on the right side of Scheme I. Dissociation of CO from **2** gives coordinatively unsaturated intermediate **6**. Coordination of ethylene leads to **7**, an intermediate in which H (rather than only SiR$_3$, as in **4**) can migrate to the alkene.[12]

In summary, Cp$_2$Ta(CH$_2$)$_2$Ir(CO)$_2$ is a unique catalytically active heterodinuclear complex. The reactions it induces appear to take place at the iridium center, but the tantalum is necessary for the chemistry observed to take place,[13] although the specific role played by the early metal remains to be elucidated. Studies are in progress aimed at obtaining further evidence for the mechanistic conclusions summarized above, understanding the solvent effect observed in the hydrogenation reaction, and modifying the structure of **1a** to increase the scope of its catalytic reactivity.

Acknowledgment. We thank Johnson-Matthey for a generous loan of iridium and the National Science Foundation (Grant No. CHE-8722801) for financial support of this work.

Supplementary Material Available: Complete spectroscopic and analytical data for **1a**,**b**, **2a**–**c**, and **9** and details of the crystal structure determination for **1b**, including crystal and data collection parameters, positional parameters, and tables of intramolecular distances and angles (6 pages). Ordering information is given on any current masthead page.

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(11) Kinetic data were collected by monitoring the disappearance of the bridging methylenes against ferrocene as an internal standard by ^{1}H NMR spectrometry.

(12) We propose that the rate-determining step of the hydrosilation reaction involves reversible loss of CO from iridium. This predicts that added CO should inhibit the hydrosilation. Unfortunately, this prediction is difficult to test because added CO (as well as other dative ligands, such as PMe$_3$) forms stable adduct **9** with **1** and retards the rate by this mechanism (Scheme I).

(13) It is not easy to find structurally analogous mononuclear iridium complexes whose catalytic properties can be compared with those of **1**. One candidate is the phosphorus/iridium compound (Ph$_2$P(CH$_2$)$_2$)Ir(CO)(PPh$_3$), which we have recently prepared and shown to have a structure similar to **1**. This material is at least 100 times less active than **1** (or its phosphine analogue Cp$_2$Ta(CH$_2$)$_2$Ir(CO)(PPh$_3$)) in hydrogenation and hydrosilation reactions (Butts, M. D.; Bergman, R. G., unpublished results). The comparative chemistry of the tantalum and phosphorus compounds will be reported in a full paper.

Use of Alkyl Substitution To Control Ring Size in the Intramolecular Ionic Diels–Alder Reaction

Paul G. Gassman* and David B. Gorman[1]

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

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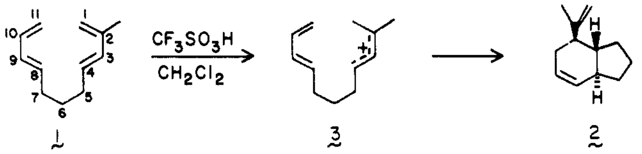
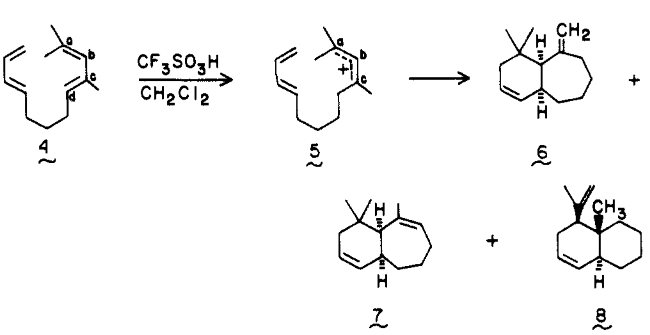
We have previously demonstrated that derivatives of the bicyclo[4.3.0]nonyl ring system could be prepared in high yield via an ionic Diels–Alder reaction from derivatives of 1,3,8,10-undecatetraene.[2] Determination of the site of protonation and the regioselectivity of the addition of the allyl cation to the 1,3-diene, through careful manipulation of the methyl substitution pattern on the tetraene,[3] has been found to allow selective formation of the bicyclo[4.3.0]nonyl, bicyclo[4.4.0]decyl, or bicyclo[5.4.0]undecyl ring skeletons.

Treatment of 2-methyl-1,3,8,10-undecatetraene (**1**) with 5 mol % of triflic acid in methylene chloride at 23 °C for 2 min gave an 86% yield[4] of **2**. Protonation of **1** occurred at C-1 to produce the more stable trisubstituted allyl cation **3**, which was the reactive intermediate in the formation of **2**.



In contrast, treatment of **4** with 10 mol % of triflic acid at −23 °C for 20 min gave products that were consistent with the protonation of **4** on C$_d$ to produce the tetrasubstituted allyl cation **5**. Subsequent *formal*[5] intramolecular Diels–Alder cyclization gave 72% of **6**, 4% of **7**, and 24% of **8** (GLC yields vs an internal standard).[6] Use of 1 equiv of the weaker methanesulfonic acid with **4** in methylene chloride at −23 °C for 2 min gave 18% of **6**, 44% of **7**, 17% of **8**, and starting material. These results suggested that **6** was a secondary product derived from **7**. Control experiments demonstrated that **7** rapidly and cleanly isomerized to **6** in the presence of triflic acid at −23 °C and that **6** was not converted into **7** under these conditions.[7]



The use of *p*-toluenesulfonic acid as catalyst (100 mol %) for 40 min at 23 °C in methylene chloride also promoted the intramolecular cycloaddition reactions of **4**. Under these conditions we obtained 27% of **6**, 3% of **7**, and 41% of **8**. As a result of the change in acid catalyst and temperature, **8** had become the major product.[9-11] While this change in major product requires only a relatively small change in transition-state energies, it is particularly auspicious because **7** (and subsequently **6**) resulted from the formal addition of the a–b portion of the allyl cation of **5** to the diene while **8** resulted from the b–c portion of the allyl cation of **5** being the 2π component of the cycloaddition.

For rigorous structural assignments, **6** and **8** were each treated with excess dichlorocarbene to give the crystalline adducts **9** and **10**, respectively. Single-crystal X-ray structural determination

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(1) Rohm and Haas Fellow, 1988–1989.

(2) Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 6085. Gassman, P. G.; Singleton, D. A. *J. Org. Chem.* **1986**, *51*, 3075.

(3) The various substituted tetraenes were prepared by straightforward synthetic approaches, which will be described in a full paper on this subject. Satisfactory elemental analyses and exact mass molecular weights have been obtained on all new compounds. All new compounds had IR, ^{1}H NMR, and ^{13}C NMR spectra that were consistent with the assigned structures.

(4) Operating on an 81-mg scale, the yield of **2** was 86% by analytical GLC analysis vs an internal standard (undecane) and 56% by isolation by preparative GLC.

(5) The stepwise vs concerted nature of these cycloadditions is discussed in the following communication in this issue.

(6) On a 76-mg scale, **6** and **8** were isolated in 53% and 22% yields, respectively, from **4** by preparative HPLC.

(7) This is in contrast to the direction of the analogous isomerization of α-himachalene to β-himachalene.[8] Apparently, the location of the *gem*-dimethyl groups on the seven-membered rings of the himachalenes vs that on the six-membered rings of **6** and **7** results in a significant change in the conformational stability of the two analogues, with the himachalenes being more stable with the double bond endocyclic, while our system is more stable with the double bond exocyclic.

(8) Harref, A. B.; Bernardini, A.; Fkih-Tetouani, S.; Jacquier, R.; Viallefont, P. *J. Chem. Res., Synop.* **1981**, 372. Mehta, G.; Singh, B. P. *J. Org. Chem.* **1977**, *42*, 632. Challand, B. D.; Hikinko, H.; Kornis, G.; Lange, G.; de Mayo, P. *J. Org. Chem.* **1969**, *34*, 794.

(9) We have found that yields and product ratios for a variety of ionic Diels–Alder reactions are dramatically dependent on both the acid catalyst and the temperature. For additional examples, see the following communication.

(10) Control experiments demonstrated that **8** was not interconverted with either **6** or **7** under the reaction conditions.

(11) With 100 mol % of methanesulfonic acid as the catalyst, the ratio of (**6** + **7**)/**8** systematically declined as the temperature increased: −23 °C, 3.6; 0 °C, 2.4; 23 °C, 1.3; 40 °C, 0.8.

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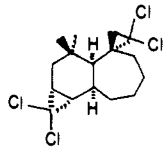
confirmed the structures of **9** and **10** and, by extrapolation, the structures of **6** and **8**.



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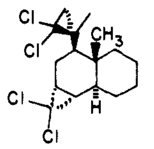
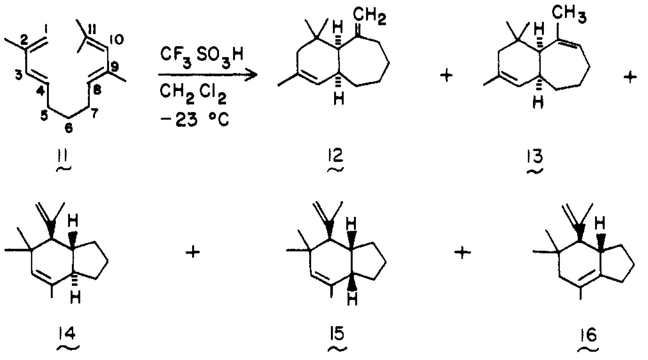
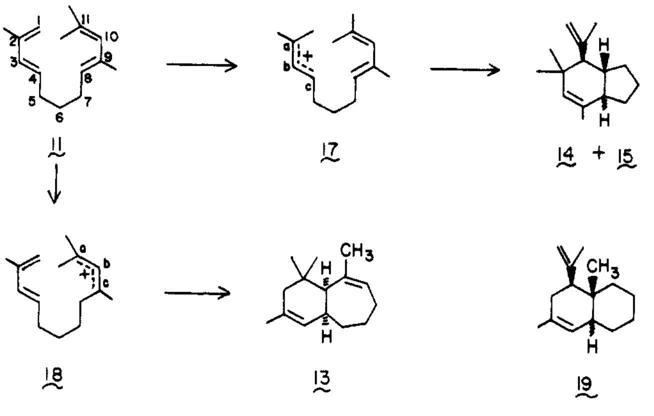


10

The addition of another methyl group of **4** resulted in major changes. When **11** was treated with 10 mol % of triflic acid in methylene chloride at −23 °C for 2 min, we obtained 43% of **12**, 5% of **13**, 15% of **14**, 15% of **15**, and 14% of **16**.[12,13] When the reaction was carried out at −78 °C for 1.5 h, the yields were 21% of **12**, 15% of **13**, 12% of **14**, 12% of **15**, and less than 1% of **16**. This indicated that **12** and **16** were secondary products that resulted from the acid-catalyzed isomerization of **13** and of **14** and **15**, respectively. This was confirmed by isomerization studies on **13**, **14**, and **15**.



Treatment of **11** with 40 mol % of *p*-toluenesulfonic acid in methylene chloride at 23 °C for 1 h gave 4% of **12**, 2% of **13**, 20% of **14**, 20% of **15**, and 30% of **16**.[12,13] Again, a change in acid and temperature resulted in a major change in product ratio. These changes are best understood through examination of the mechanistic pathways involved in the formation of **13**, **14**, and **15**. Product structures dictate that the allyl cation **17** must be involved in the formation of **14** and **15**. This requires protonation of C-1 of **11** to produce the trisubstituted allyl cation **17**, followed by exclusive *formal* cycloaddition of the b–c portion of the allyl cation to the diene moiety of **17**. In order to form **13**, **11** must be protonated at C-8 to give the tetrasubstituted allyl cation **18**. The complete absence of **19** shows that, in contrast to the reactions of **5**, **18** underwent *formal* intramolecular cycloaddition of only the a–b portion of the allyl cation **18**.



In summary, the bicyclo[4.3.0]nonyl, bicyclo[4.4.0]decyl, or bicyclo[5.4.0]undecyl ring systems can be produced from 1,3,8,10-undecatetraene through a judicious choice of methyl substitution, acid catalyst, and temperature. This is particularly useful in the case of the bicyclo[5.4.0]undecanes, which are not readily available.[14]

Acknowledgment. We are indebted to the National Institute of General Medical Sciences of the National Institutes of Health for a grant that supported this investigation. We thank Professor D. Britton for his assistance in the structure determination.

Supplementary Material Available: Spectral and other analytical data for **2**, **6–10**, and **12–16** and crystallographic experimental details, ORTEP drawings, and tables of positional and thermal parameters and significant distances and angles for **9** and **10** (20 pages). Ordering information is given on any current masthead page.

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(12) Two additional products were detectable by GLC in 5–7% combined yield.

(13) Under the reaction conditions, **12** and **13** were not interconverted with **14**, **15**, and **16**.

(14) For previous syntheses of the bicyclo[5.4.0]undecane skeleton via intramolecular Diels–Alder reactions, see: Wenkert, E.; Naemura, K. *Synth. Commun.* **1973**, *3*, 45. Oppolzer, W.; Snowden, R. L. *Helv. Chim. Acta* **1981**, *64*, 2592.

Stepwise Mechanism for the Formation of 2π + 4π Cycloadducts in the Ionic Diels–Alder Reaction

Paul G. Gassman* and David B. Gorman[1]

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

Received August 16, 1990

The term Diels–Alder reaction[2] has long been used to describe 2π + 4π cycloaddition reactions in which cyclohexene derivatives are formed. The mechanistic details of these cycloadditions have been much discussed and widely debated.[3,4] Theoretical studies have suggested that transition states for various Diels–Alder reactions range from a concerted synchronous process for the addition of ethylene to 1,3-butadiene[3,4] to very asynchronous pathways for the reactions of acrolein or cyanoalkenes with butadiene[4] and for certain Lewis acid catalyzed cycloadditions.[5] Completely stepwise "formal" 2π + 4π cycloaddition processes have been suggested in a few cases for the "classical" Diels–Alder reaction.[6-8] Since we have extensively investigated "ionic" Diels–Alder reactions in recent years,[9,10] we became intrigued with the mech-

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(3) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779. Fukui, K. *Acc. Chem. Res.* **1971**, *4*, 57. Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley and Sons: New York, 1976. Woodward, R. B.; Hoffman, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim/Berlin, Germany; Academic Press: New York, 1970; p 145.

(4) For recent leading references, see: Back, R. D.; McDonall, J. J. W.; Schlegel, H. B. *J. Org. Chem.* **1989**, *54*, 2931. Burke, L. A. *Int. J. Quantum Chem.* **1986**, *29*, 511. Houk, K. N.; Lin, Y.-T.; Brown, F. K. *J. Am. Chem. Soc.* **1986**, *108*, 554. Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 209. Dewar, M. J. S.; Olivella, S.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1986**, *108*, 5771. Loncharich, R. J.; Brown, F. K.; Houk, K. N. *J. Org. Chem.* **1989**, *54*, 1129. Houk, K. N.; Loncharich, R. J.; Blake, J. F.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 9172. Gajewski, J. J.; Peterson, K. B.; Kagel, J. R.; Huang, Y. C. J. *J. Am. Chem. Soc.* **1989**, *111*, 9078.

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(6) Gupta, R. B.; Frank, R. W. *J. Am. Chem. Soc.* **1987**, *109*, 5393.

(7) Jensen, F.; Foote, C. S. *J. Am. Chem. Soc.* **1987**, *109*, 6376.

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(10) Gassman, P. G.; Gorman, D. B. *J. Am. Chem. Soc.*, preceding paper in this issue.

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