidenecyclopropane (10) reacts rapidly with 2 to form the 2:1 adduct 12 ($\underline{m/e}$ calcd for C₂₆H₂₀N₆O₄: 480,158. Found: 480,154). The ir spectrum of the 2:1 adduct displays typical urazole ring absorption bands, but no N-H bands in the 4000-3200 cm⁻¹ region. The presence of a cyclopropyl function in the 2:1 adduct was clearly evident by the presence of high-field multiplets in the nmr spectrum at δ 1.00 (2H), 1.82 (1H) and 2.66 (1H) (3); the remainder of the nmr spectrum being essentially identical with the nmr spectrum of the 2:1 adduct of 2 with styrene (4). The formation of 12 is pictured as occurring



via 11; an intermediate similar to that proposed by Baldwin and Peavy (5) to be formed (13) in the reaction of diarylmethylenecyclopropanes with tetracyano-



(4-Phenylbutylidene)-cyclopropane (15) reacts with 2 only via an "ene" reaction to produce the 1:1 adduct 16. The ir spectrum of 16 displays an N-H absorption band at 3435 cm^{-1} along with the typical urazole ring absorption bands. Retention of the cyclopropyl function in 16 was immediately evident from the nmr spectrum by the presence of AA'BB' multiplets at δ 1.01 and 1.32. The vinyl and methylene hydrogens appear as an AMX₂ system at δ 5.68 (dt, $J = 15.6$ and 5.6 Hz), 5.40 (d, $J = 15.6$ Hz) and 3.36 (d, $J = 5.6$ Hz, 2H).



The extreme reluctance of the methylenecyclopropanes 5, 10 and 15 to react with 2 in $[(\sigma_2 + \pi_2) + \pi_2]$ cycloaddition reactions is in distinct contrast to the extremely facile analogous reactions of alkenylidenecyclopropanes with 2 (1). The only difference between the methylene- and alkenylidenecyclopropanes is the presence of the C₄-C₅ π -bond in the latter which allows for an "eight-electron" reaction process. The very interesting orbital interactions present in 1, and in the frontier orbital interactions present in the transition state for cycloaddition leading to the high degree of reactivity with 1 (but not with the methylenecyclopropanes) will be discussed in a forthcoming article on the cycloaddition reactions of alkenylidenecyclopropanes with 2 (6).

References:

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2. R. Noyori, N. Hayashi, and M. Kato, *ibid.*, 93, 4948 (1971).
3. The rather significant dissimilarity in the chemical shifts of the hydrogens of the cyclopropyl function is due to long-range shielding by the urazole ring. A molecular model of 12 indicates that one of the methylenes of the cyclopropyl function resides almost in the plane of the urazole ring and suffers extensive deshielding. Similar deshielding

effects have been observed in the alkenylidenecyclopropane-2 adducts (1,6).

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