after loss of the CH_2OH group and found only in the presence of the NCHO group, must be on the formylated ring.

The chemical effect of the N-formyl group is manifest in two novel variations on the reactions above. (1) Further phosphorus–hydriodic acid reduction of IV gives only V, and no III. The ultraviolet spectrum of V shows it to contain the two isolated pyridone nuclei shown.[8] Since no III is formed, the formyl group is apparently required for reduction of the pyridone ring; otherwise, the central ring is the more readily reduced. (2) Treatment of IV and VII with concentrated nitric acid does not give quinones analogous to VIII, but instead gives dinitro compounds.

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(8) H. Specker and H. Gawrosch, *Ber.*, **75**, 1338 (1942).

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PRODUCTION, STABILIZATION, AND REACTIONS OF SIMPLE HYDROCARBON CARBANIONS. I. ACTIVATION OF C-H BONDS IN HYDROCARBON OLEFINS

Sir:

The production of carbanions from simple hydrocarbons has been the subject of much study.[1] Recently, Price has shown that allyl ethers undergo an anionic isomerization reaction in homogeneous media at mild conditions.[2] We have had a program in this area for some time and these recent results prompt us to communicate our findings concerning the anionic activation of hydrocarbon olefins. We have found that the low temperature, homogeneous, base catalyzed isomerization of hydrocarbon olefins is possible in certain media. In this communique, only the solvent dimethyl sulfoxide will be discussed.

The base used in this research was sublimed potassium *tert*-butoxide. At $55°$, a dimethyl sulfoxide solution 1.0 molar in 2-methylpentene-1 and 1.0 molar in potassium *tert*-butoxide was found to yield 2-methylpentene-2. Starting with either 2-methylpentene-1 or 2 methylpentene-2, no 4-methylpentene-1 or *cis* and *trans* 4-methylpentene-2 was observed after 55 hours at $55°$. Analyses were performed on a 21 ft. gas chromatographic column of 3% squalane on firebrick. This system was sensitive to 0.1% of the olefin isomers. On starting with 2-methylpentene-2, the product distribution remained constant for hours 15 to 55 at 88.1% 2-methylpentene-2 and 11.9% 2-methylpentene-1.

Although both olefins gave rise to the same isomer distribution, it may be that equilibrium in-

(1) H. Pines, "Advances in Catalysis and Related Subjects," Vol. 12. Academic Press, New York, N. Y., 1960.

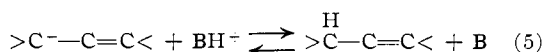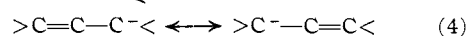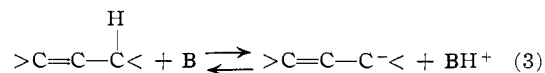(2) C. C. Price and W. H. Snyder. *J. Am. Chem. Soc.*, **83**, 1773 (1961).

volving the 4-methylpentene isomers would be achieved on longer standing. However, these data clearly show that the rate of base-catalyzed isomerization past a tertiary carbon hydrogen bond (Eq. 1) is much slower than that involving primary–secondary bonds (Eq. 2). This falls in line with

$$(1)$$

$$(2)$$
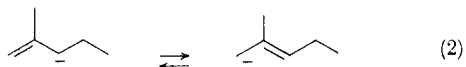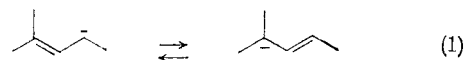
the order of carbanion stability, *vis.*, primary > secondary > tertiary. The rate constant at the 1.0 molar base level was 1.2×10^{-4} sec.$^{-1}$. Small amounts of *tert*-butyl alcohol slow the rate appreciably. A solution that is 1.0 molar in potassium *tert*-butoxide, 1.0 molar in *tert*-butyl alcohol and 1.0 molar in olefin has a rate that is $1/100$ that of the solution not containing any alcohol. This may be interpreted on the basis of complex formation between alcohol and base and the effect is being investigated further.[3] No noticeable conversions were obtained in pure *tert*-butyl alcohol, tetrahydrofuran or 1,2-dimethoxyethane over very long time periods at $55°$.

With olefins that may form *cis* and *trans* isomers, the reaction is kinetically controlled and initially gives rise to more *cis* than *trans* olefin. As an example, butene-1 is 96% selective to *cis*-butene-2 at 80% butene-1 conversion. This stereoselective isomerization reaction was discovered by Pines using sodium on alumina although the degree of stereoselectivity was not as marked.[4] The question of the transition state is important. Both Pines and Price arrive at similar activated complexes although the catalysts are different.[2,4] To shed light on this point, tritium tracing experiments were carried out. Although the structure of the transition state is unknown, we have found that the reactant olefin exchanges protons with the solvent at roughly the same rate at which the isomerization reaction proceeds.

In general, it has been postulated[2,4] that the base catalyzed isomerization reaction proceeds via carbanion formation (step 3), rearrangement of the intermediate (step 4) and finally reformation of the isomerized olefin hydrocarbon[1] (step 5).

$$>C{=}C{-}\overset{H}{\underset{}{C}}< + B \rightleftarrows >C{=}C{-}C^{-}< + BH^{+} \quad (3)$$

$$>C{=}C{-}C^{-}< \longleftrightarrow >C^{-}{-}C{=}C< \quad (4)$$

$$>C^{-}{-}C{=}C< + BH^{+} \rightleftarrows >\overset{H}{\underset{}{C}}{-}C{=}C< + B \quad (5)$$

The question arises as to whether the reaction is strictly intramolecular, a 1–3 shift, or whether the anion abstracts a proton from another olefin or whether it abstracts a proton from the solvent. These three mechanisms can be clearly distinguished by carrying out the isomerization of mixed olefin reagents with one olefin tagged with H^3 in the allylic position. If no H^3 appears in the untagged olefin and the activity of the tagged olefin

(3) D. J. Cram, *et al.*, *ibid.*, **81**, 5740 (1959).

(4) W. O. Haag and H. J. Pines, *ibid.*, **82**, 389 (1960).

(5) R. Wolfgang and R. S. Rowland. *Anal. Chem.*, **30**, 903 (1958).

remains constant, the reaction is clearly intramolecular. If the carbanion intermediate abstracts a proton from another olefin, H^3 will appear in the untagged olefin. Finally, if the intermediate abstracts a proton from the solvent there will be a decrease in the total activity of the tagged olefin.

The present study was carried out by isomerizing a 0.7 molar solution of a 50–50 weight mixture of pentene-1 and hexene-1 in a 0.9 molar solution of sublimed potassium *tert*-butoxide in dimethyl sulfoxide. The pentene reagent contained 0.01 mc./mM. of tritium. Analysis of the pentene as received from The New England Nuclear Corporation showed that it contained about 3% of pentene-2 and that his 3% contained 99% of the tritium. The pentene was tritiated by contacting pentene-1 with sulfuric acid-H^3. Analyses of reactants and products were obtained on a radioassaying gas chromatograph of the type described by Wolfgang.[5] This system can count tritium at essentially 100% efficiency.

It was found that the 1-olefins were converted completely in 24 hours but there was no measurable H^3 in the isomerized hexenes after 312 hours. (If 1% of the initial H^3 were in the hexenes, it would have been detected easily). At the end of this 312 hour period, the pentenes and hexenes were at thermodynamic equilibrium and the H^3 was equally distributed among the three pentene isomers. There was a gradual decrease in the total H^3 content of the pentenes and at the conclusion of the experiment, the activity had fallen to 65% of its initial value. Thus, the conclusion is reached that the intermediate is exchanging protons with the solvent. Analysis of the dimethyl sulfoxide on the radio-assaying gas chromatograph showed that the solvent contained essentially all of the tritium that had been lost from the pentene.
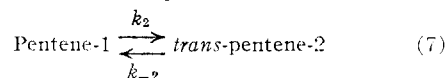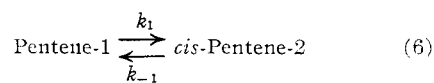
ISOMERIZATION OF LABELED OLEFIN

7.0 cc. of dimethylsulfoxide; 0.7 g. of KOC_4H_9, 0.38 g. of olefin mixture.

Hours	Feed	1	4	24	48	144	312
Composition, wt. %							
Pentene	47.5	8.7	4.3	1.3	1.8	1.3	1.5
Pentene-2-*t*	1.0	4.1	11.3	20.7	28.1	37.6	33.7
Pentene-2-*c*	0.6	40.1	34.6	21.0	18.0	10.9	9.0
Hexene-1	50.9	7.0	3.3	2.5	1.4	0.8	0.9
Hexene-3	...	...	1.2	9.1	10.6	13.2	14.1
Hexene-2-*t*	...	4.3	6.4	16.0	19.5	24.6	29.5
Hexene-2-*c*	...	35.7	38.9	29.3	20.6	11.7	11.3
Rel. sp. act.[a]							
Pentene-1	2.9	27	50	69	76	72	78
Pentene-2-*t*	3300	972	337	147	117	77	70
Hexene-2-*c*	3300	45	66	55	53	66	74
Total activity	100	105	103	89	82	67	64

[a] Defined as the ratio of the radio peak area divided by the chemical peak area.

In order to obtain a more quantitative estimate of the rate of exchange with the solvent, as compared with the rate of isomerization, it is possible to make a simplified kinetic analysis of the reaction. The values for forward rate constants for reactions

(6) and (7) can be obtained at low conversion from

$$\text{Pentene-1} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} cis\text{-Pentene-2} \qquad (6)$$

$$\text{Pentene-1} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} trans\text{-pentene-2} \qquad (7)$$

equations (8), (9) and (10). Since most of the

$$[\text{pentene-1}] = [\text{pentene-1}]_0 e^{-kt} \qquad (8)$$

$[cis\text{-pentene-2}] = [cis\text{-pentene-2}]_0 +$
$\qquad (k_1[\text{pentene-1}]_0/k)(1 - e^{-kt}) \quad (9)$

$[\text{Pentene-2-}t] = [\text{pentene-2-}t]_0 +$
$\qquad (k_2[\text{pentene-1}]_0/k)(1 - e^{-kt}) \quad (10)$

where: $k = k_1 + k_2$

H^3 is in the pentene-2 isomers the reactions of interest are the reverse of (6) and (7), represented by k_{-1} and k_{-2}. These are obtained by dividing the forward rate constants k_1 and k_2 by the appropriate equilibrium constants. Values for the four rate constants are shown in the table.

k_1	4.8×10^{-4} sec.$^{-1}$	$K_{-1} = 7.83$
k_{-1}	6.1×10^{-1} sec.$^{-5}$	
k_2	3.0×10^{-1} sec.$^{-5}$	$K_{-2} = 25.9$
k_{-2}	1.2×10^{-4} sec.$^{-6}$	

A plot of the log of the total activity remaining *vs.* time shows the decay in radioactivity to be first order and to proceed with a rate constant of 1.2 $\times 10^{-6}$ sec.$^{-1}$. Insufficient information about the detailed mechanism is available to apply an isotope effect but it is clear that exchange with the solvent is occurring at roughly the same rate as isomerization.

The foregoing data lead to the postulation of an intimate complex between base, solvent and reactant olefin. Additional work is presently in progress that should shed more light on the nature of this complex.

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UNUSUAL MAGNETIC PROPERTIES OF SOME SIX-COÖRDINATE COBALT(II) COMPLEXES[1]—ELECTRONIC ISOMERS

Sir:

If attention is restricted to octahedral transition element complexes, for metal ions such as Fe(II), Co(II), etc., an extended series of ligands of increasing ligand field strength would be expected to produce spin-free compounds at the low field extremity and spin-paired compounds at the high field extremity of the series. In the vicinity of that interval within which the pairing energy is comparable to the excess stabilization energy of the spin-paired state, the two spin states are expected to coexist.[2] Here a true electronic isomerism

(1) Presented at the 136th National Meeting of the American Chemical Society, Atlantic City, New Jersey, 1959.

(2) L. E. Orgel, *J. Chem. Phys.*, **23**, 1819 (1955); Report to the Xth Solvay Council, Brussels, May, 1956.