Electrophilic Substitution at Saturated Carbon. XXIX. Relationships between Position of Protonation of Allylic Anions and the Kinetic and Thermodynamic Stabilities of the Olefinic Products[1]

Stephen W. Ela[2] and Donald J. Cram

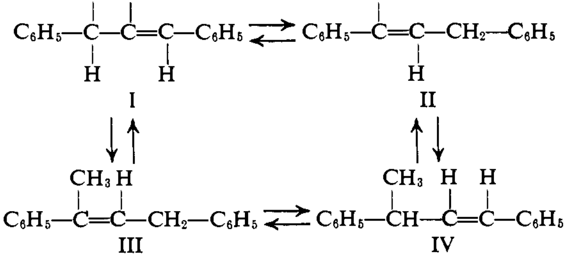
Contribution No. 1953 from the Department of Chemistry, The University of California at Los Angeles, Los Angeles, California 90024. *Received August 15, 1966*

Abstract: The relationship between the kinetic and thermodynamic stabilities of proton-tautomeric olefins and the position of protonation of their derived allylic anions has been examined. The four 1,3-diphenylbutenes were synthesized, characterized, and interconverted in *t*-butyl alcohol–potassium *t*-butoxide. At 40° the equilibrium proportions were 32% *trans*-1,3-diphenyl-1-butene (I), 52% *cis*-1,3-diphenyl-2-butene (II), 15% *trans*-1,3-diphenyl-2-butene (III), and 1% *cis*-1,3-diphenyl-1-butene (IV). The second-order rate constants (l./mole sec) for isomerization of the olefins at 40° were as follows: I, 5.1×10^{-5}; II, 3.2×10^{-5}; III, 1.8×10^{-6}; and IV, 7.5×10^{-8}. The ratio of rate constants for isotopic exchange and isomerization (k_e/k_i) was estimated for each olefin in *t*-butyl alcohol-O-*d*: I, <0.3; II, 17; III, 21; IV, <0.07. Configurationally discrete isomeric allylic carbanions (A and B) are required to explain the interconversions of I and II on the one hand and of I and III on the other. The energy barrier for direct interconversion of the two allylic anions is estimated to be greater than 3 kcal/mole at 40°. The large difference in reactivity between IV and the other three olefins is discussed in terms of a third allylic anion less stable than the other two. The stabilities of the allylic anions are correlated with the magnitudes of the 1,3 steric interactions between substituents *cis* to one another in the plane of the anion. The ratios of k_e/k_i, corrected for intramolecular proton transfer, were used to estimate the "collapse ratios" of the isomeric allylic anions. Protonation of carbanion A to form II was about 35 times faster than protonation to form I. Protonation of carbanion B to form III was about 40 times faster than to form I. These unbalanced "collapse ratios" of carbanions A and B are attributed to the inductive effects of the methyl groups, which direct protonation to the less substituted sites. The relative ground-state stabilities of the olefins appear to have little influence upon the magnitudes of the collapse ratios.

Proton tautomerism was extensively studied by the Ingold school in the 1920–1940 period, and the results have been summarized.[3] Much effort was devoted to determination of the effects of substituents upon equilibrium constants and relative kinetic acidities of tautomers, and upon the position of predominant protonation of anionic intermediates in the interconversion of tautomers. Many results were summarized in terms of the Ingold rule, which stated: "When a proton is supplied by acids to the mesomeric anion of weakly ionizing tautomers of markedly unequal stability, then the tautomer which is most quickly formed is the thermodynamically least stable; it is also the tautomer from which the proton is lost most quickly to bases." The systems studied usually involved anions stabilized by nitro, cyano, keto, and ester groups. These groups were intact in the more stable tautomer, but protonation occurred faster at the position of higher electron density.[4] For example, nitrocarbanions when carefully acidified gave *aci*-nitro compounds, and these compounds reverted to the anions faster than did their tautomers.

Recently, exceptions to the Ingold rule have been found. In the base-catalyzed interconversions of α-benzylstyrene and *cis*- and *trans*-α-methylstilbene,[5] and of 3-phenyl-1-butene and *cis*- and *trans*-2-phenyl-2-butene,[6] the first part of the rule was violated. In the base-catalyzed interconversions of 1-methylsulfinyl-1-dodecene and 1-methylsulfinyl-2-dodecene,[7] both parts of Ingold's rule were broken.

The present study was initiated to explore further the relationship between thermodynamic and kinetic acidities of olefins, and the positions of preferred protonation in their derived anions. The interconversions of olefins I–IV were studied in *t*-butyl alcohol–potassium *t*-butoxide at 40°. This system was chosen for the following reasons. (1) The compounds involved are hydrocarbons and do not contain any electronegative elements. (2) The compounds lend themselves to determination of their relative kinetic acidities at reasonable temperatures in a hydroxylic solvent. (3) By comparisons of the rates for base-catalyzed hydrogen–deuterium exchange between hydrocarbon and solvent and the rates of isomerization for the olefins,



$$C_6H_5-\underset{H}{\overset{CH_3}{C}}-\underset{H}{\overset{H}{C}}=C-C_6H_5 \rightleftarrows C_6H_5-\overset{CH_3}{C}=\underset{H}{C}-CH_2-C_6H_5$$

$$C_6H_5-\overset{CH_3}{C}=\overset{H}{C}-CH_2-C_6H_5 \rightleftarrows C_6H_5-\overset{CH_3}{C}H-\overset{H}{C}=\overset{H}{C}-C_6H_5$$

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[2] National Science Foundation Predoctoral Fellow, 1962–1964, and U. S. Rubber Company Predoctoral Fellow, 1964–1965.

[3] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter 10.

[4] (a) A. J. Birch, *Quart. Rev.* (London), **4**, 69 (1950); (b) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, New York, N. Y., 1961.

[5] D. H. Hunter and D. J. Cram, *J. Am. Chem. Soc.*, **86**, 5478 (1964).

[6] D. J. Cram and R. T. Uyeda, *ibid.*, **86**, 5466 (1964).

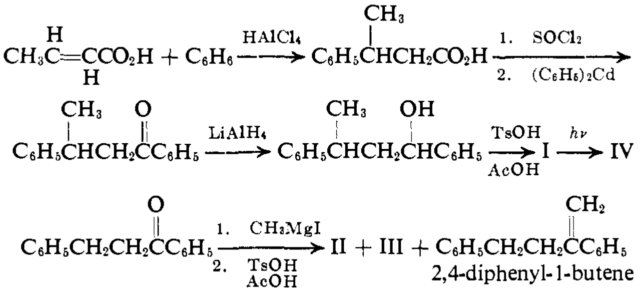
[7] D. E. O'Connor and C. D. Broaddus, *ibid.*, **86**, 2267 (1964).

the relative rates of protonation at the two ends of the allylic anions can be estimated. (4) The systems give allylic anions symmetrical except for the methyl group. (5) The system permits an examination to be made of the stability of geometrically isomeric allylic anions.

Methods and Results

The preparation and characterization of olefins I–IV, their acid- and base-catalyzed equilibrations, and the determination of their rates of base-catalyzed isomerization and hydrogen isotopic exchange with solvent are described in the following sections.

Preparation and Characterization of Starting Materials. Olefins I–IV were prepared by the methods formulated. Only the final steps are discussed. Treatment of a diastereomeric mixture of 1,3-diphenyl-1-butanols with *p*-toluenesulfonic acid in acetic acid at 100° gave *trans*-1,3-diphenyl-1-butene (I). Photoisomerization of I with α-naphthyl phenyl ketone as photosensitizer gave a high yield of *cis*-1,3-diphenyl-1-butene (IV).[8] Both olefins were purified by preparative vapor phase chromatography (vpc). Dehydration of 2,4-diphenyl-2-butanol with *p*-toluenesulfonic acid in acetic acid gave a 3:1 mixture of *cis*- to *trans*-1,3-diphenyl-2-butenes (II to III) as well as about 7% of 2,4-diphenyl-1-butene. The thermodynamically more stable *cis* isomer (II) was found to undergo photoisomerization very efficiently to give the *trans* isomer (III). The substances were purified by preparative vpc.



$$\mathrm{CH_3\overset{H}{C}{=}\underset{H}{C}CO_2H + C_6H_6 \xrightarrow{HAlCl_4} C_6H_5\overset{CH_3}{\overset{|}{C}}HCH_2CO_2H \xrightarrow[2.\ (C_6H_5)_2Cd]{1.\ SOCl_2}}$$

$$\mathrm{C_6H_5\overset{CH_3}{\overset{|}{C}}HCH_2\overset{O}{\overset{\|}{C}}C_6H_5 \xrightarrow{LiAlH_4} C_6H_5\overset{CH_3}{\overset{|}{C}}HCH_2\overset{OH}{\overset{|}{C}}HC_6H_5 \xrightarrow[AcOH]{TsOH} I \xrightarrow{h\nu} IV}$$

$$\mathrm{C_6H_5CH_2CH_2\overset{O}{\overset{\|}{C}}C_6H_5 \xrightarrow[2.\ TsOH,\ AcOH]{1.\ CH_3MgI} II + III + \underset{2,4\text{-diphenyl-1-butene}}{C_6H_5CH_2CH_2\overset{CH_2}{\overset{\|}{C}}C_6H_5}}$$

Although mixtures of I and IV and of II and III were easily separated by analytical vpc techniques, complete resolution of mixtures that contained all four isomers was not accomplished. Optimal conditions produced only a partial separation of III and IV, although the other separations were accomplished. The vpc data, coupled where necessary with data derived from acid-catalyzed isomerization of that material (see next section), indicated that each of the four starting olefins was >99.5% pure with no more than 0.3% contamination from any one isomeric olefin. Only when olefin III was prepared by photoisomerization of II was the possible limit of impurity higher; it was not demonstrated that this sample of III did not contain less than about 1% of IV. Analytical methods for analysis of I–IV based on vpc and acid isomerization are detailed in the Experimental Section.

The nuclear magnetic resonance (nmr) spectra readily distinguished I and IV from II and III. The nmr spectra of the latter pair were in agreement with published values.[9] The ultraviolet spectra in hexane led to configurational assignments. Compounds assigned structures II and III exhibited λ_{max} 245 mμ (ε 15,600) and 230 mμ (ε 9500), respectively. These data harmonize with those reported for *cis*- and *trans*-2-phenyl-2-butene:[10] 243 mμ (ε 12,100) and 235 mμ (ε 8200), respectively. The ultraviolet absorption maxima for I and IV were at 252 mμ (ε 21,500) and 241 mμ (ε 14,200), respectively. These values agree well with those reported for *trans*- and *cis*-propenylbenzene:[11] 250 mμ (ε 17,300) and 241 mμ (ε 13,800), respectively. The acid-catalyzed isomerization data of the next section serve to confirm the structural assignments.

Equilibrations of the 1,3-Diphenylbutenes (I–IV). Table I lists the results of acid-catalyzed isomerizations of the four olefins at about 100°. In runs 1 and 2, reaction times were chosen to establish equilibrium between II, III, and 2,4-diphenyl-1-butene before leakage to I and IV occurred. Similarly, I and IV in runs 3 and 4 became equilibrated before crossover to II and III was observed.

Table I. Equilibrations of *cis*- and *trans*-1,3-Diphenyl-2-butenes (II and III) and of *cis*- and *trans*-Diphenyl-1-butenes (IV and I) in 98% Glacial Acetic Acid–2% Acetic Anhydride (by Volume), 0.10 *M* in *p*-Toluenesulfonic Acid Monohydrate at 99.1 to 99.5°

Run no.	Substrate[a]	Time, hr	% IV	% I	% II	% III	% terminal olefin[b]
1	II	8.0	0.0[c]	<0.2[d]	70.8	22.6	6.6
2	III	8.0	0.0[c]	<0.2[d]	70.8	22.3	6.9
3	IV	168	2.8	97.2[e]	<0.2[d]	0.0[f]	<0.1[d]
4	I	168	2.9	97.1[e]	<0.2[d]	0.0[f,g]	<0.1[d]

[a] 0.098 *M*. [b] 2,4-Diphenyl-1-butene. [c] Assumed from absence of IV in starting material and lack of formation of I during reaction. [d] Estimated lower limit of detection. None was visible by vpc. [e] 1–2% of suspected indane isomers present but not included in percentages (see Experimental Section). [f] Assumed due to lack of formation of II during reaction. [g] Assumed due to absence in starting material.

The acid-catalyzed equilibrium values for II, III, and 2,4-diphenyl-1-butene are subject to a minor uncertainty. Any 2-acetoxy-2,4-diphenylbutane produced in equilibrium concentration in the mixture would not survive the vpc conditions used for analysis and would probably give terminal olefin in higher than the 7% equilibrium value. The related tertiary alcohol eliminated water under vpc conditions to give about 50% terminal olefin. However, the equilibrated mixture before vpc exhibited no hydroxyl or carbonyl bands in its infrared spectrum, and no compounds slower moving than the olefins were observed by thin layer chromatography (tlc). Furthermore, dehydration of the tertiary alcohol at 75° in the same reaction mixture gave a mixture of the three olefins in which acetate at most was a very minor component.

Analysis of the products from runs 3 and 4 showed less than 1% of a long retention time component (vpc) judged to be the acetate of secondary alcohol, 1,3-diphenyl-1-butanol. Besides olefins I and IV and the trace of secondary acetate, two additional components were observed in the equilibrium mixture (1–2%). More vigorous reaction conditions increased the yield of these suspected products. This acid-catalyzed ring

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(8) The authors are indebted to Dr. G. S. Hammond who suggested this photosensitizer.

(9) R. M. Parkhurst, J. O. Rodin, and R. M. Silverstein, *J. Org. Chem.*, 28, 120 (1963).

(10) D. J. Cram, *J. Am. Chem. Soc.*, 71, 3883 (1949).

(11) R. Y. Mixer, R. F. Heck, S. Winstein, and W. G. Young, *ibid.*, 75, 4094 (1953).

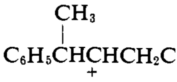
Table II. Base-Catalyzed Equilibrations of *cis*- and *trans*-1,3-Diphenyl-1-butene (IV and I) and *cis*- and *trans*-1,3-Diphenyl-2-butene (II and III) in *t*-Butyl Alcohol–Potassium *t*-Butoxide

Run no.	Substrate[a]	Base, *M*	Temp, °C[b]	Time, hr	% II	% I	% III + IV	Cor av equil values, %[c]
5	II	0.351	99.5	16.5	50.4	31.4	18.2	II, 50.4 I, 31.6 III, 17.1 IV, 1.0
6	II	0.351	99.5	277	50.5[d]	31.6	17.9	
7	I	0.351	99.5	16.5	50.0	31.7	18.3	
8	IV	0.351	99.5	259	50.7	31.5	17.9	
9	II	0.354	75.0	1004	50.4	31.6	17.8	II, 50.6 I, 31.7 III, 16.6, IV, 1.0
10	I	0.354	75.0	1005	51.1	31.7	17.2	
11	IV	0.354	75.0	1049	50.4	31.8	17.8	
12	II	0.39	40.0	970	52.9	32.0	15.1	II, 52 I, 32 III, 15, IV, 1
13	I	0.39	40.0	3080	52.0	31.9	16.2	
14	III[e]	0.39	40.0	1940	51.4	31.7	16.9	

[a] Concentration, 0.098 *M*. [b] ± 0.1°. [c] Acid-catalyzed equilibrium value at 99.5% of I/IV = 32 was used to calculate III and IV. [d] About 0.3% 2,4-diphenyl-1-butene was present, but was not included. [e] Tube was kept first at 100° for 44 hr, then the remainder of the time at 40°.

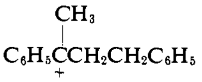
closure has precedence.[12] The absence of II in the product of run 3 establishes that the starting material (IV) was contaminated with no more than 0.3% of III. Run 2 demonstrated that under these conditions III would equilibrate with II.

The slowness of interconversion of I and IV to II and III under acid catalysis reflects the instability of the secondary dialkyl carbonium ion (V) as compared with tertiary and secondary benzyl carbonium ions (VI and VII). These results indicate that protonation to give ions VI or VII and their deprotonation is fast compared to intramolecular 1,2 or 1,3 hydride shifts leading to interconversion of the benzylic carbonium ions, and to intermolecular hydride shifts leading to saturated hydrocarbons and allylic carbonium ions.



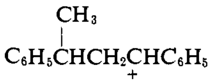
$C_6H_5\overset{CH_3}{\overset{|}{C}}H\underset{+}{C}HCH_2C_6H_5$

V



$C_6H_5\underset{+}{\overset{CH_3}{\overset{|}{C}}}CH_2CH_2C_6H_5$

VI



$C_6H_5\overset{CH_3}{\overset{|}{C}}HCH_2\underset{+}{C}HC_6H_5$

VII

The 1-butenes (I and IV) equilibrated more slowly than the 2-butenes (II and III). Under conditions of run 3, IV gave only about 50% conversion to I after 24 hr, whereas, at equilibrium, I was present to the extent of 97.2%. This result is in accord with the expectation that the tertiary benzylic carbonium ion (VI) is more stable and hence more easily formed than is the secondary benzylic carbonium ion (VII).

The values of Table I allow equilibrium constants at 99° to be calculated: *K* for I/IV = 32; *K* for II/III = 3.14.

The equilibrium percentages of II, III, and terminal olefin are similar to the equilibrium percentages of 75.5, 20.4, and 4.1% for *cis*-2-phenyl-2-butene, *trans*-2-phenyl-2-butene, and 2-phenyl-1-butene, respectively, observed at 100° with the same catalyst and solvent mixture.[13]

Olefins I–IV were also equilibrated at 100, 75, and 40° in *t*-butyl alcohol, 0.35 *M* in potassium *t*-butoxide. Table II lists the results. Runs 8 and 11 involve IV as starting material. This isomer is shown in the next section to be the slowest to react under these conditions. No attempt was made to isomerize IV at 40°. Run 12, made at 40° with II as starting material, is undoubtedly low in IV owing to incomplete equilibration, but is included to illustrate the constancy of the II/I ratio. Preliminary runs at 40° demonstrated that these two olefins were at equilibrium at 40° after about 100 hr. At that time, III and IV constituted only about 4% of the mixture.

The final corrected equilibrium values are based on the assumptions that at 100° the change in solvent mixtures from the acid-catalyzed experiments to the base-catalyzed does not greatly affect the equilibrium ratio of I/IV, and that this equilibrium ratio does not change much with a 60° change in temperature. Justification for these assumptions is found in other work. Thus the equilibrium ratios of *cis*- and *trans*-α-methylstilbene and α-benzylstyrene do not change appreciably with change from acetic acid to *t*-butyl alcohol.[5] The equilibrium values of *cis*- and *trans*-2-phenyl-2-butene and 2-phenyl-1-butene changed little over a 50° range in temperature.[13] Comparison of values of II/III from runs 1 and 2 made at 99° in glacial acetic acid (3.14) with those from runs 5–8 made at 99° in *t*-butyl alcohol (2.95) indicates a difference close to experimental error. Thus the errors produced by these assumptions are insignificant.

Base-Catalyzed Isomerization Rates of the 1,3-Diphenylbutenes (I–IV). Table III summarizes the kinetic data obtained from isomerization of the four olefins (I–IV) in *t*-butyl alcohol–potassium *t*-butoxide solutions. All runs were made with about 20 mg of mixture per kinetic point, either in sealed tubes or in stoppered flasks, and were analyzed by vpc (see Experimental Section). Preparative isomerizations were also carried out, and the high yields of reisolated olefin mixtures indicate the absence of side reactions.

Olefins I and II were found to interconvert readily at 40°. The rate constant for run 15 is an average initial rate constant for conversion of I to II, and was obtained by the method of Benson[14] for analysis of the rates of two components going to equilibrium making use of the raw rate data and the equilibrium constant (*K* = II/I = 1.63 from runs 12, 13, and 14). The appearance of III was slow in this run. After 35% reaction, about 0.5% of the mixture was composed of a peak corresponding in retention time to III and IV. This small amount of competing reaction was neglected in the calculation of the rate constant for run 15. The rate constant for conversion of II to I was calculated from the equilibrium constant and the rate constant of run 15.

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[12] B. B. Corson, W. J. Heintzelman, H. Moe, and C. R. Rousseau, *J. Org. Chem.*, **27**, 1636 (1962).

[13] D. J. Cram and M. R. V. Sahyun, *J. Am. Chem. Soc.*, **85**, 1257 (1963).

[14] S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., New York, N. Y., 1960, p 96.

Table III. Kinetics of Isomerization of *cis*- and *trans*-1,3-Diphenyl-1-butene (IV and I) and of *cis*- and *trans*-1,3-Diphenyl-2-butene (II and III) in *t*-Butyl Alcohol–Potassium *t*-Butoxide

Run no.	Substrate[a]	Base, *M*	Temp, °C[b]	No. of points	k_2, l./mole sec[c]
15	I	0.349 ± 0.003	40.0	6[d]	$5.13 \pm 0.07 \times 10^{-5}$
...[e]	II	0.349	40.0	..	$3.15 \pm 0.06 \times 10^{-5}$[e]
16	III	0.327 ± 0.003	40.0	6[f]	$1.79 \pm 0.04 \times 10^{-6}$
17[g]	IV	0.329 ± 0.004	100.0	6[h]	$6.26 \pm 0.46 \times 10^{-5}$
18	IV	0.354 ± 0.002	99.5	6[h]	$6.72 \pm 0.15 \times 10^{-5}$
19[i]	IV	0.351 ± 0.002	75.0	6[h]	$5.47 \pm 0.18 \times 10^{-6}$
...[j]	IV	0.35	40.0	..	$7.5 \pm 0.4 \times 10^{-8}$

[a] 0.10 *M*. [b] ±0.1°. [c] Second-order rate constants calculated on the assumption that the isomerizations are first order in base (see D. J. Cram, B. Rickborn, C. A. Kingsbury, and P. Haberfield, *J. Am. Chem. Soc.*, **83**, 3678 (1961)); rate constants for run 15 are average of initial rate constants calculated by the Benson procedure (ref 14), and ± values are standard deviations. [d] Points taken over first 35% of reaction. [e] Calculated from the rate constant of run 15 and the equilibrium value of 1.63 ± 0.02 for II/I from averages of runs 12–14, Table II. [f] Points taken over first 20% of reaction. [g] Run was made in *t*-butyl alcohol-O-*d*, 0.98 atom of deuterium per molecule (combustion and falling-drop analysis). [h] Points taken over first three half-lives of reaction. [i] Activation parameters: E_a = 26.6 ± 1.0 kcal/mole, ΔF^* = 29.6 ± 0.9 kcal/mole at 75°, ΔH^* = 26.0 ± 1.0 kcal/mole at 75°, ΔS^* = −10 ± 4 eu at 75°. [j] Calculated utilizing activation energy derived from runs 18 and 19.

The isomerization rate for III at 40° was slow compared with those of I and II. Listed for run 16 is the initial second-order rate constant for disappearance of III. Both I and II appeared as products. Under the conditions of the run, these products underwent appreciable interconversion. It is assumed (see below) that no IV (analytically indistinguishable by vpc from starting material) was produced during the first 20% reaction. Table IV gives a complete description of run 16. The value of I/II falls from 2.2 to 0.79 as the reaction proceeds from 16 to 96 hr. This change suggests that I is produced initially, but it equilibrates with II with time.

Table IV. Ratios of *trans*-1,3-Diphenyl-1-butene (I) to *cis*-1,3-Diphenyl-2-butene (II) and the Individual First-Order Rate Constants for Disappearance of *trans*-1,3-Diphenyl-2-butene (III) in Run 16

Point no.	Time, hr	% reaction	I/II	$k_1 \times 10^7$, sec^{-1}
1	16.0	3.24 ± 0.10	2.2 ± 0.4	5.64
2	32.0	6.62 ± 0.12	1.27 ± 0.04	5.97
3	48.0	9.74 ± 0.20	0.997 ± 0.012	5.93
4	64.0	12.7 ± 0.1	0.881 ± 0.005	5.92
5	80.0	15.6 ± 0.0	0.825 ± 0.010	5.91
6	96.0	18.2 ± 0.1	0.787 ± 0.008	5.81

k_1(av) = $5.86 \pm 0.12 \times 10^{-7}$ sec^{-1}
k_2 = $1.79 \pm 0.04 \times 10^{-6}$ l./mole sec

A temperature of 100° was necessary to produce a convenient isomerization rate for IV in deuterated solvent (run 17), and temperatures of 100 and 75° in protonated solvent (runs 18 and 19). The rate constant at 40° for IV in protonated solvent was obtained by extrapolation.

The inability to distinguish between III and IV by vpc required the assumption that in runs 17, 18, and 19 the three product olefins were present in equilibrium proportions for each point. The amount of III present was calculated through use of $K_{\mathrm{II/III}}$ and the sum of III and IV present for each point. Table V records the individual first-order rate constants as well as the observed II/I ratios for runs 17, 18, and 19. Clearly, olefins II and I were in equilibrium throughout runs 18 and 19, since the equilibrium value of 1.63 is constant for each point. In run 17 in deuterated solvent, the ratio is high at early reaction times, falls as the reaction proceeds, and reaches the value of about 1.6 only after roughly 50% isomerization. An explanation of this behavior will be offered below. The above procedure yielded kinetic data of a fair degree of precision, which suggests that III was also in equilibrium with I and II throughout runs 18 and 19. However, no direct evidence bearing on this point is available.

Table V. Ratios of *cis*-1,3-Diphenyl-2-butene to *trans*-1,3-Diphenyl-1-butene (II/I) and Individual Rate Constants for Isomerizations of *cis*-1,3-Diphenyl-1-butene (IV)

Run 17, 100°, 0.329 *M* potassium *t*-butoxide in *t*-butyl alcohol-O-*d*

Point no.	Time, min	% reaction	II/I	IV isomerizn, $k_1 \times 10^5$, sec^{-1}
1	60	6.78 ± 0.28	2.55 ± 0.20	1.96
2	120	12.3 ± 0.2	1.91 ± 0.04	1.82
3	180	20.9 ± 0.6	1.91 ± 0.12	2.18
4	240	25.5 ± 0.9	1.84 ± 0.03	2.05
5	480	46.9 ± 0.1	1.68 ± 0.01	2.20
6	1506	85.3 ± 0.4	1.58 ± 0.02	2.12

k_1 = $2.06 \pm 0.15 \times 10^{-5}$ sec^{-1}

Run 18, 99.5°, 0.354 *M* potassium *t*-butoxide in *t*-butyl alcohol

Point no.	Time, min	% reaction	II/I	$k_1 \times 10^5$, sec^{-1}
1	120	15.7	1.68	2.38
2	240	29.7	1.62	2.44
3	360	40.3	1.67	2.39
4	480	50.1	1.58	2.43
5	720	64.1	1.55	2.37
6	1453	86.4	1.57	2.29

k_1 = $2.38 \pm 0.05 \times 10^{-5}$ sec^{-1}

Run 19, 75.0°, 0.351 *M* potassium *t*-butoxide in *t*-butyl alcohol

Point no.	Time, hr	% reaction	II/I	$k_1 \times 10^6$, sec^{-1}
1	23.6	15.0	1.61	1.95
2	47.7	27.2	1.68	1.84
3	71.9	37.7	1.59	1.84
4	96.5	49.4	1.65	1.97
5	144	64.0	1.61	1.97
6	295	87.0	1.61	1.92

k_1 = $1.92 \pm 0.06 \times 10^{-6}$ sec^{-1}

Isomerization and Isotopic Exchange of 1,3-Diphenylbutenes (I–IV) in *t*-Butyl Alcohol-O-*d*–Potassium *t*-Butoxide. Each of the olefins (I–IV) was partially isomerized in *t*-butyl alcohol-O-*d*-potassium *t*-butoxide solution, reisolated, and submitted to nmr analysis for deuterium incorporation. An aliquot of the reaction product was submitted to vpc analysis for the per cent isomerization. The remainder was flash distilled and the per cent olefin recovery calculated. The starting olefin was then obtained by preparative vpc and submitted to nmr analysis of the exchangeable benzyl

Table VI. Results of Potassium *t*-Butoxide Catalyzed Hydrogen–Deuterium Exchange between *cis*- and *trans*-1,3-Diphenyl-1-butene (IV and I), *cis*- and *trans*-1,3-Diphenyl-2-butene (II and III), and *t*-Butyl Alcohol-O-*d*[a]

Run no.	Substrate[b]	Base, *M*	Temp, °C[c]	Time, hr	% recovered[d]	% isomerizn[e]	Labile H in Starting material[e,f]	Labile H in Recovered starting material[e,f]	Atoms of D in recovered starting material
20	IV	0.316	101.3	9.0	86	55.7 ± 1.1[g]	0.99 ± 0.02	0.98 ± 0.02[h,i]	<0.04
21	I	0.353	40.0	1.0	90	12.4 ± 0.4[j]	1.02 ± 0.02	1.03 ± 0.02[h,k]	<0.04
22	II	0.353	40.0	1.0	94	4.2 ± 0.5[l]	2.03 ± 0.03	0.57 ± 0.02[k]	1.43
23	III	0.373	40.0	12.5	92	3.4 ± 0.3[m]	1.99 ± 0.03	0.76 ± 0.04[n]	1.24

[a] 0.98 atom of deuterium per molecule (combustion and falling-drop method). [b] 0.10 *M*. [c] ± 0.1°. [d] Based on recovered olefin mixture after flash distillation; corrected for weighed aliquot used for vpc analysis and removed from undistilled mixture. [e] ± mean deviation. [f] C-3 methinyl proton in IV and I, two C-1 methylene protons in II and III. Analysis by nmr integration compared to 3.0 methyl protons of each olefin. [g] Average of two analyses. II/I = 1.68 ± 0.04 (vpc); II/I = 1.86 ± 0.06 (methyl group integration of mixture recovered from preparative vpc). From the amount of I (vpc), the calculated IV/III ratio of 4.7 ± 0.2. [h] The absorption pattern of the C-3 methinyl proton was identical with that observed in the spectrum of protio material. [i] Observed IV/III = 5.5 ± 0.2 (integration of methyl groups). At high sensitivity no signal for protons at C-1 in III was visible. [j] Average of six analyses. [k] Trace of isomerization product present (see Experimental Section). [l] Average of four analyses. [m] Average of three analyses. Ratio of I/II = 4.5 ± 0.2. [n] No trace of other olefins observable.

hydrogens, with the methyl hydrogen signals as standards. Deuterium incorporation at other sites was negligible. For each olefin, the nmr method gave good precision. Table VI records the results.

Since III and IV were not separable by vpc, the mixture of these two separated from the other olefins was analyzed by nmr. In run 20, with IV as starting material, III was present but did not interfere with the analysis of IV. In run 23, with III as starting material IV was not detectable. Thus III does not isomerize appreciably to IV, a fact that justifies neglect of IV in calculation of the initial rate constants for isomerization of III (run 16, Table III).

Calculation of the Ratios of Rates of Exchange to Rates of Isomerization for Each of the 1,3-Diphenylbutenes (I–IV). The data of Table VI indicate that II and III undergo methylene proton–deuterium exchange much faster than they undergo isomerization. Conversely, IV and I isomerize to products faster than their methine protons exchange. In the following analysis, the exchange and isomerization processes for each olefin are assumed to proceed through a carbanionic intermediate, whose nature needs not be specified. In each run the amount of exchanged starting material measures the extent to which starting material (SM) has proceeded to carbanion (C) and back to exchanged starting material (SM*), or SM → C → SM*. The amount of isomerization measures the extent of process SM → C → P, where P is product. If the exchange and isomerization processes are kinetically

$$\begin{tikzcd}
\mathrm{SM} \arrow[r] & \mathrm{C} \arrow[r] \arrow[dl] & \mathrm{P} \\
\mathrm{SM}^{*} & &
\end{tikzcd}$$

independent and competing processes are each first order in substrate, the ratio of exchanged starting material to products is equal to the ratio of the corresponding rate constants, k_e/k_i,[15] for those processes. For runs 20–23, this relationship (eq 1) rigorously holds only at time zero. However, the data of Table VI allow a semiquantitative estimation of the k_e/k_i values for each run.

$$\mathrm{SM} \xrightarrow{k_i} \mathrm{P} \qquad \mathrm{SM} \xrightarrow{k_e} \mathrm{SM}^{*} \qquad \frac{\mathrm{SM}^{*}}{\mathrm{P}} = \frac{k_e}{k_i} \tag{1}$$

The kinetic scheme of eq 1 does not provide for return of products to starting material, but in none of runs 20–23 could the back reaction have been appreciable. The percent of product(s) is uniformly small compared to the relevant equilibrium percentages. Back reaction in runs 20 and 21 that involved IV and I is slow owing to rapid incorporation of deuterium into the product olefins once formed.

In each run exchanged starting material possesses the same order of reactivity as original protio-starting material. If exchange and isomerization occur at comparable rates, the amount of exchange observed for the starting material could be corrected for the exchanged starting material that has isomerized. In none of the four runs is this correction considered significant. No exchange of IV and I was observed, and the per cents isomerization in runs 22 and 23 with II and III as starting material are small compared to the observed amounts of exchange.

Table VII reports one-point, second-order rate constants for isomerization (k_i^{obsd}) calculated from the isomerization data of Table VI. The value for IV has been extrapolated to 40° with the assumption that the activation energy for isomerization in deuterated solvent is the same as that for isomerization in protio solvent (Table III).

The k_i^{obsd} values for IV and I are good approximations of the initial isomerization rates of protio substrates in deuterated solvent, for each starting material has undergone little or no exchange. However, the k_i^{obsd} values for II and III are undoubtedly low since the per cents of exchange are appreciable. As starting olefins become increasingly more deuterated, the isomerization rates will drop because of the growing influence of primary substrate isotope effects. In both runs 22 and 23 (Table VII), $k_{\text{RH}}/k_{\text{RD}}$, are expected to be large. As a model, $k_{\text{RH}}/k_{\text{RD}}$ for the isomerizations of 3-phenyl-1-butene and 3-phenyl-1-butene-3-*d* at 75° in potassium *t*-butoxide–*t*-butyl alcohol is estimated as 3.5.[6]

A corrected initial isomerization rate constant (k_i^{cor}) for II-*h* in deuterated solvent is estimated on the assumptions that k_i^{obsd} of run 21 for I is indeed the initial isomerization rate constant in deuterated solvent, and that K for I $\rightleftarrows$ II (for protio substrates) does not change appreciably with change from protio to deu-

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(15) A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 160.

Table VII. Isomerization Rate Constants and Ratios of Isotopic Exchange Rate Constants to Isomerization Rate Constants for the 1,3-Diphenylbutenes in Potassium *t*-Butoxide–*t*-Butyl Alcohol-O-*d* at 40°

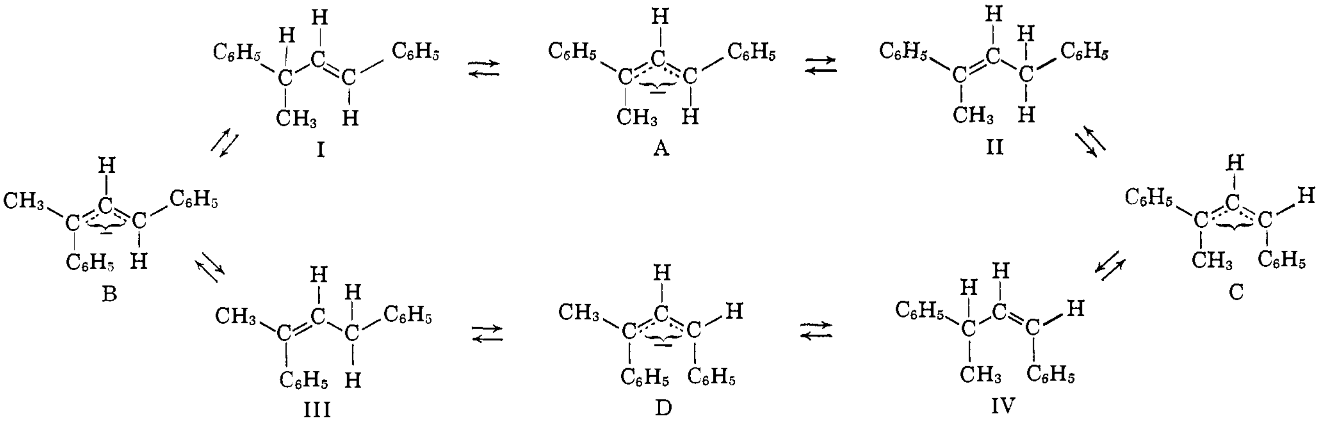
Run no.	Olefin	k_i^{obsd}, l./mole sec[a]	k_i^{cor}, l./mole sec[b]	$\left[\frac{100 \times (\text{atoms of D incorpd})}{\% \text{ isomerization}}\right]$[c]	k_e/k_i[d]
20	IV	8.6×10^{-8}[e]	...	<0.07	<0.07
21	I	$1.0 \pm 0.05 \times 10^{-4}$	...	<0.3	<0.3
22	II	$3.1 \pm 0.4 \times 10^{-5}$	6.3×10^{-5}	34	17
23	III	$2.1 \pm 0.2 \times 10^{-6}$	3.6×10^{-6}	36	21

[a] One-point, second-order rate constants for isomerization based on data of Table VI. [b] Twice the relevant rate constant for isomerization in protio solvent (Table III). [c] Calculated from data of Table VI. [d] [100 × (atoms of D incorpd)/% isomerization] × k_i^{obsd}/k_i^{cor}. [e] Observed value at 101° extrapolated to 40° with use of the activation energy derived from runs 17 and 18 of Table III.

terio solvent. Thus, in deuterated solvent at time zero, $(k_i^{cor})_{II} = (k_i^{obsd})_I/K$ (for I $\rightleftarrows$ II) = 6×10^{-5} l./mole sec.

The rate constant of run 15 for isomerization of I in protio solvent and the rate constant of Table VII for isomerization of I in deuterio solvent serve to establish the solvent isotope effect, $(k^{ROD}/k^{ROH})_I = 2$. As a result the value of $(k_i^{cor})_{II\text{-}h}$ in deuterated solvent comes out to be about twice the value of k_2 for II obtained in protonated solvent (Table III). The fact that in run 22, k_i^{obsd} for II in deuterio solvent is the same as the isomerization rate of II-*h* in protio solvent (Table III) suggests that when about 1.4 atoms of deuterium have been incorporated into II, the isomerization rate-retarding effect of deuterium incorporation has just counterbalanced the rate-enhancing solvent isotope effect.

Chart I



The same cancellation of solvent and primary isotope effects is visible in the rate data for isomerization of III. In run 16 for III-*h* in protonated solvent, $k_2 = 1.8 \times 10^{-6}$, whereas in run 23 for III-*h* + III-*d* in deuterated solvent, $k_i^{obsd} = 2.1 \times 10^{-6}$. The amount of deuterium incorporated into III in run 23 was slightly less than that incorporated into II in run 22. This difference parallels the small difference in the two k_i's for III. These facts suggest that the solvent isotope effect $(k^{ROD}/k^{ROH})_{III} \sim 2$. Use of this relationship allows the estimate $(k_i^{cor})_{III} = 3.6 \times 10^{-6}$ l./mole sec to be made ($2 \times 1.8 \times 10^{-6}$, k_2 value for III-*h* in protio solvent). Table VII records the values of k_i^{cor}.

Table VII also includes values of the ratio [100 × (atoms of deuterium incorporated)/% isomerization] calculated for each olefin from the data of Table VI. This ratio serves as a good upper limit for k_e/k_i with I and IV as starting materials. With II and III as starting materials, this ratio is high because k_i^{obsd} is less than the initial isomerization rate, k_i^{cor}. A more accurate estimate of k_e/k_i for II and III is obtained from the relationship, $k_e/k_i = [k_i^{obsd}/k_i^{cor}][100 \times$ (atoms of deuterium incorporated)/% isomerization]. These final estimates of the ratios of exchange to isomerization rate constants (k_e/k_i) are listed in Table VII.

Discussion

In the following sections, these subjects are treated in turn: models for the mechanism of the isomerization reactions; fits of the data to the models; failure of ground-state stabilities to correlate with either position of protonation of allylic anions or with relative kinetic acidities of tautomers.

Mechanistic Models for the Base-Catalyzed Reactions of the 1,3-Diphenylbutenes (I–IV). Chart I outlines a mechanistic scheme which will serve as a model for correlating the equilibrium, kinetic, and isotopic exchange data for interconversion of olefins I–IV. In this scheme, each olefin by proton removal can generate either of two allylic carbanions which differ only in the spacial disposition of the attached groups. Proton capture by each of the carbanions (A, B, C, and D) produces two olefins, depending on the point of capture. For example, I can give either anion A or B, depending on the conformation of I at the time of proton removal. Anion A, by proton capture, can give either I or II, depending on whether charge is neutralized at the methine or methylene carbon. In the following discussion, these reasonable assumptions are made: (1) the ground-state conformations of olefins I–IV equilibrate much faster than carbanions are generated; (2) the transition states for carbanion formation resemble the carbanions in geometry; (3) charge delocalization in the carbanions tends to make the systems as planar as steric effects permit. Purposefully excluded from Chart I is any path in which one carbanion passes directly to a second. Evidence will be presented that carbanions A and B are protonated much faster than they interconvert, but evidence on this point is lacking for C and D.

These carbanions in *t*-butyl alcohol undoubtedly exist as ion pairs and are hydrogen bonded.[6] The cations and solvent molecules are omitted from Chart I and are not needed to rationalize the data.

The rates at which the four carbanions undergo isomerization, coupled with the equilibrium data for the four olefins, allow inferences to be made about the relative stabilities of the four carbanions. Implicit in this treatment is the reasonable assumption that the activation energies for proton capture by the four carbanions are very low compared to those for proton abstraction, and that the former change much less than the latter with structure.

Of the four olefins, I and II are the most thermodynamically stable and the most readily interconverted. Only these two olefins have carbanion A available as an initial intermediate. Carbanions B and D are available to olefin III. This olefin is slightly less thermodynamically stable than I or II, but it undergoes isomerization at a rate an order of magnitude slower than either I or II. The fourth olefin, IV, is markedly less thermodynamically stable than the other three. With only carbanions C and D initially available as intermediates, IV isomerizes at by far the slowest rate. These facts clearly indicate the following stability order for the carbanions: $A > B > C \gtrless D$.

This stability order harmonizes with that predicted upon consideration of the steric interactions that exist within each carbanion. Two types of steric interactions differentiate the isomeric allylic anions: a pair of 1,2 interactions across the *top*, and a single 1,3 interaction across the *bottom* of the anion. The above stability order suggest that the 1,3 steric interaction is the dominant factor controlling the stability of each carbanion. Thus the 1,3 steric interactions increase in the same order that the carbanion stabilities decrease: $CH_3{>}\!{-}\!{<}H < C_6H_5{>}\!{-}\!{<}H < CH_3{>}\!{-}\!{<}C_6H_5 < C_6H_5{>}\!{-}\!{<}C_6H_5$.

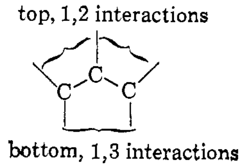
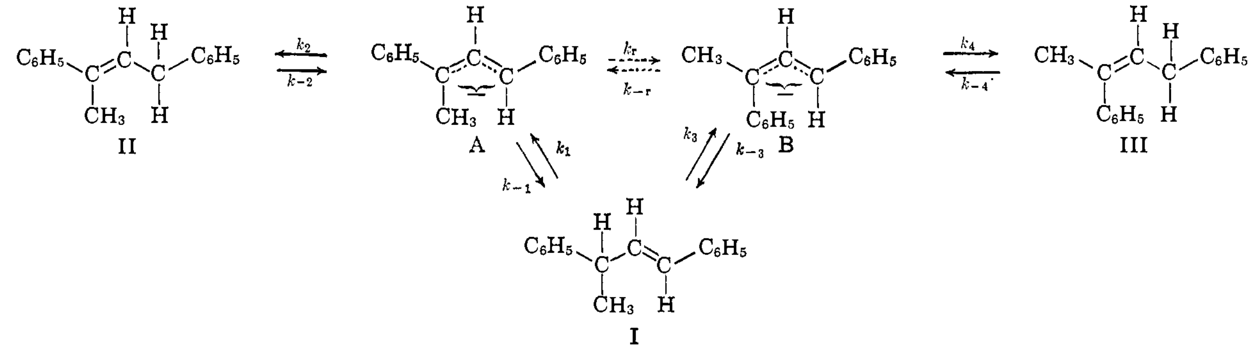
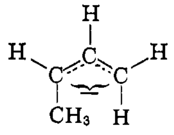
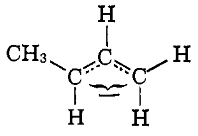


Chart II



A number of alkenes that lead to mono- and dialkyl-substituted allylic anions have been shown to rearrange largely to *cis* products rather than to the more thermodynamically stable *trans* products.[16] As an explanation applicable to the isomerization of 1-butene to predominantly *cis*-2-butene, it has been proposed that the *cis*-butenyl anion is intrinsically more stable than the *trans* anion because of favorable dipole interactions in the former.[17]


cis-anion


trans-anion

A stability order for A–D based on the rationale that methyl is better placed on the bottom of an allylic anion leads to the prediction that A > B, C > D, and that C > B in stability. The last prediction is in conflict with observation. The stability order is undoubtedly a composite of pole–dipole interactions, direct steric effects, and steric effects resisting the coplanarity requirement for full charge delocalization.

Fits of Data to the Models for the Mechanism of the Base-Catalyzed Reactions of the 1,3-Diphenyl-1-butenes. In Chart I, olefins I and IV initially have available carbanions that are adjacent to each other in the predicted stability order. Thus I can give A or B, and IV can give C or D. In contrast, II and III initially have available only carbanions that are not adjacent to each other. Thus II can give A or C, and III, B or D. Very likely II and III react almost exclusively through the more stable carbanions, A and B. If the kinetically most sluggish olefin (IV) is temporarily disregarded, and if the above deduction is valid, the mechanism of Chart I reduces to that of Chart II.

If the rate constants for direct carbanion interconversion (k_r and k_{-r}) are large compared to the protonation rate constants (k_{-1}, k_{-2}, k_{-3}, and k_{-4}), the two configurationally isomeric carbanions become kinetically indistinguishable from one another. Only one intermediate then needs to be postulated to achieve internal consistency among the kinetic and exchange data. However, if one intermediate is to describe the reactions of I–III in Chart II, the ratios of products derived from that intermediate must be independent of the olefin employed to generate that intermediate.

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(16) (a) A. Schreisheim and C. A. Rowe, Jr., *Tetrahedron Letters*, 10, 405 (1962); (b) M. D. Carr, J. R. P. Clarke, and M. C. Whiting, *Proc. Chem. Soc.*, 333 (1963).

(17) (a) S. Bank, A. Schriesheim, and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, 87, 3244 (1965); (b) S. Bank, *ibid.*, 87, 3245 (1965).

The k_e/k_i ratios of Table VII clearly do not meet this requirement. The major product from II is deuterated II, while the major product from III is deuterated III. These facts negate the possibility of rapidly equilibrating carbanions and indicate unambiguously that A and B are distinct species that protonate faster than they interconvert.

This conclusion is stated in kinetic terms as follows. Making use of the definitions of Chart II, k_e and k_i are related to the rate constants for carbanion generation and capture by eq 2-4, k_r and k_{-r} being small valued compared to k_{-1}, k_{-2}, k_{-3}, and k_{-4}. Thus the ratio, k_e/k_i, for each olefin measures the "collapse ratio" of

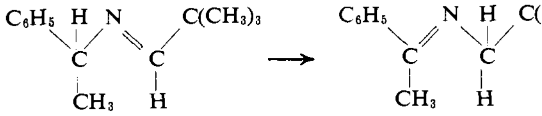
$$[k_e]_{II} = k_2[k_{-2}/(k_{-1} + k_{-2})] \qquad [k_e]_{III} = k_4[k_{-4}/(k_{-3} + k_{-4})] \quad (2)$$

$$[k_i]_{II} = k_2[k_{-1}/(k_{-1} + k_{-2})] \qquad [k_i]_{III} = k_4[k_{-3}/(k_{-3} + k_{-4})] \quad (3)$$

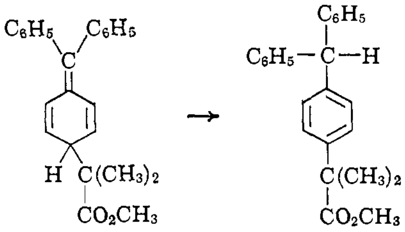
$$[k_e/k_i]_{II} = k_{-2}/k_{-1} \qquad [k_e/k_i]_{III} = k_{-4}/k_{-3} \quad (4)$$

the discrete allylic carbanion formed from that olefin. The ratios of k_e/k_i of Table VII for the four olefins are equal to the collapse ratios of the relevant carbanions with a correction.

Recently base-catalyzed allylic rearrangements have been shown to occur with varying amounts of intramolecularity.[18] Since isotopic exchange either greatly leads isomerization in rate, or products once formed exchange under rearrangement conditions, the amounts of intramolecularity associated with isomerizations of olefins I-IV cannot be determined. However, fractions of intramolecular transfer for potassium *t*-butoxide catalyzed isomerizations in *t*-butyl alcohol-O-*d* have been measured in a variety of systems closely related to I-IV. Isomerization of α-benzylstyrene to *cis*-α-methylstilbene at 75° gave 0.55; to *trans*-α-methylstilbene, 0.36.[5] For 3-phenyl-1-butene to *cis*-2-phenyl-2-butene at 75° the intramolecularity was 0.51. For imine VIII to imine IX at 75°, a value of 0.47 was measured.[19] At 25° the 1,5 proton shift of X to XI was 0.50.[18] Allylbenzene to *trans*-propenylbenzene isomerization at 25° gave a value of 0.59.[20]



VIII IX



X XI

The fractions of intramolecularity are all close to a value of 0.5, and the pK_a values of these compounds probably lie on both sides of olefins I-IV. Therefore, this value is adopted as a reasonable estimate of the fraction of intramolecularity in the isomerizations of olefins I-IV. It is also reasonable to assume that the fraction of intramolecularity is a property of the allylic anion and not of the parent olefins. In other words, if an olefin isomerizes with a certain fraction of intramolecularity, collapse of carbanion to starting olefin also occurs with the same fraction of intramolecularity.

Table VIII. Collapse Ratios Derived from Runs 20–23 and Values of k_e^{cor} and k_{ionzn} for the 1,3-Diphenylbutenes in Potassium *t*-Butoxide–*t*-Butyl Alcohol-O-*d* at 40°

Run no.	Substrate	Collapse ratio[a]	k_e^{cor}, l./mole sec[b]	k_{ionzn}, l./mole sec[c]
20	IV	<0.14	$<1.2 \times 10^{-8}$ [d]	9×10^{-8}
21	I	<0.6	$<6 \times 10^{-5}$	1×10^{-4}
22	II	34	2.1×10^{-3}	2.1×10^{-3}
23	III	42	1.5×10^{-4}	1.5×10^{-4}

[a] Calculated from k_e/k_i ratios of Table VII, and an assumed value of I_h of 0.5. [b] Defined as k_i^{cor} × collapse ratio. [c] Defined as ($k_e^{cor} + k_i^{cor}$). [d] At 40° by extrapolation of k_i^{obsd} at 101°; see Table VII.

Incorporation of this correction into one of the kinetic expressions of eq 4 provides eq 5, where I_h represents the fraction of intramolecularity characteristic of the isomerization, and k_{-2}/k_{-1} is the collapse ratio of anion A. Table VIII lists values of the collapse ratios obtained from each of runs 20–23. The values for runs 21 and 22 that involve I and II as starting materials are interpreted as indicating the collapse ratio of carbanion A. The limiting value of k_{-1}/k_{-2} of <0.6 for run 21 is consistent with the value of $k_{-2}/k_{-1} = 34$ for run 22, or $k_{-1}/k_{-2} = 0.03$. The collapse ratio obtained from run 23 with III as starting material is assigned to carbanion B. The data of run 20 with IV as starting material will be discussed later.

$$k_{-2}/k_{-1} = \frac{1}{1 - I_h}[k_e/k_i]_{II} = 2[k_e/k_i]_{II} \quad (5)$$

Table VIII also includes values of k_e^{cor}, which is defined in eq 6. The values of k_e^{cor} measure the rate of formation of returned (both deuterio and protio) starting material.

$$k_e^{cor} = k_i^{cor}(k_e/k_i)[1/1(1 - I_h)] \quad (6)$$

Also listed in Table VIII are rate constants for "ionization" (k_{ionzn}) of the four olefins; k_{ionzn} is defined as the sum of k_e^{cor} and k_i^{cor}, and measures the rate of proton loss, or the kinetic acidity, of each olefin.

Since no exchange of starting material was detected in runs 20 and 21, k_{ionzn} for both I and IV is equal to the rate constant for isomerization of each olefin in deuterated solvent. Since exchange of both II and III was much faster than isomerization, k_{ionzn} for these two olefins equals k_e^{cor}.

These estimates of the kinetic acidities, together with those of the collapse ratios and the values of the ground-state, free-energy differences (Table II) define the energy diagram of Figure 1 for the reactions of protio-II, I, and III in 1 *M* potassium *t*-butoxide–*t*-butyl alcohol-O-*d* at 40°. The free energies of the ground and transition states in Figure 1 are established experimentally. The carbanion free energies are not, and

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(18) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, p 176.

(19) D. J. Cram and R. D. Guthrie, *J. Am. Chem. Soc.*, **87**, 397 (1965).

(20) S. W. Ela and D. J. Cram, *ibid.*, **88**, 5791 (1966).

their positions relative to one another are illustrated in accordance with Hammond's postulate.[21]

The transition state for direct conversion of carbanion B to A must lie above the highest of the four transition states (that between I and B) of Figure 1. The transition state between I and B is established from the estimated initial rate constant for disappearance of III in deuterated solvent (run 23). Both I and II were produced and in a ratio (I/II) of 4.5. Under the conditions of run 23, I once formed is expected to isomerize to II. But if it is assumed that the II produced arose entirely from direct isomerization of B to A, then a lower limit of the transition-state energy for *carbanion isomerization* may be estimated. The estimated initial rate constant for disappearance of III was 3.6×10^{-6} l./mole sec, division of which by 4.5 yields a rough estimate of 8.0×10^{-7} l./mole sec for the rate constant of the process III → B → A → II. This rate constant corresponds to a ΔF^* of 27.0 kcal/mole at 40° in 1 *M* base. This limiting value for the transition-state energy for conversion of B to A is higher by 3.2 kcal/mole than the transition-state energy for protonation of B to form III. Thus B converts to A not more than once every 175 times it is formed. Probably this value is much greater than 175, since much, if not all, of II produced involves I as intermediate.

The estimate that the lower limit of the transition state for interconversion of A and B is 27.0 kcal/mole above the ground-state energy of III sets lower limits for the activation energies of the processes A to B and B to A. If the free energy of A is no lower than the transition state between it and II (protonation of A to give II has near-zero activation energy), then the activation energy for conversion of A to B is no less than (27.0 + 0.8 − 22.2) or 5–6 kcal/mole. Likewise, if B is no lower than 23.8 kcal/mole above III, the activation energy for B → A is no lower than about 3 kcal/mole.

The relative rates at which I isomerizes to II and III may be estimated in several ways. If it is assumed that I is the sole product in the isomerization of III in protio solvent, division of the rate constant for isomerization of III (run 16) by the I/III equilibrium value gives a calculated rate constant of 8.5×10^{-7} l./mole sec for the isomerization of I to III. This value is about $^1/_{60}$th the value of the rate constant for the isomerization of I to II in protio solvent (run 15). Application of the same procedure to the data obtained in deuterated solvent reveals that I → II is about 70 times faster than I → III. These values agree well with the observation that in protio solvent (run 15), after 35% of I was converted to II, about 0.5% of suspected III was formed. The data for the partitioning of I also compare well to the value of 60 found for the partitioning of 3-phenyl-1-butene to *cis*-2-phenyl-2-butene in preference to *trans*-2-phenyl-2-butene obtained in the same solvent–base system at 75°.[6] The fact that I forms A 60 times as fast as it forms B strengthens the hypothesis that II reacts exclusively through A, and III through B.

The behavior of *cis*-1,3-diphenyl-1-butene (IV) is unique compared to the other three isomers. Although IV is of the highest energy of the four olefins (only about 1% exists in the equilibrium mixture), it isomerizes at a rate considerably slower than the rates for the other isomers (Table III). The activation parameters or IV (runs 18 and 19) closely resemble those found for the isomerization of α-benzylstyrene in the same solvent–base system;[5] in particular, the values for ΔS are both $-10(\pm 4)$ eu.

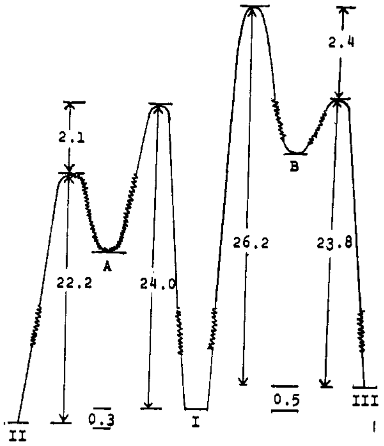

Figure 1. Reaction profile for the isomerization and exchange reactions of *cis*-1,3-diphenyl-2-butene (II), *trans*-1,3-diphenyl-1-butene (I), and *trans*-1,3-diphenyl-1-butene (III) in 1 *M* potassium *t*-butoxide–*t*-butyl alcohol-O-*d* at 40°. Numbers express free energy in kcal/mole.

Compound IV isomerizes more slowly by a factor of about 700, than its *trans* isomer (I), although both IV and I undergo isomerization faster than isotopic exchange (runs 20 and 21). Thus the difference in rates reflects the difference in kinetic acidities of the two olefins. The difference in free energies of the transition state for each olefin isomerization is the sum of the difference of the free energy of activation ($\Delta\Delta F^*$) and of the difference in ground-state free energies ($\Delta\Delta F$), and amounts to about 6 kcal/mole at 40° in 1 *M* potassium *t*-butoxide–*t*-butyl alcohol. This difference is ascribed mainly to the difference in the 1,3 steric interactions across the bottom of the two configurationally isomeric carbanions that are formed.

Similar steric interactions are present (but to lesser degrees) in the ground states for the two olefins. The magnitude of the nmr coupling constant between vicinal vinyl and allylic protons depends on their conformation.[22] If the conformer in which the two protons are *trans* is highly preferred, the coupling constant is in the neighborhood of 11 cps. If no one conformer is preferred (*e.g.*, with 1-butene), the coupling constant is about 6.5 cps. The coupling constants for the adjacent allylic and vinyl protons of IV and I are 10(±0.5) and 7(±0.5) cps, respectively. These data indicate that little or no conformational preferences exist in I, but that in IV the conformation with the two protons *trans* to each other predominates. This preference reflects the bulk of the two phenyl groups. As IV proceeds toward the geometry of the transition states for proton removal, 1,3 interactions between the two phenyl groups (D as anion) or the phenyl and methyl groups (C as anion) must increase markedly.

One piece of experimental evidence suggests that IV gives anion C in preference to D. The ratios of II to I produced in run 17 (deuterated solvent at 100°, Table

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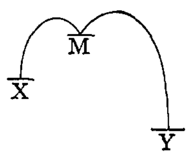
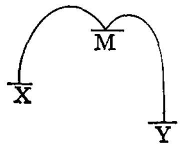
(21) G. S. Hammond, *J. Am. Chem. Soc.*, 77, 334 (1955).

(22) A. A. Bothner-By, C. Naar-Colin, and H. Günther, *ibid.*, **84**, 2748 (1962).

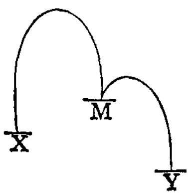
$$X \underset{k_{-a}}{\overset{k_a}{\rightleftarrows}} M \underset{k_{-b}}{\overset{k_b}{\leftrightarrows}} Y$$



Case 1: $Y/X > 1$; $k_{-b}/k_{-a} < 1$; $k_a/k_b >> 1$



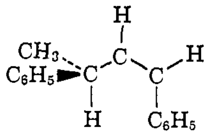
Case 2: $Y/X > 1$; $k_{-b}/k_{-a} > 1$; $k_a/k_b > 1$



Case 3: $Y/X > 1$; $k_{-b}/k_{-a} >> 1$; $k_a/k_b < 1$

Figure 2. Three possible reaction-coordinate–free-energy profiles for the interconversion of two ground states through a single intermediate.

V) undergo a steady decrease from 2.5 at 7% reaction to 1.7 at 47% reaction. This fact suggests that II is an initial product and implicates C as the probable intermediate. Preconceptions based on the relative strains in C and D also point to C as a more probable intermediate than D.



preferred conformer of IV

The differences in reactivities of the four 1,3-diphenylbutenes are strikingly larger than the differences in their ground-state energies and do not correlate with the latter. Thus detailed description of both kinetic and thermodynamic behavior is necessary for mechanistic characterizations of base-catalyzed isomerization reactions of olefins.

Failure of the Ingold Rule to Correlate the Kinetic and Thermodynamic Acidities of the 1,3-Diphenylbutenes and the Collapse Ratios of Their Derived Anions. In the interconversion of two tautomers, X and Y, through a single high-energy intermediate, M, three kinds of reaction-coordinate–free-energy profiles, can be envisioned. These are drawn in Figure 2. Equation 7

$$X \underset{k_{-a}}{\overset{k_a}{\rightleftarrows}} M \underset{k_{-b}}{\overset{k_b}{\leftrightarrows}} Y$$

defines the rate and equilibrium constants that relate X, M, and Y. The ratio k_a/k_b is the ratio of rate

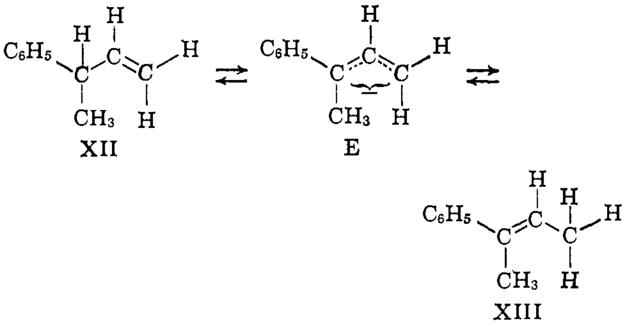
$$K = \left(\frac{k_a}{k_b}\right)\left(\frac{k_{-b}}{k_{-a}}\right) = \frac{(Y)}{(X)} \tag{7}$$

constants for formation of M and as applied to base-catalyzed proton tautomerism is termed the *kinetic acidity ratio*. The ratio k_{-b}/k_{-a} is the ratio of rate constants for formation of tautomers from anion and is labeled the *collapse ratio*. If K is arbitrarily fixed as greater than unity, the kinetic acidity collapse ratios can be varied in three ways and the conditions of eq 7 still be satisfied. These three cases correspond to the three profiles of Figure 2.

Case 1 is that formulated by Ingold[3] in which the anion collapses preferably to the thermodynamically less stable tautomer, which is the kinetically stronger acid. Case 2 violates the first part of Ingold's rule but not the second; that is, anion protonation favors the thermodynamically stable tautomer, which is the kinetically weaker acid. Case 3 violates both parts of Ingold's rule; the anion predominantly gives the thermodynamically more stable tautomer, which is the kinetically stronger acid.

Estimates of the collapse ratios of carbanions A and B indicate that A forms II about 34 times faster than it forms I, and that B forms III about 42 times faster than it forms I. Although the uncertainties connected with the data and with the undetermined fractions of intramolecularity do not allow differentiation of these values, the salient point is that protonation occurred at the secondary benzylic carbon 30 to 40 times faster than at the tertiary benzylic carbon.

These collapse ratios are numerically about the same as the collapse ratio of carbanion E present in the conversion of 3-phenyl-1-butene (XII) to *cis*-2-phenyl-2-butene[6] (XIII). In potassium *t*-butoxide-*t*-butyl alcohol-O-*d* at 75°, the collapse ratio of E favors XIII by a factor of 35 to 40.[23] At equilibrium, XII/XIII ~ 0.002.[24]



These three systems, which all possess similar-valued collapse ratios, illustrate the three possible energy profiles of Figure 2. Interconversion of I and III through B follows Ingold's rule and case 1 of Figure 2. Interconversion of XII and XIII follows the first half of Ingold's rule but violates the second, and is represented by case 2 of Figure 2. Interconversion of II and I through A violates both parts of Ingold's rule and is represented by case 3 of Figure 2. These facts suggest that the factors that dictate the relative ground-state stabilities play little part in determining the relative transition-state stabilities. Clearly, the effects present in the carbanions themselves play the major role in controlling the energies of the transition states.

The imbalance in the collapse ratios of these systems appears to be due to the common methyl substituent.

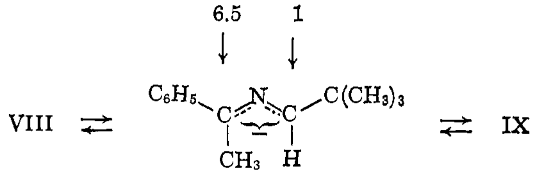
[23] This value is derived by application of the refined kinetic treatment of ref 5 to the data of run 6, ref 6.

[24] The rate constants calculated for runs 6 and 19 of ref 6 measure the kinetic acidities of XII and XIII, and $k_{XII}/k_{XIII} \sim 15$. Multiplication of this value by the collapse ratio (35–40) gives the reciprocal of XII/XIII.

Carbanion A is symmetrical except for the methyl group. Substitution of hydrogen for the methyl group of B produces a carbanion that is unsymmetrical only in the sense that one of the two phenyl groups lies on the *top* of the anion and the other at the *bottom*. The collapse ratio of the symmetrical anion must be unity; that of the unsymmetrical anion is expected to be close to unity, since no significant difference exists in the collapse ratios of A and B. Since the collapse ratio of carbanion E is about equal to that of A and B, the imbalance in the collapse ratio of E is also primarily due to the methyl group. A major implication of this conclusion is that a phenyl substituent has little effect upon the collapse ratio of an allylic anion. This inference is experimentally tested in the paper that follows.[20,25]

The collapse ratios of carbanions A, B, and E are compatible with the hypothesis that the negative charge in these anions is largely concentrated at the ends of the three-carbon allylic system, and that the electron-releasing effect of a methyl group on one of these carbons favors accumulation of charge on the other. If the pK_a's of the carbon acid and that of the alcohol that acts as solvent differ by many units (*i.e.*, 10), protonation must occur with very little activation energy, and the solvated carbanion serves as a model for the transition state. Since solvation by hydrogen bonding is higher where charge is concentrated, protonation should also be favored at this position, the end carrying the least number of alkyl groups.

If the steric effect of a methyl group should influence the collapse ratio, that of a phenyl should be even larger, and yet the phenyl group appears to have minor influence. Perhaps the best case of a steric effect possibly influencing a collapse ratio lies in the system composed of imines VIII and IX connected by anion F.[19] At 75° in potassium *t*-butoxide-*t*-butyl alcohol-O-*d*, collapse of F to the covalent state favors protonation at the benzyl carbon by a factor of 6 or 7. However, a prediction of this collapse ratio based solely on charge-density arguments is qualitatively in the right direction. Taft[26] lists σ^* values for *t*-butyl and methyl groups as -0.165 and -0.100, respectively.



F

Alkyl groups play a dual role in directing protonation to the less substituted end of an allylic anion. Alkyl substituents stabilize double bonds by their inductive effect, and thus are expected to partially localize the double bond of the allylic anion at the end more highly substituted with alkyl groups. Thus, in allylic anions, the two aspects of the inductive effect of alkyl groups reinforce one another and provide fairly high collapse ratios favoring protonation at the less substituted carbon atom.

In allylic cations, the two aspects of the inductive effect of alkyl substituents oppose one another, and as expected, collapse ratios are much lower valued than for allylic anions. Thus, in cases where the same composition of products was obtained from solvolysis of isomeric substituted allylic halides, the collapse ratios in hydroxylic solvents are small.[27] For example, with butenyl cation in water, the ratio of secondary to primary alcohols produced was 1.9; in acetic acid, the ratio of acetates was 1.2.

Experimental Section

General. Nuclear magnetic resonance spectra were recorded with a Varian A-60 instrument. Solvent for all spectra was spectral-grade carbon tetrachloride with 2–5% added tetramethylsilane. The percentages given throughout the experimental refer to the weight of sample in total weight of solution. Infrared spectra were recorded with a Beckman IR-5 machine, with the exception of the spectra of the 1,3-diphenylbutenes which were recorded on a Perkin-Elmer 421 instrument. The solvent was carbon tetrachloride unless otherwise stated. Concentrations are expressed as percentages of the weight of the sample divided by the weight of solution. A 200-w medium-pressure Hanovia lamp (Type No. 54A36) served as light source in the photoisomerization experiments. All melting points are uncorrected unless otherwise stated. All boiling points are uncorrected. Anhydrous magnesium sulfate was uniformly used as drying agent; "brine" refers to a saturated aqueous solution of sodium chloride.

Solvents and Bases. Previously described procedures[6] were employed for purification of *t*-butyl alcohol, preparation of *t*-butyl alcohol-O-*d*, and preparation of basic solutions of both. The *t*-butyl alcohol-O-*d* contained 0.98 atom of deuterium per molecule, as determined by the combustion and falling-drop analysis performed by J. Nemeth of Urbana, Ill.

Vapor Phase Chromatography. Various high-temperature vpc liquid phases were found to give little or no separation of II and I before Epon 1001, an epoxy resin of bisphenol A and epichlorohydrin, was found to give complete separation of the two olefins. Unless otherwise specified, analyses were carried out on 10 ft × 0.25 in. aluminum columns packed with 20% Epon 1001 on 60–80 mesh firebrick. The columns were installed in a Wilkens A90P gas chromatograph (thermal conductivity detection) coupled to a Leeds and Northrup 1-mv recorder equipped with a disk integrator. Column oven temperatures ranged between 205 and 220°. Injector and detector oven temperatures were 250 and 275°, respectively, and the flow rate of helium carrier gas was 100 ml/min.

Slow bleeding of the liquid phase was observed under these conditions; during an analysis the base line was steady, but after 18 hr of running time the retention times of the olefins were appreciably shortened, and II and I were incompletely resolved. When complete separation of these isomers was no longer possible, a freshly packed column was installed and preconditioned for 6 hr at operating temperatures with a low helium flow. Good precision was obtained for multiple analyses of the same sample on different columns.

No attempt was made to correct for possible differences in thermal conductivities among the four isomeric olefins. Thus, for all analyses, peak area ratios are assumed to equal molar ratios of the 1,3-diphenylbutenes.

Some of the olefin analyses during the synthetic work were performed on a 5 ft. × 0.25 in. aluminum column packed with 20% Epon 1001 on 60–80 mesh firebrick and installed in a Perkin-Elmer Model 154 machine (thermal conductivity). This 5-ft column is designated "column D."

Preparative vpc work was carried out on a machine built in these laboratories. Three Epon 1001 columns were used. For preparative separation of II from I, a 6 ft × 3/8 in. aluminum column (designated column A) packed with 20% Epon 1001 on 60–80 mesh firebrick was employed. With sample sizes of about 80 mg. of mixture, close to complete separation of the isomers was obtained. For synthetic work either a 4 ft × 0.75 in. column (column B) packed with 10% Epon 1001 on 60–80 mesh firebrick, or a 6 ft. × 0.75 in. column (column C) packed with the same mixture was used.

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(25) The collapse ratios of the isomeric 1-phenylpropenyl anions were determined.

(26) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 595.

(27) R. H. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956).

3-Phenylbutanoic Acid.[28] Anhydrous aluminum chloride (Baker and Adamson sublimed reagent), 420 g, was added in portions to a cooled (ice–brine bath) solution of crotonic acid (Eastman technical grade, bp 179–182°, cut from one short-path distillation), 129 g, in 600 ml of molecular seive dried benzene. When aluminum chloride addition was complete, anhydrous hydrogen chloride was gently bubbled through the mixture for 30 min. The flask was capped with a drying tube and the mixture allowed to stand for 92 hr. The product was isolated in the usual way[28] to yield 199 g (81%) of 3-phenylbutanoic acid, bp 112–114° (0.25 mm).

1,3-Diphenyl-1-butanone. Phenylmagnesium bromide was prepared under nitrogen from 1.51 g, of magnesium turnings, 9.67 g, of bromobenzene (Eastman White Label), and 40 ml of molecular seive dried diethyl ether in a 250-ml flask equipped with Teflon stirring bar and condenser. The mixture was cooled to 0° and cadmium dichloride (anhydrous, Baker and Adamson, dried at 110° and stored over phosphorus pentoxide), 6.14 g, was added. After 5 min the mixture was warmed and refluxed for 2 hr. At this point most of the ether was allowed to evaporate, and 50 ml of molecular seive dried benzene was introduced into the flask. The water-bath temperature was raised to boiling and, after one-half of the benzene had distilled, the remainder was allowed to reflux. After 15 min the mixture was again cooled to 0° and 3.00 g of 3-phenylbutyroyl chloride in 25 ml of dry benzene was added over 0.5 min. After 1 min the hot-water bath was reinstalled and the mixture refluxed for 15 min. The flask and mixture were then quickly cooled and the reaction was hydrolyzed with ice and, when a water layer was visible, 40 ml of 3 *M* sulfuric acid.

The mixture was filtered through a plug of glass wool into a 500-ml separatory funnel. The mixture was shaken and separated, and the aqueous phase was washed with ether and discarded. The combined organic phases were washed with water, saturated sodium bicarbonate solution, and brine, then dried, filtered, and evaporated under reduced pressure. The residual yellow oil gave crystals from pentane (in later experiments hexane was used more advantageously); two crops gave 2.68 g of 1,3-diphenyl-1-butanone, mp 72.5–73.5°, lit.[29] 72–73°.

Evaporation of the mother liquors from the second crystallization gave a light yellow solid that was chromatographed on 30 g of neutral activity 1 alumina to yield 0.4 g of biphenyl, 0.18 g of ketone, and 0.16 g of material presumed to be 1,1,3-triphenyl-1-butanol. The total yield of recovered ketone was 2.86 g, 78% of theory.

Similar runs were performed on up to 40 g of acid chloride with yields in the range of 65–75%. The larger runs necessitated longer times for the addition of the acid chloride, but the reflux time following addition was closely held to 15–20 min.

Mixture of *threo*- and *erythro*-1,3-Diphenyl-1-butanols. A solution of 1,3-diphenyl-1-butanone, 15 g, in 280 ml of ether was slowly added to a stirred mixture of 1.4 g of lithium aluminum hydride in 200 ml of ether at 0° under nitrogen. After addition was complete the mixture was warmed and refluxed for 1 hr. The reaction mixture was cooled and hydrolyzed first with ice and then with 1 *N* sulfuric acid. The mixture was transferred to a separatory funnel and shaken; the organic phase was separated from the aqueous phase and the latter twice washed with ether. The combined organic extracts were washed with water, saturated bicarbonate, and brine solutions, then dried, filtered, and evaporated. Flash distillation of the viscous light yellow oil gave 14.1 g (94%) of colorless liquid.

The product showed bands in the infrared spectrum (chloroform) at 2.8, 2.9, 3.3–3.5, 6.25, 6.7, 6.9, and 7.3 μ. The nuclear magnetic resonance spectrum (20%) of the diastereomeric mixture showed a distorted singlet (10 H) at γ 2.9, a multiplet (1 H) at 5.5–6.0, a singlet (1 H) at 7.1 superimposed upon a multiplet (1 H) at 7.0–7.5, distorted quartet (2 H) at 8.0–8.4, and a doublet (3 H) centered at 8.9. Thin layer chromatography of the diastereomeric mixture on silica gel in a number of solvent mixtures uniformly showed only two spots of similar R_f values and of similar intensity (iodine chamber). Under the analytical vpc conditions used for the olefin mixtures, the diastereomeric mixture gave only two incompletely resolved peaks of roughly equal size and of retention times roughly three times that of I.

***trans*-1,3-Diphenyl-1-butene (I).** A mixture of the diastereomeric 1,3-diphenyl-1-butanols, 5.03 g, and 56 ml of acetic acid, 2% in acetic anhydride and 0.1 *M* in *p*-toluenesulfonic acid monohydrate (Eastman White Label), was placed in a stoppered flask which was placed in a 100° bath for 3 hr. The reaction mixture was cooled and poured into a separatory funnel containing 400 ml of pentane and 400 ml of water. After the mixture was shaken and separated, the aqueous phase was washed with one 200-ml portion of pentane. The combined organic extracts were washed with 300-ml portions of water and brine, then dried, filtered, and evaporated on the steam bath under nitrogen.

The crude reaction mixture, 4.64 g, was chromatographed on 100 g of silica gel using a 5% ether–95% pentane solution. Two 250-ml fractions gave 4.40 g of olefin mixture that was purified by preparative vpc, column B, 160°, 16 psi. Flash distillation of the major component gave 3.51 g, or 76% of theoretical.

The distilled olefin (I) showed no traces of isomeric olefins by analytical vpc under conditions that would have detected 0.1% of IV, III, or 2,4-diphenyl-1-butene, and 0.2% of II.

The olefin, n^{25}D 1.5920, showed bands in the infrared, 20%, at 3082 (medium), 3061 (medium), 3025 (strong), 2966 (strong), 1645 (weak), 1371 (medium), and 965 (strong) cm^{-1}. The nuclear magnetic resonance spectrum, 29%, gave a singlet (10 H) at τ 2.88, a closely spaced and unsymmetrical pair of doublets (2 H, J = 2.5 cps) at 3.67–3.78, a partially resolved quartet of triplets (1 H J, = 7 and 2.5 cps) centered at 6.50, and a doublet (3 H, J = 7 cps) at 8.64. The ultraviolet spectrum in hexane showed λ_{max} 252 mμ (ϵ 21,500), 284 (1800), ad 293 (1300). *Anal.* Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.16; H, 7.88.

Photoisomerization of *trans*-1,3-Diphenyl-1-butene (I) to *cis*-1,3-Diphenyl-1-butene (IV). Solutions of I, 0.84 g, and benzene, 8.0 ml, 0.05 *M* in α-naphthyl phenyl ketone[30] (mp 75.5–75.8°), were added to three 18 × 150 mm Pyrex test tubes that had been drawn out to facilitate sealing and fitted with 10/30 joints. The tubes were degassed, sealed, thawed, and irradiated for 48 hr. The tubes were then opened and the contents chromatographed on 75 g of silica gel with 95% pentane–5% ether solution. Three 250-ml fractions yielded 2.62, 0.07, and 0.16 g of material, respectively. The first fraction showed two peaks by analytical vpc; the major one preceded that of starting olefin and predominated by a factor of 10.4:1. The liquid second fraction was discarded, as was the third which turned solid and was presumed to be ketone. The mixture from the first fraction was separated by preparative vpc, column B, 164°, 15 psi. The product olefin was washed from the collector with pentane, the solvent removed, and the olefin flash distilled to give 2.02 g of colorless liquid, 80% based on 2.52 g of starting olefin.

The olefin showed no traces of either II, I, or 2,4-diphenyl-1-butene under vpc conditions that would have showed less than 0.1% of each. Since acid-catalyzed isomerization of IV showed less than 0.2% of II under conditions that were shown to equilibrate III and II, IV is demonstrated to contain less than 0.2% of III as well.

The olefin, n^{25}D 1.5819, showed bands in the infrared, 20%, at 3081 (medium), 3060 (medium), 3026 (strong), 2964 (strong), 1368 (medium), and 695 (strong) cm^{-1}. The nuclear magnetic resonance spectrum, 19%, gave a singlet (10 H) at τ 2.68, a doublet (1 H, J = 12 cps) centered at 3.44, a distorted triplet (1 H, J = 12 and 10 cps) from 3.90 to 4.35, a doublet of quartets (1 H, J = 10 and 7 cps) centered at 5.93, and a doublet (3 H, J = 7 cps) centered at 8.60. The ultraviolet spectrum in hexane showed λ_{max} 241 mμ (ϵ 14,200), λ_{sh} 269 mμ (ϵ 1600). *Anal.* Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.40; H, 7.55.

***cis*- and *trans*-1,3-Diphenyl-2-butene (II and III).** The ketone, 1,3-diphenyl-1-propanone,[31] was prepared as follows. Benzalacetophenone (Eastman White Label), 20.5 g, was placed in a Parr hydrogenation bottle and dissolved in 150 ml of molecular seive dried ethyl acetate. The bottle was swept with nitrogen, and 0.1 g of platinum oxide (MCB) was added. The hydrogenation was carried out on a Parr hydrogenation apparatus under an initial hydrogen pressure of 25 psi. When the theoretical amount of hydrogen had been absorbed, the reaction was stopped, the mixture filtered through Celite, and solvent removed under reduced pressure. This procedure was repeated; the combined products from the two runs were crystallized three times from 95% ethanol. The crystallizations were followed by vpc; the last gave 20.2 g of white crystals of ketone, mp 70.5–71.0°, that showed one and only one peak by vpc.

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[28] G. Baddeley and W. Pickles, *J. Chem. Soc.*, 2855 (1957).

[29] J. H. Brewster and M. W. Kline, *J. Am. Chem. Soc.*, 74, 5179 (1952).

[30] G. Baddeley, *J. Chem. Soc.*, S99 (1949).

[31] This procedure is patterned after that of R. Adams, J. W. Kern, and R. L. Shriner in "Organic Syntheses," Gillman and Blatt, Ed., Coll. Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1941, p 101.

This ketone was converted to 2,4-diphenyl-2-butanol as follows. A solution of 19.0 g (0.091 mole) of 1,3-diphenyl-1-propanone in 200 ml of ether was added slowly to a refluxing solution of Grignard reagent prepared from magnesium (3.36 g, 0.139 g-atom) and methyl iodide (19.5 g, 0.137 mole) in 300 ml of ether. The mixture was refluxed for 1 hr, then cooled and hydrolyzed with concentrated ammonium chloride solution. The mixture was filtered into a separatory funnel, and, after shaking, the aqueous phase was removed and washed with three 200-ml portions of ether. The combined organic phases were washed with water and brine, then dried, filtered, and evaporated to dryness. The crude product was chromatographed on 400 g of silica gel, the alcohol appearing in the 90% pentane–10% ether fractions. Distillation yielded 18.8 g (92%) of the alcohol, bp 115° (0.2 mm), $n^{25}\text{D}$ 1.5664. The infrared spectrum, 10%, showed peaks at 2.8, 3.3, 3.4, 6.2, 6.7, 6.9, and 7.3 μ. The nuclear magnetic resonance spectrum, 30%, contained a multiplet (10 H) from τ 2.5 to 3.0, a multiplet (5 H) from 7.3 to 8.2, and a singlet (3 H) at 8.52.

The tertiary benzylic alcohol, 5.00 g, and 49.0 ml of a solution of acetic acid, 2% in acetic anhydride and 0.1 *M* in *p*-toluenesulfonic acid monohydrate (Eastman White Label), were mixed in a dry, round-bottomed flask which was stoppered and placed in the 75° bath for 9 hr. The solution was cooled and poured into a separatory funnel containing 300 ml of pentane and 400 ml of water. After the mixture was shaken and separated, the aqueous phase was washed with two 150-ml portions of pentane. The combined pentane extracts were washed with 200-ml portions of water, 5% sodium hydroxide solution, water, and brine, then dried, filtered, and evaporated on the steam bath under nitrogen. The crude reaction mixture, 4.61 g, 99% of theory, showed no hydroxyl or carbonyl bands in the infrared spectrum and no slow-moving components by tlc. Flash distillation of the residue gave 4.33 g (93% of theory) of a mixture of olefins that consisted of 73.8% II, 20.0% III, and 6.3% 2,4-diphenyl-1-butene. The mixture was separated by preparative vpc (column B, 174°, 20 psi), and the collected isomers were flash distilled to give 2.56 g of II and 0.64 g of III. Analysis of the distillates by vpc showed no traces of isomeric olefins: less than 0.1% of any of the four isomeric olefins could have been readily detected in the distilled II; less than 0.1% of II, I, or 2,4-diphenyl-1-butene was present in the distilled III. Since the crude reaction mixture showed no trace of I by vpc, the purified III is considered to be free of IV. Any rearrangement to produce IV in preference to I during the reaction is considered highly unlikely in view of the equilibration data at 100° for the latter olefins.

Structural assignments were made from the following data. For II, $n^{25}\text{D}$ 1.5903, the infrared spectrum, 20%, showed peaks at 3080 (medium), 3060 (medium), 3022 (strong), 2980 (medium), 2860 (medium), and 1377 (medium) cm^{-1}. The nuclear magnetic resonance spectrum,[9] 21%, showed a singlet (10 H) with maximum at τ 2.88, a triplet of partially resolved quartets (1 H, J = 7 and 1 cps) centered at 4.12, a doublet (2 H, J = 7 cps) centered at 6.54, and a partially resolved doublet (3 H, J = 1 cps) centered at 7.93. The ultraviolet spectrum in hexane gave $\lambda_{\max}$ 245 mμ (ϵ 15,600), λ_{sh} 269 mμ (ϵ 4700). *Anal.* Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.27; H, 7.62.

For III, $n^{25}\text{D}$ 1.5753, the infrared spectrum, 20%, showed peaks at 3081 (medium), 3062 (medium), 3027 (strong), 2970 (medium), 2850 (medium), and 1373 (medium) cm^{-1}. The nuclear magnetic resonance spectrum, 10%, showed a pair of singlets (10 H) with maxima at τ 2.80 and 2.90, a triplet of partially resolved quartets (1 H, J = 7 and 1 cps) centered at 4.38, a doublet (2 H, J = 7 cps) centered at 6.73, and a partially resolved doublet (3 H, J = 1 cps) centered at 7.93. The ultraviolet spectrum in hexane gave λ_{sh} 230 mμ (ϵ 9500), 262 (1900), and 268 (1000). *Anal.* Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.48; H, 7.68.

The third and thermodynamically least stable olefin was assigned the 2,4-diphenyl-1-butene structure by confirmation of the highly distinctive nuclear magnetic resonance spectrum reported for this isomer by Parkhurst, *et al.*[9] The spectrum, 9%, gave an overlapping pair of singlets (10 H) with maxima at τ 2.72 and 2.89, a pair of singlets (2 H) at 4.77 and 4.98, and one sharp singlet (4 H) at 7.25.

Photoisomerization of *cis*-1,3-Diphenyl-2-butene (II) to *trans*-1,3-Diphenyl-2-butene (III). Solutions of II, 0.627 g, and sodium-dried benzene, 0.05 *M* in α-naphthyl phenyl ketone, 8.0 ml, were made up in two 18 × 150 mm Pyrex test tubes that had been drawn out to facilitate sealing and fitted with 10/30 joints. The tubes were degassed, sealed, and irradiated for 67 hr. The tubes were then opened and the contents removed, and solvent was evaporated under reduced pressure. The residue appeared homogeneous; at this point 20 mg was removed for vpc analysis. A small amount of 95% pentane–5% ether solution was added to the remainder and the mixture chromatographed on 40 g of silica gel using pentane–ether of the above composition. The first 100-ml fraction gave 1.203 g of clear liquid upon evaporation of solvent; this material was subjected to preparative vpc (column B). The III collected weighed 1.092 g; the small amount of II was not collected. Flash distillation gave 1.061 g of III that was identical by nuclear magnetic resonance spectra and relative vpc retention times with the fully characterized sample of III isolated from the dehydration reaction. Analysis by vpc showed no trace of II or IV with conditions under which 0.2% of either would have been readily detected. Analysis by nmr at high sensitivity showed no trace of the methyl group of IV under conditions that would have been expected to show 1% of this impurity.

Analysis by vpc of the 20-mg aliquot of the crude reaction mixture showed 98.2% III and 1.8% II (average of three analyses), or a III/II ratio of 55.

Acid-Catalyzed Isomerizations of the 1,3-Diphenylbutenes. The appropriate olefin, 21 mg, was added to a clean, dry 10 × 75 mm test tube that had been drawn out to facilitate sealing. The tube was flushed with purified nitrogen and, at room temperature, 1.00 ml of a solution of 98% acetic acid, 2% (by volume) in acetic anhydride and 0.1 *M* in *p*-toluenesulfonic acid monohydrate, was added with a microburet. With nitrogen still gently sweeping through the tube, the tube was partially immersed in a Dry Ice–acetone bath and immediately sealed. The tube was placed in the 100° bath, thawed, shaken, and let stand for the appropriate number of hours. The tube was then removed from the bath, cooled, washed, and opened, and its contents was poured into a 125-ml separatory funnel containing 25 ml of pentane and 25 ml of water. After the mixture was shaken and separated, the aqueous phase was washed with 25 ml of pentane. The combined organic phases were washed with 25-ml portions of 5% sodium hydroxide solution, water, and brine, then dried, filtered, and evaporated on the steam bath under a stream of nitrogen. The residue was transferred with pentane to a sample vial and solvent evaporated on a warm-water bath under a stream of nitrogen. Final traces of solvent were removed under aspirator pressure at room temperature. Approximately 0.1 ml of *n*-decane (MBC) was added, the solution swept with nitrogen, and the flask capped and stored in the cold until analyzed.

The olefin percentages were determined by analytical vpc. The mixtures from II and III contained only three components: the two above olefins and the expected 2,4-diphenyl-1-butene. The mixtures from the 1,3-diphenyl-1-butenes contained no structurally isomeric olefins, a trace of suspected acetates at about twice the retention time of I, and two new components with retention times of 0.69 and 0.75 relative to I. These components were present in about equal amounts and together totaled 1–2% of the total mixture. Their retention times precluded any of the olefins from the equilibrations of the 2-butenes; these new compounds are probably the diastereomeric 1-methyl-3-phenylindanes.[12]

Base-Catalyzed Equilibrations of the 1,3-Diphenylbutenes. These runs were conducted in sealed 10 × 75 mm test tubes using the general procedure outlined for the acid-catalyzed equilibrations with the following exceptions: the solution added was 1.00 ml of *t*-butyl alcohol, 0.4 *M* in potassium *t*-butoxide; in order to break emulsions between the aqueous and pentane layers during work-up, either the aqueous phase was partially neutralized by adding *ca.* 0.5 *M* sulfuric acid dropside, or 3 ml of saturated brine was added; the combined pentane solutions were washed only with 20 ml of brine.

During the base-catalyzed equilibration and kinetic runs, the isomerized solutions were occasionally checked for loss of total base. At no time was loss of base observed. The sample was added directly to 15 ml of water, 2 drops of bromocresol green–methyl red mixed indicator was added, and the basic solution was titrated with 0.0511 *N* sulfuric acid. The aqueous solution was then added to pentane in a separatory funnel and worked up as described above, with the inclusion of 25-ml washes with 1% sodium hydroxide solution and water. The equilibration of IV at 75° is illustrative of the lack of base consumption: titration of the potassium *t*-butoxide–*t*-butyl alcohol solution before the run gave 0.354 *M* total base; titration of the reaction solution after 1049 hr at 75° gave 0.357 *M*.

Procedures for Kinetic Runs. For IV at 75 and 100°, and III at 40°. The desired amount of olefin was weighed into a clean, dry, 20-ml pear-shaped flask equipped with a side arm that was fitted with a serum cap. The flask was fitted with a nitrogen inlet and outlet tube modified from a vacuum takeoff apparatus and then thoroughly swept with purified nitrogen. With a clean and dry graduated pipet, enough potassium *t*-butoxide–*t*-butyl alcohol solution was added to make the resulting solution 0.1 *M* in olefin. The flask was swirled, and a positive pressure of nitrogen was maintained over the room temperature solution. With a microburet that was purged with nitrogen after each sample was transferred, 1.0-ml aliquots were removed from the flask and added to clean and dry 10 × 75 mm test tubes that were continually swept with nitrogen. The tubes were sealed as described in the acid equilibrations, stored on Dry Ice, then placed in the constant temperature bath, thawed, shaken, and let stand. At an appropriate time a tube was removed, cooled, washed, and opened, and the contents was worked up in the same manner as were the tubes in the base-catalyzed equilibration runs.

In each run, after a majority of the tubes had been loaded, a 1.00-ml aliquot of the reaction solution was added to 15 ml of water, titrated, and worked up as described for the titrated base-catalyzed equilibrations. The olefin recovered from this "zero point" was checked for purity by vpc; in no run was any isomerized olefin detected. In each run at least one of the tubes corresponding to a high per cent reaction was titrated in the usual way; in no instance was consumption of base observed. The olefin mixtures from each aliquot were subjected to vpc analysis.

For I at 40°. The olefin, 146 mg, was added to a clean, dry, 10-ml pear-shaped flask, and, after the flask was thoroughly swept with purified nitrogen, 7.0 ml of a solution of potassium *t*-butoxide in *t*-butyl alcohol was introduced. The flask was quickly swirled to bring the olefin into solution, a 1.00-ml aliquot was withdrawn for titration, the flask was capped with a stopper fitted with a small stopcock, and the flask and contents were frozen in a Dry Ice–acetone bath. The flask was then placed in the 40° bath, the contents melted (complete melting denoted time zero), swirled, and let stand. At appropriate times the stopcock was opened and, with the aid of a syringe and hypodermic needle, 1.0-ml aliquots were withdrawn and added to pentane–water mixtures in separatory funnels. These aliquots were worked up in the usual manner. The last point was obtained by removing the stopcock and pipetting 1.00 ml of the reaction solution into 15 ml of water; this solution was then titrated and worked up by the modified procedure described in the base-catalyzed equilibration section. The initial and final titrations were identical and indicated 0.35 *M* total base. The samples were analyzed by the usual analytical vpc method described above.

Procedures for the Exchange Runs. For IV. The olefin, 329 mg, was introduced into a clean, dry Carius tube. The tube was flushed with purified nitrogen and 15.8 ml of *t*-butyl alcohol-O-*d* (0.98 atom of deuterium per molecule), 0.32 *M* in potassium *t*-butoxide, was added. The tube was again flushed with nitrogen, the contents were frozen by immersing the tube in a Dry Ice–acetone bath, and, after warming the constriction of the tube, a drying tube was fitted to the opening of the Carius tube and the latter immediately sealed. The sample was then thawed, the tube was checked for leaks and, after thorough mixing of the contents, immersed in an oil bath at 101° for 9 hr. The tube was then frozen, opened, and fitted with a drying tube, and the contents were allowed to thaw. Two 1.00-ml aliquots were removed and titrated in the usual way (total base was 0.316 ± 0.004 *M*), and the titrated solutions then were added to a separatory funnel that contained the remainder of the reaction mixture, 125 ml of water, and 200 ml of pentane. The mixture was shaken and the aqueous phase separated and washed with a 100-ml portion of pentane. The combined organic extracts were washed with 150-ml portions of water, 1% sodium hydroxide solution, and brine, then dried and partially evaporated on the steam bath under nitrogen. The residue was transferred to a tared flask and the residual solvent removed on the rotary evaporator. To the oily reaction mixture, 320 mg, there was added 197 mg of *n*-hexane, and 29 mg (corresponding to 18 mg of reaction mixture) of the resulting solution was removed for vpc analysis. The remainder was transferred to a distilling apparatus, the solvent removed, and the residue flash distilled into a tared sample vial to yield 266 mg of distillate: yield $[266 + (266/302) \times 18]/329 \times 100 = 86\%$.

The distillate was mixed with a small amount of *n*-decane and subjected to preparative vpc (column C), 185°, 15 psi. The fraction that contained IV and III was washed from the collector with methylene chloride; evaporation of solvent gave 124 mg that was diluted with 239 mg of carbon tetrachloride containing 2% tetramethylsilane. The resulting 34% solution was subjected to nmr analysis with a 35% solution of authentic protio-IV as reference sample.

The second fraction from the vpc separation contained both II and I. The sample was worked up as above to yield 88 mg that was then diluted to make a 22% solution in carbon tetrachloride for nmr analysis.

For I and II. Each olefin, 247 mg of II and 248 mg of I were weighed out into a clean, dry, 25-ml pear-shaped flask. The flasks were thoroughly swept with purified nitrogen and, with nitrogen continually passing into the flasks, 11.9 ml of potassium *t*-butoxide–*t*-butyl alcohol-O-*d* solution was added to each flask. The flasks were then immediately stoppered and chilled in Dry Ice–acetone baths. Immediately before and after transfer of the solvent, 1.00-ml portions of the solvent were added to 15-ml portions of water and titrated in the usual manner. These duplicate titrations established total base concentration as 0.353 ± 0.001 *M*. The stoppers (equipped with Teflon sleeves) were then wired on, the flasks placed in the bath, and the contents thawed with continued swirling. When the solvent was completely melted the timer was started; the flasks were given final swirls and then let stand at 40.0 ± 0.1° for 62.5 min. At this time the flasks were removed from the bath, the outsides washed with acetone and ether, the stoppers removed, and the contents poured into separatory funnels, each of which contained 200 ml of pentane, 125 ml of water, and 25 ml of brine. After the mixtures were shaken, each aqueous phase was separated and washed with an additional 100 ml of pentane. The combined organic phase of each run was washed with 100-ml portions of water and brine, then dried, and filtered, and solvent was evaporated on the steam bath under nitrogen. Each of the residues was then sampled for vpc analysis and flash distilled in the same manner as described for the IV experiment above. By that technique the recoveries of the olefin mixtures were: from I, 90%; from II, 94%.

The distillate, 207 mg, from I as starting material was resolved by preparative vpc, column A, 167°, 20 psi. The collected I was washed from the collector into a 250-ml flask using spectral-grade carbon tetrachloride. After concentration of this solution on the rotary evaporator, the solution was transferred to a tared 25-ml pear-shaped flask and solvent removed in the same way. The remaining olefin, 116 mg, was diluted with 278 mg of carbon tetrachloride containing 2% tetramethylsilane, and the resulting 29% solution analyzed by nmr against a 29% solution of authentic protio-I. The nmr spectrum of the exchanged sample showed a trace of II, its methyl group present as a discernible singlet one-fifth the height of one of the methyl doublets of I after a 50-fold increase in the spectrum amplitude and fourfold increase in the radiofrequency field.

The distillate, 217 mg, from II as starting material was handled in a similar manner as that from I. Preparative vpc involved column A at 171° and 20 psi. The recovered II, 177 mg, was diluted with carbon tetrachloride and the resulting 41% solution analyzed by nmr against a 42% solution of authentic protio-II. A broad singlet, perhaps ascribable to the methyl group of partially deuterated I, was present at high sensitivity in the spectrum of reacted II; with a 25-fold increase in spectrum amplitude and sixfold increase in the radiofrequency field, this peak was one seventh the height of the II methyl group at usual sensitivity. The per cent isomerization in each run was determined by analytical vpc.

For III. In the same way as described above for I and II, the olefin, 184 mg, was weighed into a pear-shaped flask, 8.65 ml of potassium *t*-butoxide–*t*-butyl alcohol-O-*d* solution was added, and the mixture was allowed to react at 40.0° for 12.5 hr. Titration of the base solution in the usual way showed 0.373 *M* total base. The flask was cooled and its contents poured into a separatory funnel that contained 200 ml of pentane, 150 ml of water, and 20 ml of brine. After the mixture was shaken and separated, the aqueous phase was washed with a 100-ml portion of pentane; the combined organic phases were then washed with 150-ml portions of water and brine, then dried, filtered, and evaporated on the steam bath under nitrogen. The crude reaction mixture was sampled for vpc analysis and flash distilled in the way described for IV; the yield of distilled olefins was 92%. III was isolated by preparative vpc, column C, 168°, 20 psi. The collected olefin, 92 mg, was handled in the same way as described for I and II. The nmr solution, 19%, was integrated against a 19% solution of authentic protio-III. At high sensitivity, no trace of other olefins was visible in the nmr spectrum of reacted III.

Deuterium Analyses by Nuclear Magnetic Resonance Spectroscopy. With the Varian A-60 spectrometer at a sweep time of 100 sec, and with the "integral amplitude" and "spectrum amplitude" at approximately the settings required to give full-scale deflection for the methyl peak, the drift in the integrator base line was steadied by varying the "detector zero" at the extreme field limits (*i.e.*, 1000 cps downfield and 500 cps upfield from TMS), and by varying the "detector phase" at positions slightly upfield and downfield from the peaks to be integrated. The radiofrequency field was decreased as much as was possible to still produce a reasonable steady base line. The integral amplitude and spectrum amplitude were then varied to give roughly 0.8 full-scale deflection for the methyl group, always in such a manner as to keep the "signal level" meter on scale. The base line was then checked, and, if not steady under these conditions, it was returned following the above procedure at these new integral amplitude and spectrum amplitude settings. This general procedure was repeated until optimum conditions were secured. The relevant absorptions in the spectrum were then each integrated 12 times, the highest and lowest values neglected, the remaining 10 values averaged, and standard deviations for each absorption found. The average deflection for the methyl group was assumed to equal 3.00 protons and the number of protons corresponding to the other absorptions in question calculated from their average deflections. The same procedure was used in the integrations of the authentic protio-olefin standards. Precision of this procedure was found to be independent of any time-variable idiosyncrasies of the spectrometer. For example, multiple analyses of exchanged III on different days gave values of 62 ± 3, 62 ± 2, and 63 ± 2% for exchange.

Electrophilic Substitution at Saturated Carbon. XXX. Behavior of Phenylallylic Anions and Their Conjugate Acids[1]

Stephen W. Ela[2] and Donald J. Cram

Contribution No. 1955 from the Department of Chemistry, The University of California at Los Angeles, Los Angeles, California 90024. *Received August 15, 1966*

Abstract: Allylbenzene (I) and *cis*- and *trans*-propenylbenzene (*cis*- and *trans*-II) were each equilibrated at 25° in dimethyl sulfoxide–potassium *t*-butoxide to give 97.75% *trans*-II, 2.20% *cis*-II, and about 0.05% I. Equilibrium mixtures at 97° in *t*-butyl alcohol–potassium *t*-butoxide contained 93.95% *trans*-II, 5.73% *cis*-II, and 0.32% I. The isomerization and exchange reactions of each olefin were studied in potassium *t*-butoxide–*t*-butyl alcohol. The second-order rate constant for isomerization of allylbenzene at 25° was 1.5×10^{-5} l./mole sec, and *trans*-II was formed 12.9 times faster than *cis*-II. The *trans*-allylic anion intermediate underwent proton capture to give *trans*-II about three times as fast as to give I at 25°. Isotopic exchange of *cis*-II in deuterated solvent at 98° was six to seven times faster than isomerization. Under the same conditions, exchange of *trans*-II was three to six times faster than isomerization. The balanced collapse ratio of the *trans*-allylic anion is discussed in terms of the ability of a phenyl group to stabilize both a carbanion and an olefinic double bond. The relative stabilities of *cis* and *trans* carbanions are discussed. The rates of loss of allylic protons from 12 methyl- and phenyl-substituted propenes are calculated.

Recent studies have probed the effects that influence the collapse ratios of allylic carbanions.[3] The allylic anion that is an intermediate in the conversion of 3-phenyl-1-butene to *cis*-2-phenyl-2-butene[3b] produced the latter olefin 35–40 times faster than the former olefin.[3b] Studies of the interconversions of the four 1,3-diphenylbutenes suggested that the methyl substituent of the derived allylic anions was primarily responsible for the imbalance of the collapse ratios, and that the phenyl substituent played little part in producing the observed values of 35–40. Again, protonation favored the more substituted olefin.

Although it has been demonstrated that allylic anions are capable of maintaining their configurational identities,[3a,c] the roles played by steric and electronic effects in determining the free-energy difference between any pair of configurationally isomeric carbanions are not thoroughly understood. Direct determination of the energy differences between configurationally isomeric allylic anions has yet to be reported, although the energy differences between structurally and configurationally isomeric enolate anions have been investigated.[4] The relative stabilities of a pair of configurationally isomeric allylic anions have been inferred from kinetic studies in which the transition states for carbanion formation were used as models for the allylic anions themselves.[3a]

The results of an investigation of the interconversions of allylbenzene (I) and *cis*- and *trans*-propenylbenzene (*cis*- and *trans*-II) are reported here. The *cis*- and *trans*-allylic anions (B and A, respectively) derived from this system have only one substituent, a phenyl group (see Chart I). Thus, the hypothesis that phenyl and hydrogen have about the same effect on the collapse ratios of allylic anions can be tested.[3a] This system is simpler than the others reported in this series of papers, and its study should yield data bearing on the relative stabilities and interconvertibility of configurationally related allylic anions. Allylbenzene has recently been subjected to base-catalyzed isomerization, but the proportions of *cis*- and *trans*-II produced were not reported.[5]

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(3) (a) S. W. Ela and D. J. Cram, *J. Am. Chem. Soc.*, **88**, 5777 (1966); (b) D. J. Cram and R. T. Uyeda, *ibid.*, **86**, 5466 (1964); (c) D. H. Hunter and D. J. Cram, *ibid.*, **86**, 5478 (1964).

(4) (a) H. O. House and V. Kramer, *J. Org. Chem.*, **28**, 3362 (1963); (b) H. O. House and B. M. Trost, *ibid.*, **30**, 2502 (1965).

(5) A. Schreisheim, C. A. Rowe, Jr., and L. Naslund, *J. Am. Chem. Soc.*, **85**, 2111 (1963).