

Table I. Stereoselectivity of Olefin Isomerization as a Function of Base and Solvent^a

Base	Solvent	10 ³ <i>k</i> , sec. ⁻¹	(<i>cis</i> / <i>trans</i>) <i>t</i> → 0 ^b
1-Butene, 55°			
NaO- <i>t</i> -Bu	DMSO ^c	0.01	37
KO- <i>t</i> -Bu	DMSO	1.16	26
RbO- <i>t</i> -Bu	DMSO	2.84	16
CsO- <i>t</i> -Bu	DMSO	4.47	25
KO- <i>t</i> -Bu	TMU ^d	0.0174	23
KO- <i>t</i> -Bu	N-Methyl-2-pyrrolidone	0.0785	26
KO- <i>t</i> -Bu	HMPA ^e	0.201	19
1-Pentene, 55°			
KOMe	DMSO	0.00569	14
KO- <i>t</i> -Bu	DMSO	0.717	13
KO- <i>t</i> -Bu	DMSO + 0.5% <i>t</i> -BuOH	0.605	11
KO- <i>t</i> -Bu	DMSO + 1% <i>t</i> -BuOH	0.493	10
KO- <i>t</i> -Bu	DMSO + 2% <i>t</i> -BuOH	0.433	10
KO- <i>t</i> -Bu	DMSO + 4% <i>t</i> -BuOH	0.256	10
KO- <i>t</i> -Bu	DMSO + 8% <i>t</i> -BuOH	0.044	10

^a Experimental details will be presented in a future publication.

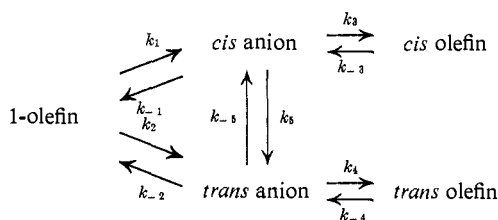
^b The uncertainty in these values is ±10% of the ratios. At least five points at low conversions were taken in each run.

^c DMSO, dimethyl sulfoxide. ^d TMU, tetramethylurea. ^e HMPA, hexamethylphosphoramide.

upon the rate of isomerization will be discussed in a future publication.

The work reported here shows clearly that there is no correlation between the stereoselectivities and the rates, the cation, the anion, or the solvent involved in the isomerization. Therefore any explanation for the stereoselectivity must evolve from a property that is common to all of these systems, that is, a fundamental or intrinsic property of the system. We propose that this intrinsic property of the system is that for simple olefins the *cis*-allylic anion is thermodynamically more stable than the *trans* form.

That such an assumption can explain the kinetic results is seen by the following kinetic scheme. For simplicity ion pairs have been neglected in the formulation; their inclusion does not affect the over-all conclusion. With $k_{-5} > k_5$ the *cis*-allylic anion is more



stable than the *trans* form. Both k_{-5} and k_5 are expected to be small, perhaps insignificant, for the eventual *cis* to *trans* olefin conversion; nonetheless the allylic anions once formed are expected largely to maintain their geometry.¹⁰ The reprotonation of the anions is probably diffusion controlled and most reasonably the same for both anions. Then with $k_{-3} > k_{-4}$ the reaction initially produces more *cis* olefin, but with time the more stable *trans* olefin predominates.

While the kinetics are amply accounted for by the assumption that the *cis*-allylic anion is more stable than the *trans* form, some external justification is desirable. For this purpose halo-substituted olefins and Grignard reagents are used as models for the allylic

(10) D. H. Hunter and D. J. Cram, *J. Am. Chem. Soc.*, **86**, 5478(1964).

anion formed in the base-catalyzed isomerization of simple olefins.

Recent data^{11,12} have shown that halo-substituted propenes show unusual thermodynamics, namely, the *cis* form is more stable than the *trans*. Favorable dipole-dipole van der Waals interactions present only in the *cis* form have been invoked to account for the results.

The halopropenes are a better model for the allylic anions than the parent olefin for several reasons. First, the electronegativity of the anionic system is better represented both directionally and in magnitude by the halo-substituted compounds. Second, the dipole of the anionic system is expected to be as great or greater than that of the halo compounds. From these considerations the *cis*-allylic anion, in analogy with the *cis*-halopropenes and unlike the parent olefin, is expected to be more stable than the *trans* form. In addition, U-shaped pentadienyl anions are more stable than other planar forms although the corresponding transoid dienes are more stable than the cisoid dienes.¹³

Equally convincing support is found in the fact that a preference for the *cis* form is found in quenching butenyl Grignard reagents.¹⁴ As a model, the fact that Grignard reagents are solvated and agglomerated makes them an excellent choice for the highly solvated anion formed in the isomerization reaction.

(11) K. E. Howell and L. F. Hatch, *ibid.*, **77**, 1682 (1955).

(12) J. W. Crump, *J. Org. Chem.*, **28**, 953 (1963).

(13) R. B. Bates, R. H. Carnighan, and C. E. Staples, *J. Am. Chem. Soc.*, **85**, 3030, 3031 (1963).

(14) W. G. Young, S. Winstein, and A. N. Prater, *ibid.*, **58**, 289 (1936).

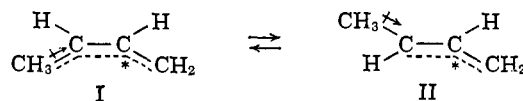
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Received April 15, 1965

Thermodynamic Stability of Allylic Intermediates

Sir:

A previous communication presents evidence that the stereoselectivity observed in the base-catalyzed olefin isomerization is the result of the fact that the *cis*-allylic anion is thermodynamically more stable than the *trans* form.¹ Favorable dipole attractive forces in the *cis* form were offered to account for the thermodynamic reversal relative to the parent hydrocarbons. In the present communication the extension of this simplified scheme to other reactive intermediates is considered. Of compelling interest is the conclusion that the thermodynamic stabilities of these intermediates can be derived from charge and dipole considerations.

There will be interactions of the dipole of a methyl group and the dipoles of the various allylic intermediates, Ia-c and IIa-c (where a, b, and c are 0, 1, and 2 π -electrons).



It is the purpose of this communication to demonstrate that the thermodynamic isomeric preferences can be predicted by a consideration of these interactions.

(1) S. Bank, A. Schriesheim, and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, **87**, 3244 (1965).

For Ic and IIc (the allylic anions), the system has a net charge of -1 and there will be attractive forces between the methyl group and the *cis*-allylic form. For Ia and IIa (the allylic carbonium ions), the system has a net charge of $+1$ and in the absence of other factors (*vide infra*) there will be repulsive forces between the dipole of the methyl group and the *cis*-allylic cation. Finally for Ib and IIb, the system has no net charge and neither strong attractive or repulsive forces are expected.

Consideration of these expected dipole interactions leads to the following stability predictions: Ic > IIc; IIa >> Ia; and IIb > Ib. The last prediction evolves from the fact that for the neutral species the thermodynamic stabilities of the several isomers is principally determined by steric repulsive forces in the absence of charge considerations. For this purpose, the parent hydrocarbons serve as a convenient model and, since the stability of simple olefins is *trans* > *cis*, similar isomeric stabilities are expected for the radicals (Ib and IIb).

Data favoring the conclusion that the *cis*-allylic anion is more stable than the *trans* form are outlined in the previous paper.¹ With respect to the cationic species, a test of the proposed scheme is afforded by the silver ion assisted solvolyses of α -methylallyl chlorides.² As expected theoretically, the allylic cations maintain configurational stability. Of greater interest is the fact that "the high predominance of *trans* in the primary alcohol from hydrolysis of α -methylallyl chloride suggests that α -methylallyl chloride IS gives rise nearly exclusively to the *trans*-butenyl cation IVT."² Additional support is derived from the observation that the order of reactivities of crotyl chlorides is *trans* > *cis*. Insofar as the energetics of the transition states for these reactions accurately reflect the stabilities of the various intermediates, a reasonable assumption, then the *cis*-allylic cation is less stable than the *trans* form.

For the radicals, experimental evidence for the relative stabilities of the *cis* and *trans* form is derived from a study of the allylic chlorination of butenes with *t*-butyl hypochlorite.³ As is now commonly accepted for these allylic intermediates, the radicals thus formed are configurationally stable. Of direct implication to the concepts in the present work is the observation that, although the *cis* form is statistically favored, the final product has a 1.85:1 preference for the *trans* compound. Significantly the *trans* preference, after correction for the statistical factor, is 3.7:1, which is very similar to that of the parent hydrocarbons (3:1). Thus the available evidence on the stabilities of *cis*- and *trans*-allylic radicals also supports the proposed scheme.

The simple dipole argument presented above is supported by data on the isomeric preferences of the three intermediates. Nevertheless, some consideration of other factors possibly influencing stabilities is warranted. The proposed scheme that charge dipole attractions and repulsions control the isomeric preference neglects significant contributions from induced dipoles, hydrogen bonding, and nonclassical structures. For example, a reasonable case could be made that the

(2) W. G. Young, S. H. Sharman, and S. Winstein, *J. Am. Chem. Soc.*, **82**, 1376 (1960).

(3) C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961).

cis-allylic cation would be favored over the *trans*-if contributions from some or all of these factors were important. Insofar as the stability of the *cis*- and *trans*-allylic cations is successfully derived from simple charge dipole repulsions, these factors must be relegated to secondary roles.

Finally the isomerization of 1-butene over various solid acid catalysts produces ratios of *cis*-2-butene to *trans*-2-butene from 1.5 to 6.5.⁴ These results contrast with the ion stabilities outlined in this paper and supported by the solvolyses. Of significant importance, the isomerization of 1-butene in homogeneous acid solution does not exhibit a stereochemical preference to the *cis* olefin.⁵ In actual fact the ratios of *cis*- to *trans*-2-butene in dilute sulfuric and phosphoric acids are 1. The *trans*:*cis* ratio of 1 observed in the homogeneous acid-catalyzed isomerization is amply accounted for as proceeding through a 2-butyl cation. Insofar as the stereochemical control is observed only on supported systems and insofar as many possible catalyst surface effects can explain the results, they do not constitute a serious objection to the proposed cation stabilities.

We are currently examining a wide variety of data in the light of the proposed hypothesis. The more detailed description of these results will be published later.

Acknowledgment. The author wishes to express his appreciation to Dr. Alan Schriesheim for stimulation and continued interest. He is grateful to the Esso Research and Engineering Co. for permission to publish this research.

(4) (a) P. J. Lucchesi, D. L. Baeder, and J. P. Longwell, *ibid.*, **81**, 3235 (1959); (b) W. O. Haag and H. Pines, *ibid.*, **82**, 2488 (1960).

(5) W. B. Smith and W. B. Watson, Jr., *ibid.*, **84**, 3174 (1962). For possible exception, see, however, ref. 4b.

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Received April 15, 1965

exo Vicinal Hydride Shift in the 3-*endo*-Methyl-2-norbornyl Cation¹

Sir:

The behavior of the 3-*endo*-methyl-2-norbornyl cation (**8**) serves as a standard of comparison for the 3-*exo*-methyl-2-norbornyl case, where stringent stereo-electronic prohibition of *endo* vicinal hydride shift is observed.² It also provides a measure of the competition between solvent capture and vicinal hydride shift in a norbornyl system.

The racemic alcohol 3-*endo*-methyl-2-*exo*-norborneol (**1**, X = OH) is prepared (1) from the known³ 3-*endo*-methyl-2-*exo*-norbornanecarboxylic acid (**1**, X = CO₂H) via the "acid \rightarrow acetate" sequence: **1**, X = CO₂H \rightarrow **1**, X = COCl \rightarrow **1**, X = COCH₃ \rightarrow **1**, X = OAc \rightarrow **1**, X = OH; and (2) by hydroboration-oxi-

(1) (a) Presented in part at the Anniversary Meeting of the Chemical Society, Birmingham, England, April 6-9, 1964, Abstracts, p. 19; *Proc. Chem. Soc.*, 204 (1964). (b) Support of part of this work by the National Institutes of Arthritis and Metabolic Diseases through Grant No. AM-07505 is gratefully acknowledged.

(2) J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *J. Am. Chem. Soc.*, **87**, 3248 (1965).

(3) (a) S. Beckmann and R. Mezger, *Chem. Ber.*, **90**, 1559 (1957); (b) G. Komppa and S. Beckmann, *Ann.*, **523**, 69 (1936).