

CYCLOADDITION REACTIONS OF SUBSTITUTED VINYL-CYCLOPROPANES WITH
4-PHENYL-1,2,4-TRIAZOLINE-3,5-DIONE AND CHLOROSULFONYLISOCYANATE

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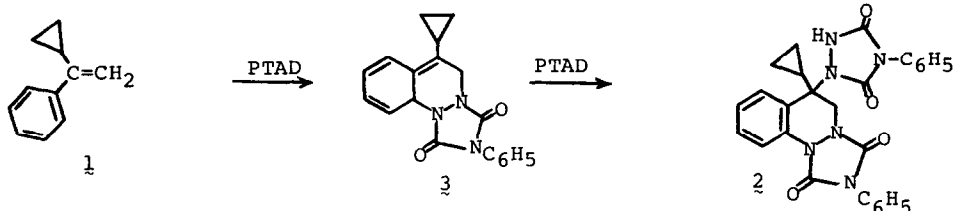
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In a continuing study of cycloaddition reactions involving cyclopropane ring-containing systems (1) we have investigated the reactions of vinylcyclopropane and some substituted vinylcyclopropanes with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) and chlorosulfonylisocyanate (CSI).

The cycloaddition of maleic anhydride with α -cyclopropylstyrene (1) to produce 4-phenyl-4-cycloheptene-1,2-dicarboxylic anhydride was reported more than a decade ago (2). Despite the seemingly important synthetic utility of this type of reaction, reports of further investigations of such reactions have not appeared. We have not, however, been able to reproduce this reaction under the reported reaction conditions. (We have not explored the possibility that the earlier report might have involved a catalyzed addition).

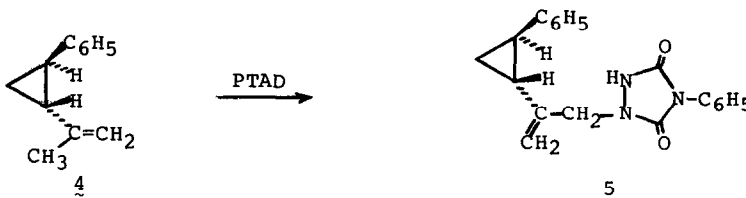
We then resorted to the use of the very much more reactive dienophile PTAD with 1 which resulted in a very fast reaction with 1 to produce the 2:1 adduct 2 [mp 231-232°; m/e calcd for C₂₇H₂₂N₆O₄: 494.173. Found: 494.176; ir: ν_{N-H} 3492 cm⁻¹; nmr: (DMSO-d₆) δ 0.25 (m, 2H), 0.65 (m, 2H), 1.70 (m, 1H), 4.24 (d, J = 12.5 Hz, 1H), 4.68 (d, J = 12.5 Hz, 1H), 7.12 (br.s, 1H), 7.4 (m, 15H), and 8.2 (m, 1H)]. The retention of the cyclopropane ring in the product was clearly evident from the very high-field multiplets in the nmr.



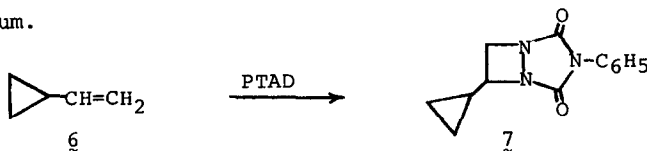
The 2:1 adduct is easily visualized as being formed via cycloaddition of PTAD across the styrene chromophore of 1, instead of the vinylcyclopropane moiety,

to give 3 followed by an "ene" reaction to regenerate the aromatic system.

trans-2-Phenylisopropenylcyclopropane (4) reacts rapidly with PTAD (15 min at 25° in CH₂Cl₂) to give only the "ene" product 5 [91%; mp 43-46°; m/e calcd for C₁₇H₂₂N₃O₂: 330.145. Found: 330.147; nmr: (CDCl₃) δ 0.85-1.30 (m, 2H), 1.35-1.55 (m, 1H), 1.60-2.10 (m, 1H), 4.23 (br.s, 2H), 4.93 (br.s, 2H), 7.1 (m, 5H), and 7.35 (s, 5H); ir: ν_{N-H} 3450 cm⁻¹]. The retention of the cyclopropane ring in the adduct is clearly indicated by the high-field multiplets appearing in the nmr spectrum.



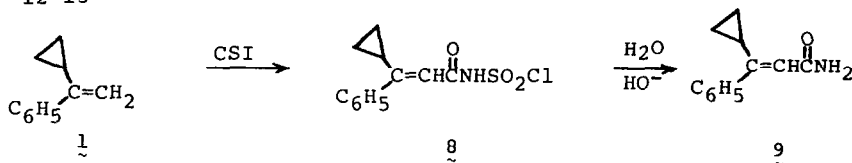
In order to remove the potentiality for possible "ene" or other cycloaddition reactions, the reaction of vinylcyclopropane itself was carried out with PTAD. Vinylcyclopropane (6) reacted more slowly (45 min at 25°) with PTAD to produce only the (2 + 2) cycloaddition product 7 [87%; mp 128-130°; m/e calcd for C₁₃H₁₃N₃O₂: 243.108. Found: 243.109; nmr: (CDCl₃) δ 0.3-0.7 (m, 4H), 1.25 (m, 1H), 3.6-4.3 (m, 3H), 7.36 (br.s, 5H)]. Again, the presence of a cyclopropane moiety in the product is clearly indicated by the nmr spectrum.



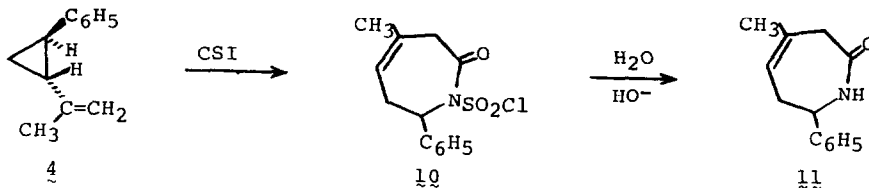
Thus, even in the absence of other more facile reaction pathways, vinylcyclopropane is extremely reluctant to undergo cycloaddition to the vinylcyclopropane system, reacting instead in a (2 + 2) manner. Methylene-cyclopropanes similarly are extremely reluctant to undergo cycloaddition reactions to produce methylenecyclopentane-type products (1b); however, alkenylidenecyclopropanes undergo facile cycloaddition with PTAD (1a, 1c). A molecular orbital analysis of vinylcyclopropanes, similar to that presented for alkenylidenecyclopropanes (1c), indicates that appropriate molecular orbitals are available

for a concerted cycloaddition to a vinylcyclopropane. A number of differences, however, exist between the alkenylidene- and vinylcyclopropanes. The bond length between the double bond and the three-membered ring is different, as well as is the Walsh- π bond interorbital angles. These differences must reduce the effective orbital overlap in the transition state for a concerted cycloaddition reaction, thus allowing other reaction pathways to effectively compete.

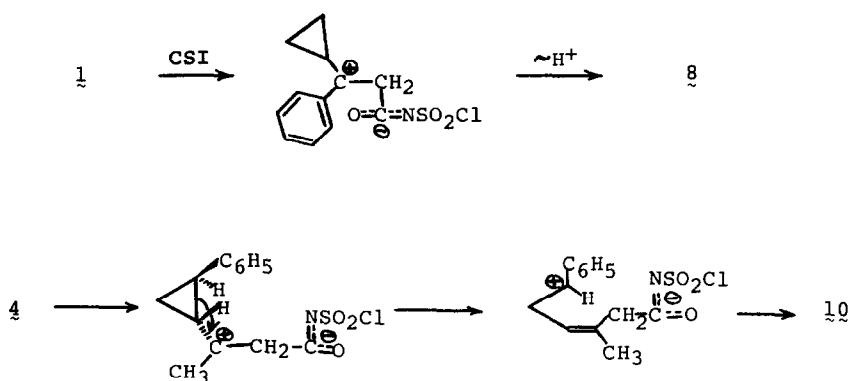
Treatment of 1 and 4 with CSI leads to different types of reactions. Reaction of 1 with CSI in CH_2Cl_2 at 0° produced only the cyclopropane ring retained product 8 of unknown stereochemistry [88%; mp $109-110^\circ$; ir: $\nu_{\text{N-H}}$ 3300 cm^{-1} ; nmr: δ 0.55-1.05 (m, 4 cyclopropyl H's), 1.55-1.94 (m, 1H), 6.05 (s, =CH-), 7.25 (m, 5H), and 9.3 (br. s, NH)]. Hydrolysis of 8 with aqueous base produced the corresponding unsaturated amide 9 [mp $100-101^\circ$; m/e calcd for $\text{C}_{12}\text{H}_{13}\text{NO}$: 187.100. Found: 187.098].



In contrast, 4 reacts with CSI to produce the cyclopropane ring-opened product 10 (92% as a viscous liquid). The structure of 10 was derived from the spectral properties of the lactam 11 derived by the hydrolysis of 10 [mp $113.0-113.5^\circ$; m/e calcd for $\text{C}_{13}\text{H}_{15}\text{NO}$: 201.116. Found: 201.119; ir: $\nu_{\text{N-H}}$ 3397 cm^{-1} ; nmr: δ 1.83 (br. s, 3H), 2.50 (br. s, 2H), 2.77 (br. d, $J = 16.0$ Hz, 1H), 3.77 (br. d, $J = 16.0$ Hz, 1H), 4.88 (four overlapping doublets, $J = 10.0, 5.0, \text{ and } 4.2$ Hz, 1H), 5.49 (br. s, 1H), 6.05 br. s, 1H), and 7.35 (s, 5H)]. The position of the phenyl in 11 was demonstrated by saturation of the ^{14}N resulting in a doublet ($J = 5.0$ Hz) for the N-H resonance.



The distinctly different behavior between 1 and 4 with CSI must be due to the different stabilization afforded the cationic portion in the dipolar intermediate; in the case of the reaction of 1 the phenyl group offering stabilization, whereas in the intermediate derived from 4 no stabilization is afforded and the cyclopropane ring undergoes ring opening to produce a benzyl cation.



References:

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