Procedure A was used for measuring the slower rates at 20° and 35°; procedure B was used for the faster rates at 20° and 35° and for the rates at higher temperatures. For the latter, it was necessary to employ sodium iodide since, at the concentrations used, potassium iodide precipitated out of solution. Most of the rate data were taken from the first 20–30% of the reactions, although several reactions were followed to 50–70% completion. No significant drifts in rate constants were observed.

The electric timer used was manufactured by the Standard Time Co. and was graduated in hundredths of a minute. The thermostat temperature regulators were set using a total immersion thermometer range 0 to 250°, graduated in 0.5°, calibrated by the U. S. Bureau of Standards.

The sample volumes varied from 5 to 15 ml.; N_{KIO_3} was 0.003082 for all reactions. The other concentrations varied, with N_{KI} or N_{NaI} between 0.015 and 0.025 and N_{KBr} between 0.05 and 0.1, accurate for 5 decimals.

The second-order rate constants were obtained from the equation $K = 1/t(a-b) \times \ln[b(a-x)/a(b-x)]$ which, with the appropriate substitutions, gives $k = 2.303/t(M-1) \times \log [M-Z/M[1-Z)]$, where Z = fraction of inorganic iodide consumed at time t, M = ratio of organic halide to inorganic iodide. A plot of *kt versus* time gave straight lines which passed through the origin and whose slopes were the velocity constants. The rates reported are the average values determined from not less than four separate runs.

Since the concentrations of the reagents were all based on a solvent temperature of 20°, corrections had to be made for the thermal expansion of acetone. The true value of k will be obtained by multiplying the calculated value by the factor obtained by dividing the volume of acetone at $t°$ by the volume of acetone at 20°. This factor was measured in a capillary tube by meniscus difference.

The activation energies were calculated from the equation $E_a = 2.303 T_2 T_1/(T_2 - T_1) \times \log k_2/k_1$ from which the activation entropies were obtained according to the expression $S^* = R \ln k_1 + E_a/T_1 - R \ln (R_2 + T_2)/2 \times k/(n - R)$, with $T_1 + T_2/2 = T_{av}$. After rearrangement and evaluation of constants, one obtains $S^* = 2.303 \log k_1 - E_a/T_1 - 2.303 R \log (2.084\ T_{av}) - 47.76$. The frequency factors B are given by the expression $\log B = \log k + 0.4342 E_a/RT$.

Reagents. **Potassium iodide and sodium iodide** (Baker analyzed) were recrystallized twice from distilled water, dried for 2 hours at 110°, and cooled in a desiccator.

Potassium iodate (Baker analyzed) was recrystallized twice from distilled water, dried for 2 hours at 140°, and cooled in a desiccator. Commercial **acetone** was purified by the method of Conant and Kirner[17]; although it is known that acetone thus purified still contains some water, the drying procedure was reproducible, as comparable results were obtained with different batches of acetone (see also Hine[9]). Commercially available **alkyl halides** were purified by rectification through a standard Todd column.

The following fluoroalkyl halides were prepared by known procedures: 3,3,3-trifluoro-1-bromopropane,[20] 3,3,4,4,5,5,5-heptafluoro-1-bromopentane,[21] 2,2,2-trifluoro-1-bromoethane[20] and 2,2,3,3,4,4,4-heptafluoro-1-bromobutane.[22]

***trans*-4,4,4-Trifluorocrotyl Chloride.**—A mixture of 4,4,4-trifluoro-2-butene-1-ol, (36 g., 0.29 mole) and tosyl chloride (60 g., 0.32 mole) was cooled to 0° in an ice-bath, and dry pyridine (45 g., 0.57 mole) was added dropwise with stirring. After continued stirring for 5 hours at 0°, the mixture was poured onto crushed ice and 30 g. of concentrated hydrochloric acid. The hydrolysis mixture was extracted 7 times with ether (emulsion), the ether extracts were dried over magnesium sulfate and the ether removed by distillation. Vacuum distillation of the residue gave a fraction boiling at 25–35° (39 mm.). Redistillation at atmospheric pressure gave 12 g. (29%) of *trans*-4,4,4-trifluorocrotyl chloride, b.p. 81–81.5°; n^{20}_D 1.3638,[23] d^{20}_4 1.2720.

Anal. Calcd. for $C_4H_4F_3Cl$: C, 33.25; H, 2.79; Cl, 24.54; M_D, 25.11. Found: C, 33.55; H, 2.96; Cl, 24.28; M_D, 25.22.

The product was shown to be isomerically pure by vapor phase chromatography; *trans* configuration was assigned on the basis of the infrared spectrum, with strong absorptions at 5.88 μ (1700 cm.$^{-1}$) and at 10.27 μ (974 cm.$^{-1}$).

Acknowledgment.—Financial support by the Hooker Chemical Corporation is gratefully acknowledged.

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[20] R. N. Haszeldine, *J. Chem. Soc.*, 3372 (1953).

[21] O. R. Pierce, E. T. McBee and R. E. Cline, *J. Am. Chem. Soc.*, **75**, 5618 (1953).

[22] E. T. McBee, D. H. Campbell and C. W. Roberts, *ibid.*, **77**, 3149 (1955).

[23] J. A. Pegolotti and W. G. Young, *ibid.*, **83**, 3256 (1961), report b.p. 82.5–83°, n^{25}_D 1.3610.

[Contribution from Esso Research and Engineering Co., Linden, N. J.]

Anionic Activation of C–H Bonds in Olefins. III. Solvent Effect on the Isomerization of 2-Methyl-1-pentene

By A. Schriesheim and C. A. Rowe, Jr.

Received January 9, 1962

The isomerization of 2-methyl-1-pentene was studied in a homogeneous medium consisting of potassium *tert*-butoxide in dimethyl sulfoxide. It was found that the use of dimethyl sulfoxide allowed the double bond isomerization to take place with ease and high selectivity at moderate temperatures. The reaction is first order in olefin and of varying order in base. Activation parameters are E_a = 22 kcal./mole, $\Delta H^{\ddagger}$ = 21.6 kcal./mole and $\Delta S^{\ddagger}$ = −16.7 e.u. It was also determined that 2-methyl-1-pentene and 2-methyl-2-pentene rapidly interconvert, but that the 4-methyl-1-pentene isomers are only formed at very long contact times. This is interpreted on the basis of different stabilities of the anionic intermediates.

A recent communication reported that dimethyl sulfoxide was an effective medium for the potassium *tert*-butoxide catalyzed isomerization of olefins.[1] This reaction technique is of some importance since it represents a tool for activating weakly acidic C–H bonds in a variety of molecules. As an example, Price and Snyder[2] have recently reported the use of the same system for the rearrangement of allyl ethers, and Cram, *et al.*, have speculated on the use of similar systems for a variety of base-catalyzed reactions.[3]

Anionic activation of C–H bonds in olefins is a relatively unexplored area. The reason for the lack of information in this area has been due to the use of strong base systems that are relatively difficult to handle and reproduce.[4] Olefin isomerization has been accomplished with sodium-organosodium catalysts prepared *in situ*[5] and alkyl-sodium com-

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

[2] C. C. Price and W. H. Snyder, *ibid.*, **83**, 1773 (1961).

[3] D. J. Cram, B. Rickborn, C. A. Kingsbury and P. Haberfield, *ibid.*, **83**, 3678 (1961).

[4] For a literature review, see: H. Pines and L. A. Schaap in Volume XII of "Advances in Catalysis," Academic Press Inc., New York, N. Y., 1960.

[5] H. Pines, J. A. Vesely and V. N. Ipatieff, *J. Am. Chem. Soc.*, **77**, 347 (1955); H. Pines and H. E. Eschinazi, *ibid.*, **78**, 6314, 7178, 6950 (1956).

pounds at their decomposition temperatures.[6] These systems are heterogeneous and require elevated temperatures. A more active heterogeneous system is one extensively used by Pines and co-workers composed of a high surface alkali metal usually supported on alumina.[4,6]

Homogeneous catalysts include lithium in ethylene diamine[7] and potassium amide in liquid ammonia.[8] These systems have not been investigated in any detail.

The reaction conditions discussed in this paper have the advantage of being experimentally simple and of being homogeneous in olefin and base, so that reaction kinetics and energetics may be determined. This paper is concerned with preliminary work on the nature of the catalytic system and the following paper discusses the rate-determining step.[9]

Results

The disappearance of 2-methyl-1-pentene in the base–solvent system, potassium *tert*-butoxide-dimethyl sulfoxide, obeys good first-order kinetics over the temperature range 40–75° (Fig. 1). The concentrations of olefin and base were 0.734 and 0.70 molar, respectively. No noticeable deviation from linearity is noted up to 70% reaction. A plot of the log *k* *vs.* $1/T$ is linear. The activation energy and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are shown in Table I along with the rate constants at 40, 55 and 75°.

TABLE I

ISOMERIZATION OF 2-METHYL-1-PENTENE

2-Methyl-1-pentene in 0.70 *M* KO*t*Bu/DMSO[a]				
Temp., °C.	*k*, sec.$^{-1}$ × 10^4	Ea, kcal./mole	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, e.u.
40	0.21			
55	1.2	22.0	21.4	−16.7
75	8.3			

[a] Dimethyl sulfoxide.

Stability of the potassium *tert*-butoxide–dimethyl sulfoxide mixtures appears to be good. Table II shows the results of isomerization experiments in which the olefin was injected into base–solvent systems that had been stored in the dry-box for varying lengths of time. Over a period of 280 hours the individual rates of isomerization were reproducible to within ±10%.

TABLE II

STABILITY OF BASE–SOLVENT SYSTEM

	DMSO[b] solvent, 0.734 *M* 2-methyl-1-pentene, 0.70 *M* KO*t*Bu					
Storage time, hr.[a]	0.5	1	10	20	100	280
k, sec.$^{-1}$ × 10^4	1.0	1.1	0.9	1.0	1.2	0.8

[a] Storage of base–solvent in dry-box for the indicated number of hours before addition of olefins. [b] Dimethyl sulfoxide.

At the end of 80 hours over the temperature range of 40° through 60° there was no noticeable loss of olefin to side products such as polymer although darkening of the solution occurred. Such color formation might be due to slight decomposition of solvent through an unknown side reaction.

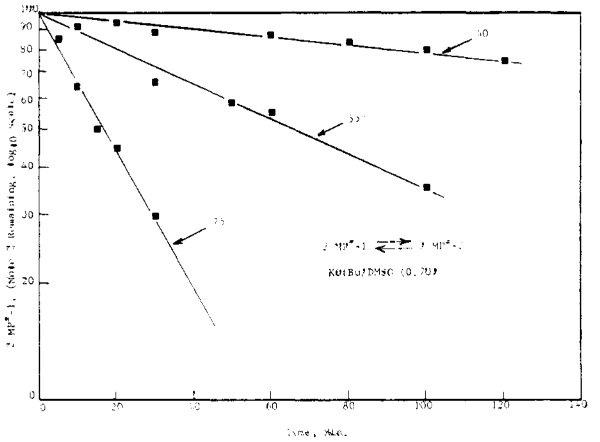

Fig. 1.—Effect of temperature on the rate of isomerization of 2-methyl-1-pentene.

The variation in rate as a function of base and olefin concentration was also studied. The limit of olefin solubility, while not rigorously determined, is of the order of 15 vol. %. Base solubility is rather difficult to obtain. At high base concentrations the entire solution becomes viscous and actually seems to form a gel whose fluidity is a marked function of temperature. When the amount of olefin is increased to the point where the solution becomes heterogeneous and two phases are present—base/solvent/olefin lower phase and olefin upper phase—the reaction is still first order in olefin. Sampling of both phases gave equal reaction rate with good stirring.

A plot of the log of the first-order rate constant at constant olefin concentration *vs.* the log of base molarity is shown in Fig. 2. At low base concentrations, 0.05 to 0.2 molar, the reaction is 1.92 order in base; however, above this point the reaction order changes and from 0.25 to 1.5 molar the rate is independent of base concentration. Attempts were made to obtain kinetics below 0.05 molar base; however, the results at these low base concentrations were not reproducible, possibly because of traces of moisture.

The isomerization of 2-methyl-1-pentene gives rise to 2-methyl-2-pentene initially. After a relatively long time (750 hr.) 4-methyl-1-pentene and *cis*- and *trans*-4-methyl-2-pentene appear (Fig. 3). Isomerization of 2-methyl-2-pentene produces 2-methyl-1-pentene initially and, again, only after a relatively long reaction time do 4-methyl-1-pentene and *cis*- and *trans*-4-methyl-2-pentene appear. A series of experiments was then performed in which solutions containing all five methylpentenes in their approximate equilibrium concentrations were contacted with base–solvent at 55°. Analyses were periodically obtained until no further change in composition occurred (459 hr.). The equilibrium olefin concentrations found are shown in Table III along with the calculated values. In addition, a comparison was made between the free energy changes for isomerization using 2-methyl-2-pentene as the reference isomer (Table IV). This is a standard technique for comparing

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(6) H. Pines and W. O. Haag, *J. Org. Chem.*, **23**, 328 (1958).

(7) L. Reggel, S. Friedman and I. Wender, *ibid.*, **23**, 1136 (1958).

(8) A. I. Shatenstein, L. N. Vasil'eva, N. M. Dykhno and E. A. Izrailevick, *Doklady Akad. Nauk, SSSR*, **85**, 381 (1952); *C. A.*, **46**, 9954d (1952).

(9) A. Schriesheim, R. J. Muller and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, **84**, 3164 (1962).

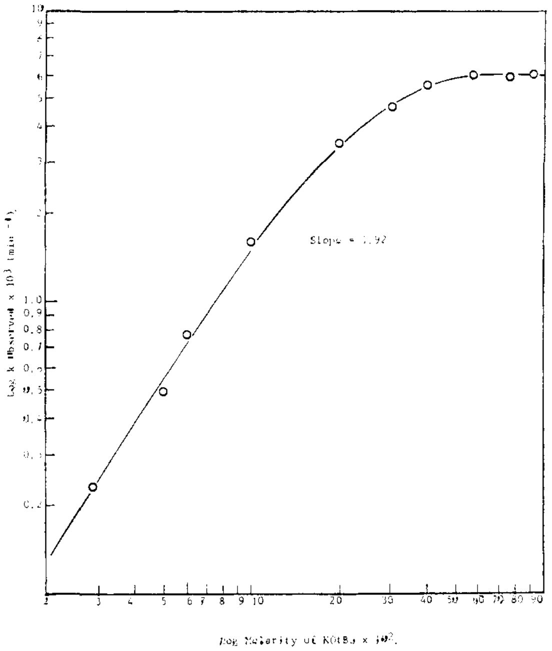

Fig. 2.—Plot of the log of the base concentration *vs.* the log of the rate of 2-methyl-1-pentene isomerization at 55°.

experimental isomerization equilibrium values with calculated ones.[10] The method of analysis used gives a limit of confidence of ±0.5 kcal./mole. Thus, there is excellent correspondence between the observed and calculated values with the major discrepancy being only 0.64 kcal./mole.

TABLE III

EQUILIBRIUM ISOMER COMPOSITION AT 55°

Pentene	Mol. % Obsd.	Mol. % Calcd.[a]
2-Methyl-2-	80.0	80.7
2-Methyl-1-	11.3	11.0
4-Methyl-1-	0.3	1.0
trans-4-Methyl-2-	7.2	5.5
cis-4-Methyl-2-	1.2	1.8

[a] "The Science of Petroleum," Vol. V., Part 1, Oxford University Press, New York, N. Y., 1950.

TABLE IV

ISOMER EQUILIBRIUM THERMODYNAMICS

Pentene	ΔF, kcal./mole at 55° Obsd.	Calcd.[a]	Diff[b]
2-Methyl-2-	0	0	0
2-Methyl-1-	1.28	1.31	−0.03
4-Methyl-1-	3.66	2.92	+ .64
trans-4-Methyl-2-	1.58	1.76	− .18
cis-4-Methyl-2-	2.76	2.50	+ .26

[a] Calculated from the data of column 3, Table III. [b] Difference is the observed minus the calculated value in kcal./mole.

The homogeneity of the reaction was also investigated. Since slight traces of impurities (K_2CO_3) in the potassium *tert*-butoxide were insoluble in the dimethyl sulfoxide solution, Tyndall beam experiments were not possible. However, with experiments that were conducted at various stirring rates at olefin concentrations that produced only one phase, no observable trend in rates was noted. Indeed, solutions that were not stirred, other than an initial shake of the vial, had the same rate, within experimental error, as solutions stirred at 2700 r.p.m. It is concluded, therefore, that under these conditions the reaction is homogeneous in olefin, base and solvent.

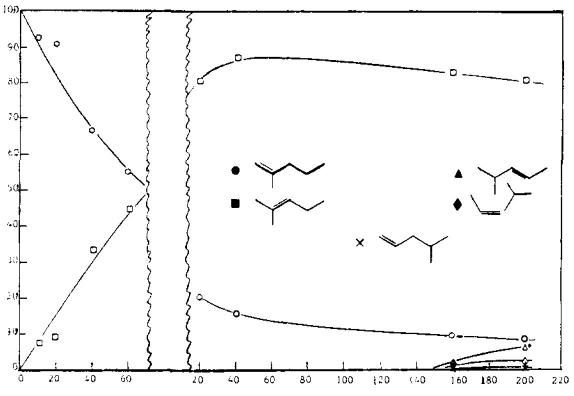

Fig. 3.—Isomerization of 2-methyl-1-pentene; isomer composition *vs.* time at 55°.

TABLE V

HOMOGENEITY OF SOLUTION

DMSO[a] solvent, 0.734 *M* 2-methyl-1-pentene, 0.70 *M* KOBu-*t*

Stirring rate, r.p.m.	0	100	500	1000	2000	2700
k, sec.$^{-1}$ × 10^4	0.9	1.0	1.1	0.8	1.0	1.1

[a] Dimethyl sulfoxide.

The effects of *tert*-butyl alcohol, a hydroxylic species, on the rate of isomerization of the olefin in dimethyl sulfoxide containing from 0.5 to 10 vol. % of the hydroxylic species were determined. Isomerizations were carried out in the usual manner. The results depicted in Table VI show no obvious correlation between the dielectric constant of the medium employed and rate of isomerization.

TABLE VI

ISOMERIZATION OF 2-METHYL-1-PENTENE AS EFFECTED BY ADDITION OF *tert*-BUTYL ALCOHOL

t-BuOH added, vol. %	*t*-BuOH / KO*t*Bu mol. ratio	ϵ^b	k,[a] sec.$^{-1}$ × 10^5
0	0.0	45.0	8.7
0.5	.05	45.0	3.6
1	.10	44.5	2.9
3	.25	44.5	2.6
6	.50	44.0	1.6
12	.90	42.0	0.2

[a] First-order rate constant. Total volume of solution, olefin concentration (0.734 *M*) and KO-Bu-*t* concentration (0.70 *M*) maintained constant. [b] Sargeant model V oscillometer at 25°, calibrated *vs.* several standard liquids.

Discussion

It may be postulated that the base-catalyzed isomerization of an olefin in the highly basic system used here involves carbanion formation. A reasonable mechanism suggested by others in similar systems[2,4] involves the formation of the carbanion (step 1), allylic resonance of the intermediate

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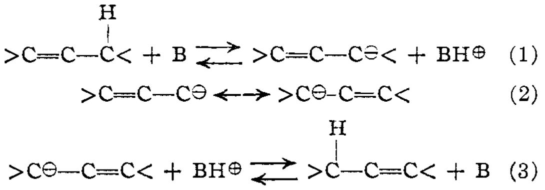
[10] G. M. Kramer and A. Schriesheim, *J. Phys. Chem.*, **64**, 849 (1960).

(step 2) and finally, reformation of the isomerized olefin hydrocarbon (step 3). Many questions arise concerning such a reaction in the present system. These include the question of whether the reaction is strictly a 1–3 intramolecular shift or whether the anion abstracts a proton from another olefin or whether it abstracts a proton from the solvent; the question of the rate-determining step, *i.e.*, is the acidity of the allylic C–H bond rate controlling or is it the proton reabstraction reaction (step 3); questions also arise concerning the nature of the catalytic system and the degree of freedom of the ionic or partially ionic species.



$$>C{=}C{-}\overset{H}{\overset{|}{C}}< + B \rightleftharpoons >C{=}C{-}C^{\ominus}< + BH^{\oplus} \quad (1)$$

$$>C{=}C{-}C^{\ominus} \longleftrightarrow >C^{\ominus}{-}C{=}C< \quad (2)$$

$$>C^{\ominus}{-}C{=}C< + BH^{\oplus} \rightleftharpoons >\overset{H}{\overset{|}{C}}{-}C{=}C< + B \quad (3)$$

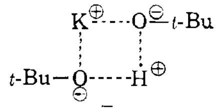
A detailed discussion of the rate-determining step will not be undertaken here since it is the subject of the following paper. We have also reported[1] that the solvent is not "aprotic" and that proton exchange does occur between the olefin and solvent so that no scrambling is noted between a tagged and an untagged olefin. The reaction scheme (steps 1 to 3) indicates that the rate should probably depend on both olefin and base. At base concentrations below about 0.2 molar the rate expression has the form

$$\text{rate} = k(\text{base})^{1.82}(\text{olefin})^{1}$$

However, at higher base concentration the rate becomes independent of base. This rate dependence on base concentration is analogous to that recently found by Cram, *et al.*,[3] while studying the base-catalyzed racemization of (+)-2-methyl-3-phenylpropionitrile in 97% dimethyl sulfoxide–3% methanol mixtures. At base concentrations below 0.06 M the racemization is first order in base, while above 0.06 M the reaction is second order in base (1.94 order) up to about 0.2–0.3 M.

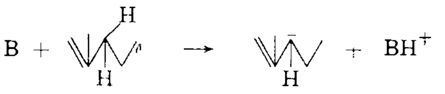
At low base concentrations the base is almost all if not completely ionized. As the concentration of base increases ion pairing occurs and eventually agglomeration takes place. In such highly concentrated basic solutions, a constant supply of monomeric or, perhaps, dimeric base would be available for reaction and further addition of base would not have an observable effect on the rate of isomerization.

The effect of the addition of *tert*-butyl alcohol to dimethyl sulfoxide is interesting in light of the well-known tendency to consider the alkoxide–alcohol mixtures as strong base systems. A marked decrease in rate is observed with increasing concentration of *tert*-butyl alcohol. This situation can be explained as the result of the formation of the species (KOBu-*t*)(*t*-BuOH). Preliminary work on allylbenzene isomerization shows the latter species to be about 10^3–10^4 times less active than the uncomplexed potassium *tert*-butoxide. Such a situation presumably arises because of the formation of complex I which is a weaker base than the non-hydrogen bonded *tert*-butoxide anion. Further support of this view is shown in Table IV where the dielectric constant values for mixtures of alcohol-dimethyl sulfoxide solutions are shown. There is no obvious relationship between isomerization rate and dielectric constant of the alcohol–dimethyl sulfoxide mixtures.



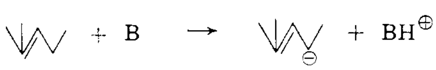
I

The relatively rapid interconversion of 2-methyl-1-pentene and 2-methyl-2-pentene compared to the slow appearance of the 4-methyl-1-pentene isomers can be rationalized in terms of different carbanion stabilities. This explanation is based on the rate-determining step being the ionization of the allylic hydrogen. Such a step will be shown in the following paper to be, indeed, rate controlling.[9] Thus the rate of proton abstraction from 2-methyl-1-pentene (step 4) or 2-methyl-2-pentene (step 5) is probably higher than the rate of proton abstraction to give species II in step 6. Steps 4 and 5 involve the same mesomeric anion III. This anion has two extreme forms, one of which is a primary ion and the other a secondary ion (eq. 7). The mesomeric anion produced in step 6, however, can be considered to have two extreme forms involving secondary and tertiary ions (eq. 8). Because of the methyl groups, the latter situation (eq. 8) is not favored compared to the formation of mesomer III.



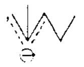
(4)

(5)

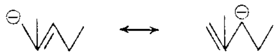


(6)

II



III



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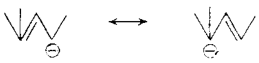


(8)

This would seem to be a rather clear illustration of the lower stability of tertiary carbanions compared to secondary or primary carbanions. This effect is being investigated further.

Acknowledgment.—The authors would like to acknowledge the advice and encouragement provided by Professors W. von E. Doering and H. C. Brown, and the ever present optimism of Mr. D. L. Baeder. They would also like to thank the Esso Research & Engineering Co. for permission to publish this research and Mr. Lars Naslund for much of the experimental work.

Experimental

Potassium *tert*-butoxide was obtained from Mine Safety Appliance Co. This material was received as the sublimed, white powder. Analysis of this powder indicated the presence of up to 1.5% K_2CO_3 as an impurity. Samples that were below this 98.5% purity level were rejected. Dimethyl sulfoxide was dried and distilled over Linde 13X molecular sieves. Infrared, gas chromatographic and mass spectrometric techniques showed the presence of only one compound. The olefins used, 2-methyl-1-pentene, 2-methyl-2-pentene, 4-methyl-1-pentene and *cis*- and *trans*-4-methyl-2-pentene, were all API samples and contained at the most 0.5% impurity. The hydrocarbons were analyzed on a model #154 Perkin–Elmer gas chromatograph equipped with a 21-ft. column containing 3% squalane on firebrick. Operating conditions amenable for complete separations were attained at 25° with 10 p.s.i.g. of helium pressure.

All solutions of potassium *tert*-butoxide in dimethyl sulfoxide were prepared in a nitrogen-blanketed dry-box. Maximum water content was 10 parts per million as detected by a moisture conductivity cell. Solutions were prepared to give a desired molarity and then placed in the appropriate flask or vial fitted with an air-tight rubber cap. The vial was then set in a constant temperature bath (±0.5°). Usually no more than 5–10 cc. of dimethyl sulfoxide was used. Prethermostated olefin was then injected into this base solution by means of a glass syringe after complete temperature equilibration. If a nonstirred vial was used, the olefin–dimethyl sulfoxide base solution was shaken for a few seconds by hand and set back into the constant temperature bath. Samples were obtained by inserting a hypodermic syringe through the self-sealing neoprene diaphragm. These samples were either directly injected into the gas chromatograph or else 0.5-cc. samples were quenched by injection into 5 cc. of ice-water. In the latter case, a small amount of n-pentane (0.2–0.5 cc.) was added to the solution and the mixture shaken. The miscible water–dimethyl sulfoxide layer was frozen out on Dry Ice. A sample of supernatant pentane extract was then analyzed on the gas chromatograph. Analysis by both methods gave similar results. In certain experiments an inert hydrocarbon was added along with the olefin to the solvent–base system as an internal standard to determine whether the olefin was reacting to form materials other than the isomers in question.

Dielectric constants were measured at 25 ± 0.5° using a Sargeant oscillometer, model V.

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

Anionic Activation of C–H Bonds in Olefins. IV. Effect of Ring Size on Rate of Formation of Anions from Alkylidenecycloalkanes and Cycloalkanones

BY A. SCHRIESHEIM, RENÉ J. MULLER AND C. A. ROWE, JR.

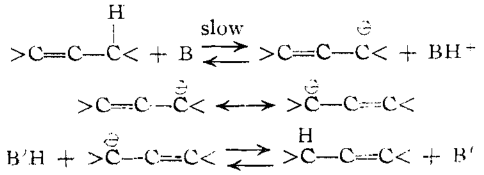
RECEIVED JANUARY 9, 1962

The isomerization of cyclic olefins in which the starting double bond is exocyclic to the ring has been studied. A homogeneous catalyst system, potassium *tert*-butoxide–dimethyl sulfoxide was used and the rate constants, activation energies and entropies were obtained. It was found that the isomerization rates were a function of ring size and the following order of reactivities holds at 55°: C_4-ring, 1070; C_5-ring, 454; C_6-ring, 1; C_7-ring, 5.8; C_8-ring, 17. A linear free-energy relationship was obtained between the isomerization rates and the rates for the base-catalyzed bromination of structurally similar ketones. The results are interpretable on the basis of a rate-determining step involving the removal of a proton followed by p-π-bond rehybridization to form an allylic anionic system. Stereoelectronic factors are postulated to play a key role in establishing such a system.

Since Freund[1] synthesized cyclopropane in 1882, a considerable amount of research effort has been expended on elucidating the chemistry of small-, common-, medium- and large-membered rings.[2] The reactivities of these cyclic compounds exhibit peculiarities which have been accounted for by several theories. For example, in a study of the reactivity of cyclic compounds. Brown introduced the now well-known concept of I-strain (from "internal"). The I-strain theory has been tested by Brown and others and has been somewhat modified.[3-8] Certain aspects have been criticized but, on the whole, I-strain provides a correlation for a vast amount of data. These correlations have been recently reviewed,[9] and Table I summarizes the effects of ring size on reaction rate for a number of mechanistically different reactions.

Several cases are known which do not follow the above predictions,[9] and Roberts[10-12] has presented data showing that electrical effects in small rings may be important.

Recently, strongly basic systems have been developed which are capable of activating C—H bonds in olefins at moderate temperatures.[13a,b,c] The system used in these studies was the base solvent combination potassium *tert*-butoxide–dimethyl sulfoxide. The postulated intermediates are allylic carbanions and the rate-determining step in the double bond isomerization is thought to be the abstraction of an allylic hydrogen by base.



$$>C{=}C{-}\overset{\overset{H}{|}}{C}< + B \underset{}{\overset{\text{slow}}{\rightleftarrows}} >C{=}C{-}\overset{\ominus}{C}< + BH^{+} \quad (1)$$

$$>C{=}C{-}\overset{\ominus}{C}< \longleftrightarrow >\overset{\ominus}{C}{-}C{=}C< \quad (2)$$

$$B'H + >\overset{\ominus}{C}{-}C{=}C< \rightleftarrows >\overset{H}{C}{-}C{=}C< + B' \quad (3)$$

There has not been any work reported on the rates of base-catalyzed movement of the *exo* to the

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(2) Terminology is that of H. C. Brown, R. S. Fletcher and R. B. Johannesen, *J. Am. Chem. Soc.*, **73**, 212 (1951).

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(9) For references, see the extensive review on "Strain and Reactivity in Monocyclic Systems," by Ya. I. Goldfarb and L. I. Belenkii, *Russian Chem. Rev.*, (*Uspekhi Khimii*), **29**, No. 4, pp. 214–235 (1960).

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