p$K_R{}^+$ Determinations.—The dipropyl and tripropyl cations were titrated against a glass electrode, since neither they nor their neutralization products had ultraviolet spectra which could be used for the *pK* determinations. A standard method was devised, and checked against cations whose *pK* previously had been determined spectrophotometrically. To calibrate the method, 66.3 mg. of trianisylcyclopropenyl bromide[3] was added to a mixture of 20 ml. of acetonitrile and 10 ml. of 0.10 *N* HCl. The *p*H was observed on a Beckman model G *p*H meter after the stepwise addition of standardized 0.10 *N* NaOH solution. The forward titration gave an apparent *pK* of 6.54 from the usual plot, and 6.41 by back titration (reptd.[3] *pK* 6.4 in 23% aqueous ethanol by spectrophotometric titration). Similar titration of dianisylphenylcyclopropenyl bromide[3] in this 50% aqueous acetonitrile solution gave an apparent *pK* of 5.16 (rept.[3] 5.2 in 23% aqueous ethanol) and titration of triphenylcyclopropenyl bromide[3] gave *pK* 3.1 (rept.[3] 2.8).

To 20 ml. of acetonitrile containing 10.5 mg. of tripropylcyclopropenyl perchlorate was added 20 ml. of a premixed solution of 10 ml. each of 0.10 *N* NaOH and 0.10 *N* HCl (to reproduce the medium but avoid prolonged exposure of the compound to neutral aqueous solutions). Then eight portions of 0.1 *N* NaOH were added such that the total was equivalent to the cyclopropenyl cation, and the *p*H's were observed after each addition. A classical titration curve was obtained whose midpoint was taken as the *pK*. The solution remained clear during the titration, and the curve was reversible up to the *pK*, although above that point some irreversibility was observed. The *pK* observed is 7.2.

To 7.1 mg. of dipropylcyclopropenyl perchlorate in 20 ml. of acetonitrile was added a mixture of 10 ml. of 0.10 *N* HCl and 9.7 ml. of 0.10 *N* NaOH. Then the NaOH solution was added in increments of 0.1 ml. The initial and final *p*H values over this range were 2.65 and 2.92, while a standard titration in which the cation was omitted went from 2.88 to 7.0. The solution remained clear during the titration. Since at these low concentrations and *p*H's hydrolysis of the cation is appreciable, the titration curve was constructed by plotting base *consumed* by the cation against *p*H, rather than simply base *added*. When the data were plotted in this way, which required correcting the observed titration curve by use of the points of the above standard titration, a titration curve was obtained whose inflection point was taken as the *pK*. In several runs this ranged from 2.65 to 2.70.

The $pK_R{}^+$ of propyldiphenylcyclopropenyl fluoroborate was determined in "23%" aqueous ethanol as described previously for other cations,[3] using a spectrophotometric procedure. A solution of 1.2 mg. of the cation in 5.27 ml. of 95% ethanol was diluted to 10 ml. with 0.2 *N* aqueous HCl, and 1.0 ml. of this solution was diluted to 10 ml. with 20% ethanolic acid or buffers. The ultraviolet spectra were immediately examined in 10-cm. cells, and were constant over the few minutes required for measurement. The absorbancy at 305 mμ, which is characteristic of the cation, was plotted against *p*H, determined with a Beckman model G *p*H meter calibrated against standard buffers, and the resulting titration curve had its inflection point at 3.80.

[CONTRIBUTION OF THE CHEMISTRY DEPARTMENT, TEXAS CHRISTIAN UNIVERSITY, FORT WORTH, TEX.]

Studies of Ionic Elimination Reactions in the *sec*-Butyl System

BY WILLIAM B. SMITH[1] AND WILLIAM H. WATSON, JR.

RECEIVED MARCH 5, 1962

A variety of reactions which presumably proceed *via* the *sec*-butyl cation have been studied with respect to the nature of the butenes produced on elimination. In the cases of the isomerization of 1-butene over either dilute sulfuric acid or phosphoric acid and the reaction of *sec*-butyl bromide with silver nitrate in *t*-butyl alcohol the ratio of *trans*- to *cis*-2-butene was *ca.* 1. Under typical E_2 conditions *sec*-butyl bromide gives a *trans*- to *cis*-2-butene ratio of *ca.* 2.8. In none of the cases studied did the *trans* to *cis* ratio go below 1. The mechanistic implications of these results are considered.

Introduction

Cram[2] has characterized the stereochemistry of the E_1 reaction as being "vastly complicated by the multistage nature of the mechanism and by the difficulties of identifying the geometry and capabilities of the intermediates involved." The implications of this statement are nowhere more evident than in the various studies reported in recent years which purport to explain the distribution and the geometries of products obtained from the *sec*-butyl cation.

Brown and co-workers[3] have studied the acetolysis of 2-butyl tosylate at 118° and have reported a *trans* to *cis* ratio of 2-butenes as being *ca.* 1.1. Lucchesi, *et al.*,[4] have reported the stereospecific isomerization of 1-butene over a silica–alumina catalyst to give ratios of *cis-/trans*-2-butene as high as 6.5 and have proposed a hydrogen-bridged butyl cation to explain their results. Rather similar observations have been made by Pines and Haag[5] for the isomerization of 1-butene over various alumina catalysts and by phosphoric acid where values of *cis-/trans*-2-butene of 1.5 to 4.4 were reported. The dehydration of 2-butanol over the same catalysts has been observed also to lead to higher values for *cis-* than *trans*-2-butene (*cis/trans* = 3.0 at 350°).[6]

The results of Pines[5,6] and of Lucchesi[4] and their respective co-workers are considerably different from the results reported by Brown.[3] Streitwieser and Schaeffer[7] have commented on the elimination of a proton from a *sec*-butyl cation and have concluded that one should expect approximately equivalent amounts of the geometrical 2-butene isomers. In order to clear the anomaly existing in the literature, we have now investigated several systems where *sec*-butyl cations might be reasonably expected. In order to clarify further the role of steric effects in these systems some examples of the E_2 type elimination in the *sec*-butyl system were also studied.

Experimental

Gas analyses were carried out by vapor phase chromatography using a 3.7-m. column of dimethyl sulfolane and ethylene glycol saturated with silver nitrate on Chromosorb P (Johns-Manville) and then a 3.7-m. column of hexadec-

---

[1] Robert A. Welch Visiting Scientist, 1960–1961.

[2] D. J. Cram in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chap. 6.

[3] (a) H. C. Brown and M. Nakagawa, *J. Am. Chem. Soc.*, **77**, 3614 (1955); (b) H. C. Brown and I. Moritani, *ibid.*, **77**, 3607 (1955).

[4] P. J. Lucchesi, D. L. Baeder and J. P. Longwell, *ibid.*, **81**, 3235 (1959).

[5] W. O. Haag and H. Pines, *ibid.*, **82**, 2488 (1960).

[6] H. Pines and W. O. Haag, *ibid.*, **83**, 2847 (1961).

[7] A. Streitwieser and W. D. Schaeffer, *ibid.*, **79**, 2888 (1957).

ane on firebrick. The butyl bromides and amines used in this study were Eastman Kodak Co, white label grade. The butenes were C.P. grade from the Matheson Co.

Isomerization of Butenes over Sulfuric Acid.—The reaction vessel consisted of a horizontal glass tube fitted with three vertical side-arms. The end side-arms were fitted with stopcocks and the central arm was closed with a serum cap for easy sample removal. Each tube was filled with thirty-five glass beads (6 mm.) to provide a larger surface area. The resulting volume was 66 ml.

Sulfuric acid (2.0 ml., 18.7 *N*) was added to the reaction vessel which was then placed in the constant temperature bath at 72.6°. The vessel next was pumped down and flushed several times with the appropriate butene. The desired butene was then metered into the vessel to a pressure of approximately 4.5 p.s.i. above atmospheric pressure. A preliminary study showed the rate of isomerization was extremely slow at room temperature under these conditions.

At various time intervals samples were withdrawn by gas tight syringes and analyzed by v.p.c. By this procedure the rates of isomerization of 1-butene to *cis*- and *trans*-2-butene and *cis*-2-butene to 1-butene and *trans*-2-butene, and *trans*-2-butene to 1-butene and *cis*-2-butene were studied. The data for the isomerization of 1-butene, shown in Fig. 1, are a composite of seven runs and illustrate the reproducibility of the method.

The isomerization of each butene at 72.6° was followed until equilibrium was reached. The equilibrium values were determined to be 6 ± 1% 1-butene, 26 ± 1% *cis*-2-butene and 68 ± 1% *trans*-2-butene. While the formation of the isomeric butenes indicated a complex reaction path, the initial changes in concentration (150–200 min.) of the isomers very closely approximated a straight line. Starting with 1-butene the rate of formation of *cis*-2-butene (C) and *trans*-2-butene (T) can be written as $dC/dt = k_3(\text{I}) - k_{-3}(\text{C})$ and $dT/dt = k_2(\text{I}) - k_{-2}(T)$, where (I) represents the concentration of some intermediate. The rate constants are as given in the scheme in the discussion. Because the concentrations of *cis*- and *trans*-2-butene are small at the start, the initial rates of formation can be written as $dC/dt = k_3(\text{I})$ and $dT/dt = k_2(\text{I})$. With no knowledge of the reaction mechanism and only assuming the intermediate (I) is the same for the formation of both isomers, we can find the ratio of the rate constants from the initial rates of formation of the isomers, *i.e.*, $(\Delta C/\Delta t)/(\Delta T/\Delta t) = k_3/k_2$. The ratios of the rate constants obtained graphically from the initial rates of formation of the isomers are shown in Table I.

TABLE I

RATIO OF RATE CONSTANTS FOR THE ISOMERIZATION OF THE VARIOUS BUTENES AT 72.6°

k_1 = rate of formation of 1-butene; k_2 = rate of formation of *trans*-2-butene; k_3 = rate of formation of *cis*-2-butene

Reactant	Ratios of rate constants k_2/k_1	k_2/k_3	k_3/k_1
1-Butene	..	1.1	..
cis-2-Butene	11.1	..	..
trans-2-Butene	..	1.0[a]	11.4

[a] Calculated from $(k_2/k_1)/(k_3/k_1)$.

The Isomerization of 1-Butene over Phosphoric Acid.—A tube 36 cm. high containing 85% phosphoric acid was heated to 100° and 1-butene was bubbled through for *ca.* 1 hr. with a contact time of 1-2 sec. per bubble. After this time a sample of gas was analyzed then another flush period of 1 hr. was allowed. The second gas sample agreed in analysis with the first. By increasing the rate of flow a contact time of somewhat less than 1 sec. was obtained. The results of these two experiments are given in Table II.

The Deamination of *n*-Butyl- and *sec*-Butylamine.—A solution of 22 g. (0.3 mole) of the appropriate amine in 60 g. of acetic acid and 200 ml. of water was heated to 70° in a 500-ml. 3-necked flask fitted with a dropping funnel and condenser. The latter was connected to a trap cooled in Dry Ice–acetone. The flask was flushed with argon to remove oxygen. A solution of 69 g. of sodium nitrite in 100 ml. of water was slowly added at a rate that allowed the temperature to be maintained at 70–75°. The reaction was heated 1–2 hr. following the final addition.

The trap was allowed to warm to room temperature and the gaseous material was collected over brine. The yield of butenes from *n*-butylamine was 26% based on both the volume of gas and the loss in weight in the trap. The analysis of this gas is given in Table II. The yield from *sec*-butylamine was 39%, and the analysis is also given in Table II.

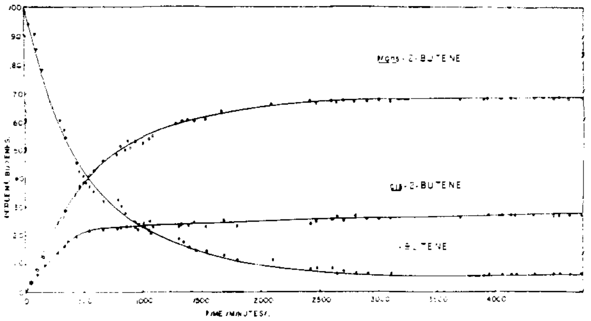

Fig. 1.—The isomerization of 1-butene as a function of time over sulfuric acid (18.7 *N*) at 72.6°.

TABLE II

PRODUCT ANALYSES FOR ELIMINATION REACTIONS IN THE BUTYL SYSTEM AT *ca.* 73°

Reactant	Reagent	Product distribution 1-Butene	*cis*-2-Butene	*trans*-2-Butene	*trans*/*cis*
1-Butene	Sulfuric acid				1.0[a]
1-Butene	Phosphoric acid	92.2	3.8	4.0	1.0[b]
		96.2	1.8	2.0	1.1[b]
s-BuOTs	H_2O	7	46	47	1.0
s-BuOTs	*t*-BuOH	5	46	49	1.1
s-BuOTs	Acetic acid	10.3	43	46	1.1[c]
n-BuBr	$AgNO_3$(*t*-BuOH)	96	2	2	1.0
s-BuBr	$AgNO_3$(*t*-BuOH)	24	35	41	1.2
n-BuBr	$AgNO_3(H_2O)$	78	9	13	1.4
s-BuBr	$AgNO_3(H_2O)$	5	41	54	1.3
n-$BuNH_2$	$HNO_2(H_2O)$	60	15	25	1.7
s-$BuNH_2$	$HNO_2(H_2O)$	22	25	53	2.1
		27	22	51	2.3[d]
s-BuBr	H_2O	10	33	57	1.7
s-BuBr	10% KOH	15	23	62	2.7
s-BuBr	$NaOC_2H_5$	23	18	59	3.3
s-BuBr	KOC_4H_9	56	16	28	1.8
Equilibrium values		6	26	68	2.6[e]

[a] Taken from the initial rates of formation of *cis*- and *trans*-2-butene. [b] Reaction at 100° with contact times of 1–2 sec. (upper) and less than 1 sec. (lower). [c] Ref. 3b. [d] Reaction in the presence of silver ion. [e] Equilibrium values taken from the isomerizations of the three butenes over sulfuric acid.

In one experiment the possible effect of complexing by silver ion on the ratios of the reaction products was determined by generating the nitrous acid from 0.2 mole of silver nitrite plus 0.1 mole of sodium nitrite to 0.1 mole of *sec*-butylamine. The gas analysis is given in Table II.

The Reactions of *sec*-Butyl Tosylate.—The method of Tipson[8] was used to prepare *sec*-butyl tosylate. The entire process including product workup was carried out at 0–5°. The crude product in chloroform was washed with cold dilute sulfuric acid then cold dilute sodium bicarbonate. After drying the solution (magnesium sulfate) the chloroform was removed on a rotary evaporator keeping the flask cold throughout. The crude tosylate was used directly.

The decomposition of the tosylate was carried out by stirring 12 g. of the above in 200 ml. of the chosen solvent at 75°. Experiments were carried out in water and *t*-butyl alcohol, respectively. In each case, heating overnight produced *ca.* 300 ml. of gas. The analyses are given in Table II.

The Reactions of *n*-Butyl Bromide and *sec*-Butyl Bromide with Silver Nitrate.—A solution of 34 g. of silver nitrate in

---

[8] R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

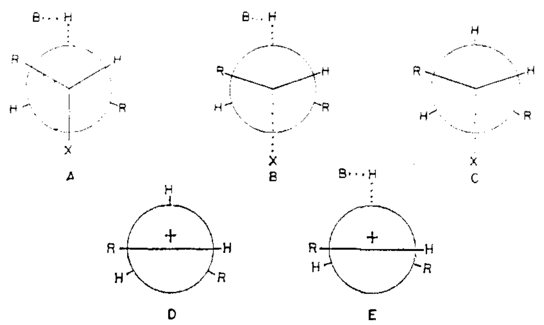

Fig. 2.—The various transition states and intermediates possible for E1 and E2 reactions.

200 ml. of water was heated to 70°, and 13.7 g. (0.1 mole) of the desired bromide was added. The reaction flask was connected through a condenser directly to a gas collection bottle filled with brine.

Using *n*-butyl bromide the gas evolution ceased after 17 hr. The yield of butenes was *ca.* 100 ml. (4%). The analysis is given in Table II. The yield of silver bromide was 88% of the theoretical amount.

The yield of gas with *sec*-butyl bromide was 700 ml. (29%), and the analysis appears in Table II. The gas evolution stopped after 4 hr., and the yield of silver bromide was 84%.

The above experiments were repeated using *t*-butyl alcohol in place of water. The silver nitrate did not completely dissolve. On heating overnight *n*-butyl bromide evolved 300 ml. (12%) of butenes while *sec*-butyl bromide gave 400 ml. (16%) after 4 hr. when gas evolution ceased. Both analyses are given in Table II.

The Reaction of *sec*-Butyl Bromide with Water and with 10% Potassium Hydroxide.—A mixture of 13.7 (0.1 mole) of *sec*-butyl bromide and 250 ml. of water was heated and stirred for 3.5 days at 70°. The gas was collected and analyzed as before (Table II); yield 200 ml. (8%).

This experiment was repeated using 250 ml. of 10% potassium hydroxide. After 2.5 hr. all gas evolution had ceased; yield 1 l. (40%); analysis in Table II.

In a further experiment, the above reaction was repeated incorporating 10 g. of potassium bromide with the potassium hydroxide solution. The analysis of the first 400 ml. of gas evolved agreed exactly with that reported in Table II for the reaction with potassium hydroxide. The same was true for the second 400 ml., collected separately, indicating that the ratios of the various butenes does not vary with time and that additional potassium ion does not influence the mechanism.

The Reaction of *sec*-Butyl Bromide with Sodium Ethoxide. A solution of 0.3 mole of sodium ethoxide in 200 ml. of ethanol was heated to 70° with 13.7 g. of *sec*-butyl bromide. The yield of gas was 1 l. (40%) when the reaction ceased after 1 hr. The analysis is given in Table II.

In a control experiment *cis*-2-butene was allowed to stand over alcoholic sodium ethoxide at 70° for 48 hr. A trivial amount of isomerization (*ca.* 1%) occurred.

The Reaction of *sec*-Butyl Bromide with Potassium *t*-Butoxide.—A solution of 0.3 mole of potassium *t*-butoxide in 250 ml. of *t*-butyl alcohol was heated to 70° and 13.7 g. of *sec*-butyl bromide was added. The evolution of gas ceased after *ca.* 4 hr. The reaction mixture was heated overnight. The total yield of gas was 900 ml., and the analysis is given in Table II.

Results and Discussion

Current chemical theory provides a variety of transition states and intermediates which can be evoked to explain ionic elimination reactions.[2,9,10,11] In order to elucidate some of these reactions, mixtures of *cis*- and *trans*-2-butenes and 1-butene have been prepared by a variety of methods in an attempt to see whether the same or at least conformationally similar intermediates are involved. The most important of these are shown in Fig. 2 as Newman projections.

Since the E_2 reaction is perhaps the simplest mechanistically, it seemed desirable to compare the results of the various reactions with those which might be expected to favor a true E_2 elimination process. Possible variations in the E_2 transition state are shown in Fig. 2a, b and c.[2] The reactions of 2-bromobutane with 10% potassium hydroxide, with sodium ethoxide in ethanol, and with potassium *t*-butoxide in *t*-butyl alcohol were assumed to be typical E_2 reactions. While the hydroxide gave a value of *trans*-/*cis*-2-butenes near the thermodynamic ratio, the elimination with ethoxide gave a slightly higher value and the reaction with *t*-butoxide a somewhat lower value (Table II).

It seems reasonable to assign 2-b to the usual state achieved by an alkyl halide, such as 2-bromobutane, when treated with a moderately strong base in a good solvating medium.[2,11,12] Since bond breaking at C-α and C-β has progressed considerably in 2-b, the transition states leading to *trans*- and *cis*-olefins will have energy differences roughly reflecting the difference in the product olefins. This simple picture neglects any influences which additional eclipsing effects by the base or solvent might have on the energy difference of the two possible transition states and predicts a maximum ratio of *trans*- to *cis*-olefin equal to the thermodynamic ratio. While this picture holds for the reaction of 2-bromobutane with hydroxide in water, it is evident that some additional factor produces a ratio somewhat above the thermodynamic value when the halide is treated with ethoxide in ethanol. Presumably this enhanced ratio reflects additional eclipsing interactions introduced by the ethoxide in ethanol.

With a stronger base, such as *t*-butoxide, in the relatively poor solvating *t*-butyl alcohol the transition states will be shifted toward a carbanion mechanism (Fig. 2a).[2,12] Since the double bond is not so well developed in this transition state, eclipsing effects will not be so important and a smaller *trans*/*cis* ratio would be expected. The experimental result with 2-bromobutane supports this contention.

The opposite extreme in E_2 transition states (Fig. 2c) marks the borderline between the E_2 and E_1 reactions. Here the halogen bond has stretched considerably but little or no elongation of the β-hydrogen bond has occurred. Most reasonably this transition state would be achieved in a good ionizing solvent in the absence of a strong base. As above, little progress has been made toward olefin formation, and eclipsing should play a smaller role in determining the ratio of *trans*/*cis* isomers. The treatment of 2-bromobutane with neutral water illustrates the expected behavior producing 2-butenes with a *trans*/*cis* ratio of 1.7.

While the E_2 reaction proceeds in a synchronous fashion from reactants through a high energy transition state before collapsing into products, the E_1 reaction should be characterized by a dip in the

---

(9) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., Chap. VIII.

(10) B. V. Banthorpe, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 4054 (1960).

(11) D. Y. Curtin, *Record Chem. Prog.*, **15**, 111 (1954).

(12) D. J. Cram, F. D. Greene and C. H. DePuy, *J. Am. Chem. Soc.*, **78**, 790 (1956).

energy curve corresponding to the formation of a carbonium ion intermediate. Since rotational barriers are small in the butyl system, the usual assumption of rapid internal rotation compared to the life time of the intermediate should hold. Thus, the products derived from a free 2-butyl cation should not reflect any conformational differences in starting materials. Furthermore, since the formation of the olefinic products from the 2-butyl cation should be an exothermic process, the transition states for the process should resemble the intermediate in character,[13] *i.e.*, the β-H is very slightly stretched, eclipsing effects are negligible, and rapid rotation about the central carbon-carbon bond leads to the complete equivalence of the hydrogens at the β-carbon. Silver[14] recently has observed deuterium isotope effects of *ca.* 2–3 in the E_1 elimination reactions of the *t*-pentyl cation, a result in keeping with the concept that only small progress in breaking the β-hydrogen bond has occurred in the transition state from ion to olefin. The preferential formation of *trans*- or *cis*-olefins from a free 2-butyl cation would not be expected then in a true E_1 elimination.

A number of reactions believed to proceed by an E_1 mechanism giving 2-butyl cations was studied. The elimination reactions of butyl bromides, tosylates and amines were investigated, and the composition of the product butenes was determined.

Treatment of 2-bromobutane with silver nitrate in water or in *t*-butyl alcohol at 70° was found to produce elimination according to the Saytzeff rule leading to a preponderance of the 2-butene isomers. The distribution of products is given in Table II. While the results of the reaction of *n*-butyl bromide with silver nitrate in either water or *t*-butyl alcohol gave low yields of olefins, it is interesting to note (Table II) that the ratio of *trans-/cis*-2-butene closely parallels the results with the secondary bromide.

The acetolysis of *sec*-butyl tosylate has been shown kinetically to proceed by an E_1 path with a *trans-/cis*-2-butene ratio of 1.1.[3] These results are in accord with the assumed carbonium ion mechanism. For comparison purposes we have examined the same reaction in water and in *t*-butyl alcohol and have found the same ratio of *trans*- to *cis*-2-butene, as seen in Table II.

The elimination products from the nitrous acid deamination of *n*-butyl- and *sec*-butylamine have been reported in acetic acid at room temperature.[7] Since *sec*-butylamine is proposed to react with the nitrous acid largely by a carbonium ion mechanism, it seemed desirable to repeat these reactions in water at 70° in order to compare the results with those obtained above. The results, recorded in Table II, agree well with the distribution of products found by Streitwieser and Schaeffer[7] at the lower temperature.

In order to draw conclusions regarding the possible influence of π-complexing with silver ions as a product-determining factor, the deamination of *sec*-butylamine with silver nitrite was carried out. The results, Table II, indicate no appreciable change in the *trans-/cis*-2-butene ratio in the presence of silver ion.

A variety of evidence is now available pointing to the abnormal behavior of ionic elimination reactions proceeding *via* the nitrous acid deamination of amines.[7,15] Streitwieser and Schaeffer consider that the *trans/cis* ratio of 2.9 (*ca.* 2.1 at 70° in our study) for the 2-butenes supports the concept of a concerted *trans* elimination of nitrogen and hydrogen from the 2-butyldiazonium ion. Our over-all results are consistent with their interpretation; however, there are several points which are still not satisfactorily explained.

Another point of interest brought out by the data in Table II is the *trans-/cis*-2-butene ratio produced by ionic eliminations in the 1-butyl system. The accumulated data[7] indicate that solvolytically produced 1-butyl cations do not noticeably rearrange to 2-butyl cations. In order to explain the much greater formation of the 2-butenes from the deamination of 1-aminobutane, Streitwieser and Schaeffer[7] postulated a concerted loss of nitrogen from the primary diazonium ion and a hydride shift to the primary carbon. Whether or not the end result of this process was to be considered as a normal 2-butyl cation was not discussed. In view of the fact that the ratio of *trans-/cis*-2-butene was reported to be near the thermodynamic ratio, it seems most likely that such is not the case. Again an over-all concerted process of nitrogen loss, hydride shift and elimination of the hydrogen on carbon-3 may be evoked. Since the final transition state of the reaction will have proceeded well toward olefin formation, the same energy considerations will be brought into play as discussed previously for the E_2 reaction.

Only a slight modification of this picture is needed to accommodate the results of treating 1-bromobutane with silver ion in *t*-butyl alcohol or in water. Since the *trans-/cis*-2-butene ratio is close to unity in these two cases, it seems reasonable to postulate 2-butene formation from a 2-butyl cation. The latter is most likely formed by a concerted process in which the silver ion pulls off the bromine accompanied by a 1,2-shift of hydride.

The Isomerization of the Butenes.—The isomerization of the three *n*-butenes at 72.6° over dilute sulfuric acid was studied as a function of time. The reactions were followed until equilibrium was attained. The same equilibrium values were reached in each case (Table II). While no isobutylene was formed from either 1-butene or *cis*-2-butene, there was an indication of a trace of isobutylene in the v.p.c. curve during the *trans*-2-butene isomerization. A composite plot of the data from seven runs on the isomerization of 1-butene is given in Fig. 1. The data clearly reflect the reproducibility of the experimental technique.

Two points of interest arise from the plot shown in Fig. 1. First, the production of *cis*-2-butene does not pass through a maximum as has been observed by Haag and Pines[5] in the case of the isomerization of 1-butene over alumina at 230°. Second, at no point was there more *cis*-2-butene than *trans*-2-butene observed.

---

(13) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(14) M. S. Silver, *ibid.*, **83**, 3487 (1961).

(15) M. S. Silver, *ibid.*, **83**, 3482 (1961).

A crude mechanism for the isomerizations of the butenes may be written as

$$\begin{tikzcd}
\text{1-butene} + \mathrm{H}^+ \arrow[r, shift left, "k_{-1}"] & \text{intermediate} \arrow[l, shift left, "k_1"] \arrow[r, shift left, "k_2"] \arrow[d, shift left, "k_3"] & \textit{trans}\text{-2-butene} + \mathrm{H}^+ \arrow[l, shift left, "k_{-2}"] \\
 & \textit{cis}\text{-2-butene} + \mathrm{H}^+ \arrow[u, shift left, "k_{-3}"] &
\end{tikzcd}$$

By determining the initial rates of formation of the two products from a given starting olefin one may compute the ratios k_2/k_3, k_3/k_1 and k_2/k_1 unhindered by considerations of the reversibilities of the above steps since at t_0 the reverse reactions will not have been established. Plots of the data for the isomerization of each of these olefins were linear over the first 150–200 minutes of reaction time. The ratios of rates of formation of the various butenes calculated from these slopes are given in Table I. It should be remembered for future discussion that the rates of production of *trans*- and *cis*-2-butene from the reaction intermediate were nearly equal.

Haag and Pines[5] have reported a higher initial rate of conversion of 1-butene to *cis*-2-butene than to *trans*-2-butene on bubbling the gas through phosphoric acid. The ratio of *cis* to *trans* was found to increase at higher temperatures and with shorter contact times with the acid. Since these results ran counter to our observations with sulfuric acid, we have attempted to repeat these experiments using 85% phosphoric acid at about 100°. The details of the experiments are given in the Experimental section. Even at very short contact times (1 sec. or less) the amounts of the two 2-butene isomers were nearly the same with the *trans* isomer slightly in excess (Table II). The concentration of the phosphoric acid in the work of Haag and Pines was not given.

The classical picture of the acid-catalyzed isomerization of the *n*-butenes involves the 2-butyl cation as a common intermediate. On repeated formation, the ultimate result should be the thermodynamic equilibrium mixture of butene isomers. However, by studying the acid-catalyzed isomerization at short reaction times before the various reversible steps have assumed importance it has been shown that the formation of *trans*- and *cis*-2-butenes occurs at equal rates in either sulfuric acid or phosphoric acid. Clearly no special hydrogen-bridged structures or protonium ions need be evoked, and the reaction can be described as simply proceeding through a 2-butyl cation.

Both Pines and co-workers[5,6] and Lucchesi, *et al.*,[4] have proposed non-classical bridged structures to explain the greater rate of formation of *cis*-2-butene than *trans*-2-butene in various isomerization and elimination reactions of the 2-butyl system over alumina and silica–alumina catalysts, respectively. In none of these studies was the question of the role of the catalyst surface raised. In view of results and reasoning given above, it seems most unlikely that non-classical hydrogen bridged ions play any important role in E_1 reactions in the 2-butyl system. There is no evidence that they would be formed in a high temperature heterogeneous reaction, nor is there any *ad hoc* line of thought which suggests that they would occur more readily under these conditions than in the reactions studied here. Keeping in mind our present inexact knowledge of heterogeneous reactions, one may readily imagine several possible surface effects which could explain the results reported.

Acknowledgment.—Part of the research reported here was supported by a grant from the Robert A. Welch Foundation (W. H. W.). Grateful acknowledgment for this support is hereby given. The authors also wish to acknowledge the help of Mr. Charles Wall (National Science Foundation Undergraduate Research Participant) in determining the isomerization rates of the butenes over sulfuric acid.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIF.]

Reactions of the 2-Bornyl Radical. I. The Decarbonylation of 2-Formylbornane[1]

BY JEROME A. BERSON AND CARL J. OLSEN[2]

RECEIVED MARCH 2, 1962

The di-*t*-butyl peroxide-induced decarbonylation of 2-formylbornane in the liquid phase at 138° gives mainly bornane and traces of bornene and tricyclene as the sole C_{10}-hydrocarbon products. The hypothetical rearrangement product 2,3,3-trimethylnorbornane (isocamphane) is not observed and cannot be present to an extent greater than about 0.1% of the total volatile hydrocarbon formed. The chain length for carbon monoxide production in the decarbonylation varies with the ratio of peroxide to aldehyde used and ranges from about 0.4 to about 4.8 as the ratio changes from about unity to about 0.1. At high initial ratios, the yields of disproportionation products (bornene and tricyclene) increase at the expense of bornane, suggesting an increased importance of radical–radical reactions relative to hydrogen abstraction.

As part of a study of the reactions of the bornyl free radical, we report here on the *t*-butyl peroxide-induced decarbonylation of 2-formylbornane (2-formylcamphane)[3] (I). The radical is of potential

---

[1] (a) This research was supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF18-(600)-1544. Reproduction in whole or in part is permitted for any purpose of the United States Government. Also supported in part by the Office of Ordnance Research under Contract No. DA-04-495-ORD-532. We are indebted to these agencies and to the Alfred P. Sloan Foundation and the Richfield Oil Corporation for support. (b) Taken from a portion of the dissertation submitted by C. J. Olsen in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (c) For a preliminary report, see J. A. Berson, C. J. Olsen and J. S. Walia, *J. Am. Chem. Soc.*, **82**, 5000 (1960).

[2] Richfield Oil Corporation Fellow, 1956–1957.

[3] The nomenclature used in this and the following paper[4] is con-