

**Acknowledgment.**—We are indebted to Dr. A. H. Struck and Mrs. R. Barritt for the mass spectral meas-

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[CONTRIBUTION FROM ESSO RESEARCH AND ENGINEERING CO., LINDEN, N. J.]

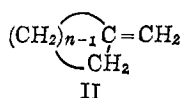
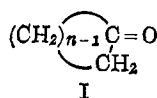
## Anionic Activation of C-H Bonds in Olefins. V. Influence of Structure on Reaction Rate

By A. SCHRIESHEIM, C. A. ROWE, JR., AND L. NASLUND

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The base-catalyzed proton migration rates of a series of terminal olefins of varying structure were studied in a homogeneous system using potassium *tert*-butoxide–dimethyl sulfoxide between 35 and 55°. The steric and electronic effects of substituents on four classes of olefinic structures were studied. It was found that the effect of substitution of the various alkyl groups for hydrogen gave rise to the same change in rate in each series. Correlations employing a Taft–Hammett type treatment show that both the inductive and steric effects of the alkyl groups are important. It has also been shown that the ease of reaching a coplanar transition state plays a large role in determining the C–H bond activity of acyclic olefins. In addition, electron delocalization effects are quite important in these prototropic shifts and a comparison of steric, inductive and electron delocalization effects is made.

Several recent papers have discussed the anionic activation of allylic C–H bonds<sup>1a–d</sup> for prototropic migrations in olefinic hydrocarbons in potassium *tert*-butoxide–dimethyl sulfoxide solution. The system is homogeneous and allows proton migration rates to be determined simply and reproducibly. Of considerable interest was the finding of a linear correlation between logarithms of the relative rates of base-catalyzed bromination of alicyclic ketones (I) and isomerization of methylenecycloalkanes (II).<sup>1d</sup> The suggestion of rate-determining allylic proton removal has been further substantiated by the observance of a large deuterium isotope effect.<sup>2</sup>



Variations in ring size from cyclobutyl to cyclooctyl in I and II lead to substantial rate differences, although these structures encompass small changes in inductive effects. Rate enhancements in small rings (cyclobutyl) were attributed to the proper geometry of the allylic C–H bond with respect to the  $\pi$ -orbitals of the unsaturated linkage in contrast to the unfavorable geometry of the allyl system in methylenecyclohexane.<sup>1d</sup>

It was of interest to determine the effect on rate of appropriate electron-withdrawing and -donating substituents in various positions of acyclic olefins and to demonstrate the direction and magnitude of their inductive and steric effects.

### Results

The rate of base-catalyzed isomerization of 2-ethyl-1-butene (III) was compared with the rate of base-catalyzed bromination of 3-pentanone (IV). Plots of the log values of these two quantities fit on the same graph recently reported for the comparison of alkylidenecycloalkanes and cycloalkanones<sup>1b</sup> (Fig. 1). These results clearly establish similarities in the transition state



profiles of the cyclic–acyclic olefin isomerization reaction and the cyclic–acyclic ketone bromination reactions.

(1) (a) A. Schriesheim, J. E. Hofmann and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, **83**, 3731 (1961); (b) A. Schriesheim and C. A. Rowe, Jr., *Tetrahedron Letters*, No. 10, 405; (c) A. Schriesheim and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, **84**, 3160 (1962); (d) A. Schriesheim, R. J. Muller and C. A. Rowe, Jr., *ibid.*, **85**, 3164 (1962).

(2) S. Bank, C. A. Rowe, Jr., and A. Schriesheim, *ibid.*, **85**, 2115 (1963).

The rates of isomerization of a number of terminal olefins of varying complexity are listed in Table I. All reactions were carried out in dimethyl sulfoxide–potassium *tert*-butoxide solutions at 55° with the exception of allylbenzene and 1,4-pentadiene. The latter two compounds isomerized at extraordinarily rapid rates and it was necessary to obtain their rates at 30° in a dimethyl sulfoxide–*tert*-butyl alcohol–potassium *tert*-butoxide solution.<sup>1c</sup> The rate constants were obtained from the slopes of first-order plots up to 30–50% conversion and are statistically corrected for reactable hydrogens. In addition, they have all been compared to 1-butene as the standard and are placed in order of descending rates. Where available,  $\Delta E_{\text{act}}$ ,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are listed. The 2-isomer predominates over the 1-isomer at equilibrium except in the case of 2,4,4-trimethyl-1-pentene where there is about 85% of the terminal olefin at equilibrium at 55°. Further reaction leading to other internal isomers are found when no structural limitations are present. However, these isomers are usually formed at a slow rate and do not complicate the rate studies.

Four basic olefin structures have been classified in the manner shown in Table II. Class I and II compounds are treated essentially as 3-substituted-1-propene and 3-substituted-2-methyl-1-propene derivatives, while class III and IV are 3-substituted-1-butene and 2-substituted-1-butene derivatives. The rates are listed relative to a methyl substituent in each class.






It was found that structural variation in the class I and II olefins gives rise to definite trends in reaction rates. Thus, as the substituents are varied from methyl to *tert*-butyl, the rate progressively decreases. The methyl-substituted compounds isomerize about 120–150 times faster than the *tert*-butyl substituted materials. Rate enhancements of a much greater magnitude result when electron-withdrawing groups such as phenyl or vinyl are present in series I olefins. Thus, allylbenzene and 1,4-pentadiene isomerize about 10<sup>5</sup> times faster than 1-butene. The effects of the various substituent groups upon the relative rates are therefore: vinyl  $\cong$  phenyl  $\gg$  methyl  $>$  ethyl  $\cong$  propyl  $>$  isopropyl  $>$  *tert*-butyl.

Class III and IV olefins give rise to the same trends within the scope of the substituents studied. Hydrogen substitution leads to a rate increase. In series III the hydrogen substituted material (1-butene) isomerizes 4.13 times faster than the methyl substituted compound 3-methyl-1-butene. The variation of substituent effect upon the rate is: hydrogen  $>$  methyl  $>$  ethyl  $>$  isopropyl.

TABLE I  
 SUMMARY OF RATE DATA

Olefin CH <sub>2</sub> =CR <sub>1</sub> CHR <sub>2</sub> R <sub>3</sub>			Ref.	Rate constant <sup>a</sup> k, sec. <sup>-1</sup> at 55°	k/kbutene	E <sub>a</sub> , kcal./mole	ΔH <sup>‡</sup> , kcal./mole	ΔS <sup>‡</sup> , e.u.
R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>						
H	H	CH=CH <sub>2</sub>	<sup>c</sup>	(3.6 × 10 <sup>-3</sup> ) <sup>b</sup>	(1.4 × 10 <sup>6</sup> ) <sup>b</sup>			
H	H	C <sub>6</sub> H <sub>5</sub>	<sup>c</sup>	(1.6 × 10 <sup>-3</sup> ) <sup>b</sup>	(6.1 × 10 <sup>4</sup> ) <sup>b</sup>			
H	H	CH <sub>3</sub>	<sup>c</sup>	8.4 × 10 <sup>-4</sup>	1.0	17.2	16.6	-22.3
H	H	CH <sub>2</sub> CH <sub>3</sub>	<sup>c</sup>	4.8 × 10 <sup>-4</sup>	0.57			
H	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	<sup>c</sup>	4.7 × 10 <sup>-4</sup>	.56			
H	CH <sub>3</sub>	CH <sub>3</sub>	<sup>c</sup>	2.0 × 10 <sup>-4</sup>	.24			
H	H	CH(CH <sub>3</sub> ) <sub>2</sub>	<sup>c</sup>	1.5 × 10 <sup>-4</sup>	.18	22	21.6	-16.7
CH <sub>3</sub>	H	CH <sub>3</sub>	<sup>c</sup>	1.3 × 10 <sup>-4</sup>	.15			
H	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	<sup>c</sup>	1.1 × 10 <sup>-4</sup>	.13			
CH <sub>2</sub> CH <sub>3</sub>	H	CH <sub>3</sub>	<sup>c</sup>	7.6 × 10 <sup>-5</sup>	.091			
CH <sub>3</sub>	H	CH <sub>2</sub> CH <sub>3</sub>	<sup>c</sup>	6.5 × 10 <sup>-5</sup>	.078			
CH <sub>3</sub>	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	<sup>c</sup>	5.6 × 10 <sup>-5</sup>	.067			
H	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	<sup>c</sup>	3.0 × 10 <sup>-5</sup>	.036			
CH <sub>3</sub>	H	CH(CH <sub>3</sub> ) <sub>2</sub>	<sup>c</sup>	1.6 × 10 <sup>-5</sup>	.019			
CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	<sup>c</sup>	5.9 × 10 <sup>-6</sup>	.011			
H	H	C(CH <sub>3</sub> ) <sub>3</sub>	<sup>c</sup>	6.0 × 10 <sup>-6</sup>	.0072	21.0	20.3	-21.6
CH <sub>3</sub>	H	C(CH <sub>3</sub> ) <sub>3</sub>	<sup>c</sup>	1.1 × 10 <sup>-6</sup>	.0013			

## Miscellaneous olefins

	<sup>d</sup>	2.3 × 10 <sup>-3</sup>	2.7	13.9	13.3	-27.3
	<sup>d</sup>	9.8 × 10 <sup>-4</sup>	1.2	17.9	17.3	-17.0
	<sup>d</sup>	3.7 × 10 <sup>-5</sup>	0.043	17.4	16.8	-25.4
	<sup>d</sup>	3.5 × 10 <sup>-6</sup>	0.0042	20.3	19.7	-18.0
	<sup>d</sup>	2.5 × 10 <sup>-6</sup>	0.0026	27.4	27.1	+ 0.7

<sup>a</sup> These rate constants have been calculated on a per hydrogen basis. Thus in order to obtain absolute rates the rate for the compound in question should be multiplied by the number of reactable hydrogens, e.g., 1 hydrogen for 3-methyl-1-butene and 4 hydrogens for 2-ethyl-1-butene. <sup>b</sup> It was necessary to obtain the isomerization rates of allylbenzene and divinylmethane (1,4-pentadiene) in a dimethyl sulfoxide solution that was 5 M in *tert*-butyl alcohol and 0.1 M in potassium *tert*-butoxide and 0.7 M in olefin at 30°. At these conditions the rate constant per hydrogen for 1-butene is 2.6 × 10<sup>-3</sup> sec.<sup>-1</sup>. <sup>c</sup> This work. <sup>d</sup> Ref. 1d.

 TABLE II  
 OLEFIN CLASS

Class Olefin	I CH <sub>2</sub> =CHCH <sub>2</sub> R	II CH <sub>2</sub> =CCH <sub>2</sub> CH <sub>2</sub> R	III CH <sub>2</sub> =CHCHRCH <sub>3</sub>	IV CH <sub>2</sub> =CRCH <sub>2</sub> CH <sub>3</sub>	
R	kI/k <sup>0</sup> I <sup>a</sup>	R	kIII/k <sup>0</sup> III <sup>d</sup>	R	kIV/k <sup>0</sup> IV <sup>e</sup>
H	...	H	4.13	H	6.5
Me	1	Me	1	Me	1
Et	0.57	Et	0.43	Et	0.58
Pr	.55	Pr	.50	...	...
<i>i</i> -Pr	.17	<i>i</i> -Pr	.12	<i>i</i> -Pr	0.15
<i>t</i> -Bu	.0074	<i>t</i> -Bu	.0085	...	...
Vinyl <sup>b</sup>	20 × 10 <sup>5</sup>	...	...	...	...
Phenyl <sup>b</sup>	9.4 × 10 <sup>5</sup>	...	...	...	...

<sup>a</sup> k<sup>0</sup>I = 8.4 × 10<sup>-4</sup> sec.<sup>-1</sup>. <sup>b</sup> See footnote b, Table I. <sup>c</sup> k<sup>0</sup>II = 2.6 × 10<sup>-4</sup> sec.<sup>-1</sup>. <sup>d</sup> k<sup>0</sup>III = 2.04 × 10<sup>-4</sup> sec.<sup>-1</sup>. <sup>e</sup> k<sup>0</sup>IV = 2.60 × 10<sup>-4</sup> sec.<sup>-1</sup>.

## Discussion

The interrelation of structural factors for acyclic and alicyclic olefins is established by consideration of the linear free energy relationship in Fig. 1. Since the acyclic olefin III and ketone IV fit the same linear plot defined by alicyclic olefins and ketones, factors that control reaction rates for alicyclic olefins are expected similarly to influence reaction rates in acyclic olefins. These findings suggest rate-determining proton removal and outline the structural effects that influence reaction rate.

The rate-determining step in proton migration was established as proton abstraction<sup>2</sup> using deuterium isotope effects. Cram<sup>3</sup> has recently placed a lower limit of 54% of the intramolecular nature of proton migration in optically active (+)-3-phenyl-1-butene. Proton migration in perdeuterio-1-pentene<sup>2</sup> has been shown to proceed almost exclusively in an intramolecular manner. These factors coupled with the high negative entropy of activation (Table I) support a rigid transition state.

These considerations can be expressed in terms of

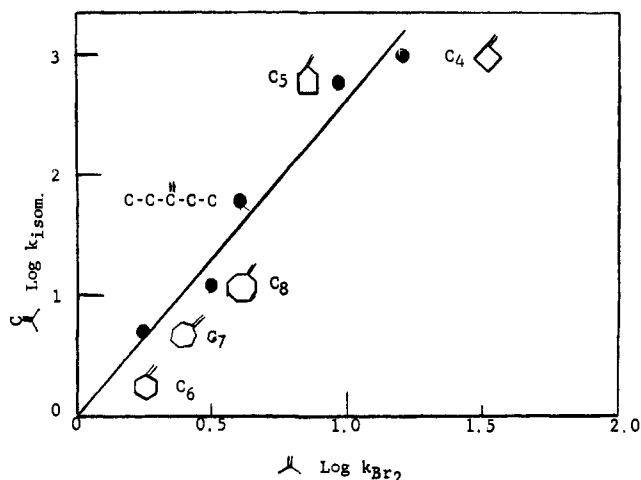
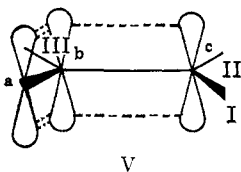


Fig. 1.—Log reaction rate for base-catalyzed olefin isomerization vs. log reaction rate for base-catalyzed ketone bromination.

the idealized intermediate V. Such a species will be characterized by an increase or decrease in energy by virtue of the inductive or electron delocalization



effects of substituents situated in the vicinity of the reaction site. The relative importance of the inductive effect of alkyl substituents situated on carbon atoms a, b and c should be reflected in the reactivity of the carbon-hydrogen bond on carbon a, for example. The migrating proton has not been placed in this picture and this aspect is discussed in the following paper.<sup>2</sup>

Consideration of the steric factors leads to a twofold problem: (i) the inherent bulk steric requirements of the approach of base to the allylic carbon-hydrogen bond and (ii) deformation of the idealized transition state. Thus, it is expected that transition state stabilization is maximized by strong overlap of the p-orbital formed when a proton is removed from carbon atom (c) with the  $\pi$ -orbital between carbon atoms b and a. These three carbon atoms, therefore, tend to be coplanar and, indeed, bonds I, II and III must necessarily also tend toward coplanarity with the a-b-c plane for maximum  $\rho$ - $\pi$ -overlap. It may be postulated that any factor forcing bonds I, II and III out of the a-b-c plane will tend to reduce transition state stability. This deviation from coplanarity will lower the C-H bond reactivity on atom c and result in a lower reaction rate.

For alkyl substitution in the four classes of olefins studied it was found that effects of a given substituent upon the relative rate in each class are similar (Table II). For example, introduction of an ethyl group decreases rates by a factor of 1.7–2.2 relative to methyl. Indeed, the logarithms of the rates for the ethyl-substituted compounds relative to methyl, in each series, are the same within the experimental error ( $-0.23 \pm 0.04$ ). These considerations may be conveniently expressed by

$$\log \frac{k^a \text{I}}{k^0 \text{I}} = \log \frac{k^a \text{II}}{k^0 \text{II}} = \log \frac{k^a \text{III}}{k^0 \text{III}} = \log \frac{k^a \text{IV}}{k^0 \text{IV}} = \left( \log \frac{k^a}{k^0} \right)_{\text{av}} \quad (1)$$

where

$k^a \text{I}$ ,  $k^a \text{II}$ , etc., are the rate constants for substituent a in olefin series I, II, etc.

$k^0 \text{I}$ ,  $k^0 \text{II}$ , etc., are the rate constants for methyl-substituted compounds in series I, II, etc.

$(\log k^a/k^0)_{\text{av}} = \text{av. of series I-IV.}$

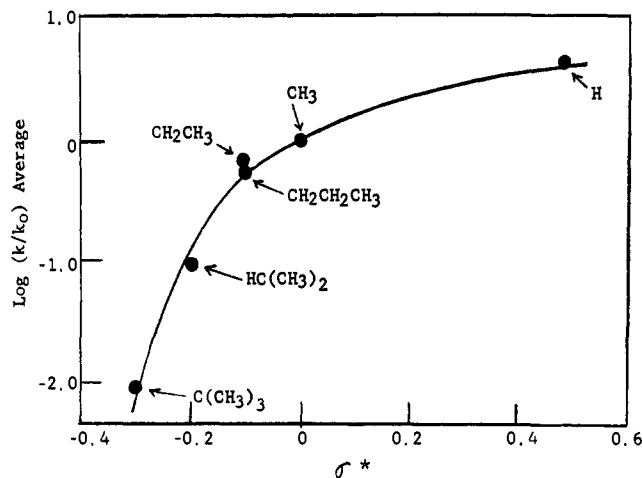


Fig. 2.—Log of average relative rates vs. Taft's  $\sigma^*$  constants.

The average values of  $\log k/k^0$  along with the  $\sigma^*$  values compiled by Taft are listed in Table III. This treatment facilitates a discussion of the substituent effects in terms of a Hammett<sup>4</sup>-Taft<sup>5</sup> type treatment.

TABLE III  
VALUES OF  $\log k/k^0$

R	Values of $\log k/k^0$ <sup>a</sup>	$\sigma^*$ <sup>b</sup>
H	+0.80	+0.490
CH <sub>3</sub>	.00	-.000
CH <sub>2</sub> CH <sub>3</sub>	-.23	-.100
CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	-.24	-.115
HC(CH <sub>3</sub> ) <sub>2</sub>	-.85	-.190
C(CH <sub>3</sub> ) <sub>3</sub>	-2.05	-.300

<sup>a</sup> Average of series I-IV. <sup>b</sup> Reference 5.

The  $\log k/k^0$  values listed in Table III are a function of both steric and inductive factors, and it would be desirable to determine to what relative extent these factors influence allylic carbon-hydrogen reactivity. In order to estimate the steric and inductive effects the  $\log k/k^0$  values of Table III were plotted vs. Taft's  $\sigma^*$ -values (Fig. 2).

The resulting plot yields a curve with a positive slope. Since the values for  $\sigma^*$  represent the polar contributions of the alkyl groups, the observed deviations indicate that other factors are important. Furthermore, the magnitude of the deviations increases as the bulk of the substituent increases. This is evidence that anionic proton migration is apparently affected by both steric and inductive effects. Such steric effects are most probably due to the factors that were previously outlined.

A quantitative observation can be made concerning the relative importance of a decrease in reactivity brought about by the electron donating effect vs. that decrease due to inability to reach the ideal planar transition state V. This analysis is carried out in Table IV.

Replacing a secondary vinyl hydrogen in 1-butene by a methyl group decreases the rate by a factor of 3.2. This probably largely represents the rate decrease brought about by the inductive effect of a methyl group in the center of an allylic anionic system. In a similar fashion replacing an allylic hydrogen by a methyl group decreases the rate by a slightly larger amount (4.2). In both cases this falls in line with the order of carbanion stabilities being primary > secondary > tertiary. Assuming that the systems are

(4) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII.

(5) R. W. Taft, "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13.

TABLE IV  
ISOMERIZATION OF  $\alpha$ - AND  $\beta$ -METHYL SUBSTITUTED BUTENES

Olefin	$k^1$ , rel. to $\text{CH}_2=\text{CHCH}_2\text{CH}_3$	Calcd. <sup>a</sup>
	1	...
	0.31	...
	.24	...
	.0071	0.074

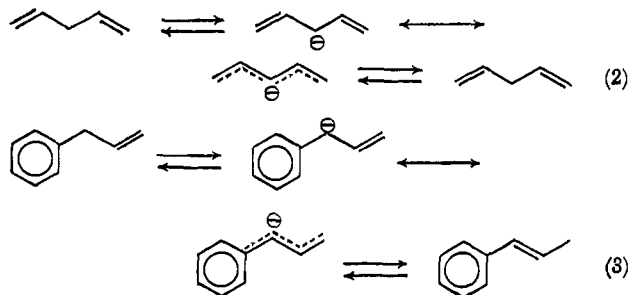
<sup>a</sup> Calculated assuming 2- and 3-methyl effects are additive, e.g.,  $k = (k^1 \text{ 2-methyl}) (k^1 \text{ 3-methyl})$

sterically similar, so that bulk of an approaching base would not affect relative rates, then the rate of proton migration in 2,3-dimethyl-1-butene relative to 1-butene would be calculated as 0.074.

The observed relative rate is one-tenth of this calculated value and this difference is well outside the experimental error. These results indicate that there is an added factor above an inductive effect that is operating to decrease the reactivity of the allylic C-H bond in 2,3-dimethyl-1-butene.

It seems most reasonable to ascribe this reactivity decrease to a marked reluctance of the tetramethylethylene system to assume the coplanar conformation necessary to maximize  $\rho$ - $\pi$  bond overlap.

In addition to the inductive and stereoelectronic control of rate, there is also the possibility of extensive charge delocalization. The two systems studied in which such delocalization is possible are 1,4-pentadiene and allylbenzene. In both systems, anionic activation of a methylene hydrogen leads to extensive  $\rho$ - $\pi$  orbital overlap. In the case of 1,4-pentadiene the negative



charge is delocalized over the 5-carbon divinylmethyl system (eq. 2) and in allylbenzene the charge is delocalized over the 9-carbon phenylvinylmethyl system (eq. 3). Calculations of the resulting delocalization energies ( $E_r$ ) are shown in Table V along with a calculated value for butene (considered as the simple allyl anion).

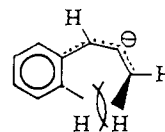
Table V offers a striking example of resonance interaction in an anionic system. Thus, proton migration rates in systems undergoing electron delocalization are over one million times faster than rates for the simple olefin 1-butene. Butene-1 is able to undergo rehybridization over only a 3-carbon system and these results clearly establish the importance of charge delocalization in the reaction of hydrocarbon anions. In addition, it is interesting to note that simple HMO-LCAO calculations correlate well with relative isomerization rates. Indeed, a plot of the logarithm of relative rates *vs.*  $\Delta E_r$  is linear; however, more than the three observed points are needed in order to confirm such a relationship. Steric effects, for example, could be important in certain cases. Thus, the slightly decreased rate found experimentally for the phenyl-substituted olefin may be attributed in part to the inability of the phenyl group

TABLE V  
TOTAL  $\pi$ -ELECTRON ENERGIES

Without $\rho$ - $\pi$ overlap	With $\rho$ - $\pi$ overlap	Delocalization $E_r$ energies <sup>a,b</sup>	$k^1$ /butene
 $E_\pi = 4\alpha + 2\beta$	 $E = 4\alpha + 2\sqrt{2}\beta$	0.82 $\beta$	1
 $E_\pi = 6\alpha + 4\beta$	 $E = 6\alpha + 5.46\beta$	1.46 $\beta$	$20 \times 10^5$
 $10\alpha + 10\beta$	 $10\alpha + 11.38\beta$	1.38 $\beta$	$9.4 \times 10^5$

<sup>a</sup> Column 2 - column 1. <sup>b</sup> Delocalization energies were calculated from a simple HMO-LCAO treatment of the anionic species. In the case of allylbenzene the secular equations were solved on the IBM 7090 computer to obtain the  $\pi$ -electron energy levels.

to achieve complete coplanarity because of interference between *ortho* and vinyl hydrogens.



Molecular models show that the extent of this interference is practically non-existent when a vinyl group is put in place of the phenyl.

It is of some importance to compare the ease of forming anions from cyclic and acyclic olefins. In Table VI rates for selective alicyclic olefins relative to a similarly substituted acyclic olefin are listed.

TABLE VI  
RELATIVE RATES OF ISOMERIZATION OF CYCLIC AND ACYCLIC OLEFINS

Structure	$k$ , sec. <sup>-1</sup> $\times 10^5$	$k$ , rel.
	2300	30.7
	970	12.9
	75	1.0
	2.2	0.029

It is evident that methylenecyclobutane and methylenecyclopentane are both more reactive than the acyclic olefin, 2-ethyl-1-butene. The cyclic olefin, methylenecyclohexane, is however about  $1/30$  as reactive as the acyclic olefin. The rate acceleration effect of the four- and five-membered rings strongly supports the previously discussed concepts of stereoelectronic control. The rate-retarding effect of the six-membered ring probably results from the introduction of non-bonded interaction and angle strain in achieving structure V. Such factors would destabilize the transition state.<sup>1d</sup>

### Experimental

The experimental procedures used were similar in all respects to those previously reported.<sup>1</sup> Detailed experimental procedures have been given for the cyclic olefins. The acyclic olefins were all API standard samples. In all cases API samples of the expected products were obtained and used to calibrate gas chromatographic equipment. The column used for the acyclic

olefins is a 10-ft. squalene on acid treated Chromosorb (42/60 mesh). A 10-ft. column of 1/1 in. o.d. stainless steel was used at 40° with a helium flow rate of 60 cc./min. and a chart speed of 15 in./hr. The average precision of the rate constant for the 25 olefins reported here is  $\pm 5\%$  of the absolute number value. Bromination of diethyl ketone was carried out as outlined in reference 1d. The pseudo-first-order rate constant under the conditions noted is  $1.33 \times 10^{-3} \pm 0.13 \text{ sec.}^{-1}$ .

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## Anionic Activation of C–H Bonds in Olefins. VI. Intramolecular Nature and Kinetic Isotope Effect of Base-Catalyzed Olefin Isomerization<sup>1</sup>

By S. BANK, C. A. ROWE, JR., AND A. SCHRIESHEIM

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The relative rates of double bond migration and of deuterium exchange of perdeuterio-1-pentene with unlabeled 2-methyl-1-pentene and solvent have been determined at 55° in the system potassium *tert*-butoxide-dimethyl sulfoxide. It was found that isomerization is 16 times faster than exchange. The base-catalyzed prototropic migration is thus shown to be intramolecular. The relative rates of isomerization, activation enthalpies and entropies of 1-pentene and perdeuterio-1-pentene were obtained. These values are compared with the values calculated for a primary isotope effect. The good agreement indicates that the carbon to hydrogen bond cleavage is largely complete in the transition state. These results are interpreted on the basis of a tightly bound ion pair.

Anionic reactions of relatively weak organic acids ( $pK_a$  10–20) are well known. Recently, the anionic protropic shifts of still weaker acids, *i.e.*, olefins, have been observed in homogeneous media under mild conditions.<sup>2</sup> The base-catalyzed proton migration of simple olefins is particularly well suited to serve as a model for carbanions of very weak acids. Indeed, the ready availability of a wide variety of olefin structures and the lack of complicating functional groups greatly facilitate mechanistic studies. It is also anticipated that knowledge obtained with such simple models could be widely applied to a broad study of anionic intermediates.

Several recent publications in this area have discussed the kinetics and the effect of solvent and olefin structure upon the rate of isomerization.<sup>2,3</sup> It has been shown with alkylidene cycloalkanes that activation of the allylic hydrogen is rate controlling. A linear relationship between the log of the rate of isomerization and the log of the rate of bromination has also been found with cyclic and acyclic olefins and structurally similar ketones.<sup>2b,c</sup> There are several questions that remain unanswered; namely, does the reaction involve ionic or partially ionic species; what is the degree of freedom of the species; is the reaction intramolecular?<sup>2,3</sup>

An examination of the rates of isomerization and deuterium exchange between a protium substituted olefin and a deuterium substituted olefin could provide meaningful answers to these questions. The extent of carbon-hydrogen bond cleavage in the transition state, as determined by the ratio  $k_H/k_D$ , bears directly on the question of ionic character. The isomerization of the labeled olefin in the presence of an unlabeled olefin is expected to provide information concerning the question posed in preceding papers concerning the intra- or intermolecular nature of the prototropic shift. Preliminary results of this work have been disclosed<sup>1</sup> and a similar study of exchange *vs.* isomerization has been investigated independently by Cram.<sup>4</sup>

(1) Presented by A. Schriesheim in a preliminary communication of the 1962 Gordon Research Conference on Catalysis, Colby Junior College, New London, N. H.

(2) A. Schriesheim, J. E. Hofmann and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, **83**, 3731 (1961).

(3) (a) A. Schriesheim and C. A. Rowe, Jr., *ibid.*, **84**, 3160 (1962); (b) A. Schriesheim, R. J. Muller and C. A. Rowe, Jr., *ibid.*, **84**, 3164 (1962);

(c) A. Schriesheim, C. A. Rowe, Jr., and L. Naslund, *ibid.*, **85**, 2111 (1963).

(4) D. J. Cram and R. T. Uyeda, *ibid.*, **84**, 4358 (1962).

## Results

The rates of isomerization of 1-pentene (Ia) and perdeuterio-1-pentene (Ib) were studied as a function of temperature. These rate measurements were carried out in dimethyl sulfoxide-potassium *tert*-butoxide solutions. Premixed solutions of each pentene olefin and equimolar quantities of 2-methyl-1-pentene were injected at time zero. Since it has been shown that the rate of isomerization of any olefin is independent of added olefin, the inclusion of 2-methyl-1-pentene serves as a convenient internal standard. The reaction is first order in olefin and, at these base concentrations, ( $>0.2 M$ ) is zero order in base.<sup>2</sup> The disappearance of  $\alpha$ -olefin was followed to greater than 75% reaction and no deviations from linearity were found in the first-order rate plots. The composition of a thermodynamic mixture of the pentene olefins at this temperature was determined to be 60.2% *trans*-2-pentene, 36.9% *cis*-2-pentene and 3.1% 1-pentene. The pertinent rate constants as well as the values for the enthalpies are summarized in Tables I and II.

TABLE I  
RATES OF ISOMERIZATION OF 1-PENTENE AND PERDEUTERIO-1-PENTENE AT 55.0°

Olefin <sup>a</sup>	Rate constant <sup>b</sup> $\times 10^4, \text{ sec.}^{-1}$	$k_H/k_D$
1-Pentene	$9.54 \pm 0.10$	
2-Methyl-1-pentene	$1.22 \pm .08$	4.4
Perdeuterio-1-pentene	$2.19 \pm .09$	
2-Methyl-1-pentene	$1.28 \pm .06$	

<sup>a</sup> Olefin concentration 0.36 M. <sup>b</sup> Using potassium *tert*-butoxide (0.4 M) in dimethyl sulfoxide.

TABLE II  
RATE CONSTANTS AND DERIVED DATA FOR THE ISOMERIZATION OF 1-PENTENE AND PERDEUTERIO-1-PENTENE

Compound	Temp., °C.	Rate constant $k_1 \times 10^4,$ sec. <sup>-1</sup>	$\Delta H^\ddagger,$ kcal./mole	$\Delta S^\ddagger,$ e.u.
	44.0	2.66		
	25.0	0.70		
Perdeuterio-1-pentene	70.0	7.15	$17.5 \pm 0.4$	$-22.2 \pm 1.2$
	55.0	2.19		
	40.0	0.56		