Cycloadditions to 1,1-Dicyclopropylethylene[1]

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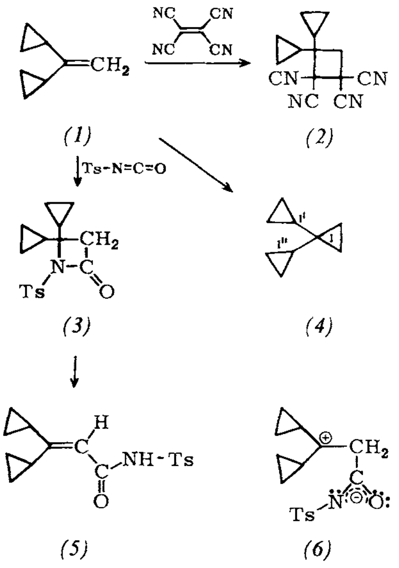
While the stabilization of cationic centers by alpha cyclopropyl groups has been verified in many instances[2,3], to the best of our knowledge nothing is known about the influence of cyclopropyl groups, as substituents, on the reaction mechanism of multiple bonds. The α-cyclopropylcarbonium ions[4] that may be formed are capable of rearrangement, thus providing additional information as to a polar or a more concerted mechanism of cycloaddition.

We have therefore investigated the reaction of 1,1-dicyclopropylethylene *(1)* with electrophiles. Reaction of *(1)* with tosyl isocyanate in ether at 0 °C leads to the formation of the β-lactam *(3)* (yield 50%, m.p. 93 °C; IR: $\nu_{C=O} = 1788\ cm^{-1}$). In boiling benzene, *(3)* rearranges to the acrylamide *(5)* (yield 100%, m.p. 98 °C; IR: $\nu_{C=O} = 1704\ cm^{-1}$, $\nu_{NH} = 3276\ cm^{-1}$) which is possible *via* the dipole *(6)* only. If the reaction of *(1)* with tosyl isocyanate is carried out at 20 °C, a mixture of *(3)* and *(5)* is formed.

Tetracyanoethylene reacts with *(1)* at 20 °C to give the cyclobutane derivative *(2)*. When the reactants are mixed in benzene the solution turns blood-red, indicating π-complex formation. Attempts at thermal isomerization of *(2)* into a substitution product corresponding to the amide *(5)* failed. On prolonged standing in $[D_6]$-DMSO, the intensity of the cyclopropyl proton signals decreases, possibly by rearrangement of a carbonium ion dipole corresponding to *(6)*.

The reactivity of compound *(1)* towards diphenylketene is much lower than towards tosyl isocyanate. Comparison with corresponding cycloadditions to enol ethers[5] shows that, relative to the R—O group (which exerts a greater mesomeric effect), the cyclopropyl group favors cycloadditions *via* polar transition states over more concerted processes.



Simmons-Smith reaction $[CH_2I_2, Zn(Cu)]$ with *(1)* affords the interesting compound 1,1-dicyclopropylcyclopropane *(4)* in moderate yields; *(4)* can be separated from the reaction mixture by gas chromatography [^{1}H-NMR: $\tau \approx 8.95$ (m/2H on $C^{1'}$ and $C^{1''}$); ≈ 9.8 (m/8H on $C^{2'}$, $C^{3'}$, $C^{2''}$, $C^{3''}$); 10.0 (s/4H on C^2 and C^3)].

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