

in Table I despite the differences in the second polyelectrolyte present. Since the properties exhibited in isolation by coatings of I or of the auxiliary homopolyelectrolytes are distinctly different and less attractive than those of the composite coatings the morphology of the coatings appears to be the dominant factor controlling their behavior. Transmission electron microscopic evidence supporting this proposal along with considerable additional experimental details are described in the full paper.

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**Registry No.**  $(-\text{NH}(\text{CH}_2)_4\text{CH}(\text{N}(\text{CH}_3)_2)\text{CO}-)_n$  (SRU), 75855-87-7; PVI (homopolymer), 26983-77-7; PVP (homopolymer), 25232-41-1.

### Distinction between Aminium Cation Radical and Protic Acid Catalyzed "Diels-Alder" Reactions

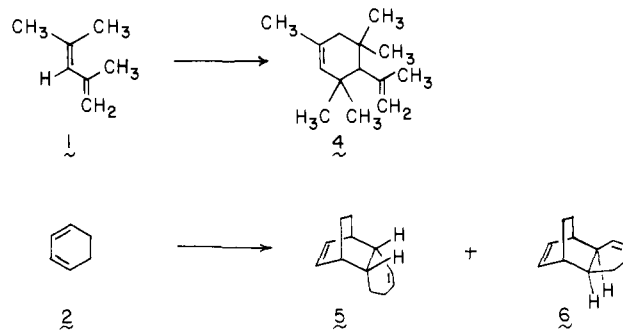
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Recently, we reported<sup>2</sup> that certain intramolecular "Diels-Alder" reactions could be catalyzed by both aminium cation radicals<sup>3,4</sup> and protic acids.<sup>5</sup> In that report<sup>2</sup> we stressed the striking similarity of the cation radical and protic acid promoted processes and questioned whether the addition of an aminium cation radical to the reaction mixture was merely leading to the generation of a protic acid, which was the true catalytic species. In order to test this concept and to extend our earlier work from intramolecular to intermolecular 2 + 4 cycloadditions, we have examined, in detail, the dimerization of 2,4-dimethyl-1,3-pentadiene (**1**) and 1,3-cyclohexadiene (**2**) as catalyzed by tris(*p*-bromophenyl)-aminium hexachloroantimonate (**3**).<sup>3,4</sup> We now wish to report that certain cation radical promoted Diels-Alder reactions can be readily distinguished from the corresponding protic acid catalyzed processes and that the previously reported<sup>3b</sup> dimerization of **1** is a protic acid catalyzed reaction and not a cation radical induced process as previously claimed.<sup>3b</sup> Lastly, we have found that the true cation radical dimerization of **1** is a relatively slow process, which leads to an entirely different dimer from that formed in the protic acid catalyzed process. These findings, when applied to other examples, will constitute a test for distinguishing between single-electron-transfer (cation radical) and protonation (protic acid induced) mechanisms for certain reactions.

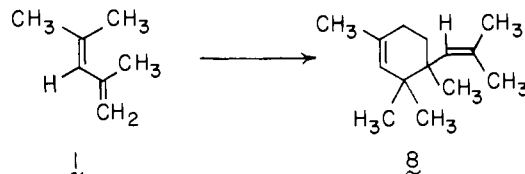
Treatment of either **1** or **2** with 5 mol % of the cation radical **3** in methylene chloride produced the Diels-Alder dimers 1,3,3,5,5-pentamethyl-4-(1-methylethenyl)cyclohexene (**4**) and a mixture of **5** and **6**, respectively, in high yield as previously reported.<sup>3a,b</sup> However, the similarity of these reactions stops at



this point. The dimerization of **1** to give **4** could be accomplished in 95% yield using either **3**<sup>3b</sup> or hydrogen bromide<sup>5</sup> as the catalyst. In matched reactions using **3** and hexachloroantimonic acid ( $\text{HSbCl}_6$ ),<sup>6</sup> we obtained an 88% yield of **4**. In contrast, attempts to catalyze the conversion of **2** into **5** and **6** with protic acid gave large amounts of intractable material and only trace amounts of **5** and **6** after prolonged periods.

With 5 mol % of **3** as catalyst, the dimerization of **1** showed an induction period at  $-42^\circ\text{C}$ . This induction period was significantly increased in base-washed glassware or in the presence of 1 mol % of 2,6-di-*tert*-butylpyridine (**7**).<sup>7</sup> When 2,6-di-*tert*-butylpyridine was added in amounts greater than **3**, the formation of **4** from **1** was completely inhibited even though the aminium cation radical **3** was present in the reaction mixture. For example, when 20 mol % of 2,6-di-*tert*-butylpyridine was present in a reaction mixture containing **1** and 5 mol % of **3** at  $-23^\circ\text{C}$ , no trace of **4** could be detected even though the blue color of the aminium cation radical persisted for 20 min. In the absence of the base, **1** was completely converted into **4** in 2 min under these conditions. In contrast to the findings with **1**, the dimerization of **2** proceeded to 27% yield with 62% of the starting material being unreacted in the presence of 20 mol % of 2,6-di-*tert*-butylpyridine at  $0^\circ\text{C}$  in 90 s, at which time the blue color of **3** disappeared and the reaction stopped.<sup>7</sup> Thus, the observed reaction of **1** was inhibited by base, while that of **2** was not.

Our observations on the dimerization of 1,3-cyclohexadiene were consistent with the cation radical chain mechanism proposed in the literature.<sup>3a</sup> In contrast, the results observed for the reactions of **1** were consistent with a protic acid catalyzed process but not with a cation radical chain process.<sup>8</sup> This suggested to us that we should determine if **1** could be dimerized in a cation radical chain process and if the product would be **4** or some other product resulting from a cation radical induced transformation. When **1** was treated with 50 mol % of **3** and 55 mol % of 2,6-di-*tert*-butylpyridine at  $25^\circ\text{C}$ , a new dimer, **8**, was obtained in 27% yield.<sup>11</sup> Similarly, irradiation of a 0.5 M solution of **1** in ace-



(6) Solutions of  $\text{HSbCl}_6$  were prepared by bubbling dry hydrogen chloride gas into  $\sim 0.1$  M  $\text{SbCl}_5$  in 1,1,2-trichlorotrifluoroethane at  $-30^\circ\text{C}$  under an inert atmosphere.

(7) 2,6-Di-*tert*-butylpyridine does not react at a significant rate with **3** by itself, as analyzed by visible absorption spectroscopy. However, it does accelerate the rate of decomposition of **3** in the presence of **1** or **2**, presumably by removing protons from cation radicals generated in the reaction of **1** or **2** with **3**.

(8) We wish to stress that the protic acid could originate from loss of protons from initially generated cation radicals<sup>9</sup> or from dimerization of cation radical intermediates followed by proton loss.<sup>10</sup>

(9) Faita, G.; Fleischmann, M.; Pletcher, D. *J. Electroanal. Chem. Interfacial Electrochem.* 1970, 25, 455. Geske, D. H. *J. Am. Chem. Soc.* 1959, 81, 4145. For an example of proton loss in a reaction of **6** and a diene, see: Barton, D. H. R.; Haynes, R. K.; Leclerc, G.; Magnus, P. D.; Menzies, I. D. *J. Chem. Soc., Perkin Trans. 1* 1975, 2055.

(10) Schäfer, H.; Steckhan, E. *Angew. Chem., Int. Ed. Engl.* 1969, 8, 518.

(1) National Science Foundation Fellow 1983-1984.  
 (2) Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* 1984, 106, 6085.  
 (3) (a) Bellville, D. J.; Wirth, D. D.; Bauld, N. L. *J. Am. Chem. Soc.* 1981, 103, 718. (b) Bellville, D. J.; Bauld, N. L. *Ibid.* 1982, 104, 2665. (c) Bauld, N. L.; Bellville, D. J.; Pabon, R.; Chelsky, R.; Green, G. *Ibid.* 1983, 105, 2378. (d) Pabon, R. A.; Bellville, D. J.; Bauld, N. L. *Ibid.* 1983, 105, 5158. (e) Bauld, N. L.; Pabon, R. *Ibid.* 1983, 105, 633. (f) Pabon, R. A.; Bellville, D. J.; Bauld, N. L. *Ibid.* 1984, 106, 2730. (g) Schutte, R.; Freeman, G. R. *Ibid.* 1969, 91, 3715.  
 (4) Bell, F. A.; Ledwith, A.; Sherrington, D. C. *J. Chem. Soc. C* 1969, 2719. Ledwith, A. *Acc. Chem. Res.* 1972, 5, 133.  
 (5) Escher, A.; Übersax, B.; Neuschwander, M. *Chimica* 1981, 35, 251.  
 Hoffmann, H. M. R.; Vathke-Ernst, H. *Chem. Ber.* 1981, 114, 1182. Giguere, R. J.; von Ilseman, G.; Hoffmann, H. M. R. *J. Org. Chem.* 1982, 47, 4948.

tonitrile saturated with 9,10-dicyanoanthracene (DCA) produced **8** in 72% yield.<sup>12,13</sup> This latter reaction is presumed to occur via a sensitized-electron-transfer process to give a cation radical intermediate, which may be associated with DCA anion radical. Ample discussion of this mechanism for the photosensitized dimerization of 1,3-cyclohexadiene exists.<sup>14,15</sup>

In summary, we believe that our results indicate that **8**, and not **4**, is the real product of a cation radical mediated dimerization of **1**. The formation of **4**, as catalyzed by **3**, appears to be a protic acid catalyzed process, while the dimerization of 1,3-cyclohexadiene apparently involves the intermediacy of cation radicals. This indicates that great care should be taken in evaluating the mechanistic discussions associated with cation radical reactions initiated by aminium cation radicals. We propose that the systematic use of the series of reactions discussed above will constitute a standard approach for distinguishing when aminium cation radicals lead to a protic acid catalyzed process and when they are involved in a cation radical chain process.

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(11) The rate of formation of **8** was at least 100 times slower than the rate of formation of **4** in the absence of base. Careful examination of the reaction of **1** with **3** in the absence of base showed the presence of trace amounts (<1%) of **8**. It should be noted that the room temperature reaction of **1** with **3** in the presence of di-*tert*-butylpyridine also gave **8** and none of **4** when acetonitrile was used as solvent.

(12) <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 5.261 (1 H, heptet, *J* = 1.4 Hz), 5.017 (1 H, heptet, *J* = 1.5 Hz), 1.90-1.86 (2 H, m), 1.86-1.76 (1 H, m), 1.749 (3 H, d, *J* = 1.4 Hz), 1.713 (3 H, d, *J* = 1.4 Hz), 1.65-1.56 (1 H, m), 1.610 (3 H, d of t, *J* = 1.5, 1.0 Hz), 1.088 (3 H, s), 0.932 (3 H, s), 0.885 (3 H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 132.51 (d), 130.79 (d), 130.05 (s), 129.91 (s), 39.78 (s), 38.50 (s), 31.49 (t), 29.07 (q), 27.91 (t), 25.96 (q), 25.32 (q), 23.23 (q), 21.07 (q), 19.24 (q); IR (neat) 3060, 2960, 2915, 1660, 1455, 1398, 1375, 1200, 1090, 1063, 1032, 986, 840 cm<sup>-1</sup>. A satisfactory elemental analysis and exact mass molecular weight has been obtained for **8**.

(13) Of special significance is the fact that no trace of **4** could be detected in either of the reactions which produced major amounts of **8**.

(14) Libman, J. J. *Chem. Soc., Chem. Commun.* **1976**, 361. Jones, C. R.; Allman, B. J.; Mooring, A.; Spahic, B. *J. Am. Chem. Soc.* **1983**, *105*, 652.

(15) The electron-transfer-sensitized dimerization of 1,3-cyclohexadiene has also been studied by others: Calhoun, G. C.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 6870. We thank Professor Schuster for informing us of his results prior to publication.

### Temperature Dependence of Stereoselectivity as a Criterion for Mechanism. Rearrangement of Bicyclo[2.1.1]hexene-5-*d* and Two Phenyl Derivatives

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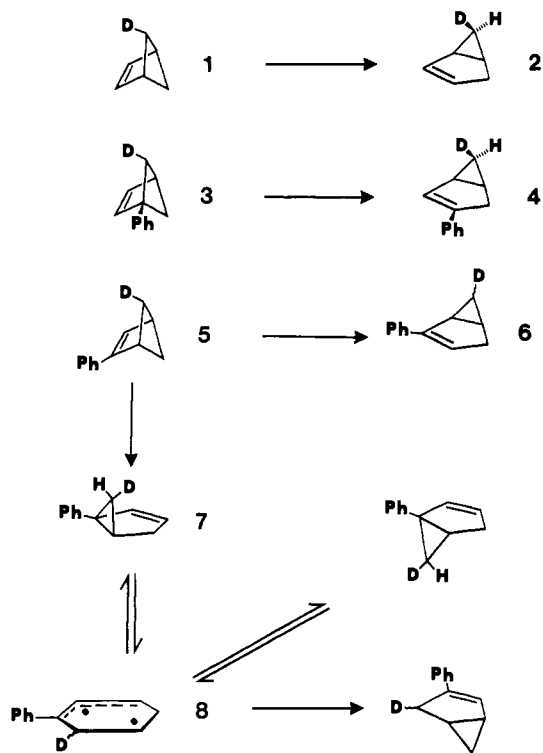
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The study of stereochemical changes at a chiral or prochiral center<sup>1</sup> can provide useful insights into mechanism. Reactions that occur with complete retention or complete inversion are generally thought of in terms of single or sequential pathways but not parallel pathways. Reactions that occur with 50% retention are generally considered to involve an intermediate that has lost the stereochemical information of the reactant; the alternative explanation of parallel inversion and retention pathways with coincidentally equal rates is implicitly treated as too improbable to be worth consideration. Problems arise when the reaction exhibits partial loss of stereochemistry. In this case parallel mechanisms are generally invoked but the single experimental

(1) We use these terms despite their imprecision (Mislow, K.; Siegel, J. *J. Am. Chem. Soc.* **1984**, *106*, 3319-3328) because the alternatives are so cumbersome in this case.

Scheme I. Main Thermal Reactions of the Bicyclo[2.1.1]hexenes<sup>a</sup>



<sup>a</sup> Only a single stereoisomer is shown for each reactant, although both were used. Only the major stereoisomer of the products from migration of the labeled bridge is shown in each case. See Table I for more details of product ratios.

observation (inversion/retention ratio) is insufficient to distinguish among the possible combinations of inversion, retention, and intermediate formation.

In the case of sigmatropic rearrangements the allowed and forbidden pericyclic mechanisms can be expected to exhibit pure retention or pure inversion. Unfortunately, the problem of interpretation of partial stereoselectivity, described above, is compounded in this case by the possibility that a biradical might have properties that allow it to retain some stereochemical information.<sup>2</sup> Thus a single pathway leading to a biradical intermediate could, perhaps, exhibit overall stereochemistry that ranges anywhere from complete stereoselectivity to complete loss of stereochemical information. This single fact has been the source of much of the contention in the study of hydrocarbon rearrangement mechanisms. In the present communication we show that by studying the temperature dependence of stereoselectivity one can considerably reduce the number of mechanistic possibilities. We further show that the stereochemistry of biradical reactions might be even more surprising than had previously been considered.

The reactions studied were the formal [1.3]-sigmatropic rearrangements of bicyclo[2.1.1]hexane-5-*d*<sup>3</sup> and its 1- and 2-phenyl derivatives (see Scheme I). Both *exo* and *endo* stereoisomers of these compounds<sup>4</sup> were used in the study. Experiments were conducted on dilute solutions of the compounds in dry, degassed isooctane. The stereochemistry of deuterium incorporation in the products was determined by <sup>1</sup>H and <sup>2</sup>H NMR, using previously reported assignments for the bicyclo[3.1.0]hex-2-ene ring system.<sup>5</sup>

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(3) For a study on the rearrangement of the unlabeled compound, see: Frey, H. M.; Hopkins, R. E.; O'Neal, H. E.; Bond, F. T. *J. Chem. Soc. D* **1969**, 1069. The stereochemistry of the rearrangement of 5-methylbicyclo[2.1.1]hexene was reported in: Roth, W. R.; Friedrich, A. *Tetrahedron Lett.* **1969**, 2607-2610.

(4) Newman-Evans, R. H.; Carpenter, B. K., unpublished results.