Cycloadditions to 1,1-Dicyclopropylethylene[1]

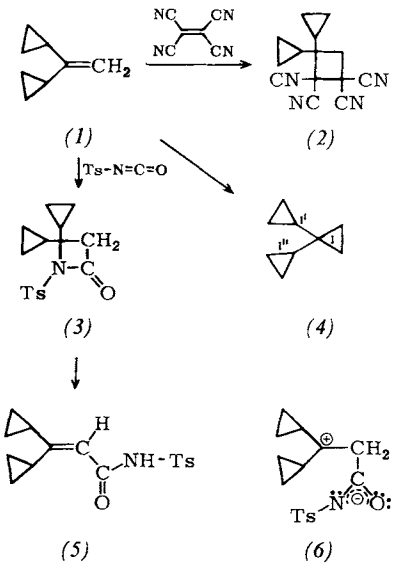
By *F. Effenberger* and *W. Podszun*[*]

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}, ν_{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: τ ≈ 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)].

Received: September 1, 1969 [Z 85 IE]
German version: Angew. Chem. *81*, 1046 (1969)

[*] Doz. Dr. F. Effenberger and W. Podszun
Institut für Organische Chemie der Universität
7 Stuttgart 1, Azenbergstrasse 14/16 (Germany)

[1] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

[2] *D. Bethell* and *V. Gold*: Carbonium Ions. Academic Press, New York 1967; *M. Hanack* and *H. J. Schneider*, Angew. Chem. *79*, 709 (1967); Angew. Chem. internat. Edit. *6*, 702 (1967); *N. C. Deno*, Progr. physic. org. Chem. *2*, 129 (1964).

[3] *S. A. Sherrod* and *R. G. Bergman*, J. Amer. chem. Soc. *91*, 2115 (1969); *M. Hanack* and *T. Bässler*, *ibid.* *91*, 2117 (1969).

[4] *R. Breslow* in *P. de Mayo*: Molecular Rearrangements. Vol. 1, Interscience, New York 1963, Chapter 4.

[5] *R. Huisgen*, *L. Feiler*, and *G. Binsch*, Angew. Chem. *76*, 892 (1964); Angew. Chem. internat. Edit. *3*, 753 (1964); Tetrahedron Letters *1968*, 4497; *F. Effenberger*, Angew. Chem. *81*, 386 (1969); Angew. Chem. internat. Edit. *8*, 306 (1969), and literature cited there.