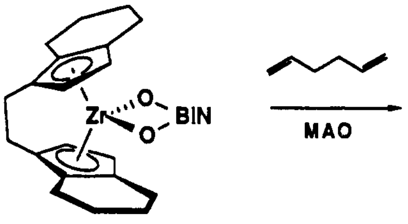
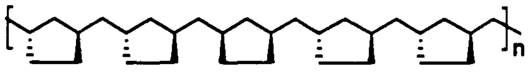
hydroindenyl)zirconium (*R*)-binaphtholate ($[\alpha]_{435}$ −1431° (*c* 1.2, CHCl$_3$))[2] and a methylaluminoxane (MAO) cocatalyst yields *optically active* poly(methylene-1,3-cyclopentane).[15] Following acidic workup, extraction of the polymer into chloroform, and precipitation with acetone, this polymer showed the molar optical rotation (per monomer unit) $[\Phi]^{28}_{405}$ +50.1° (*c* 7.8, CHCl$_3$).[16] Cyclopolymerization with (+)-(*S*)-ethylenebis(tetrahydroindenyl)zirconium (*S*)-binaphtholate ($[\alpha]_{435}$ +1848° (*c* 0.52, CHCl$_3$)) afforded the enantiomeric polymer (eq 1) with the molar optical rotation $[\Phi]^{28}_{405}$ −49.3° (*c* 7.9, CHCl$_3$).



$[\alpha]^{28}_{435}$ = +1848°



(1)

68% trans

$[\Phi]^{28}_{405}$ -49.3° (c, 7.9)

The optically active polymers contain approximately 68% trans rings and have ^{13}C NMR spectra identical with those obtained with the racemic catalyst. Since isotacticity is a requirement for chirality (for this polymer), the observation of optical activity provides an unambiguous proof for an isotactic microstructure.[17] Because of incomplete diastereoselectivity in the cyclization, the polymer obtained with chiral catalysts of the Brintzinger type is essentially an isotactic copolymer of *cis*- and *trans*-poly(methylene-1,3-cyclopentane).

Despite the presence of cis rings, the molar optical rotations (per monomer unit, $|[\Phi]^{20}_{D}|$ 22.8° (*c* 7.8, CHCl$_3$)) of the polymers are considerably higher than that of the model compound *trans*-(1*R*,3*R*)-1,3-dimethylcyclopentane, $[\Phi]^{20}_{D}$ +3.1°.[18] This suggests that the polymer adopts conformations in solution that contribute to the observed optical rotation.[5,7,8] The temperature dependence of the molar optical rotation for the polymer is consistent with this interpretation: the molar optical rotations $[\Phi]^{T}_{D}$ decrease from 26.2° at 2.5 °C to 19.5° at 51.1 °C with a slope $\Delta[\Phi]/\Delta T = -0.14°/°C$.[19]

In summary, we report the first *enantioselective cyclopolymerization to give a main-chain chiral polymer.* Because there is no requirement for chirality in the monomer, enantioselective polymerization is the most efficient means of preparing chiral polymers.[20-23] Further studies are underway to assign the absolute configuration of the polymer and to study the chiroptical and physical properties of these novel materials.

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Registry No. Cp$_2$TiCl$_2$, 1271-19-8; (±)-(EBTHI)ZrBINOL, 133868-91-4; (−)-(*R*)-(EBTHI)ZrBINOL, 123236-85-1; (+)-(*S*)-(EBTHI)ZrBINOL, 132881-66-4; 1,5-hexadiene (homopolymer), 25067-96-3; *trans*-(1*R*,3*R*)-1,3-dimethylcyclopentane, 1759-58-6.

Supplementary Material Available: Polymerization procedures and ^{13}C NMR spectra (3 pages). Ordering information is given on any current masthead page.

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[15] M_w = 35 000; M_w/M_n = 1.9 (GPC vs polystyrene).

[16] Rotations due to residual catalyst would be opposite in sign to that of the isolated polymer. Nevertheless, to rule out contributions from residual catalyst, propylene was polymerized and isolated under identical conditions with the same optically active catalyst. Residual optical activity in this sample due to the catalyst was virtually undetectable (see supplementary material).

[17] Preliminary microstructural analysis by ^{13}C NMR spectroscopy is consistent with a high degree of tacticity. Coates, G. W.; Waymouth, R. M., unpublished results.

[18] Richter, J. R.; Richter, B. *Isr. J. Chem.* **1976**, *15*, 57.

[19] Similar measurements on poly((*S*)-3-methyl-1-pentene) ($[\Phi]_D$ = +161° at 25 °C) showed temperature-dependent optical rotations with slope $\Delta[\Phi]/\Delta T = -0.36°/°C$. Pino, ref 5.

[20] Previous examples include the enantioselective cationic polymerization of benzofuran,[21] the enantioselective polymerization of pentadienes,[22,23] and the asymmetric polymerization of trityl methacrylates and chloral.[6]

[21] Natta, G.; Farina, M.; Peraldo, M.; Bressan, G. *Makromol. Chem.* **1961**, *43*, 68.

[22] (a) Natta, G.; Porri, L.; Valenti, S. *Makromol. Chem.* **1963**, *67*, 225. (b) Tsunetsugu, T.; Fueno, T.; Furukawa, J. *Makromol. Chem.* **1968**, *112*, 220. (c) Costa, G.; Locatelli, P.; Zambelli, A. *Macromolecules* **1973**, *6*, 653.

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An Unsymmetrical 1,1,3,3-Tetramethylallyl Cation

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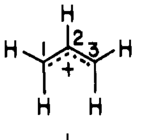
Theoreticians tell us that the allyl cation (**1**) is symmetrical.[2,3] Recent studies in our laboratory[4] have prompted us to question this concept and to carry out a detailed study of the 1,1,3,3-tetramethylallyl cation (**2**). In principle, treatment of **3** with XH



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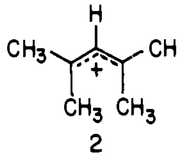

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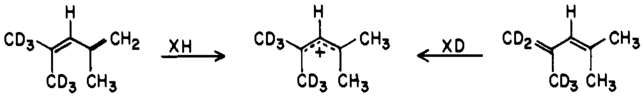
and of **4** with XD should yield the same allyl cation, **5**. We now present experimental evidence that unequivocally establishes that **3** and **4** do not yield the same allyl cation on protonation and deuteration, respectively.



3 5 4

Treatment of 2,4-dimethyl-1,3-pentadiene (**6**) with protic acid produces an allyl cation, which rapidly adds to **6** to produce the ionic Diels–Alder product **7**.[5] Thus, addition of **5** to **3**[6] and to

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[1] National Science Foundation Fellow, 1983–1986.

[2] For selected references, see: Buss, V.; Gleiter, R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 3927. Radom, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 6531. Duke, A. J. *Chem. Phys. Lett.* **1973**, *21*, 275. Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609. Gonzalez-Luque, R.; Nebot-Gil, I.; Tomas, F. *Chem. Phys. Lett.* **1984**, *104*, 203. Slee, T. S.; MacDougall, P. J. *Can. J. Chem.* **1988**, *66*, 2961. Radom, L.; Poppinger, D.; Haddon, R. C. In *Carbonium Ions Vol. V: Miscellaneous Ions, Theory and Structure*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: 1976; Chapter 38, pp 2368–2381.

[3] The rotational barrier for the allyl cation (**1**) is proposed to be approximately 35 kcal/mol in the gas phase.[2] This suggests that the planar form of **1** is about 35 kcal/mol more stable than the perpendicular form, which should represent the transition state for rotation. Alkyl substitution on the allyl cation is predicted to reduce this barrier (vide post).

[4] Gassman, P. G.; Gorman, D. B. *J. Am. Chem. Soc.* **1990**, *112*, 8623, 8624.

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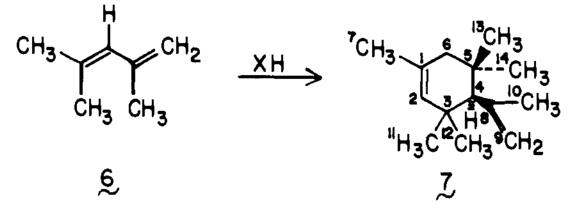
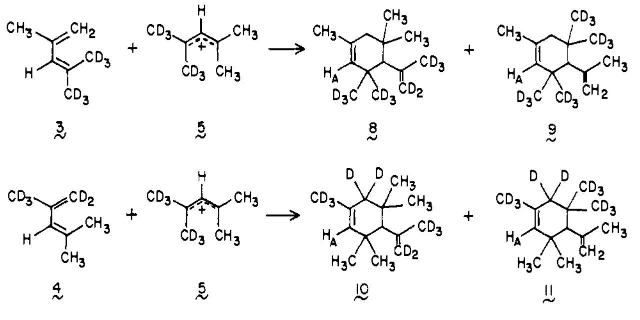


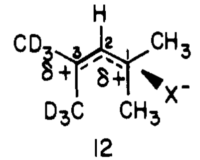
4[6] should produce an approximately equimolar mixture of **8** and **9**, and of **10** and **11**, respectively. When a methylene chloride solution of **3** was treated with 1 mol % of triflic acid for 3 min at −78 °C, the ratio of **8** to **9** was 27:73.[7,8] ^{1}H NMR analysis showed only 2% proton content in the methyls at C3 (C11 and C12), which indicated that **3** and **4** were not interconverted under these reaction conditions in excess of 2%.[7] In order to establish that the ratio of **8** to **9** was not the result of an unanticipated deuterium isotope effect in **5**, a methylene chloride solution of **4** was treated with 1 mol % of triflic acid-*d* for 3 min at −78 °C. This gave a mixture of **10** and **11** in the ratio of 68:32. ^{1}H NMR analysis showed 96% proton content in the methyls at C3 (C11 and C12), which indicated that **3** and **4** were not interconverted under these reaction conditions in excess of 4%.[7]



The data given above unequivocally establish several points. First, protonation of **3** and deuteration of **4** do not produce the same symmetrical allyl cation **5**. Second, the failure of **3** and **4** to interconvert under the reaction conditions by more than 4% indicates that if protonation (deuteration) is reversible, it must occur primarily by the microscopic reverse of the protonation (deuteration) process. This again requires that the allyl cations involved in the ionic Diels–Alder reactions be unsymmetrical (the free allyl cation **5** should have the same ratio of deprotonation to dedeuteration whether it was generated from **3** or **4**). Third, protonation of **3** and deuteration of **4** must produce different, unsymmetrical allyl cations in solution which (a) do not interconvert in excess of 4% at −78 °C or (b) do interconvert, but at a rate slower than that of their intermolecular cycloaddition (which must occur approximately 2 orders of magnitude faster than deprotonation or dedeuteration).

Additional experiments provided insight into this third point. If two unsymmetrical allyl cations are interconverting, a unimolecular process would be expected to be involved. In contrast, the intermolecular cycloaddition of the allyl cation to the starting material should be a bimolecular process which depends on both the concentration of the starting diene and the concentration of the allyl cation. If the results reported above involved two different *interconverting* allyl cations, varying the concentration of the diene and of the allyl cation (by varying acid concentration) should result in significant changes in the deuterium distribution. When 0.1 M **3** was treated with 1 mol % triflic acid at −23 °C for 3 min, the ratio of **8** to **9** was 26:74. Decreasing the acid concentration by 1 order of magnitude (0.1 mol %) gave a 27:73 ratio. Decreasing the diene concentration by 1 order of magnitude (0.01 M) gave a 27:73 ratio. Decreasing the acid concentration by 1 order of magnitude to 0.1 mol % (relative to the diene concentration of 0.01 M) gave a 23:77 ratio. In all four experiments the interconversion of **3** and **4** was 2% or less. Thus, varying the diene concentration by 10 and the acid concentration by 100 resulted in no significant change in deuterium distribution. This suggests that the unsymmetrical allyl cations generated by the protonation of **3** and the deuteration of **4** do not significantly interconvert at −23 °C or below[9] during the time required for bimolecular cycloaddition to occur.

It would appear that the allyl cation generated from **3** exists as a tight ion pair, which has either structure **12** or **13**. Extensive calculations on the 1,1,3,3-tetramethylallyl cation and on the 1,1,2,3,3-pentamethylallyl cation[10-12] indicated barriers to rotation of 27.7 and 25.3 kcal/mol, respectively.[10] The experimental barriers to rotation are reported to be 17.5 and 13.8 kcal/mol,[13,14] respectively. The lower experimental values are attributed to solvation effects.[10] The gas-phase calculations disregarded the counterion.[15] In view of these calculations and because cycloaddition occurred across both C1–C2 and C2–C3, we propose that protonation of **3** gives the unsymmetrical allyl cation **12** as a tight ion pair. If this is correct, the regiospecificity of the cycloaddition should be a function of the anion. Treatment of **3** with hexachloroantimonic acid (1 mol %) at −78 °C for 3 min gave a 9:91 mixture of **8**:**9**. Sulfuric acid (10 mol %) at 0 °C for 3 min gave a 19:81 mixture; trifluoroacetic acid (20 mol %) at 0 °C for 30 min gave a 25:75 mixture; and *p*-toluenesulfonic acid monohydrate (5 mol %) at 0 °C for 30 min gave a 35:65 mixture of **8**:**9**. Interconversion of **3** and **4** with these four systems were as follows: hexachloroantimonic acid, 1%; sulfuric acid, 2%; trifluoroacetic acid, 2%; *p*-toluenesulfonic acid monohydrate, 7%. In order to dramatically alter the size of the anion while maintaining the approximate acidity of triflic acid, Nafion-H was used at 0 °C with **3**, which gave a 45:55 mixture of **8**:**9** with less than 2% interconversion of **3** and **4**. Clearly, the counterion plays a major role.



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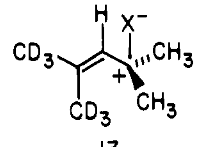

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Acknowledgment. We are indebted to the Institute of General Medical Sciences of the National Institutes of Health and to the National Science Foundation for support of this investigation.

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(6) The syntheses of **3** (99.5% specific labeling) and **4** (99.5% labeled in the methyl group and 97% labeled in the terminal methylene group) will be described in a full report on this work.

(7) The deuterium ratios were determined by the differences observed when the proton signals were integrated versus proton H_A (the proton attached to C2). On the basis of multiple experiments, the ratios of **8** to **9** and **10** to **11** were reproducible to ±3%. The values for interconversion of **3** and **4** under the reaction conditions are reproducible to ±1%. Spectra were measured on a Varian 500-MHz NMR instrument.

(8) For a detailed analysis of the ^{1}H NMR spectrum of **7**, see: Bigler, P.; Müller, C.; Bircher, H. *Magn. Reson. Chem.* **1990**, *28*, 205. Hoffmann, H. M. R.; Giguere, R. J.; Pauluth, D.; Hofer, E. *J. Org. Chem.* **1983**, *48*, 1155.

(9) At 0 °C, increased interconversion of **3** and **4** is observed. Treatment of a 0.01 M methylene chloride solution of **3** with 1 mol % of triflic acid at 0 °C gave a 32:68 mixture of **8**:**9** with 7% proton content in the methyls at C3 (C11 and C12).

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(11) MINDO/3 gave a barrier of 7.8 kcal/mol. Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1294.

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(14) Bollinger, J. M.; Brinich, J. M.; Olah, G. A. *J. Am. Chem. Soc.* **1970**, *92*, 4025.

(15) The rotational barrier for the parent ion, **1**, in liquid hydrogen fluoride, was calculated to be 21 ± 6 kcal/mol when X was fluoride ion. Cournoyer, M. E.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1984**, *106*, 5104. For earlier evidence for tight ion pairing in allyl cations, see: Nordlander, J. E.; Owuor, P. O.; Haky, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 1288.