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Cycloadditions of 1,1-Dicyclopropylallene with Activated Olefins; Dependency of the Regioselectivity upon Solvent Polarity and Lewis Acid Catalysis

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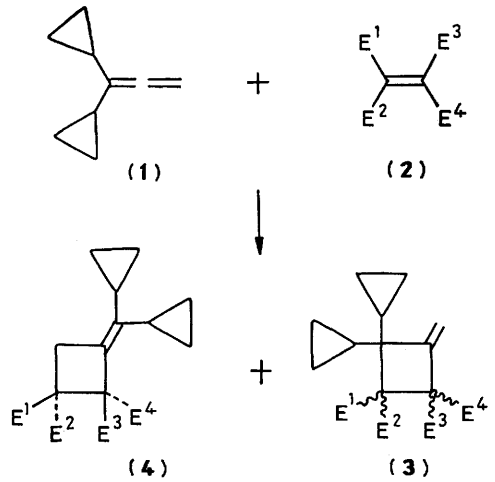
The regioselectivity of the cycloaddition of 1,1-dicyclopropylallene (**1**) with diethyl methylenemalonate (**2d**) was markedly influenced by the solvent polarity and the presence of a Lewis-acid catalyst, suggesting that a polar mechanism is operating in preferential formation of the inner adduct (**3**).

As might be expected, 1,1-dicyclopropylallene (**1**) reacts with a variety of activated olefins (**2**) in a [2 + 2] manner to give a mixture of an inner adduct (**3**) and an outer adduct (**4**). Usually, (**4**) predominated among the cycloadducts (in benzene at 200 °C) as exemplified in the reactions of (**1**) with methyl acrylate [(**2a**); (**3a**):(**4a**) = 11:89, 69%], dimethyl fumarate [(**2b**); (**4b**) exclusively, 48%], and dimethyl maleate [(**2c**); (**4b**) and (**4c**) in 30:70 ratio, 50%].†

The reaction of (**1**) with diethyl methylenemalonate (**2d**) in refluxing benzene took place similarly (81% yield after 32.5 h) with the preferential production of (**4**) [(**3d**):(**4d**) = 27:73]. However, it was interesting that the same reaction proceeded more rapidly in acetonitrile (85% after 1 h reflux) and (**3**) was the principal component in the cycloadducts [(**3d**):(**4d**) = 92:8]. This reversal of regioselectivity by a change of solvent polarity was observed only in the reaction of (**2d**). The reaction rates and regioselectivity of the cycloadditions of (**1**) with (**2a**), (**2b**), and (**2c**) were not influenced significantly by the solvent polarity.



a: $E^1 = CO_2Me$, $E^2 = E^3 = E^4 = H$
b: $E^1 = E^4 = CO_2Me$, $E^2 = E^3 = H$
c: $E^1 = E^3 = CO_2Me$, $E^2 = E^4 = H$
d: $E^1 = E^2 = CO_2Et$, $E^3 = E^4 = H$

† All new compounds described here gave satisfactory elemental analyses and spectral data.

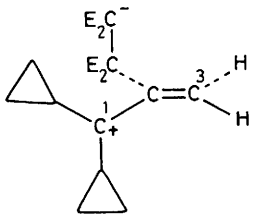
It was also interesting that Lewis acid catalysis [2] resulted in a total reversal of the regioselectivity in all the reactions described here. Thus, the inner adduct (**3**) was the exclusive cycloadduct when aluminium chloride (0.5 equiv.) was present in the reactions of (**1**) with (**2a**), (**2b**), (**2c**), and (**2d**) (CH_2Cl_2 at room temp., 67—82% yield).‡

Generally, allene cycloadditions have been discussed in terms of either a diradical stepwise mechanism or a concerted mechanism.[3] In addition, the reactions of polyalkoxy- or polyalkylthio-allenes with strongly electron-demanding olefins have been claimed to proceed *via* a zwitterionic intermediate.[4] In the present reactions, the cycloaddition of (**2c**) either in the thermal reaction or in the Lewis acid-catalysed process was found to be nonstereospecific and hence stepwise processes are suggested.‡§ Thus, the results may be best explained by a combination of a diradical and a dipolar mechanism as follows.

Since it has been established that the reagent usually attacks the central carbon atom in the reaction of 1,1-disubstituted allenes,[1] the first step of the present reaction should also be an

‡ With regard to the stereochemistry of the Lewis acid-catalysed processes, the reaction with (**2b**) gave (**3b**) exclusively, whereas a mixture of (**3b**) and (**3c**) in 27:73 ratio was obtained in the reaction with (**2c**). Lewis acid catalysis did not operate in reactions with cyano-activated olefins.

§ In acetonitrile, the reaction of (**1**) with (**2c**) gave a 43:57 mixture of (**4b**) and (**4c**). The extent of isomerization of (**2c**) under the reaction conditions was too small to account for all the nonstereospecificities described here. The reactions of 3-methylbuta-1,2-diene with (**2b**) and (**2c**), however, have been claimed as stereospecific and the concerted mechanism has been proposed (E. F. Kiefer and M.Y. Okamura, *J. Am. Chem. Soc.*, 1968, **90**, 4187).



(5)

attack of (2) at the central carbon of (1). The reactions of (1) with (2a), (2b), and (2c) either in benzene or in acetonitrile will be stepwise diradical processes, whereas the reactions yielding (3) will involve a zwitterion (5) as an intermediate. Because of the strong cation-stabilizing ability of cyclopropyl groups[5]¶ (in addition to steric strain in part), the allylic portion in (5) will not rotate to form the planar, delocalized structure. The positive charge on (5) will hence be largely associated with C-1 and the substituent cyclopropyl rings, and the cyclization will occur predominantly at this carbon atom to afford (3). In the diradical intermediate, however, only modest stabilization will be provided by the cyclopropyl groups,[6] and the charge will be mainly delocalized over the allylic portion. The cyclization can thus take place at both terminals. The steric effect may account for the predominant formation of (4) from such an intermediate.

¶ The reversal of regioselectivity by Lewis-acid catalysis was not observed in the reaction of 3-methylbuta-1,2-diene with (2).

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