a lifetime of >100 ns, then it should be possible to excite ^{3}**8** under jet conditions, since the diphenylmethyl radical is known to absorb strongly with a λ_{max} of 325–335 nm.[10] Apparently, ^{3}**8** does absorb to a significant degree and ^{3}**8*** extrudes either bis(*p*-methoxyphenyl)carbene or DPC as its primary mode of decay. However, in each of these unsymmetrical carbene additions only one of the two possible carbene extrusion processes will be observed, as the complementary extrusion process will be "invisible", since it constitutes a reversal of the reaction leading to **8**.

The mechanistic details of these carbene extrusion processes are uncertain at present. However, it seems quite likely that these carbene extrusions are β-cleavage reactions as shown in Scheme II. The photochemical β-cleavage of carbonyl-generated biradicals has been observed.[2a] Thus, β-cleavage may be emerging as a general pattern for biradical photochemistry. Furthermore, the observation of these carbene extrusions and the associated olefin metatheses adds a new dimension to triplet biradical chemistry and clearly demonstrates the utility of the laser-jet technique in the study of the photochemistry of moderately short-lived transient intermediates.

Acknowledgment. We thank the National Science Foundation (NSF CHE-8409628) for support of this research and for a grant used to assist in the purchase of high resolution mass spectrometry facilities used in this work (PCM-8219912).

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Convergent Functional Groups: Catalysis of Hemiacetal Cleavage in a Synthetic Molecular Cleft

J. Wolfe, D. Nemeth, A. Costero, and J. Rebek, Jr.*

Department of Chemistry, University of Pittsburgh Pittsburgh, Pennsylvania 15260

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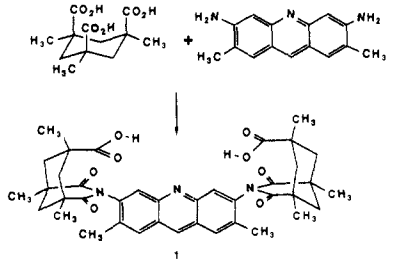
We recently reported the synthesis of diacid **1** and demonstrated its utility as a probe in molecular recognition studies.[1] The substance is readily made by the condensation of the Kemp triacid[2] and acridine yellow (eq 1). The new structure features carboxyl



(1)

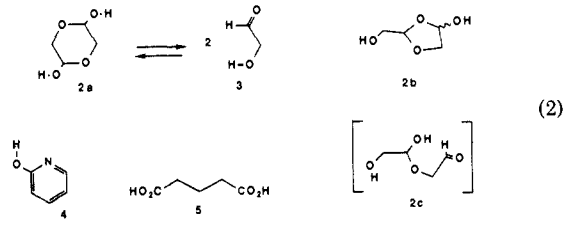
groups which are constrained to be in a convergent conformation, resembling in this respect the carboxyl groups at the active sites of lysozyme and the aspartic proteinases.[3] Here we report on some of the catalytic advantages that attend such structural constraints.

Table I. Dissociation (Eq 2) in $CDCl_3$ 25 °C

catalyst	[catalyst]	k_{obsd}	approx half-life[a,b]	k_{obsd}/[cat]
none		2.7×10^{-6}	72.1[a]	-
benzoic acid	2×10^{-4}	6.3×10^{-6}	30.8[a]	3.1×10^{-2}
glutaric acid, **5**	4.8×10^{-5}	8.6×10^{-6}	22[a]	1.8×10^{-1}
2-hydroxypyridine, **4**	5×10^{-5}	1.6×10^{-5}	12[a]	3.2×10^{-1}
7	6×10^{-5}	1.6×10^{-5}	12[a]	2.7×10^{-1}
1	2.5×10^{-6}	9.8×10^{-4}	12[b]	3.9×10^{2}

[a] Time is in hours. [b] Time is in minutes.

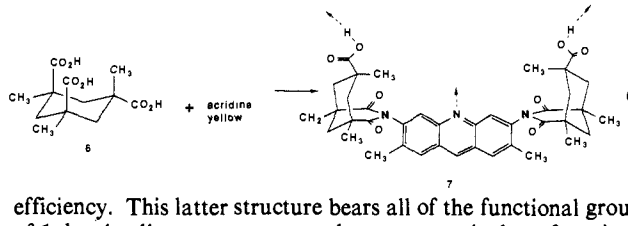
The dissociation of glycoaldehyde dimer **2a** to the monomer **3** (eq 2) has been studied by a number of workers[4] in various media. In $CDCl_3$ dissociation in the absence of catalysts is very



(2)

slow ($\tau_{1/2} \approx 3$ days). The reaction involves the rapid buildup[5] and then somewhat slower disappearance of the dioxolane isomer **2b** which remains at a steady-state concentration over most of the reaction. Substances such as 2-hydroxypyridine (**4**) and simple monocarboxylic acids, much admired for their catalysis of glucose mutarotation,[6] are quite modest in their effects on this dissociaton reaction (Table I). Dicarboxylic acids such as glutaric show little activity in this regard, and even acid–base mixtures fail to catalyze the dissociation.[7]

The convergent diacid **1** is a remarkably effective catalyst for this reaction: less than 0.5 mol% suffices to convert 2 → 3 within minutes! In contrast, the *divergent* diacid[8] **7** (eq 3) shows poor



(3)

efficiency. This latter structure bears all of the functional groups of **1**, but its divergent structure does not permit these functional groups to act in a concerted manner.

The open-chained dimer **2c** is a necessary intermediate for both forward and reverse reactions but has eluded detection.[4] In acetone, where the reverse reaction of eq 2 is favored, **1** acts as

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(5) The equilibrium constant [**2b**/**2a**] was determined by NMR to be ca. 1.6 ± 0.4 after 2–3 h, and the initial, uncatalyzed rate of **2b** formation from **2a** was 5.4×10^{-5} s^{-1}. The initial concentration of **2a** was 10^{-3} M in all reactions.

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(7) For example 2:1 mixtures of acetic acid and pyridine (several molar equivalents) were no more effective than benzoic acid. These experiments are not recorded in the table because of the difficulty in comparing systems of different molecularities.

(8) Compound **7** (dec ~ 300 °C) showed all the expected spectroscopic features. The cis/trans isomer **6** of the triacid showed mp 205–215 °C; it is obtained as a byproduct of the alkylation reaction[2b] used in the synthesis of the Kemp triacid.

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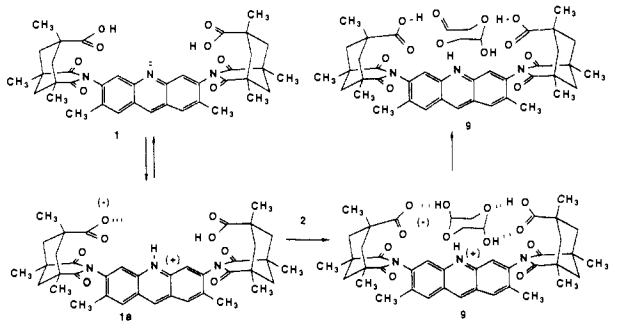
a catalyst, and the dimerization rate is first order in the catalyst. Again, the other acids and bases of Table I are quite ineffective for the dimerization reaction.

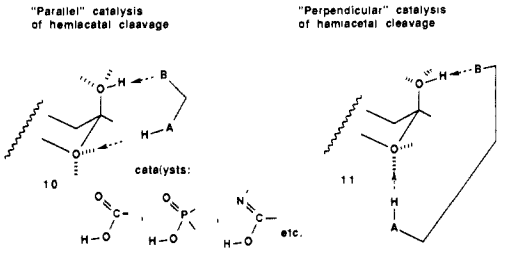
Why is **1** such an effective catalyst for this reaction? One possibility, suggested in eq 4, involves complexation before reaction



(4)

in a micromolecular version of enzymatic catalysis. Binding of a hemiacetal function to a carboxylic acid of **1** brings the other hemiacetal into contact with both acidic and basic groups. The latter are poised for general acid–base catalysis in the concerted sense suggested in **8** → **9**.

Since **1** is known[2b] to exhibit zwitterionic character (as in **1a**), the assignment of acid and base roles is ambiguous. Even so, the proposal of eq 4 incorporates favorable stereoelectronic effects at carboxyl oxygen.[9] Specifically, the syn lone pair of the carboxylate can accept the proton of the hydroxyl while the ethereal oxygen accepts a proton from acridine nitrogen. Alternatively, the carboxylic acid protonates the ethereal oxygen, while the acridine nitrogen acts as the general base. Conventional concerted catalysis of mutarotation is likely to involve parallel approaches



of acid (A–H) and base (B), as in **10**. While this mechanism may be operating in the case at hand, an intriguing additional possibility exists in **1** for the *perpendicular* approach of the two components as in **11**. Such an arrangement is expected to reduce the anomeric effect and thereby weaken the endocyclic C–O bond. In any event, the convergence of acid and base sites is unique to **1**. Other model systems for such reactions are constrained by their shapes to involve the less basic anti lone pair of the carboxylate.[10]

While the present system provides appropriate molecular shape, its activity may be specifically suited to **2** (or other substrates which can be bound within the cleft). For example, **1** shows no activity in the mutarotation of tetramethyl glucose beyond that expected for typical carboxylic acids, and CPK models show that binding a substrate of this size within the cleft of **3** does not favor the convergence of the acid–base functions in an appropriate sense for reaction. Indeed a complex is formed with **1** and tetramethyl glucose which is unreactive, i.e., modest inhibition is observed. This result underlines the importance of having the correct orientation of functional groups in the substrate–catalyst complex. Our present efforts are directed toward the construction of systems that are more general in which molecular recognition and stereoelectronic effects are appropriately combined.

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On the Lewis Acid Induced Addition of Allylstannanes to Aldehydes: A Spectroscopic Investigation

Scott E. Denmark,*[1] Thomas Wilson, and Timothy M. Willson

Roger Adams Laboratory, Department of Chemistry University of Illinois, Urbana, Illinois 61801

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The addition of allylic stannanes to aldehydes,[2] ketones,[3] acetals,[4] enones,[5] imines,[6] allylic alcohols,[7] and other functions[8] is a powerful carbon–carbon bond-forming reaction. The process is also of current interest in the context of acyclic stereoselection.[2a,9] In all of these reactions a Lewis acid (e.g., $BF_3{\cdot}OEt_2$, $TiCl_4$, $MgBr_2$, or $SnCl_4$) is employed presumably to activate the electrophilic function toward nucleophilic attack by the allylic organometallic reagent. Our previous studies in this area have served to illustrate the importance of the structure of the Lewis acid–aldehyde complex in determining the stereochemical course of intramolecular allylmetal–aldehyde condensations.[10] Nonetheless, the possibility that the Lewis acid first reacts with the allylmetal generating a new species prior to addition could not be ruled out, Scheme I. Indeed the possibility of metathetical processes has been discussed by Tagliavini,[11a] Keck,[11b] and Yamamoto[11c] based on product analysis. Furthermore, Tagliavini[11a,12a] and Gambaro[12b] have extensively studied ligand exchange to prepare allylchlorostannanes for additions to aldehydes and ketones. Herein, we report the first *direct evidence* for interaction between the *Lewis acid and the allylic stannane in the presence of the substrate aldehyde.*

All of the studies involved direct ^{13}C NMR (75.5 MHz) observation of reactions carried out in $CDCl_3/CD_2Cl_2$ 1:1 at 0.5 M between −80 and +20 °C. As control experiments we first carried out the reactions between allyltrimethylstannane (**1**) and the Lewis acids $BF_3{\cdot}OEt_2$ and $SnCl_4$. It has been known for some time that both Me_4Sn[13a] and $(allyl)_4Sn$[13b] undergo ligand exchange with $SnCl_4$ rapidly at 25 °C. However, we have found that *metathesis of either* **1** *or* $(allyl)_4Sn$ *with* $SnCl_4$ *is instantaneous and quantitative at −80 °C.* The only detectable products are $allylSnCl_3$ and Me_3SnCl. On the other hand, the reaction of **1** with $BF_3{\cdot}OEt_2$ proved to be an enigma. Already at −80 °C the resonances for

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