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THE DIELS-ALDER REACTION OF CYCLOPENTADIENE AND METHYL ACRYLATE ON γ-ALUMINA

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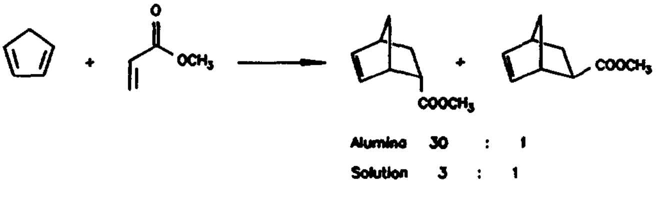
Abstract: The Diels-Alder reaction of cyclopentadiene and methyl acrylate has been run on γ-alumina. The ratio of endo to exo products is strongly dependent on the activity of the alumina. The exo adduct was also found to epimerize slowly to the endo adduct by a mechanism involving the retro-Diels-Alder reaction of the exo adduct.

The Diels-Alder reaction is a very useful reaction because it is one of the most effective methods for constructing six-membered rings; the process is stereospecific at all reaction centers and as many as four stereogenic centers are created.[1] The reaction is also catalyzed by Lewis acids.[2] Furthermore, the reaction not only occurs in solution but also on solid surfaces such as silica gel,[3,4] clays,[5] magnesium silicate[4] and alumina.[4,6]

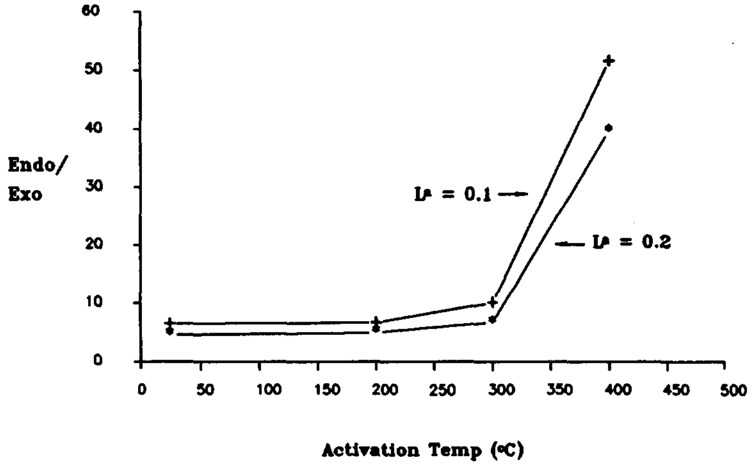
Alumina is an especially good medium on which to run Diels-Alder reactions because, according to the theories of Peri[7] and Knözinger,[8] activated Al_2O_3 possesses partially exposed aluminum cations on its surface. Indeed, Parlar and Baumann found the reaction of cyclopentadiene and methyl acrylate yielded an approximately 30:1 ratio of endo to exo adducts on activated, neutral alumina; non-activated alumina yielded a similar ratio of products.[6] By comparison a 3:1 ratio of adducts is formed in most solvents.



(1)

We have been investigating the use of activated alumina in organic reactions,[9] and have discovered that the behavior of cyclopentadiene and methyl acrylate is much more complicated than suggested in

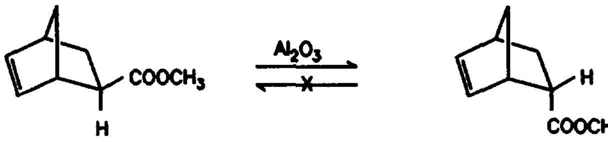
Parlar's and Baumann's preliminary report.[6] When the reaction is run at 50° for 5 hours on alumina[10] which had been activated at various temperatures and the endo to exo ratio of adducts measured, the results shown in the figure below were obtained. The endo to exo ratio is markedly temperature dependent, having a value close to 3 on unactivated, out-of- the-bottle alumina, rising slowly to values between 7 and 10, depending on loading of reactants,[11] on alumina activated at 300°, and rising sharply to values similar to those obtained by Parlar and Baumann[6] on alumina activated at 400°.



[a] L = (CP+MA):Al_2O_3, where CP+MA = 1:1 molar ratio of cyclopentadiene and methyl acrylate; (CP+MA):Al_2O_3 is a weight ratio.

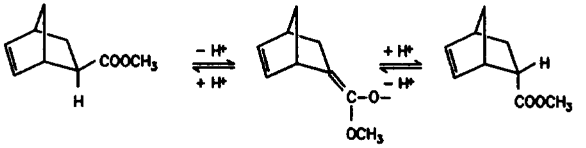
Unactivated alumina contains a top layer of hydroxyl groups and underlying aluminum cations which cannot influence the Diels-Alder reaction. On heating the solid, adjacent hydroxyl groups react to form water which is driven from the surface, thus exposing aluminum cations to the surface where they can influence the course of the reaction. The temperature at which the solid is activated determines how many aluminum cations are exposed to the surface.[7,8] This picture is in good agreement with our results shown in the above figure.

Could the dramatic change in the endo:exo ratio be due to the secondary epimerization of the endo and exo adducts? This is unlikely since the endo adduct does not epimerize under the Diels-Alder reaction conditions. The exo adduct does epimerize to the endo adduct but the isomerization is very much slower than the Diels-Alder reaction (10% endo adduct after 24 hours at 60°).



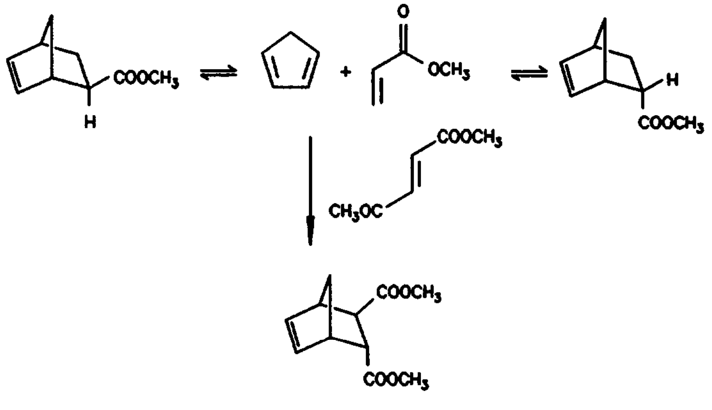
(2)

This epimerization is interesting because the thermodynamically more stable isomer isomerizes to the less stable isomer. This process could occur by two reasonable mechanisms. In the first, abstraction of the endo hydrogen at carbon-2 of the exo adduct by a basic site on the surface would yield an enolate which, on protonation from the less hindered exo face, would generate the endo adduct. If this scheme is correct, the substrates should incorporate deuterium if subjected to deuterated alumina (D/Al_2O_3), a species we previously synthesized and which is known to deuterate acidic organic compounds.[12] In fact, when the endo adduct is subjected to D/Al_2O_3, no incorporation of deuterium is observed. When the exo adduct is so treated, neither the formed endo adduct nor the recovered exo adduct contains deuterium. These results rule out the enolate mechanism.



(3)

In the alternate mechanism, the exo and endo adducts undergo a retro-Diels-Alder reaction to regenerate cyclopentadiene and methyl acrylate which then react preferentially to form the endo adduct. Lewis-acid-catalyzed retro-Diels-Alder reactions are known.[13] If this scheme is correct, it should be possible to trap cyclopentadiene with a more reactive dienophile. Indeed, when the endo adduct is treated with dimethyl fumarate on Al_2O_3, the cyclopentadiene-dimethyl fumarate adduct is generated according to equation 4.



(4)

When the trapping experiment is run on D/Al_2O_3, none of the adducts contains deuterium. This is surprising because cyclopentadiene is deuterated on D/Al_2O_3.[14] This must mean that when cyclopentadiene and methyl acrylate are formed in the retro-Diels-Alder reaction, they never escape each other's presence before they react to reform the exo and endo adducts. Had they done so, cyclopentadiene would have incorporated deuterium. Berson has observed a similar phenomenon in the solution phase isomerization of the endo cyclopentadiene-maleic anhydride adduct to the exo adduct.[15] If this premise is true, the dimethyl fumarate most likely reacts with the generated cyclopentadiene by a pre-association mechanism. Only when dimethyl fumarate is in the vicinity of the endo cyclopentadiene-methyl acrylate adduct when the retro-Diels-Alder occurs will lead to trapping.[16]

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(10) Neutral, Brockman activity I alumina, 80-200 mesh, Fisher Chemical Company.

(11) The more reactants one has on the solid, the lower the endo:exo ratio becomes, even on unactivated solid. Adding inert species such as menthol to the surface also lowers the endo:exo ratio.

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(14) When cyclopentadiene is treated with methyl acrylate on D/Al_2O_3, the cyclopentadiene dimer and Diel-Alder adduct contain deuterium. When cyclopentadiene is treated with dimethyl fumarate on D/Al_2O_3, the dimer again contains deuterium but the Diels-Alder adduct does not. The Diels-Alder reaction in the latter case is clearly much faster than the exchange reaction.

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