

THE STEREOCHEMISTRY OF THE OLEFIN METATHESIS REACTION

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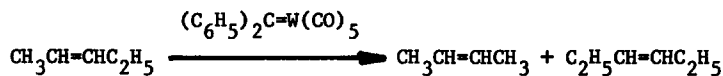
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We are reporting that the stereospecificity of *cis*-2-pentene's metathesis is much greater when the initiator is $(C_6H_5)_2C=W(CO)_5$ ¹ than when it is any other previously examined,² that this high stereospecificity is similar to that shown by cyclic olefins,³ and accordingly that no special mechanism is needed to account for why the stereospecificity of cyclic olefin metathesis is high.^{2g,4} We indicate how the stereospecificity in the previously used initiating mixtures is diminished by Lewis acids.

Trans-2-pentene with the same initiator gives ratios of *trans* and *cis* olefins similar to those at thermodynamic equilibrium:^{2b} 2.7 for 2-butene (2.6 at equilibrium), 5.0 for 3-hexene (6.2 at equilibrium).

Previous investigations have shown the metatheses of acyclic olefins effected by homogeneous tungsten-containing catalysts, as for example $WCl_6 + C_2H_5OH + C_2H_5AlCl_2$,^{2b} to be only slightly stereoselective. *Cis*-2-pentene gave 2-butenes and 3-hexenes in which the *cis* isomers predominated over the *trans* by factors of 1.0 to 2.0.^{2a,b,f,g} Similarly, *trans*-2-pentene, although studied less, gave 1.2 to 2.0 times as much *trans* olefin product as *cis*.^{2a,b,5} The slightly greater stereospecificity of heterogeneous catalysts has been attributed to surface phenomena^{2g} and the sometimes high stereospecificity of cycloolefin metatheses to intramolecular coordination of the metal by double bonds in the polymer chain,^{2g,4} but the results reported here show these postulates to be unnecessary.

Table. Stereochemistry of the Reaction

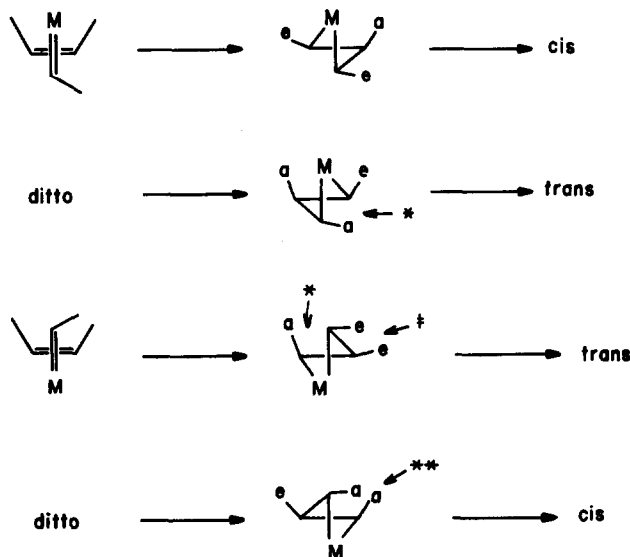
| Starting Olefin | % <i>cis</i> Olefin at Zero Conversion | | |
|-------------------------|----------------------------------------|-----------------------|----------|
| | 2-butene | 2-pentene | 3-hexene |
| <i>cis</i> -2-pentene | 94.3±1.0 | 96.0±0.4 ^a | 92.5±1.2 |
| <i>trans</i> -2-pentene | 27.2±2.7 | 0.2±0.4 ^b | 16.6±1.2 |

^a "*Cis*-2-pentene" was initially 96.4±0.2% *cis*. ^b "*Trans*-2-pentene" contained no detectable (<0.1%) *cis*.

The olefins (diluted with ca. 50% as much n-octane) and $(C_6H_5)_2C=W(CO)_5$ in molar ratios of 85-100 were combined, degassed, and sealed in a vacuum. After 14 to 40 hr at 21-25° the products were analyzed by GLPC,⁶ and the stereochemistries at zero time (summarized in the Table) were determined by extrapolating a plot of the fraction of each olefin that is cis against the extent of reaction.⁷ Even when the metathesis of the cis isomer was 87% complete, the butene, pentene, and hexene were all 86-90% cis.

These stereochemistries as well as those of the polymers formed from cycloalkenes³ can be accounted for if in the intermediate four-membered rings⁸ steric interactions are minimized between juxtaposed axial groups and ring atoms. Thus the energies of all cyclobutane conformations but the first in Scheme I must be raised by the opposition (indicated by a star) of an axial group and a ring carbon atom, and in the last conformation the interaction (indicated by two stars) must raise the energy even more. The analogous interaction

Scheme I. Metathesis of cis Olefins

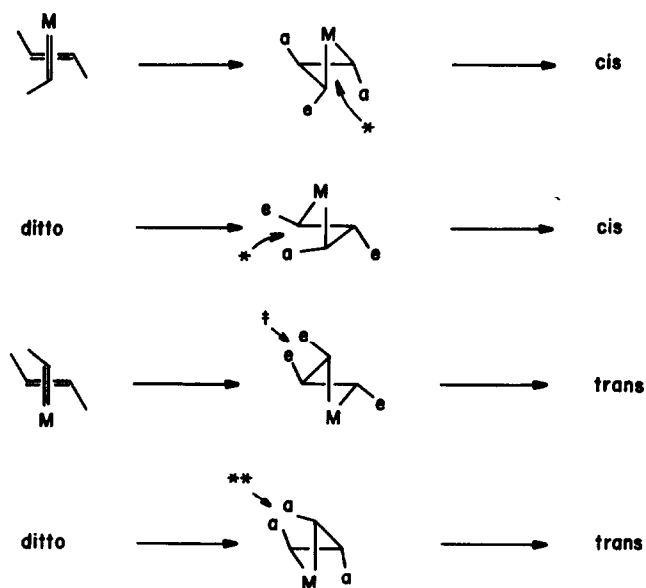


in the first conformation should raise the energy least because the axial group is juxtaposed to the tungsten (symbolized by the M) and bonds between carbon and tungsten (ca. 2.39 Å)⁹ are longer than those between carbons (1.54 Å). An indication of the effect of this distinction is provided by the structure of a four-membered ring containing platinum(II),¹⁰ in which the distance across the ring from carbon to metal is 0.3 Å greater than from carbon to carbon, and the difference should be accentuated in a tungsten metal-cycle by tungsten's greater (ca. 0.25 Å) covalent radius.⁹ Accordingly, reaction by way of this first conformation is fastest and the cis product predominates.

The stereospecificity of trans-2-pentene's metathesis, although appreciable, is not as great as that of cis-2-pentene's. The ratios of the stereoisomers are close to those at equilibrium, but are probably not determined by the products equilibrating, for in the short time the metathesis was run to determine the stereochemistry of the initial product, the precursor, trans-2-pentene, underwent only negligible isomerization.

If the stereochemistries are determined by kinetics, they should reflect conformational factors similar to those in Scheme I. The analogous scheme for trans olefin precursors, in Scheme II, shows all conformations of the four-membered ring except the third to have an axial group interacting with a ring carbon atom. Accordingly, this conformation should have the least energy, and the trans precursor should give, as it does, largely trans products.

Scheme II. Metathesis of trans Olefins



Schemes I and II might also explain why the stereospecificity is less for the trans isomer's metathesis, for a steric interaction (indicated by a dagger) that occurs when one alkyl group is rotated past another is met on the predominant path of only the trans precursor.¹¹

The reason the stereospecificities often are low when the initiator contains metal halides may be that Lewis acids facilitate cleavage of the carbon-metal bond in the metalocyclobutane, forming a 3-metallopropyl cation in which the remaining bonds rotate. In accord with this hypothesis, the stereospecificity of cyclopentene's metathesis when initiated at -30° by mixtures of WF_6 and $(C_2H_5)_3Al_2Cl_3$ diminishes with the Al/W ratio.¹³ The decrease with increasing temperature of the amounts of cis double bonds in the products of two cyclopentene metatheses¹⁴ might also be manifestations of this heterolytic cleavage reaction.

In a comparison of catalysts containing tungsten with those containing molybdenum, the latter seem to give higher stereospecificities; molybdenum catalysts have given the highest stereospecificities observed in metatheses of trans olefins^{2c,d} and in polymerizations of cyclopentene¹⁵ and norbornene.¹⁶ The reason for this and for why a molybdenum-containing catalyst was found to be the least selective in terminal olefin metathesis¹⁷ may be related: the more 3-metallopropyl cations are favored, the greater the sensitivity to the effects of substituents that determine the selectivity and the more easily the stereospecificity is

lost. Accordingly, such cations may be favored less when the metal is molybdenum than when it is tungsten.

References and Notes

- (1) C. P. Casey and T. J. Burkhardt, J. Am. Chem. Soc., **95**, 5833 (1973).
- (2) (a) J. L. Wang and H. R. Menapace, J. Org. Chem., **33**, 3794 (1968); (b) N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scott, J. Am. Chem. Soc., **90**, 4133 (1968); (c) W. B. Hughes, J. Chem. Soc., Chem. Commun., 431 (1969); (d) G. Doyle, J. Catal., **30**, 118 (1973); (e) A. Ismayel-Milanovic, J. M. Basset, M. Dufaux, H. Pralraud, and L. DeMourges, ibid., **31**, 408 (1973); (f) J. M. Basset, G. Coudurier, R. Mutin, and H. Pralraud, ibid., **34**, 152 (1974); (g) J. M. Basset, J. L. Bilhou, R. Mutin, and A. Theolier, J. Am. Chem. Soc., **97**, 7376 (1975).
- (3) T. J. Katz, S. J. Lee, and N. Acton, Tetrahedron Lett., 4247 (1976).
- (4) N. Calderon, E. A. Ofstead, and W. A. Judy, Angew. Chem., Int. Ed. Engl., **15**, 401 (1976).
- (5) P. Krausz, F. Garnier, and J. E. Dubois, J. Am. Chem. Soc., **97**, 437 (1975).
- (6) The GLPC analyses were effected with a 23' x 1/8" column at 40° of TCEP [1,2,3-tris(2-cyanoethoxy)propane] on 60/80 Chromosorb P regular.^{2b}
- (7) When the reaction of cis-2-pentene was 1.73±0.05% complete, the 2-butene formed was 92.8±5.1% cis and the 3-hexene 90.6±4.1% cis. The remaining 2-pentene was 95.9±1.9% cis, implying that 0.5% had isomerized to trans-2-pentene. Similarly, when the reaction of trans-2-pentene was 0.70±0.03% complete, the 2-butene was 24.1±4.3% cis, the 3-hexene 15.2±1.5% cis, and the 2-pentene 0.21±0.03% cis. Here percent completion is defined as 100(2-butene + 3-hexene)/(2-pentene). After 40 hr the reaction of cis-2-pentene was 87% complete and that of trans-2-pentene only 10%.
- (8) T. J. Katz and R. Rothchild, J. Am. Chem. Soc., **98**, 2519 (1976) and references there.
- (9) M. R. Churchill in "Perspectives in Structural Chemistry," volume III, J. D. Dunitz and J. A. Ibers, editors, John Wiley and Sons, New York, 1970, p. 91 ff.
- (10) D. J. Yarrow, J. A. Ibers, M. Lenarda, and M. Graziani, J. Organometal. Chem., **70**, 133 (1974).
- (11) A similar interaction has been postulated to account for the stereochemistry of epoxidation of 1,6-disubstituted cyclohexenes,^{12a} for the stereochemistry of further alkylation at the 1-position of 1-alkyl-trans-2-decalones,^{12b} and for the high barrier to inversion of nitrogen configuration in 1,2,2,6-tetramethylpiperidine.^{12c} We are grateful to Professor Gilbert Stork for pointing out his work and that of McCurry.
- (12) (a) P. M. McCurry, Jr., Tetrahedron Lett., 1841 (1971); (b) G. Stork, "XXIIIrd International Congress of Pure and Applied Chemistry---Boston, 1971," Vol. II, Butterworths, London, 1971, p. 193 ff; (c) F. A. L. Anet, I. Yavari, I. J. Ferguson, A. R. Katritzky, M. Moreno-Mañas, and M. J. T. Robinson, J. Chem. Soc., Chem. Commun., 399 (1976).
- (13) P. Günther, F. Haas, G. Marwede, K. Nützel, W. Oberkirch, G. Pampus, N. Schön, and J. Witte, Angew. Makromol. Chem., **14**, 87 and **16/17**, 27 (1971).
- (14) (a) R. J. Minchak and H. Tucker, Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem., **13**, 885 (1970); (b) G. Pampus and G. Lehnart, Makromol. Chem., **175**, 2605 (1974).
- (15) G. Dall'Asta and G. Motroni, Angew. Makromol. Chem., **16/17**, 51 (1971).
- (16) G. Sartori, F. Ciampelli, and N. Cameli, Chim. Ind. (Milan), **45**, 1478 (1963).
- (17) J. McGinnis, T. J. Katz, and S. Hurwitz, J. Am. Chem. Soc., **98**, 605 (1976).