Alternative Modes of Addition of Dienophiles to Vinylcyclopropane Systems

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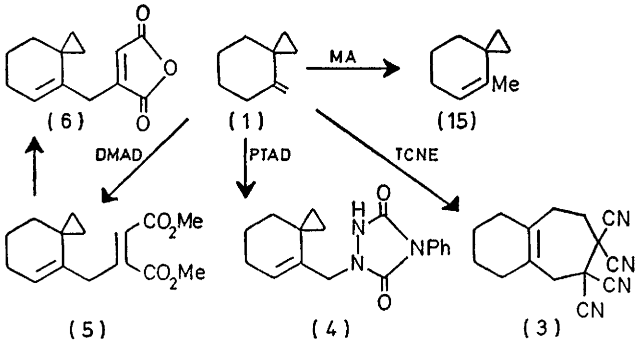
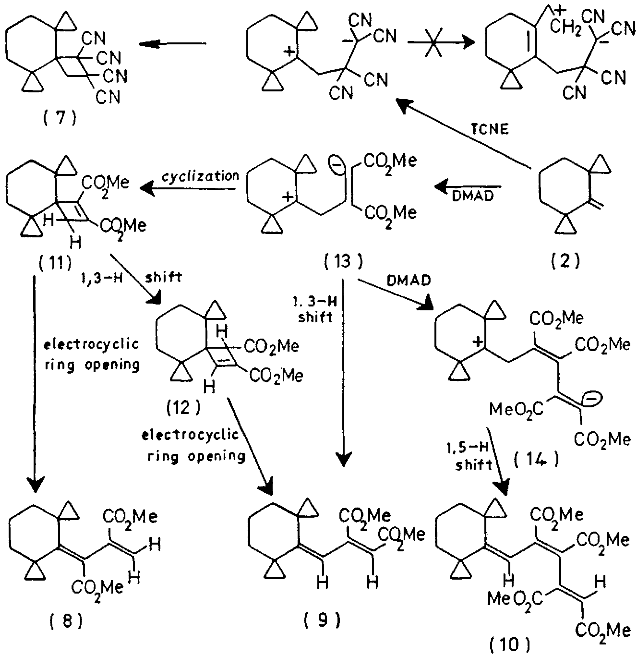
Summary Two alternative modes of addition to vinylcyclopropane systems are here described for each of two dienophiles: tetracyanoethylene is shown to react either *via* [2 + 2] or by [2 + 4] cycloadditions; and dimethyl acetylenedicarboxylate reacts either by the "ene" route or by way of insertion to the double bond.



Scheme 1

There are a few examples of [$\pi 2 + \pi 2 + \sigma 2$] cycloreactions involving 1,5-conjugative additions of dienophiles to vinylcyclopropanes to form the corresponding 7-membered ring-systems. The recorded reactions involve additions to α-cyclopropylstyrene,[1] *N*-methoxycarbonyl-2,3-homo-pyrrole,[2] bicyclo[2,1,0]pent-2-ene[3] and *trans*-2-phenylisopropenylcyclopropane.[4] The dienophiles used in these reactions include maleic anhydride (MA),[1] *N*-phenylmaleimide,[2] dimethyl acetylenedicarboxylate (DMAD),[2] tetracyanoethylene (TCNE)[3] and chlorosulphonylisocyanate.[4] It is peculiar that highly reactive dienophiles such as 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD),[4] or benzyne,[5] do not add across the vinylcyclopropane systems, and react instead either by the "ene" route or by way of [2+2] cycloaddition.[4,5]



SCHEME 2

We report a new case of a "homodienic" synthesis and a new insertion reaction in two new vinylcyclopropane systems.

The hydrocarbons (**1**) and (**2**) were synthesized from the corresponding ketones,[6] by application of a modified Wittig reaction.[7] They show molecular ions at *m/e* 122 and 148, respectively, in the mass spectrum.

An excess of (**1**) was allowed to react with TCNE for 4 h at room temp. in MeCN under N_2, and the mixture separated by g.l.c. to provide a $C_{15}H_{14}N_2$ product (*m/e* 250), shown to result from a "homodienic synthesis," in the sense that two π bonds and one σ bond were converted into two new σ bonds and one π bond with the formation of a 7-membered ring [(**3**) Scheme 1]. The disappearance of both cyclopropane and vinylic signals in the n.m.r. spectrum of (**3**) is in line with the structure assigned.

Addition of equimolar quantity of PTAD to a solution of (**1**) in acetone at room temp. (3·5 h) did not produce a 7-membered ring, but led instead to an "ene" reaction product, (**4**), as inferred from its n.m.r. spectrum, its i.r. absorption at 3170 cm^{-1} (N–H), and its mass spectrum displaying a molecular ion peak at *m/e* 297 and a base peak at *m/e* 79, which arise from successive losses of neutral species of PhNCO, HNCO, and two ethylene molecules.

A similar "ene" product, (**5**), was obtained by heating a two molar excess of DMAD with (**1**) for 20 h in a sealed tube. It was cyclized in a two-stage process into the corresponding anhydride, (**6**) (i.r.: 1845 and 1780 cm^{-1}).

Unlike (**1**), the "ene" reaction in (**2**) is precluded due to absence of allylic hydrogens, which in turn should increase the probability of the [$\pi2 + \pi2 + \sigma2$] cycloreaction. However, the reaction of equimolar quantities of (**2**) and TCNE yielded within a few minutes the 1 : 1 [2 + 2] cycloadduct (**7**) (Scheme 2). The preference of the [2 + 2] addition over that of 1,5-addition is manifested also by the emergence of (**8**) and (**9**) from the reaction of a 3-fold excess of DMAD with (**2**) (48 h, 120°). The immediate precursors of (**8**) and (**9**) are, presumably, the corresponding cyclobutene intermediates, which are the sole cycloproducts of this reaction. They arise from the collapse of the dipolar intermediate[8] (**13**), first to (**11**), and then to (**12**), *via* a 1,3-hydrogen shift. The main product of this reaction is, however, the 2 : 1-adduct, (**10**), (*m/e* 432). This clearly indicates that system (**2**) has no tendency to react with DMAD in either mode of cycloreaction, but rather reacts *via* chain insertion, yielding the trienic product.

TABLE

Compound	(3)	(4)	(7)	(8)	(9)	(10)
M.p., °C	94	124	181	58	63	106—108
λ_{max}/nm (log ϵ)	—	—	—	210(4·00)[b] 250(3·48)[b]	210(4·00)[b] 300(3·60)	208(4·02)[c] 227(3·38) 310(3·38)
τ(cyclopropyl)[a]	—	9·33	9.8—8·7	9.8—9·1	9·7—9·1	10·0—9·0

[a] 60 MHz in CCl_4. [b] In EtOH; [c] In C_6H_{14}.

The structures of (**8**)—(**10**) were based on their spectroscopic data and the oxidative degradation of their side-chains, to provide the known dispiro[2,1,2,3]decan-4-one.[6]

Finally, both (**1**) and (**2**) failed to add maleic anhydride. (**1**) isomerized into (**15**) on heating with MA (24 h).

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