Tetrahedron Letters No. 10, pp. 405-408, 1962. Pergamon Press Ltd. Printed in Great Britain.

REACTIONS OF SIMPLE HYDROCARBON CARBANIONS - II

STEREOCHEMISTRY OF THE HOMOGENEOUS OLEFIN ISOMERIZATION REACTION

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(Received 12 April 1962)

A RECENT communication[1] reported that allylic C-H bonds in olefins can be activated at mild conditions using potassium-t-butoxide in dimethylsulfoxide. It was also pointed out that the homogeneous butene-1 isomerization reaction showed a marked degree of stereoselectivity initially producing more cis-2-butene than trans-2-butene.

Determination of the factors influencing the kinetic reaction control which leads to thermodynamically less favored isomers is important. A combination of three variables might be crucial in understanding this phenomenon. These are the influence of (a) olefin structure, (b) base character, and (c) solvent type on the reaction course. An answer is desired since such knowledge would yield fundamental information concerning the geometry and reactivity of these simple hydrocarbon carbanions not now at hand.[2] The purpose of the present communication is to discuss preliminary findings concerning the effect of olefin structure on reaction stereochemistry. We have found that structural changes in the olefin profoundly influence the kinetic control exerted on the homogeneous anionic isomeri-

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[1] A. Schriesheim, J.E. Hofmann and C.A. Rowe, Jr., J. Amer. Chem. Soc. 83, 3731 (1961).

[2] H. Pines, Advances in Catalysis and Related Subjects Vol. 12. Academic Press, New York (1960).

zation of hydrocarbon olefins.

The experimental procedures used were similar to those previously reported (1). Sublimed potassium-t-butoxide was employed as the base, and the reactions were carried out at 55°C using a dimethylsulfoxide solution 0.77 molar in olefin, and 0.70 molar in base. Analyses were performed on a 21 ft gas chromatographic column of 3 per cent squalane on firebrick. This system is sensitive to 0.1 per cent of the olefin isomers. In all cases, complete isomer identification was made.

The isomerization reaction is first order in each olefin studied and typical plots of log concentration vs. time values are linear. The cis/trans ratios were calculated by extrapolating cis/trans ratio vs. time plots to zero time.[3] These zero time values provide the ratio of the forward rates, k_1 and k_2, as shown in equations (1-4).

$$\begin{tikzcd}
 & \text{\underline{cis}-2-olefin} \arrow[dl, shift left, "k_{-1}"] \arrow[dd, shift left, "k_{-3}"] \\
\text{1-Olefin} \arrow[ur, shift left, "k_1"] \arrow[dr, shift left, "k_2"] & \\
 & \text{\underline{trans}-2-olefin} \arrow[ul, shift left, "k_{-2}"] \arrow[uu, shift left, "k_3"]
\end{tikzcd} \qquad (1)$$

$$\frac{d\ \underline{cis}}{dt} = k_1\ (\text{1-olefin}) - k_{-1}\ (\underline{cis}) + k_3\ (\underline{trans}) - k_{-3}\ (\underline{cis}) \qquad (2)$$

$$\frac{d\ \underline{trans}}{dt} = k_2\ (\text{1-olefin}) - k_{-2}\ (\underline{trans}) + k_{-3}\ (\underline{cis}) - k_3\ (\underline{trans}). \qquad (3)$$

At zero time the ratio of the terms reduce to:

$$\left[\frac{d\ (\underline{cis})}{d\ (\underline{trans})}\right]_{t \longrightarrow 0} = \frac{k_1}{k_2}. \qquad (4)$$

Values of k_1/k_2 at zero time are compared in Table 1 with the values expected if "thermodynamic" or equilibrium reaction control were obtained.

The reaction stereochemistry is markedly dependent on the group adjacent to the allylic system. As the bulk of the substituting group

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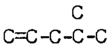
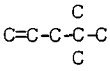
[3] W.O. Haag and H. Pines, J. Amer. Chem. Soc. **82**, 387 (1960).

TABLE 1

Cis/trans Ratios at Zero Time

1 Olefin	2 $(\text{cis/trans})^{a}_{t \rightarrow 0}$	3 $(\text{cis/trans})\ \text{eq.}^{b}$	4 $\frac{\text{cis/trans}\ t \rightarrow 0}{\text{cis/trans eq.}}$
$C{=}C{-}C{-}C$	47.4	0.25	190
$C{=}C{-}C{-}C{-}C$	10.8	0.23	47
 $C{=}C{-}C{-}\overset{C}{C}{-}C$	3.2	0.23	14
 $C{=}C{-}C{-}\overset{C}{\underset{C}{C}}{-}C$	0.25	< 0.001	> 250

[a] The uncertainty of these values is, at most, about ± 10 per cent of the ratio based on several runs, and at least 5 points below 15 per cent conversion were taken in each run.

[b] These equilibrium values were experimentally determined and the details will be shortly published. The values reported are reproducible to about ± 6 per cent.

increases through the series, methyl, ethyl, isopropyl, and t-butyl, kinetic control decreases (column 2). Indeed, results in this system seem to be generalized by the statement that "The fewer the substituents, the greater the stability of cisoid conformation relative to the transoid conformation in the transition state". A "free" carbanion reaction intermediate does not seem justified since it is difficult to rationalize selective production of cis isomers from such a species. For synthetic purposes, these results imply that steric isomers can be made from various olefins providing the starting 1-olefin structures do not contain bulky groups on certain carbon atoms.

Metal cation bonding to a β-hydrogen has been invoked to rationalize the kinetic reaction control observed when olefins are isomerized over an alkali metal-alumina catalyst.[3] A rather similar picture involving bonding to an oxygen atom has also been used to depict the kinetic control obtained in the alkoxide catalyzed isomerization of allyl ethers in dimethylsulfoxide.[4]

Such a bonding situation, at least with olefins, does not seem reasonable in light of the data obtained with 4,4-dimethyl-1-pentene. Heat of hydrogenation results[5] and the equilibrium data shown in Table 1 indicate marked interference of methyl groups in the *cis* form for this olefin. Such an unfavorable steric situation, coupled with the lack of hydrogen atoms to undergo bonding is expected to lead to ratios approaching equilibrium. The actual ratios found are very far from equilibrium and indicate kinetic control of reaction of the same type found for the less bulky olefins.

This and previous work[1] point to a transition state with a preferred conformation consisting of base, solvent and olefin. Work is continuing in this area in an effort to rationalize these results in terms of a detailed mechanism.

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[4] C.C. Price and W.A. Snyder, *J. Amer. Chem. Soc.* **83**, 1772 (1961).

[5] R.B. Turner, D.E. Nettleton, Jr. and M. Perelman, *J. Amer. Chem. Soc.* **80**, 1430 (1958).