

PROGRESS REPORT

Coalification by Clay-Catalyzed Oligomerization of Plant
Monomers.

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The next step in our systematic examination of the radical cation-initiated dimerization of plant monomers from the C₆-C₃ pool of shikimic acid metabolites was to study the dimerization of cinnamic acid and its derivatives. In order to do this we needed a radical cation initiator that has a reduction potential greater than that of BAHA ($E_{red} = 1.30$ volts), since the electron-withdrawing carboxylate functional group of cinnamates renders them inert to oxidation with BAHA. This problem was solved with the observation that DBAHA (tris-(2,4-dibromophenyl)aminium hexachloroantimonate, $E_{red} = 1.74$ volts, shown in Scheme 1) initiated the radical cation dimerization of methyl 3,4-dimethoxycinnamate (**1** in Scheme 1).

Several aspects of this reaction (Scheme 1) are worth noting. The first of these is that no Na₂CO₃ was used in this reaction, since it was felt that the acid-catalyzed dimerization of **1** would not be an important side reaction due to the more electron deficient nature of the

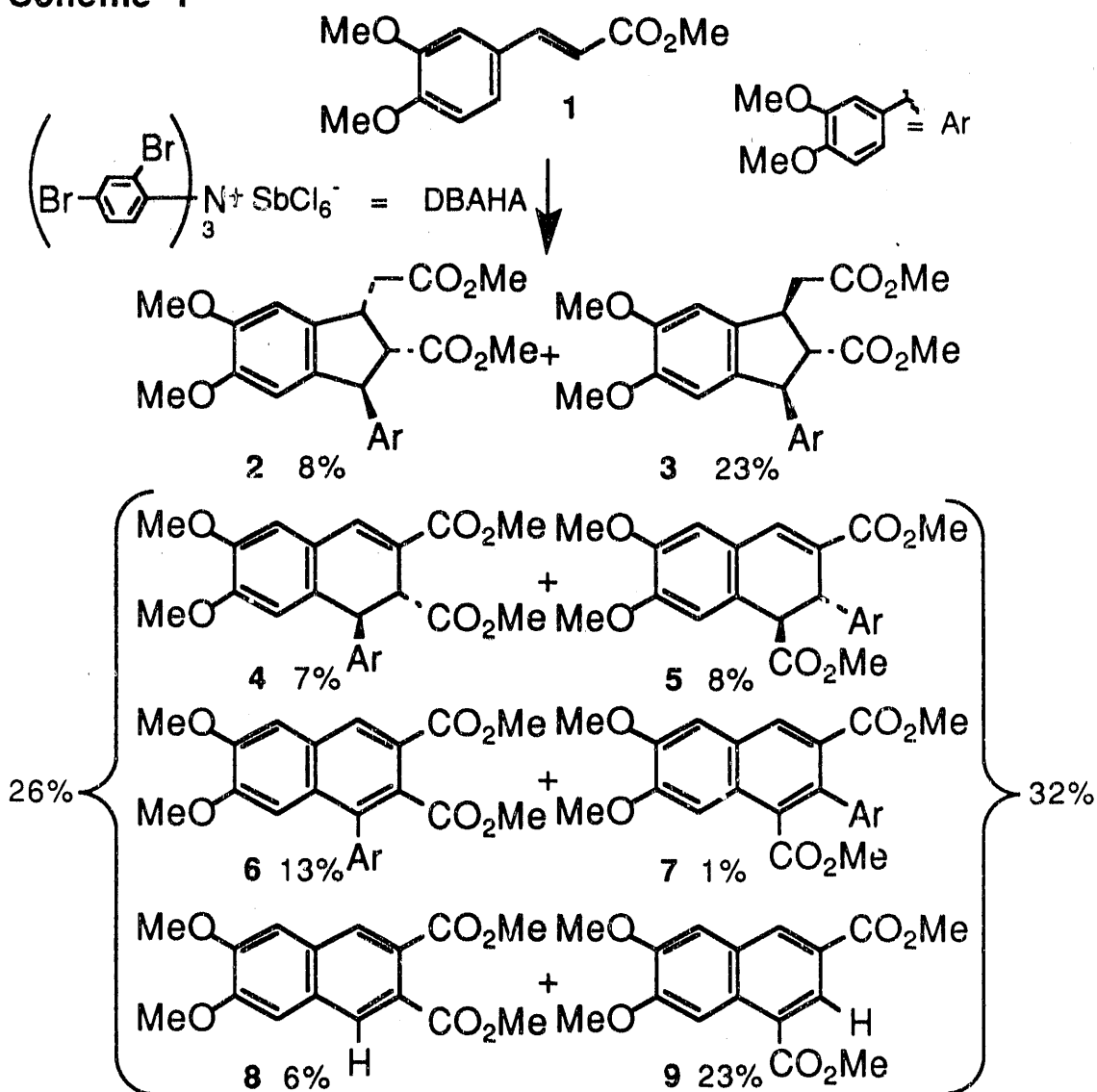
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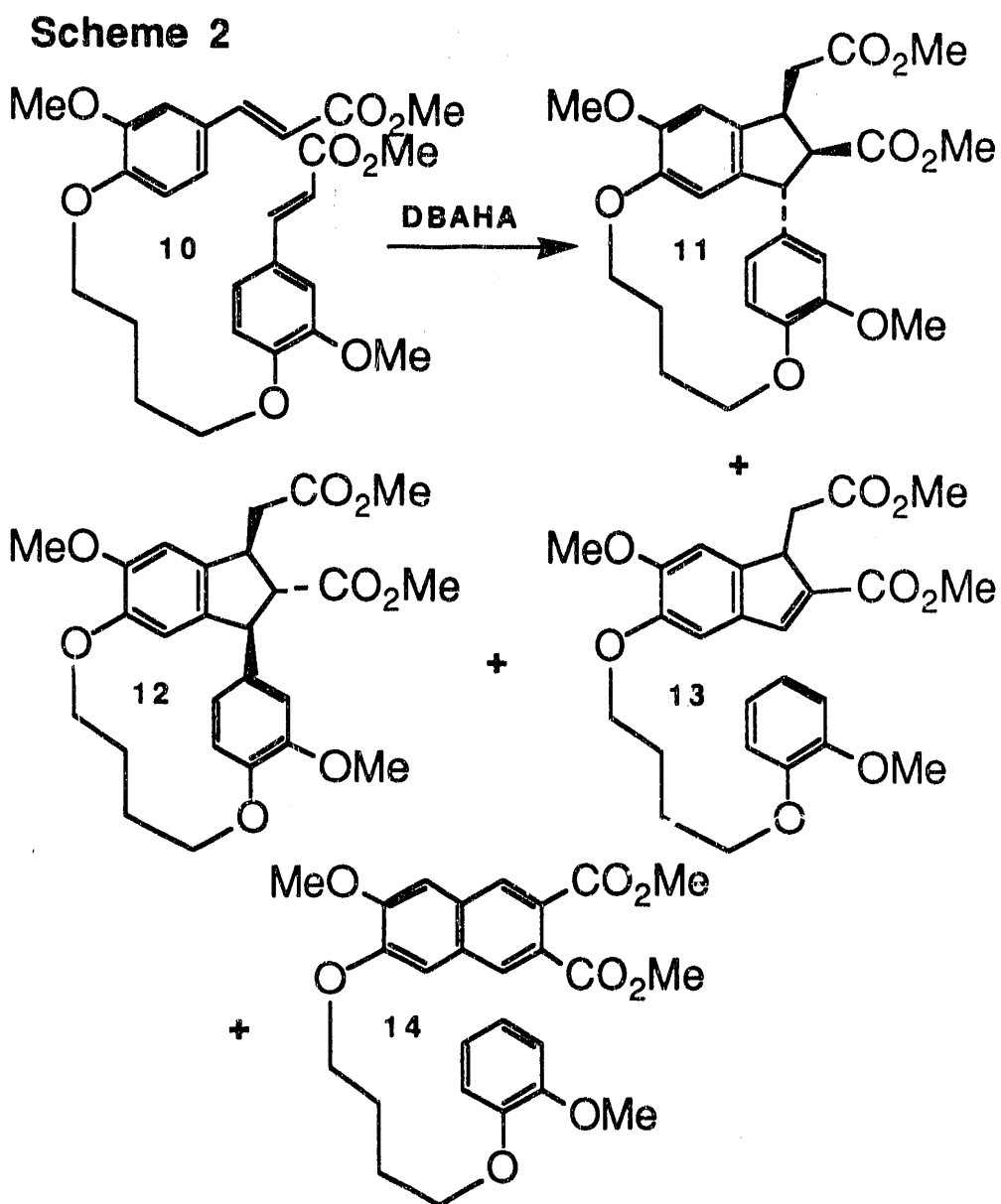
cinnamate double bond. Clearly this is not the case, as the acid-catalyzed dimers **2** and **3** are produced in this reaction. Nevertheless, the

Scheme 1



radical cation dimers **4-9** are the predominant products. Here again, as with the methylisoeugenol system, the two regioisomeric families are produced in comparable yields, $(4+6+8):(5+7+9) = 0.81$. Furthermore, this is the first instance where dihydronaphthalenes such as **4** and **5** could be

isolated. Of particular interest is the observation that **4** and **5** apparently are oxidized further to the naphthalenes **6** and **7**, respectively, via radical cation mechanisms. In addition, **4** and **5** also are converted to the dearylated naphthalenes **8** and **9**, respectively, in what appears to be acid-catalyzed processes. In this latter reaction, the companion product would be expected to be 1,2-dimethoxybenzene. However, this material could not be detected in this reaction mixture.

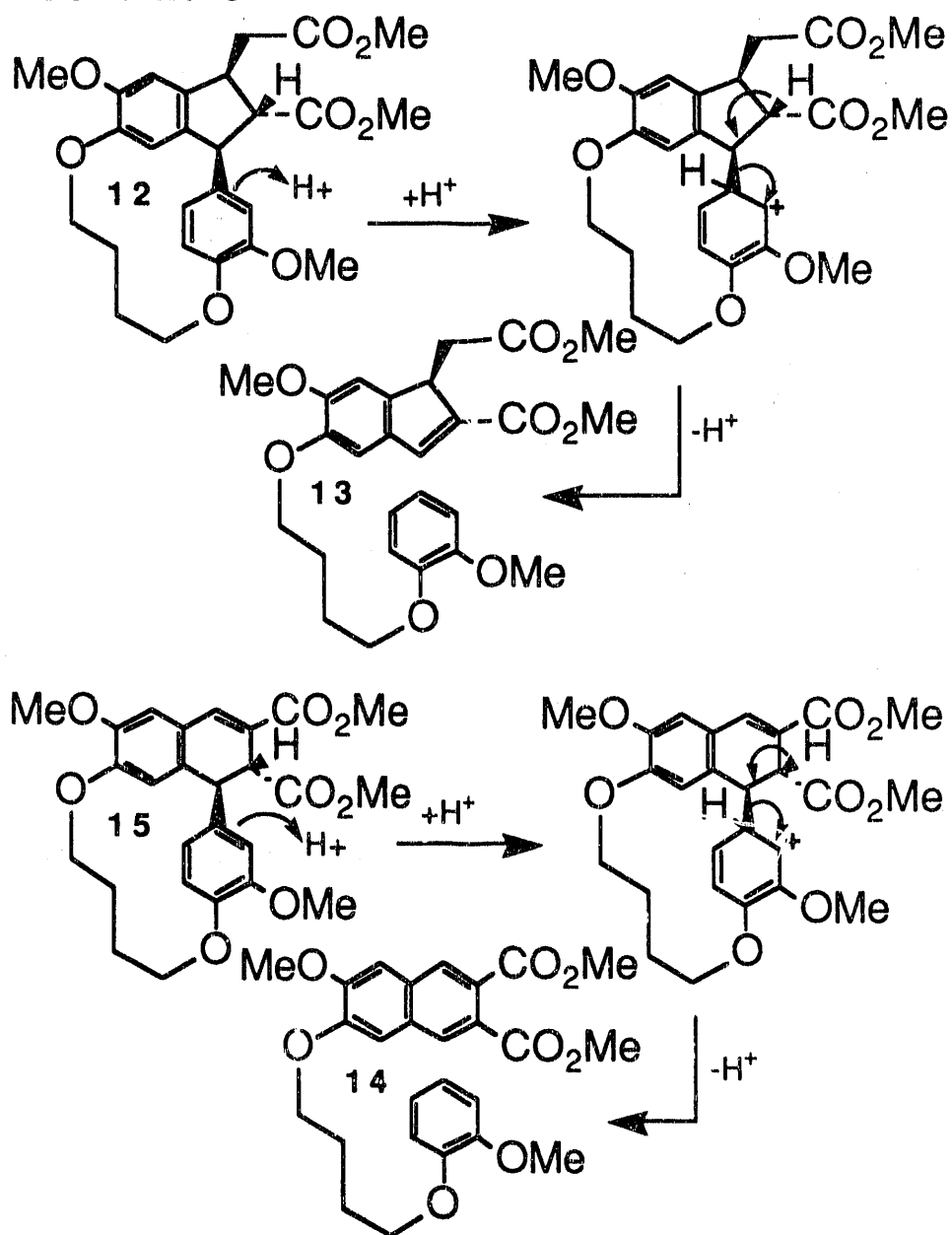


In order to inhibit the formation of the regioisomeric radical cation Diels-Alder products related to **5**, **7**, and **9** in Scheme 1, the tethered dicinnamate **10** was synthesized (Scheme 2). The short six-atom tether in **10** is only long enough to allow the two ends of the molecule to come together with a regiochemistry related to that of **4**, **6**, and **8** in Scheme 1. Furthermore, this bifunctional molecule might lead to higher oligomers more closely related to natural lignins. Thus, treatment of **10** with DBAHA, again without added Na_2CO_3 , leads to the formation two acid-catalyzed macrocycles **11** and **12**, as well as two acid-catalyzed cleavage products, the indene **13** and the naphthalene **14** (Scheme 2). The structures of both acid-catalyzed products **11** and **12** have been confirmed by X-ray crystallography. The naphthalene **14** has undergone the same dearylation process that gave rise to **8** and **9** in Scheme 1. However, in this tethered case, the fate of the cleaved aryl group is evident. The mechanism by which this cleavage proceeds has been confirmed in the cases of the indane **12** and the untethered dihydronaphthalenes **4** and **5** by the treatment of these molecules with strong acid (Scheme 3). On the basis of these correlations, it is probable that the tethered dihydronaphthalene **15** undergoes dearylation via the same acid-catalyzed mechanism (Scheme 3).

Finally, it should be noted that this acid-catalyzed cleavage is probably greatly facilitated by the electron-rich nature of the appended dialkoxybenzene ring which should be protonated easily in the initial step of the cleavage reaction, and by the relatively high acidity of the proton lost in the final step of the cleavage. If these types of arylindanes, arylindene, aryl-naphthalenes, or aryl-dihydronaphthalenes are present as units in the coal structure, then it should be possible to affect the same

type of cleavage in coal which might be of considerable utility in the liquifaction of coal. Conversely, it should be possible to suppress this acid-catalyzed cleavage by conducting the radical cation Diels-Alder reaction in the presence of a large excess of Na_2CO_3 . Whatever the future prospects of this radical cation Diels-Alder reaction might be, it is clear

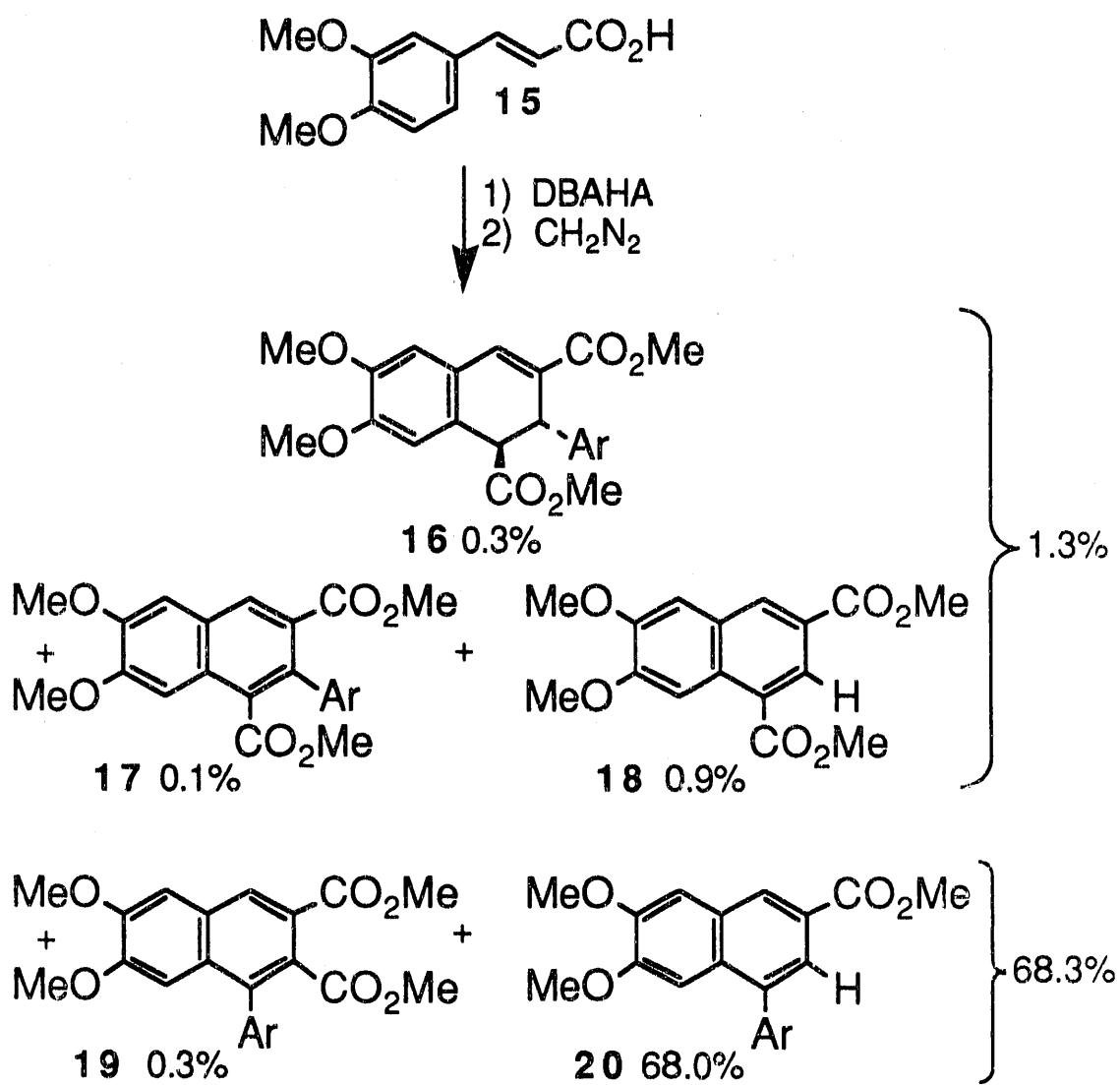
Scheme 3



at this time that the tethering approach to limiting the formation of unnatural regioisomers is a viable synthetic strategy. Therefore, we are continuing to explore the chemistry of these and related tethered cinnamates.

In the next block of research in this systematic study of the radical cation chemistry of cinnamate derivatives, we have examined the radical

Scheme 4

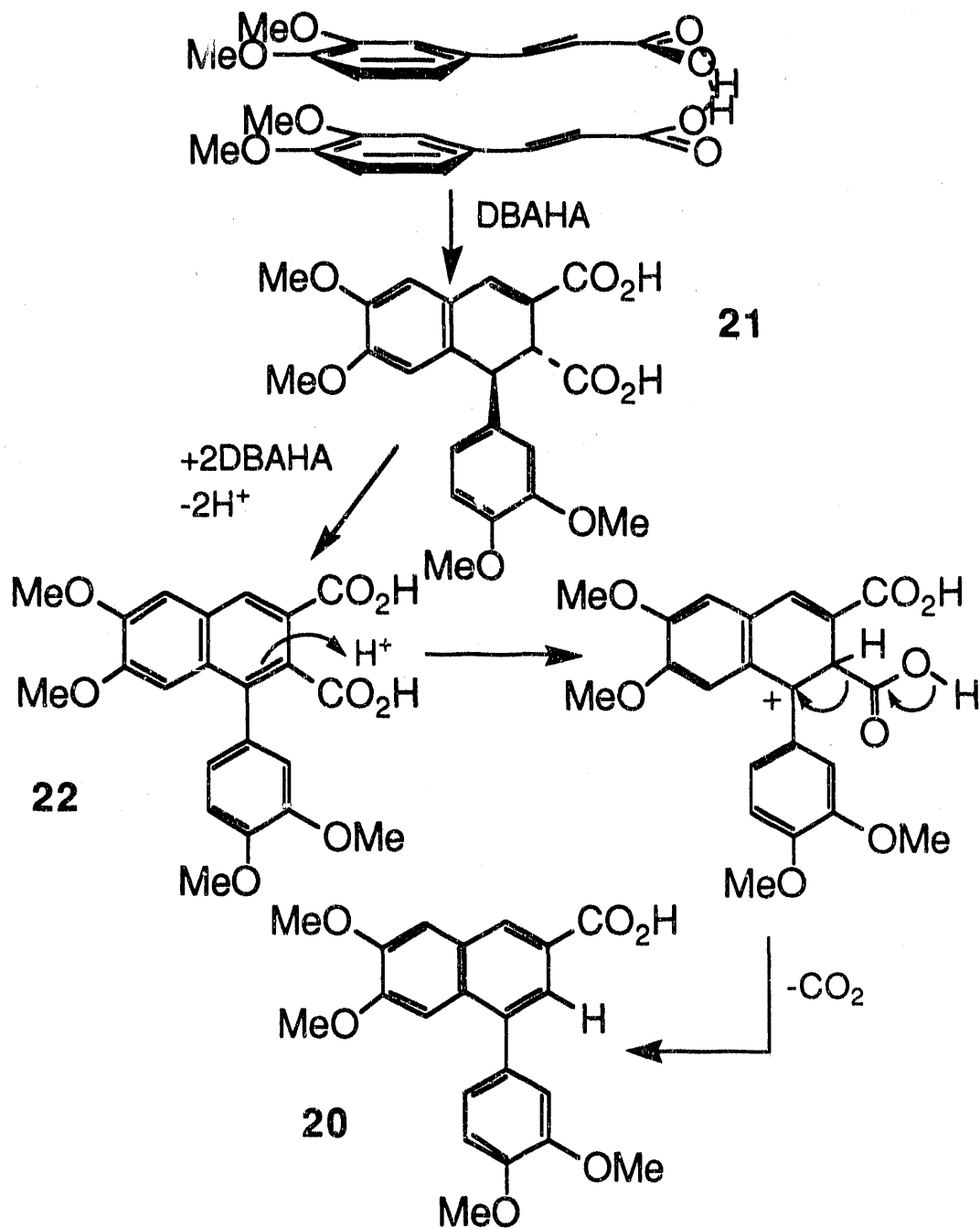


cation chemistry of the cinnamic acids themselves (Scheme 4). Thus treatment of the 3,4-dimethoxycinnamic acid (**15**) with DBAHA followed by esterification with diazomethane afforded the mixture of dihydronaphthalenes and naphthalenes shown in Scheme 4. Of particular significance here is the ratio of the regioisomeric families, (**19+20**): (**16+17+18**) = 52.3. Apparently some unanticipated factor has come into play in this cinnamic acid dimerization, and that factor greatly favors the natural regioisomers. In addition, both dearylation (**18**) and decarboxylation (**20**) have occurred with the decarboxylation pathway being favored by a considerable margin.

The simplest explanation for this unexpected regioselectivity would seem to be that the hydrogen-bonded carboxylic acid dimer is orienting the cinnamic acid molecules in a geometry that favors the natural regiochemistry as illustrated in Scheme 5. This orientation governed by the carboxylic acid dimer would lead to the dihydronaphthalene **21** and upon further oxidation by the DBAHA to the naphthalene **22**. Protonation of **22**, which should occur readily in the absence of a Na_2CO_3 , would produce decarboxylation as shown in Scheme 5. The significance of these observations is that the regiochemistry of radical cation Diels-Alder reactions apparently can be determined by strong intermolecular hydrogen bonding. This correlation tends to support the model for regiochemical control through hydrogen bonding to the montmorillonite surface developed in our last progress report. Finally, this correlation indicates that tethering may be unnecessary as a means of gaining regiochemical control. Since this approach might be most profitable in devising schemes to mimic the biosynthesis of lignins, we intend to

explore other means of achieving regiochemical control via intermolecular hydrogen bonding.

Scheme 5



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