PROGRESS REPORT

**Coalification by Clay-Catalyzed Oligomerization of Plant
Monomers.**

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During this report period, we have obtained a model of montmorillonite clay, and this model has been of great assistance in visualizing how the chemistry of substrate molecules might be altered as it occurs on the surface of the clay. A stereochemical representation of this montmorillonite model is shown in Figure 1. Of particular significance, this model indicates that hydroxyl groups are located in the center of each siloxane ring on the surface of the montmorillonite clay. These hydroxyl groups might serve to bond substrate molecules to the surface of the clay. Furthermore, when the aluminum ions in the central layer of the montmorillonite are replaced by other ions such as calcium or magnesium ions, the clay assumes a net negative charge. This charge must be compensated for by cations associated with the surface of the clay. When these cations are protons, the clay is designated K-10 and has the structure shown in Figure 2.

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Figure 1. Stereochemical views of montmorillonite clay.

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dimerizations occur on the surface of the montmorillonite clay K-10, since these two companions products are formed in Diels-Alder dimerizations of **1** initiated by radical cation reagents in homogeneous media, and since it is difficult to rationalize the co-occurrence of these products through any other mechanism.

Scheme 1

Furthermore, when the dimerization of **1** is conducted in homogeneous media, only two indanes are formed, the indanes **4** and **5** shown in Scheme 1. However, when this same dimerization is conducted

The reaction scheme illustrates the acid-catalyzed cleavage of a silylated dendritic polymer. The top structure shows a dendritic polymer with a central core of Al, Mg, and Si atoms, and a perfluorinated phenyl group. It is linked via a silyl ether bond to a dendritic structure. An arrow labeled H^+ points to the bottom structure, which is the same dendritic polymer but with the perfluorinated phenyl group removed, replaced by a hydrogen atom.

interesting, since their formation may be governed by preassociation of two molecules of **1** with the surface of the clay before the dimerization

process occurs as illustrated in Figure 3. Thus, if two molecules of **1** are bonded to the K-10 surface through hydrogen bonding, they will be oriented so as to favor the formation of the more hindered dimers **6** and **7**. The net result of this type dimerization of molecules bonded to the surface is that the dimers that result have their polar functional groups (-OMe) located as close to one another as possible. In the indanes **4** and **5**, the polar functional groups (-OMe) are situated more or less on opposite sides of the molecule. Consequently, dimerization of this regiochemistry could not take place easily between two molecules of **1** attached to a planar surface via hydrogen bonds to their methoxy groups.

Based upon these considerations, the distribution of indane isomers **4-7** in the reaction shown in Scheme 1 might indicate that dimerization is taking place both in the homogeneous medium surrounding the clay and on the surface of the clay. If this is so, and if it were possible to partially neutralize the acid on the exposed surfaces of the clay, then it might be possible to enhance the formation of indanes **6** and **7** relative to indanes **4** and **5** using partially neutralized clays. In order to test this hypothesis, samples of K-10 were pretreated with DBU, dicyclohexylamine, triphenylamine, and triton-B. In all of these cases, the pretreatment of K-10 with hindered bases completely inhibited indane formation. In addition, the partially neutralization of K-10 by the pretreatment with finely ground Na_2CO_3 was attempted. In this case, it was hoped that the particles of Na_2CO_3 should neutralized the protons on the surface of the K-10, while leaving the protons in the interlayers unaffected. Unfortunately, this procedure did not alter the ratios of indanes products from those observed with the untreated K-10. Finally, it

is thought that K-10 has a significant amount of water associated with its surface. Therefore, it was hoped that removal of this water might lead to closer association of the K-10 sheets and/or facilitate the bonding of 1 to the surface. In order to partially remove the water from the surface of K-10, the K-10 was treated with boiling benzene in an effort to azeotrope the water from the surface. While this procedure worked quite well in other dehydrations, in this case, it seemed to increase the acidity of the K-10 and the yields of the indanes, but it did not alter the ratios of the indanes.

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