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]

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

[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).

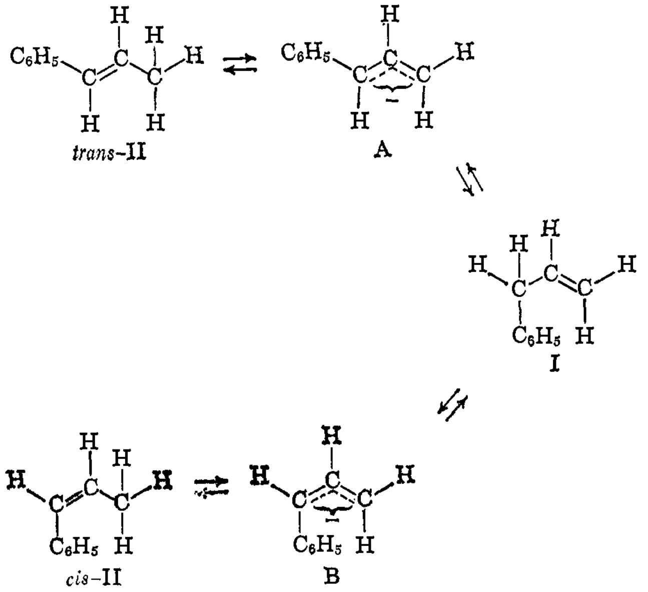
[5] A. Schreisheim, C. A. Rowe, Jr., and L. Naslund, *J. Am. Chem. Soc.*, **85**, 2111 (1963).

Table I. Results of Potassium *t*-Butoxide Catalyzed Equilibrations of Allylbenzene (I) and *cis*- and *trans*-Propenylbenzene (*cis*- and *trans*-II)

Run no.	Substrate Nature	Substrate Concn, *M*	Solvent	Base, *M*	Temp, °C[a]	Time, hr	% I	% *trans*-II	% *cis*-III
1	I	0.14	*t*-BuOH	0.42	97.0	430[b]	0.33	93.98	5.69
2	*trans*-II	0.14	*t*-BuOH	0.42	97.0	430[b]	0.32	93.95	5.73
3	*cis*-II	0.094	*t*-BuOH	0.42	97.0	430[b]	0.32	93.92	5.76
						Average:	0.32	93.95	5.73
4	I	0.20	$(CH_3)_2SO$	0.1[c]	25.0	0.5	0.05	97.78	2.17
5	*trans*-II	0.19	$(CH_3)_2SO$	0.1[c]	25.0	0.5	0.05	97.76	2.19
6	*cis*-II	0.20	$(CH_3)_2SO$	0.1[c]	25.0	0.5	0.05	97.72	2.23
						Average:	0.05	97.75	2.20

[a] ±0.5° for 97.0°; ±0.05° for 25°. [b] Tubes were immersed in 50.0° bath for 215 hr, then transferred to 97° bath for 430 hr. [c] From weight of solid potassium *t*-butoxide added to dimethyl sulfoxide.

Chart I



Results

In this section, the preparation and purification of olefins I and *cis*- and *trans*-II are described, followed by data on their base-catalyzed equilibration. The results of the kinetics of their isomerization and isotopic exchange follow, which provide data for calculations of the collapse ratios of the allylic anionic intermediates.

Preparation and Characterization of the Olefins. Allylbenzene (I) was isomerized to *trans*-propenylbenzene (*trans*-I) with potassium *t*-butoxide in *t*-butyl alcohol. The *trans* isomer was photoisomerized to *cis*-propenylbenzene (*cis*-II) with α-naphthyl phenyl ketone as photosensitizer.[6] The three olefins were purified by preparative vapor phase chromatography (vpc). Each olefin was greater than 99.9% pure by analytical vpc; the impurities present in each consisted of traces of the other two isomers. The ultraviolet and nuclear magnetic resonance (nmr) spectra,[7] as well as the compositions of the equilibrium mixtures given in the next section confirm the structural assignments.

Base-Catalyzed Equilibration of the Olefins. Each of the olefins was subjected to potassium *t*-butoxide catalyzed equilibration at 25° in dimethyl sulfoxide and at 97° in *t*-butyl alcohol. The compositions of the equilibrium mixtures were determined by vpc analyses, and Table I reports the results. Use of 3-phenylpentane as an internal standard demonstrated that loss of the olefins with *t*-butyl alcohol as solvent was negligible. No extraneous peaks were present in the vpc analyses, and in this solvent at 97°, *trans*-II/*cis*-II = 16.4. In dimethyl sulfoxide as solvent at 25°, equilibrium was established within 30 min, and 1–2% of high-boiling impurities were produced. An equilibrium constant (*trans*-II/*cis*-II) of 44.4 was observed but is subject to the following uncertainty.

Each run at 25° in dimethyl sulfoxide was conducted with a potassium *t*-butoxide to olefin ratio of about 0.5. If the pK_a of the thermodynamically most stable isomer (*trans*-II) is close to or less than the pK_a of *t*-butyl alcohol in dimethyl sulfoxide, appreciable amounts (up to 0.5) of the equilibrium mixtures of runs 4, 5, and 6 might have existed as carbanions. The results of these runs might then partially reflect the irreversible quenching of the carbanions derived from the propenylbenzenes. However, if isomerization continued during the quenching process, the results would reflect the equilibration of the three olefins in dimethyl sulfoxide–water mixtures.

The acidity of *t*-butyl alcohol in dimethyl sulfoxide at low concentrations of the alcohol is comparable to that of triphenylmethane,[8] which is 3.5 pK_a units more acidic than 1,1-diphenyl-1-propene.[9] Triphenylmethane is about 1.5 pK_a units more acidic than diphenylmethane.[10] These comparisons suggest that *trans*-propenylbenzene and 1,1-diphenyl-1-propene differ by about 1.5 pK_a units, and that *t*-butyl alcohol is more acidic by about 5 pK_a units. If this estimate is valid, the equilibrium data of runs 4, 5, and 6 are valid, and *trans*-II/*cis*-II = 44.4 at 25° in dimethyl sulfoxide. This value contrasts with the estimate of *trans*-II/*cis*-II ~ 4 at 25°, made from the free energies of formation of the olefins from the elements.[11] A theoretical treatment based on molecular orbital theory and on repulsion and tortional effects predicted *trans*-II to be 2.5 kcal/mole more stable than *cis*-II. This value corresponds to *trans*-II/*cis*-II = 65 at equilibrium at 25°.[12] The difference between the observed equilibrium

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[6] We wish to thank Dr. G. S. Hammond for suggesting use of this ketone.

[7] R. W. Fessenden and J. S. Waugh, *J. Chem. Phys.*, **30**, 944 (1959).

[8] E. C. Steiner and J. M. Gilbert, *J. Am. Chem. Soc.*, **85**, 3054 (1963).

[9] W. K. McEwen, *ibid.*, **58**, 1124 (1936).

[10] E. C. Steiner and J. M. Gilbert, *ibid.*, **87**, 382 (1965).

[11] J. E. Kilpatrick, G. W. Beckett, E. J. Prosen, K. S. Pitzer, and F. D. Rossini, *J. Res. Natl. Bur. Std.*, **42**, 225 (1949).

[12] G. Favini and M. Simonetta, *Theoret. Chim. Acta*, **1**, 294 (1963).

value of 44.6 at 25° and the value of 16.4 at 97° is consistent with the 72° difference in temperature.

The value of *trans*-II/I at 97°(290) also increased as the temperature was brought to 25° (~2000). If irreversible quenching of carbanions were a serious problem in the dimethyl sulfoxide solutions, more allylbenzene would be expected to be produced than was observed at equilibrium at 97° (0.32%). Thus, when sodium allylbenzene in liquid ammonia was quenched in methanol, 15% allylbenzene and 85% *cis*- and *trans*-II were produced.[13]

The equilibrium values are presumed to be fairly insensitive to solvent. Others[14] have found good agreement between observed equilibrium proportions of 2-methylpentenes in dimethyl sulfoxide and calculated proportions based on thermal data for the gas phase. Little change was observed[3c] in equilibrium constants of *cis*- and *trans*-α-methylstilbene and α-benzylstyrene with a change in solvent from *t*-butyl alcohol to acetic acid.

Kinetics of Base-Catalyzed Isomerization. The isomerization of allylbenzene at 25° was studied in *t*-butyl alcohol-O-*h*–potassium *t*-butoxide. Aliquots of the reaction solution were quenched periodically, and analyzed by vpc. Table II reports the results. For each aliquot, the observed *trans*-II/*cis*-II ratio and the instantaneous first-order rate constant for disappearance of allylbenzene are tabulated, along with the standard deviations for the averages. On the assumption that the rate of disappearance of allylbenzene is first order in base,[15] the average second-order rate constant for disappearance of allylbenzene is calculated. Under the same conditions in the absence of base, allylbenzene produced less than 0.2% of isomerized product.

Table II. Kinetics and Product Compositions for Isomerization of Allylbenzene[a] in *t*-Butyl Alcohol, 0.416 *M* in Potassium *t*-Butoxide at 25.0°[b] (Run 7)

Aliquot	Time, min	% reaction[c]	*trans*-II/ *cis*-II	Instant. rate const, $k_1 \times 10^6$, sec^{-1} [d]
1	60.6	2.40	13.2	6.65
2	120	4.60	12.8	6.52
3	240	8.97	13.0	6.53
4	360	12.8	12.6	6.34
5	480	16.7	13.0	6.39
6	720	24.2	12.9	6.39
7	960	30.9	13.0	6.32
8	1920	51.7	12.9	6.33
9	4330	79.9	13.1	6.19
Average (± standard deviation):			12.9 ± 0.2	6.41 ± 0.14[e]

[a] 0.095 *M*. [b] ±0.05°. [c] Equals % *trans*-II + % *cis*-II. [d] First-order rate constant. [e] Second-order rate constant, $k_2 = 1.54 \pm 0.04 \times 10^{-5}$ l./mole sec.

A similar run with allylbenzene was made at 25° in *t*-butyl alcohol-O-*d*–potassium *t*-butoxide (see Table III). The calculated first-order rate constants for the first seven points (2.6 through 40% reaction) appear constant. The ratio, *trans*-II/*cis*-II, was constant throughout the run and was equal within experimental error to the value obtained in protio solvent.

Table III. Kinetics and Product Compositions for Isomerization of Allylbenzene[a] in *t*-Butyl Alcohol-O-*d*,[b] 0.392 *M* in Potassium *t*-Butoxide at 25.0°[c] (Run 8)

Aliquot	Time, min	% reaction[d]	*trans*-II/ *cis*-II	Instant. rate const, $k_1 \times 10^6$, sec^{-1} [e]
1	30.5	2.58	13.2	1.44
2	58.0	4.66	13.2	1.37
3	123	9.45	13.3	1.35
4	243	17.8	13.3	1.34
5	364	25.2	13.1	1.32
6	470	31.8	13.2	1.33
7	652	40.1	13.2	1.31
8	1359	62.9	13.2	1.22
9	2124	76.7	13.1	1.14
10	2891	85.2	13.1	1.10
Average (± standard deviation):			13.2 ± 0.1	1.35 ± 0.05[f]

[a] 0.092 *M*. [b] 0.99 atom of deuterium per molecule. [c] ±0.05°. [d] Equals % *cis*-II + % *trans*-II. [e] Instantaneous first-order rate constant. [f] Average of points 1–7. Second-order rate constant, $k_2 = 3.45 \pm 0.13 \times 10^{-5}$ l./mole sec.

In run 8, if deuterium incorporation into allylbenzene was competitive with isomerization, and if deuterated allylbenzene isomerized with a large kinetic isotope effect, the calculated first-order rate constants should have dropped as the reaction proceeded. No drop was observed until the 63% reaction point was reached. This result suggests that exchange of allylbenzene is not faster than isomerization. The fact that after 85% isomerization the rate constant is still roughly 80% that of the initial value suggests that deuterium incorporation into starting material is slower than isomerization. Inspection of the equilibrium values of runs 1–3 indicates that in runs 7 and 8 return of the product propenylbenzenes to allylbenzene may be neglected. In both runs 7 and 8, use of 3-phenylpentane as an internal vpc standard indicated that the sum of the moles of the three olefins remained constant throughout the reactions.

Comparison of the second-order rate constants for runs 7 and 8 establishes the solvent isotope effect, $k^{\mathrm{ROD}}/k^{\mathrm{ROH}} = 2.3$. This value is about the same as those observed for the isomerizations of α-benzylstyrene[3c] at 75° and *trans*-1,3-diphenyl-1-butene[3a] at 40° in the same solvent–base systems. However, these values are larger than the values of unity found for 3-phenyl-1-butene at 75°[3b] and *cis*-1,3-diphenyl-1-butene at 100° in the same solvents.

Runs 9 and 10 (Tables IV and V) involved potassium *t*-butoxide catalyzed isomerization of *cis*-II in *t*-butyl alcohol-O-*h* and *t*-butyl alcohol-O-*d*, respectively. These runs were carried out simultaneously in sealed ampoules. In the protonated solvent, the five instantaneous rate constants are constant-valued from about 6 to 60% isomerization (run 9). However, in deuterated solvent, the instantaneous rate constants decreased markedly as the reaction proceeded (run 10). Extrapolation of the values of k_1 of run 10 to zero time yields an initial isomerization rate constant of about 6×10^{-7} sec^{-1}. Use of an internal vpc standard in these runs indicated that side reactions leading to loss

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(13) D. E. Johnson, unpublished work quoted by R. Y. Mixer and W. G. Young, *J. Am. Chem. Soc.*, **78**, 3379 (1956); see also W. G. Young and W. P. Norris, *ibid.*, **81**, 490 (1959).

(14) A. Schriesheim and C. A. Rowe, Jr., *ibid.*, **84**, 3160 (1962).

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

Table IV. Isomerization of *cis*-Propenylbenzene (*cis*-II)[a] in *t*-Butyl Alcohol-O-*h*, 0.390 *M* in Potassium *t*-Butoxide at 97.7°[b] (Run 9)

Point	Time, min	% reaction[c]	% I	Instant. rate const, $k_1 \times 10^5$, sec^{-1}
1	30.0	5.89	0.58	3.34
2	60.0	11.8	0.57	3.44
3	120	22.0	0.53	3.45
4	240	38.6	0.49	3.39
5	480	61.2	0.42	3.29
		Average (± standard deviation):		3.38 ± 0.07[d]

[a] 0.11 *M*. [b] ±0.1°. [c] Equals % I + % *trans*-II. [d] Average instantaneous rate constant, k_2 = 8.66 ± 0.20 × 10^{-5} l./mole sec.

Table V. Isomerization of *cis*-Propenylbenzene (*cis*-II)[a] in *t*-Butyl Alcohol-O-*d*,[b] 0.398 *M* in Potassium *t*-Butoxide at 97.7°[c] (Run 10)

Point	Time, min	% reaction[d]	% I	Instant. rate const, $k_1 \times 10^5$, sec^{-1} [e]
1	30.0	8.56	0.61	4.98
2	60.0	14.3	0.52	4.28
3	120	23.8	0.42	3.78
4	240	35.2	0.34	3.01

[a] 0.11 *M*. [b] 0.99 atom of deuterium per molecule. [c] ±0.1°. [d] Equals % I + % *trans*-II. [e] Instantaneous first-order rate constant.

Table VI. Potassium *t*-Butoxide (0.394 *M*) Catalyzed Isotopic Exchange between Allylbenzene (I), *cis*- and *trans*-Propenylbenzene (*cis*- and *trans*-II), and *t*-Butyl Alcohol-O-*d*[a]

	Substrate				I in product			*trans*-II in product			*cis*-II in product		
						Atoms of D in			Atoms of D in			Atoms of D in	
Run no.	Nature	Concn, *M*	Temp, °C[b]	Time, min	%	Benzyl	C_1-vinyl	%	Methyl	Vinyl	%	Methyl	Vinyl
12	I	0.20	25.0	2150	18.5	0.185[c]	0.00[d]	75.7	0.412[c]	0.00[d]	5.8	...	...
13	*cis*-II	0.19	97.7	90	0.45	...	...	19.7	...	...	79.9	1.73[c]	0.00[d]
14	*trans*-II	0.23	97.7	30	0.43	...	...	99.03	0.220[c]	0.00[d]	0.54	...	...

[a] 0.99 atom of deuterium per molecule by combustion and falling-drop analysis. [b] ±0.1°. [c] Total deuterium content determined by combustion and falling-drop method. In each case, nmr analysis agreed within experimental error (≤0.05). [d] Analysis by nmr, ≦0.05.

of olefin were of minor importance. A control experiment that involved *cis*-propenylbenzene in *t*-butyl alcohol with no added base (1320 min at 98°) showed 4% isomerization of *cis*-II to *trans*-II. A value of about 5 × 10^{-7} sec^{-1} was calculated for this control reaction, which is only about $^1/_{70}$th of the average value obtained in run 9.

In run 11 (see Experimental Section), allylbenzene was held for about 1 min at about 98° in potassium *t*-butoxide–*t*-butyl alcohol-O-*h*. Analysis by vpc showed about 33% isomerization to *cis*- and *trans*-II, and a value of *trans*-II/*cis*-II = 9.0 ± 0.1.

Base-Catalyzed Isotopic Exchange Reactions of Allylbenzene (I) and *cis*- and *trans*-Propenylbenzene (*cis*- and *trans*-II). Each of the olefins was subjected to the appropriate conditions in *t*-butyl alcohol-O-*d*–potassium *t*-butoxide, reisolated by preparative vpc, and examined for deuterium incorporation by nmr and the combustion and falling-drop methods. In each run the per cent isomerization of starting material was determined by vpc analysis. In no run was quantitative recovery of olefin attempted (in the equilibrium and kinetic experiments, no major loss of olefins was demonstrated). Run 12 with allylbenzene at 25° gave *trans*-II which contained 0.41 atom of deuterium per molecule residing exclusively in the methyl group. This result indicates that allylbenzene went to *trans*-propenylbenzene with about 59% intramolecularity, and compares to the 51% intramolecularity found in the isomerization of 3-phenyl-1-butene to *cis*-2-phenyl-2-butene in *t*-butyl alcohol-O-*d*–potassium *t*-butoxide at 75°.[3b] The results are recorded in Table VI.

Estimations of the Collapse Ratios of the Allylic Anions. The mechanistic scheme outlined in Chart I is assumed to apply to the allylbenzene–*cis*- and *trans*-propenylbenzene isomerizations. Protonations of anions A and B are presumed to occur faster than the anions interconvert, as was observed previously with other phenylallylic anions.[3a,b]

The data of run 12 allow estimation of the collapse ratio of the *trans*-carbanion (A) generated from allylbenzene (I) at 25°. Since *trans*-II is formed from I at a rate significantly faster than the rate for *cis*-II (runs 7 and 8), the isotopic exchange of I must occur mainly through A. The reaction mixture from run 12 contained 18.5% allylbenzene, which had 0.185 atom of deuterium per molecule. The fraction of intramolecularity in I → *trans*-II was observed to be about 0.59. It is reasonable to assume that the fraction of intramolecularity is a property of the carbanion,[3] and that this fraction also measures the amount of starting material regenerated from carbanion without isotopic exchange. If I* denotes the allylbenzene that has been regenerated from carbanion (both with and without exchange), the kinetic problem can be formulated and resembles the one solved for conversion of α-benzylstyrene to *trans*-α-methylstilbene.[3c] The per cent of I* is (0.185 × 18.5)/0.41 = 8.4%, and I is 10.1% in run 12. Application of the same equations used previously[3c] provides k_i/k_e = 2.8 for run 12, assuming k_H/k_D = 1.0 for the kinetic isotope effect. With k_H/k_D = 5.0,

$$\begin{tikzcd} \mathrm{I} \arrow[rr, "k_i"] \arrow[dr, "k_e"'] & & trans\text{-II} \\ & \mathrm{I}^* \arrow[ur, "k_i'"'] & \end{tikzcd}$$

k_i/k_e is calculated as equal to 3.0. Thus, a value of 2.8–3.0 appears to be a good estimate for the collapse ratio, k_i/k_e.

An implication of $k_i/k_e \sim 3$ is that a small fraction of the 0.412 atom of deuterium per molecule found by the combustion and falling-drop method in rearranged *trans*-II may reside in the vinyl position. The nmr analysis placed 0.39 ± 0.05 atom of deuterium in the methyl group and <0.05 in the vinyl position. Should

0.05 atom of deuterium reside in the vinyl position, the per cent intramolecularity would have to be increased to about 64%, which would change k_i/k_e to 2.4. Thus this small uncertainty in the intramolecularity has only a minor effect on the collapse ratio estimate.

Two additional minor sources of error exist in the estimation of the collapse ratio of A in run 12. In run 8, point 10 (taken after 85% isomerization) gave a rate constant for I → II which was 80% of the rate constant observed through the first 40% reaction. This drop was due to the isotope effect of deuterated allylbenzene that accumulated toward the end of the reaction. Taking this drop of k_i into account produces only a small correction of the collapse ratio to about 3.6. Finally, since the isomerization was carried to 80%, some I* might have undergone a second trip to carbanion and back to allylbenzene. This kinetic complication is undoubtedly minor, correction for which would decrease the collapse ratio value slightly. Thus, 3 ± 1 is a reasonable value for k_i/k_e for run 12.[16]

The data of run 13 permit a rough estimate of the collapse ratio of the *cis* carbanion (B) to be made. In run 13, *cis*-II at 98° isomerized 20.2% to give I and *trans*-II. The recovered *cis*-II possessed 1.73 atoms of deuterium per molecule by combustion and falling-drop analysis. No deuterium could be detected at the vinyl position by nmr analysis, while deuterium in the methyl group by nmr analysis was 1.77 ± 0.12 atoms per molecule.

A kinetic scheme is formulated in which k_i and k_e are defined. Assumption of two independent first-order reactions for isotopic exchange (k_e) and for isomerization (k_i) coupled with the data allow calculation of k_e/k_i. 5

$$\begin{tikzcd}
cis\text{-II} \arrow[r, "k_i"] \arrow[dr, "k_e"] & \text{I} + trans\text{-II} \\
 & cis\text{-II-}d
\end{tikzcd}$$

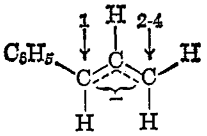
$$k_e/k_i = \frac{100(\text{atoms of D per molecule of cis-II})}{(\%\ \text{I} + \%\text{trans-II})} = 8.6$$

Four major sources of error are inherent in this crude calculation. (1) Some allylbenzene (I) formed returned to starting material. In run 11, the kinetic ratio of *trans*-II/*cis*-II formed from allylbenzene at 98° was 9. Since 19.7% of *trans*-II was observed in run 13, the per cent of *cis*-II formed from the allylbenzene generated is estimated as 19.7/9.0 or 2.2%. The error this 2.2% makes in k_e is small, but the error makes k_i 11% [100(2.2/20.2)] too low. (2) The isomerized products containing deuterium were partially formed from deuterated starting material. The amount of deuterium in *cis*-II recovered after 20% isomerization indicated that out of 100 molecules at time zero, each of the remaining 80 had undergone about 1.7 exchange events. Thus, the total number of exchange events equals 80 × 1.7 or 136. If, on a time average, each of the 20 molecules of isomerized *cis*-II had exchanged about 0.9 times before isomerization, the total number of exchange events becomes 136 + 18 or 154. This value is 13% higher than 136, and suggests that k_e is some 13% low. This source of error roughly offsets that discussed under source 1, and hence $k_e/k_i = 8.6$ when both errors are taken into consideration. (3) The isomerization rate decreased markedly from its initial value at time zero due to incorporation of deuterium into starting material. The data of run 10 suggest that the isomerization rate constant of *cis*-II in deuterated solvent drops from its initial value of about 6×10^{-5} sec^{-1} to a value of about 4.1×10^{-5} sec^{-1} after 90 min. The observed rate constant for isomerization in run 13, 4.2×10^{-5} sec^{-1}, is in good agreement. Use of 6×10^{-5} sec^{-1} as a value for k_i predicts about 27% isomerization in 90 min. Correction of k_e/k_i for this source of error gives a value of about 6.5. (4) No correction for intramolecularity in the exchange process has been applied. If the intramolecularity is about 50%, the measured exchange reaction is approximately 0.5 the rate at which *cis*-II proceeds to the carbanion and returns. Correction for intramolecularity is thus estimated to double the value of k_e/k_i. If, without this correction, the collapse ratio of B is 6 to 7 in favor of *cis*-II over I, then correction for intramolecularity gives an estimate of 10–15.

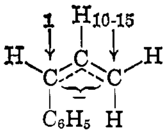
Discussion

This section is divided into three parts. The collapse ratios of the two carbanions are first discussed, followed by a rationalization of the relative stabilities of the two allylic anions. Finally, the kinetic acidities of twelve methyl- and phenyl-substituted propenes are compared.

Collapse Ratios of Allylic Anions. The results of the above calculations of collapse ratios are summarized by the numbers above the arrows in the formulas of allylic anions A and B. Thus, *trans* carbanion A at 25° collapses to *trans*-propenylbenzene (*trans*-II) two to four times faster than to allylbenzene (I). Likewise, *cis* carbanion B at 98° gives *cis*-propenylbenzene (*cis*-II) 10 to 15 times faster than allylbenzene. These data clearly indicate that isotopic exchange of allylbenzene involves little or no B as intermediate, since what little is formed proceeds to *cis*-II.



trans anion (A)



cis anion (B)

The balanced collapse ratio of anion A contrasts markedly with those of the methyl-substituted anions C, D, and E, which protonated 30–40 times faster at the carbon without the methyl substituent.[3a] While the three ground-state olefins in the systems connected by carbanions C and D are about the same in thermodynamic stability, the two ground states that lead to E are not. The equilibrium constant for *cis*-2-phenyl-2-butene/3-phenyl-1-butene has been estimated as being about 500.[3a] These facts indicate that combined inductive and steric effects of the methyl group at work in each carbanion were primarily responsible

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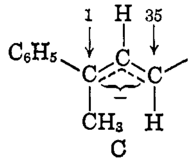
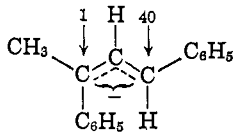
[16] The collapse ratio for allylic anion A also has been estimated from the data of run 14 (98°), in which *trans*-II served as starting material. In the calculation, account was taken of the amount of deuterium introduced directly into *trans*-II (0.05 atom per molecule), and the amount introduced in the reaction *trans*-II → I → *trans*-II (0.17 atom per molecule). Intramolecularity was assumed to be 50%, and the *cis*-II produced was assumed not to return to *trans*-II to an appreciable extent. A value of 6 was obtained, which is somewhat higher than the value of 3 ± 1 estimated above. The difference is probably associated with the 73° temperature difference between runs 12 and 14, which could well affect the intramolecularity. If the intramolecularity fell to 25% at the higher temperature, the collapse ratio would decrease to 3.2. The collapse ratio, itself, is probably not highly temperature dependent.

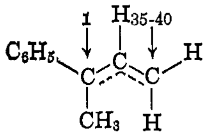
for the unbalanced collapse ratios, and that effects present in the olefinic ground states had little influence on the collapse ratios.



C



D

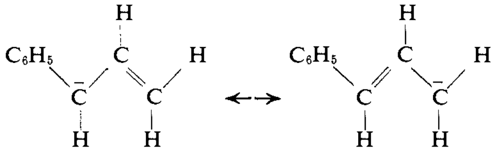


E

In the allylbenzene–propenylbenzene system, the differences in ground states are large. Thus at 25°, *trans*-II/I is ~2000. However, this imbalance in the thermodynamics of the ground states is not reflected in the transition states, since A protonates two to four times as fast to give *trans*-II as to give I. Again effects at work within the carbanion appear to determine the collapse ratio.

Simple molecular orbital theory predicts that the two terminal carbon atoms of the allylic portion of A bear equal amounts of negative charge.[17] To the extent that position of protonation reflects charge distribution, the present results confirm the prediction.

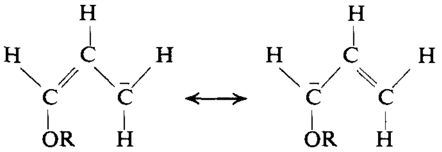
A phenyl group is known to stabilize a carbanion. Thus the pK_a of toluene has been estimated to be about 5 units less than the pK_a of methane.[18] A phenyl group also stabilizes a double bond (at 25° *trans*-II is more stable than I by a factor of about 2000). In a sense, these two effects counter each other in carbanion A, and neither one of the resonance structures (A′ and A′′) appears to be a better description of the carbanion than the other.



A′ A′′

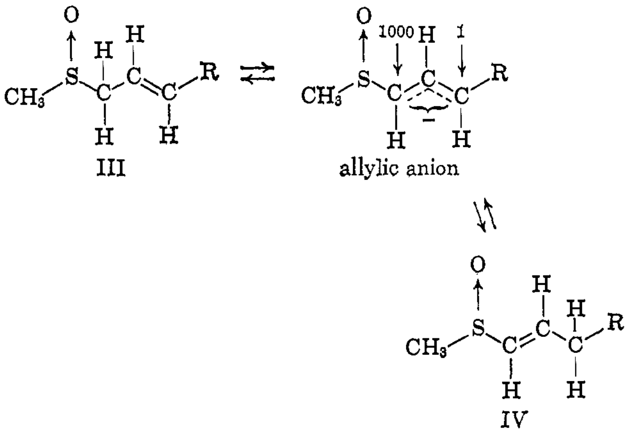
The collapse ratio of 10–15 favoring *cis*-II for the *cis* carbanion B is not as well balanced as that for carbanion A. This small dependence of collapse ratio on configuration (10–15 is about four times 2–4) is somewhat larger than has been observed in the α-benzylstyrene–*cis*- and *trans*-α-methylstilbene system,[3c] where a factor of only 1.3 was observed. Anion B is expected to distribute less charge into the phenyl group than A due to steric inhibition of coplanarity of the phenyl and allylic systems, and anion B is expected to have a larger dipole moment than A. Just how these differences between the anions affect the collapse ratios is difficult to say.

The balanced collapse ratio of carbanion A contrasts with the unbalanced collapse ratios observed for carbanions with alkoxy and alkylsulfinyl substituents. Protonation of the anion derived from an alkyl allyl ether gives predominantly the propenyl ether.[19] An alkoxy group does not appear to stabilize an attached allyl or benzyl anion greatly. The kinetic acidities of 2-phenylbutane and 1-phenylmethoxyethane were very close to one another.[20] The α proton of benzaldehyde dimethyl acetal is not greatly more acidic than the α protons of toluene.[21a] The methyl and vinyl protons of 3,3-dimethoxy-2-methylpropene exchange faster with base than the proton on carbon attached to the two methoxy groups.[21b] On the other hand, a methoxyl group stabilizes a double bond even more than a phenyl group. Thus at equilibrium, 1-methoxy-3-phenylpropene/3-methoxy-1-phenylpropene = 4.[22] Thus an alkoxysubstituted allylic anion is expected to maintain negative charge better on the unsubstituted end. In other words, resonance structure F better represents the anion than F′.



F F′

The relative abilities of a substituent to stabilize a carbanion and to stabilize a double bond are reversed in the case of an alkylsulfinyl substituent. Thus an allylic carbanion with a methylsulfinyl substituent on one end and an alkyl group at the other protonates much faster at the methylsulfinyl end.[23] From the data of the authors[23] on the isotopic exchange rate of III and isomerization rate of IV, a crude ratio of the kinetic acidities of the two isomers can be estimated. This value and the observed equilibrium constant provide a ratio that suggests that collapse of the intermediate anion to the β,γ-unsaturated compound (III) is about 1000 times faster than collapse to the α,β-unsaturated compound (IV). Part of this factor is undoubtedly due to the alkyl substituent. If a factor of 30–40 is assigned to the alkyl group, the methylsulfinyl substituent influences the collapse ratio by a factor of 25–30.



III

allylic anion

IV

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[17] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 418.

[18] D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, p 17.

[19] C. D. Broaddus, *J. Am. Chem. Soc.*, **87**, 3706 (1965).

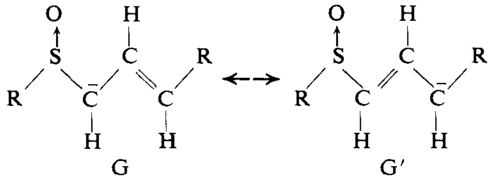
[20] D. J. Cram, C. A. Kingsbury, and B. Rickborn, *ibid.*, **83**, 3688 (1961).

[21] (a) J. P. Lorand, unpublished results; (b) H. M. Relles, unpublished results.

[22] W. von E. Doering and R. Vollrath, unpublished work reported by Broaddus.[19]

[23] D. E. O'Connor and C. D. Broaddus, *J. Am. Chem. Soc.*, **86**, 2267 (1964).

The methylsulfinyl group has a large stabilizing influence upon an attached carbanion. For example, in the above system, III underwent isotopic exchange in sodium deuteroxide–deuterium oxide at room temperature.[23] However, it has been demonstrated that an alkylsulfinyl substituent has little stabilizing effect on a double bond.[24] Thus, resonance structure G for an alkylsulfinyl-substituted allylic anion is expected to better represent the charge distribution than structure G′.


G G′

The behaviors of the sulfinyl, phenyl, and alkoxy-substituted allylic anions vary from protonation predominantly at the substituted site to roughly equal protonation at each site, to protonation predominantly at the unsubstituted site. This variation correlates with the relative abilities of each substituent to stabilize a carbanion and to stabilize a vinyl group.

Relative Stabilities of Configurationally Isomeric Allylic Anions. Equation 1 relates the rate constant for ionization of olefin (k_{ionzn}) to the rate constant for olefin isomerization (k_{isomzn}) and the collapse ratio, expressed as the rate of anion protonation to give starting material over the rate to give product. For allylbenzene at 25° in deuterated solvent (Table III) the rate constant for isomerization to *trans*-II is ${}^{13}/_{14}$ and to *cis*-II is ${}^{1}/_{14}$ the total rate constant for isomerization (3.45×10^{-5} l./mole sec). If the collapse ratio for anion A is about ${}^{1}/_{3}$ and that for anion B is about ${}^{1}/_{10}$, then I ionizes to A with $k_{\text{ionzn}} = 4.3 \times 10^{-5}$ l./mole sec, and to B with $k_{\text{ionzn}} = 2.7 \times 10^{-6}$ l./mole sec. Thus at 25°, allylbenzene ionizes to give A about 16 times faster than it ionizes to give B.

$$k_{\text{ionzn}} = k_{\text{isomzn}}(1 + \text{collapse ratio}) \qquad (1)$$

The values of the rates of ionization of I, of the collapse ratios of the carbanions, and of the equilibrium constants at 25° (Table I) together define the energy profile of Figure 1 (it is assumed that the equilibrium constants in dimethyl sulfoxide are the same as would be observed in *t*-butyl alcohol at 25°). This curve shows that both transition states leading to carbanion B are of higher energy than those leading to A, although that between *cis*-II and B is close in energy to that between I and A. If A and B do not interconvert, and the faster protonation reactions of A and B are equally close to having zero activation energies, then carbanion A is more thermodynamically stable than B.

This result is explainable on the basis of steric interactions within the carbanions. The 1,3 interaction between phenyl and hydrogen at the "bottom" of *cis* carbanion B is more serious than the 1,2 interaction across the "top" of carbanion A. Similar steric interactions are present in *cis*- and *trans*-II. The methyl and phenyl groups lie on the same side of the ethylenic linkage in *cis*-II, and this interaction destabilizes *cis*-II with respect to *trans*-II. The fact that the rates of ionization of I to give A and B ($k_{\text{I}\rightarrow\text{A}}/k_{\text{I}\rightarrow\text{B}} =$ 16) differ by less than the amount that *trans*- and *cis*-II differ at equilibrium (*trans*-II/*cis*-II = 44) simply suggests that the steric interactions in the transition states are not as large as those in the ground states.

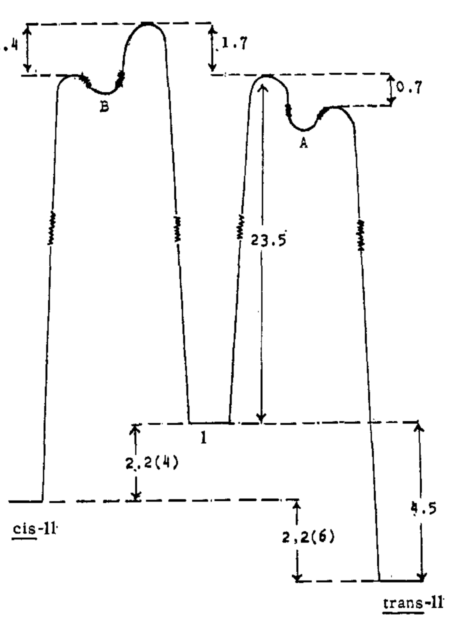
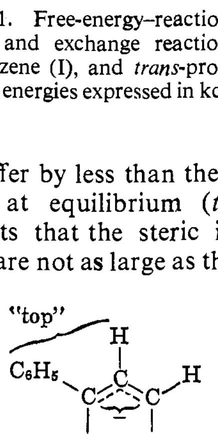
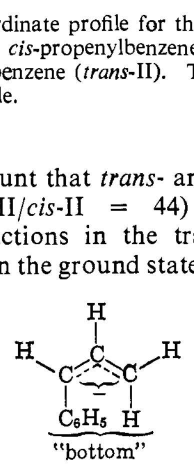


Figure 1. Free-energy–reaction-coordinate profile for the isomerization and exchange reactions of *cis*-propenylbenzene (*cis*-II), allylbenzene (I), and *trans*-propenylbenzene (*trans*-II). The numbers are energies expressed in kcal/mole.



A
1,2-phenyl–hydrogen interaction



B
1,3-phenyl–hydrogen interaction

Bank, *et al.*,[25] have called upon pole–dipole interactions to rationalize the apparent greater stability of *cis*-butenyl anion as compared to the *trans* anion. The *trans* anion A should have a lower dipole moment than the *cis* anion B, and the difference should be greater than the difference in dipole moment of *trans*- and *cis*-II. Thus, a dipole moment explanation for the greater stability of A over B would predict that the difference in activation energies for formation of A and B should be greater than the difference in the ground-state energies of *trans*- and *cis*-II. The opposite is observed and, therefore, the dipole argument is not required to explain the results.

While the dipole argument appears to correlate the relative stabilities of the butenyl anions, problems arise with more complicated systems. Alkyl group dipoles must be assumed to be larger than the net anion dipoles to explain the base-catalyzed isomerization of some of the 4-octene isomers.[26] The rearrangements of allyl ethers to *cis*-propenyl ethers[18,27] are not satisfactorily

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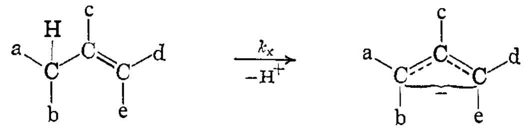
(24) D. E. O'Connor and W. I. Lyness, *J. Am. Chem. Soc.*, **86**, 3840 (1964).

(25) (a) S. Bank, A. Schriesheim, and C. A. Rowe, Jr., *ibid.*, **87**, 3244 (1965); (b) S. Bank, *ibid.*, **87**, 3245 (1965).

(26) M. D. Carr, J. R. P. Clarke, and M. C. Whiting, *Proc. Chem. Soc.*, 333 (1963).

(27) (a) T. J. Prosser, *J. Am. Chem. Soc.*, **83**, 1701 (1961); (b) C. C. Price and W. H. Snyder, *ibid.*, **83**, 1773 (1961); (c) C. C. Price and W. H. Snyder, *Tetrahedron Letters*, **2**, 69 (1962).

Table VII. Estimated Second-Order Rate Constants for Ionization[a] of Methyl- and Phenyl-Substituted Propenes at 25° in 1 *M* Potassium *t*-Butoxide–*t*-Butyl Alcohol-O-*d*



Entry	Olefin and anion substitution					k, l./mole sec	k rel to k_x for I → A	Ref
	a	b	c	d	e			
1	C_6H_5	H	H	H	H	4×10^{-5}	1	...[b]
2	H	C_6H_5	H	H	H	3×10^{-6}	6×10^{-2}	...[b]
3	H	H	H	C_6H_5	H	1×10^{-7}[c]	3×10^{-3}	...[b]
4	H	H	H	H	C_6H_5	6×10^{-7}[c]	2×10^{-2}	...[b]
5	H	C_6H_5	C_6H_5	H	H	4×10^{-7}[c]	1×10^{-2}	3b
6	C_6H_5	H	C_6H_5	H	H	4×10^{-8}[c]	1×10^{-3}	3b
7	H	H	C_6H_5	H	C_6H_5	1×10^{-7}[c]	3×10^{-3}	3b
8	H	H	C_6H_5	C_6H_5	H	3×10^{-8}[c]	8×10^{-4}	3b
9	C_6H_5	CH_3	H	H	H	3×10^{-7}[c]	8×10^{-3}	3c
10	CH_3	C_6H_5	H	H	H	5×10^{-9}[c]	1×10^{-4}	3c
11	H	H	H	C_6H_5	CH_3	2×10^{-8}[c]	5×10^{-4}	3c
12	C_6H_5	CH_3	H	C_6H_5	H	1×10^{-5}[c]	3×10^{-1}	3a
13	CH_3	C_6H_5	H	C_6H_5	H	2×10^{-7}[c]	5×10^{-3}	3a
14	C_6H_5	H	H	C_6H_5	CH_3	3×10^{-4}[c]	8	3a
15	C_6H_5	H	H	CH_3	C_6H_5	2×10^{-5}[c]	5×10^{-1}	3a
16	C_6H_5	CH_3	H	H	C_6H_5	1×10^{-8}[c]	3×10^{-4}	3a

[a] Corrected for return to starting material. [b] Present work. [c] Corrected to 25° with $\Delta H^* = 25$ kcal/mole.

explained by a dipole argument, nor are the rearrangement of allylamines.[27b]

Rates of Ionization of Methyl- and Phenyl-Substituted Propenes. The rates of isomerization of a number of olefins and the collapse ratios of the relevant allylic anions have now been determined in potassium *t*-butyl alcohol–potassium *t*-butoxide.[3] Equation 1 relates the ionization rate of an olefin to its rate of isomerization and the collapse ratio of the anion involved. Table VII lists 12 olefins and the 16 rate constants for ionization of these to discrete allylic anions. When ionization leads to isomeric anions, the rate of ionization of each olefin to each anion is listed. Each value is for protio olefin in 1 *M* potassium *t*-butoxide in *t*-butyl alcohol-O-*d* at 25°. Extrapolations of ionization rates measured at higher temperatures were based on an assumed energy of activation of 25 kcal/mole.[28] All collapse ratios were corrected for intramolecularity. In those cases where per cent intramolecularity was not determined, a value of 50% was assumed (in 7 systems where it has been measured, it varied between extremes of 36 and 59%).[3a] The ionization rates of the olefins relative to that of allylbenzene to A are also listed in Table VII.

The generalizations that may be extracted from the data of Table VII are limited by several ambiguities. The ratio of any pair of rate constants represents both a difference in transition-state and in ground-state energies. Ground-state energy differences between olefins are known from equilibrium data only when the olefins are isomeric. For example, the relative stabilities of allylbenzene and α-benzylstyrene are not known. In α-benzylstyrene a phenyl group has replaced the C-2 hydrogen of allylbenzene. This change is expected to stabilize both the carbanions and the ground state, the carbanions primarily by an inductive effect and the ground state by a conjugative effect. Comparison of the rates of ionization of the two systems indicate that the rates for the α-benzylstyrene are slower. Thus, entry 1 has a rate 10^3 times that of entry 6, and entry 2 has a rate six times entry 5. Steric inhibition of resonance in the anion formation clearly is responsible for the slow rate of entry 6.

The ambiguities caused by unknown ground-state energies become more serious when a phenyl group replaces a hydrogen atom on a terminal carbon of an allylic system. For example, *trans*-1,3-diphenyl-1-butene (entries 12 and 13) is only 30–50 times more reactive than 3-phenyl-1-butene (entries 9 and 10). Entries 12 and 9 compare sterically analogous carbanions, and provide a ratio of 28. Entries 13 and 10 do likewise and give a ratio of 50. In these comparisons, a stabilizing phenyl group has been placed on a vinyl carbon in the ground state of *trans*-1,3-diphenyl-1-butene which is absent in that of 3-phenyl-1-butene. If phenyl is placed on carbon from which the proton is removed, the effect is dramatic. Thus, *cis*-1,3-diphenyl-2-butene (entry 14) is 1.6 × 10^4 more kinetically acidic than *cis*-2-phenyl-2-butene (entry 11). The relative ground-state energies of these two compounds are probably quite similar.

Ratios of ionization rates are also sensitive to steric effects in the transition states in question. Comparisons have only a chance of being meaningful if the interactions across the "tops" and "bottoms" of the two carbanions are not grossly different. An interesting example of the role that steric effects play comes from comparison of the kinetic acidities of 3-phenyl-1-butene (entry 9) with *cis*-1,3-diphenyl-1-butene (entry 16). Here the olefin with one phenyl group is about 30 times more acidic than the olefin with two phenyl substituents. This order is exactly opposite to that noted above for entries 9 and 12. Undoubtedly, the carbanion of entry 16 is badly warped and, therefore, destabilized because of the large 1,3 repulsions along its bottom side.

Several gross estimates of the effect of methyl group

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(28) For isomerization of *cis*-1,3-diphenyl-1-butene, $\Delta H^* = 26 \pm 1$ kcal/mole in *t*-butyl alcohol–potassium *t*-butoxide.[3a] For isomerization of α-benzylstyrene, $\Delta H^* = 23.0$ kcal/mole in the same medium.

substitution can be made. Allylbenzene is about 125 times more kinetically acidic than 3-phenyl-1-butene when the favored carbanions are compared (entries 1 and 9). Ionization to the less favored carbanions in each case (entries 2 and 10) differs by a factor of about 600. In the diphenylbutene series, *cis*-1,3-diphenyl-2-butene is 27 times more acidic than *trans*-1,3-diphenyl-1-butene (entries 12 and 15). The same carbanion is generated in each case. Likewise, *trans*-1,3-diphenyl-2-butene (entry 15) is roughly 100 times more acidic than *trans*-1,3-diphenyl-1-butene (entry 13). Again the two substances give the same anion. Both of these two comparisons pit direct methyl substitution against vinyligous methyl substitution. Finally, *trans*-propenylbenzene is only six times more acidic than *cis*-2-phenyl-2-butene (entries 3 and 11).

The most striking aspect of the data of Table VII is that the total range of the kinetic acidities is so small. The largest difference is a factor 8×10^4 (entries 4 and 10). The differences in reactivities in an abbreviated series of methyl- and phenyl-substituted allylic halides, which solvolyze through allylic carbonium ion intermediates, is on the order of 5×10^5.[29] In contrast to the factors of 6 to 600 for the decreases in ionization rates caused by methyl substitution in the carbanion series, crotyl chloride solvolyzes about 4000 times faster than allyl chloride; α-methylallyl chloride reacts some 6000 times faster than allyl chloride. There are potentially large differences between allylic halide solvolyses and base-catalyzed olefin isomerizations. The modes of solvation are different, and the degrees of solvation, particularly of the transition states, may be very different. The transition states for the two series may vary in the degrees of bond breakage. However, one consideration leads to a prediction that the effects of methyl substitution should be greater in the carbanion than in the carbonium ion series. Replacement of hydrogen by methyl should stabilize both the ground states and transition states in allylic carbonium ion chemistry, but should stabilize the ground states and destabilize the transition states in allylic carbanion reactions.

The differences in reactivities caused by phenyl substitution are also smaller in allylic carbanion chemistry than in allylic carbonium ion chemistry. Cinnamyl chloride solvolyzes some 5×10^5 times faster than allyl chloride.[29] The factor of 1.6×10^4 between the kinetic acidities of *cis*-1,3-diphenyl-2-butene and *cis*-2-phenyl-2-butene has been mentioned above (entries 11 and 14).

Experimental Section

Starting Materials. Allylbenzene (Aldrich Chemical Co.) was subjected to preparative vpc on column A (see below) at 86°, 10 psi, to give a clear, colorless liquid, n^{25}D 1.5086, which by analytical vpc contained less than 0.05% of either *cis*- or *trans*-propenylbenzene. The nmr spectrum (26% in carbon tetrachloride) gave a singlet (5 H) at τ 2.90, a complex multiplet of at least 13 peaks (1 H) from 3.6 to 4.6, two singlets (2 H) each containing complex fine splitting at 4.92 and 5.11, and a rather broad doublet (2 H, J = 7 cps) centered at 6.73.

Allylbenzene (I) was converted to *trans*-propenylbenzene as follows. Under dry, pure nitrogen, 3.01 g of I was heated at 50° for 10 hr in 30 ml of *t*-butyl alcohol about 0.4 M in potassium *t*-butoxide. The mixture was cooled and shaken with water, brine, and purified pentane. After further extraction of the aqueous layer and washing of the organic layer, the latter was dried and evaporated under reduced pressure to give 2.80 g of straw-colored liquid. Analysis of this material on a 6 ft × 0.25 in. vpc column packed with 23% 4-methyl-4-nitropimelonitrile on 42–60 mesh firebrick (90°, 15 psi) showed 1% allylbenzene, 14% *cis*-II, and 84% *trans*-II. This analysis was performed with a thermal conductivity detector; peak area ratios were not corrected to molar ratios. During a second preparation of *trans*-II, an aliquot was taken after 2 hr at 50° and analyzed by the calibrated vpc column described below to give 32% reaction with *trans*-II/*cis*-II = 11.5. The main portion of the first preparation was flash distilled at about 30 mm (2.60 g or 87%) and subjected to preparative vpc (column A, 85°, 10 psi). The major component was passed through a column of 40 g of silica gel with 98% pentane–2% ether as eluent and flash distilled to give 2.03 g of clear, colorless liquid, n^{25}D 1.5477 (lit.[30] n^{25}D 1.5473). This material contained about 0.06% *cis*-propenylbenzene and less than 0.01% allylbenzene by vpc analysis. The nmr spectrum (15% in carbon tetrachloride) gave a singlet (5 H) at τ 2.78, a complex multiplet (2 H, nine peaks) from 3.40 to 4.2, and a doublet with further fine structure (3 H) centered at 8.17. This spectrum is in qualitative agreement with that for *trans*-propenylbenzene at 40 Mc reported previously.[7] The ultraviolet spectrum was identical with that previously reported[30] for *trans*-II. The minor product from the isomerization reaction was collected by vpc to give 0.152 g of *cis*-II. The nmr spectrum (21% in carbon tetrachloride) gave a singlet (5 H) at τ 2.80, a doublet of quartets (1 H, J = 11.5 and ~1.5 cps) centered at 3.58, a doublet of quartets (1 H, J = 11.5 and 7.0 cps) centered at 4.30, and a doublet of doublets (3 H, J = 7.0 and ~1.5 cps) centered at 8.15. The material was flash distilled and identified as *cis*-II by its ultraviolet spectrum in 95% ethanol, λ_{max} 240.5 mμ (ϵ 13,200), lit.[30] λ_{max} 240.6 mμ (ϵ 13,800).

A larger sample of *cis*-propenylbenzene was prepared as follows. Solutions of *trans*-II, 0.60 g, n^{25}D 1.5479, and sodium-dried benzene, *ca.* 0.05 M in α-naphthyl phenyl ketone, were prepared in two 18 × 150 mm Pyrex test tubes that had been drawn out to facilitate sealing.

The tubes were degassed three times, sealed, thawed, and positioned *ca.* 5 cm from a Hanovia medium pressure Type No. 54A36 200-w lamp. The tubes were irradiated for 78 hr and then opened and the contents chromatographed through 20 g of silica gel with 98% pentane–2% ether as eluent. After the benzene solutions were placed on the column, two 100-ml fractions were collected; the first of these was partially evaporated to give 1.95 g of material which showed a *cis*-propenylbenzene/*trans*-propenylbenzene ratio of 7.1 by vpc analysis. The second fraction was evaporated under reduced pressure to give 0.053 g of material which was discarded. The contents of the first fraction were subjected to preparative vpc (column A, 91°, 11 psi); the major component was collected, passed through a filter column of silica gel, and flash distilled to give 0.66 g (55%) of *cis*-propenylbenzene, n^{25}D 1.5408 (lit.[30] n^{25}D 1.5400). This material contained *ca.* 0.05% *trans*-propenylbenzene and *ca.* 0.01% allylbenzene by vpc analysis. The nmr spectrum was identical with that of the *cis*-propenylbenzene isolated during the preparation of *trans*-propenylbenzene.

Purification of 3-Phenylpentane. A sample of 3-phenylpentane (Shell Chemical Co.) was subjected to vpc purification through a 20 ft. × 3/8 in. column packed with 20% SE-30 on 60–80 firebrick. The purification was carried out on a Wilkens "Autoprep" machine; oven temperature, 200°; helium flow, 85 ml/min; injection volume, *ca.* 0.15 ml of a *ca.* 2:1 solution of hexane and 3-phenylpentane. A post-collection timer was employed to eliminate traces of high-boiling impurities. The collected hydrocarbon was flash distilled at aspirator pressure to give 0.77 g of 3-phenylpentane, n^{25}D 1.4863 (lit.[31] n^{25}D 1.4868). Analysis of this material by vpc (see below) indicated no low-boiling impurities; a high-boiling impurity (no more than 0.1%) appeared as a shoulder on the tail of the main peak.

Solvents and Solutions. The purification of *t*-butyl alcohol, the preparation of solutions of potassium *t*-butoxide in *t*-butyl alcohol and *t*-butyl alcohol-O-*d*, and the procedure for standardization of these solutions have been described previously.[3c] The *t*-butyl alcohol-O-*d* was prepared by the method previously reported.[32]

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[29] P. D. B. de la Mare in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Division of John Wiley and Sons, Inc., New York, N. Y., 1963, p 43.

[30] R. Y. Mixer, R. F. Heck, S. Winstein, and W. G. Young, *J. Am. Chem. Soc.*, **75**, 4094 (1953).

[31] D. J. Cram., *ibid.*, 74, 2152 (1952).

[32] D. J. Cram and B. Rickborn, *ibid.*, **83**, 2178 (1961).

Analysis of Olefin Mixtures by Vapor Phase Chromatography. Analyses of olefin mixtures were carried out on a Wilkens Model 204 gas chromatograph equipped with flame ionization detectors. The recorder employed was a Leeds and Northrup Model W equipped with a disk integrator. The column used was 10 ft. × $^{1}/_{8}$ in. (outer diameter) copper tubing packed with 5% SE-30 silicone gum and 0.5% Atpet 80 (anti-tailing agent) on 80–100 mesh HMDS-treated Chromosorb W (0.22 g/ft). The injection block, column oven, and detector oven temperatures were *ca.* 150, 65, and 120°, respectively. Nitrogen served as carrier gas; the flow was *ca.* 30 ml/min. Under these conditions, *trans*-propenylbenzene was eluted in *ca.* 16 min. Retention time ratios, relative to *trans*-propenylbenzene, were: allylbenzene, *ca.* 0.50; *cis*-propenylbenzene, *ca.* 0.75; 3-phenylpentane, *ca.* 1.50.

Calibration of Olefin–3-Phenylpentane Mixtures. Weighed amounts of each olefin and 3-phenylpentane were mixed thoroughly and stored in the freezer under nitrogen. Portions of each of the three mixtures were subjected to the work-up procedures described below and analyzed. With each mixture multiple analyses established an average ratio of peak area of olefin to peak area of standard 3-phenylpentane. This area ratio was divided into the known molar ratio (olefin to standard) to yield an area to moles correction factor for each mixture. The correction factor for each mixture was: for allylbenzene, 1.31 (±0.01); for *cis*-propenylbenzene, 1.27 (±0.01); for *trans*-propenylbenzene, 1.28 (±0.01). In the kinetic runs that involved 3-phenylpentane as internal standard, the peak area of each olefin was multiplied by its correction factor, and the sum of the corrected areas was compared to the measured area of the 3-phenylpentane peak. In runs not involving internal standard, each peak area was multiplied by the appropriate correction factor, and the relevant molar ratio of olefins was calculated. With each olefin–3-phenylpentane mixture, it was established that the peak area ratio was not dependent on injection sample size. All data in the Results section are expressed in molar ratios.

Calibration of Olefin Mixtures. The linearity of detector response was tested by analysis of olefin mixtures of known composition. A carbon tetrachloride solution of *cis*-propenylbenzene and *trans*-propenylbenzene that was 3.39 mole % in the former olefin was prepared and subjected to work-up by procedure B outlined below. Three analyses gave 3.31 mole % *cis*-propenylbenzene. The difference (0.08 or 2.5%) between the found and expected values is within experimental error; there was a *ca.* 1% weighing error associated with the 24 mg of *cis*-propenylbenzene, and the six dilution operations carried out in preparing the standard solution account for the remaining 1.5% error. In a similar manner a carbon tetrachloride solution of allylbenzene–*trans*-propenylbenzene, 0.51 mole % in the former olefin, was analyzed. Four analyses gave 0.54 ± 0.02% allylbenzene.

Preparative vapor phase chromatography was performed upon a machine designed and constructed in these laboratories by Mr. Richard Gillespie. Thermal-conductivity detection was employed. Two columns were used for preparative separation of mixtures of the olefins. Column A was 6 ft × 0.75 in. copper tubing packed with 23% 4-methyl-4-nitropimelonitrile on 42–60 mesh firebrick. Column B was 6 ft. × $^{3}/_{8}$ in. aluminum tubing packed with 20% SE-30 silicone gum on 60–80 mesh HMDS-treated Chromosorb W (5.1 g/ft). Collection of the pure olefins was efficient when a *ca.* 18-in. coil of 9-mm tubing packed with glass helices was employed. In the exchange runs, in order to minimize the volume of the solvent necessary to wash the sample from the collector, a *ca.* 10-in. U-tube of 5-mm glass was employed. With this apparatus, collection was much less efficient and marked aerosoling of the sample was observed.

Nuclear Magnetic Resonance Analyses. All spectra were recorded at 60 Mc on a Varian Associates Model A-60 spectrophotometer as solutions in spectral grade carbon tetrachloride. (Concentrations are expressed as wt/wt % in the relevant places in the Experimental Section.) Tetramethylsilane (2–5%) was used as internal standard in the spectra for characterization of the olefins; in the spectra of the exchanged olefins it was omitted. In the exchange experiments, the relevant signals of samples of reacted olefin and authentic protio olefin were each integrated 12 times; the highest and lowest values were discarded, the remaining 10 averaged, and the standard deviation calculated. In a sample of reacted olefin, the integrated area of a signal due to protons that were suspected of having suffered exchange was divided by the integrated area of a signal due to protons that were considered not to have suffered exchange in the course of the experiment. This ratio was subtracted from the corresponding ratio found in the spectrum of the protio material. The corresponding ratio for the protio material was divided by the number of exchangeable protons and the resulting number divided into the difference in ratios between protio and reacted material to give the fraction exchange per exchangeable proton. As an example, in the case of exchanged *trans*-propenylbenzene, one set of analyses gave a methyl/phenyl ratio of 0.604 for standard material and 0.559 for reacted material. The former less the latter gives 0.045; this divided by one-third of 0.604, or 0.201, gives 0.224, or 22.4% of one methyl proton exchanged. The standard deviations associated with each experimental error were carried through the calculations; hence the final standard deviation in each per cent exchange represents random errors in integration and in no way represents systematic errors inherent in the sample or machine.

Isolation Procedures for Vapor Phase Chromatographic Analyses. A general procedure was adopted for vpc analysis of solutions containing the three olefins and internal standard. An aliquot of the reaction solution was taken up in a syringe and added to a 5-ml centrifuge tube that contained 3.0 ml of a solution of 98% water–2% saturated brine (by volume) and a known volume of spectral grade carbon tetrachloride. The tube was stoppered, shaken vigorously, and hand-centrifuged. The organic layer was transferred to an empty 5-ml centrifuge tube and a fresh portion (3.0 ml) of the water-brine solution added. This tube was stoppered, shaken, centrifuged, and cooled to 0° until the organic solution was analyzed. This tube was then warmed to 25° and *ca.* 0.6 μl of the organic layer drawn into a 10-μl syringe. Immediately after removal of an aliquot, the tube was again stoppered and cooled.

Upon prolonged standing the solutions of the olefins were observed to selectively lose allylbenzene and, to a much lesser extent, *cis*-propenylbenzene. It was not determined whether this loss was strictly an evaporative process or if absorbance of the olefins by the cork played a role. It was observed that the use of a tightly fitting rubber serum cap instead of a cork accelerated the loss. The loss of allylbenzene was not a serious source of error; for example, with samples containing a small (*ca.* 1%) of allylbenzene, a period of 4 or 5 days produced a loss of *ca.* 0.1%. Likewise with *ca.* 2:1 mixtures of allylbenzene and 3-phenylpentane, the measured ratio changed by *ca.* 5 to 10% in a week's time. The loss did not appear to be a function of the number of times the tube was uncorked for removal of vpc samples. In general, analyses were performed within 4–6 hr after isolation. No data represent analyses performed longer than 24 hr after isolation.

Three different sets of reaction aliquot and carbon tetrachloride volumes were employed. Procedure A involved 1 ml of *t*-butyl alcohol *ca.* 0.4 *M* in potassium *t*-butoxide and, in general, 0.1 *M* in olefin as the reaction aliquot and a carbon tetrachloride volume of 0.5 ml. Procedure B involved 0.25 ml of *t*-butyl alcohol–potassium *t*-butoxide–olefin aliquot and 0.25 ml of carbon tetrachloride. Procedure C involved 0.25 ml of dimethyl sulfoxide–potassium *t*-butoxide–olefin aliquot and 0.25 ml of carbon tetrachloride. Mixtures of each olefin and 3-phenylpentane were analyzed by each procedure. The ratios of olefin to internal standard did not vary with the procedure employed.

Base-Catalyzed Equilibration of Allylbenzene and *cis*- and *trans*-Propenylbenzenes at 97° in *t*-Butyl Alcohol. Portions (*ca.* 17 mg) of the standard allylbenzene–3-phenylpentane mixture were added to clean and dry 10 × 75 mm test tubes that had been drawn out to facilitate sealing. Purified nitrogen was swept through each tube and 1.00 ml of a solution of *t*-butyl alcohol 0.42 *M* in potassium *t*-butoxide was added with a microburet. Each tube was swept with nitrogen, immersed in a Dry Ice–acetone bath, and sealed. The same procedure was repeated with portions of the *trans*-propenylbenzene–3-phenylpentane mixture and with *cis*-propenylbenzene. The tubes were thawed, shaken, and initially placed in a 50° bath. After 9 days at 50°, a tube that initially contained *trans*-propenylbenzene–3-phenylpentane was opened and subjected to isolation by procedure A. Analysis showed only *ca.* 0.6% of *cis*-propenylbenzene. The tubes were then transferrred to the 97° bath and let stand for 18 days. After this time a total of three tubes, each one originally having contained a different olefin, were cooled and the contents subjected to procedure A isolation. Analyses by vpc appear in the tables. The tube that originally contained allylbenzene and 3-phenylpentane gave an olefin to internal standard ratio of 1.92 (the original molar ratio was 2.00). The tube that originally contained *trans*-propenylbenzene and 3-phenylpentane gave an olefin to internal standard ratio of 2.09 (the original molar ratio was 2.07).

At 25° in Dimethyl Sulfoxide. Potassium *t*-butoxide (MSA Corp.), 0.118 g or 0.00105 mole, was quickly weighed and added to a clean, dry 25-ml flask that had been thoroughly swept with purified nitrogen. The flask and contents were again swept with nitrogen and then capped with a stopper fitted with a Teflon sleeve, stopcock, and serum cap. Dimethyl sulfoxide (Baker Chemical Co.), 10 ml, was withdrawn in a dry syringe and added to the flask, the solution was swirled, and the flask was set in the 25° bath. A *ca.* 36-mg portion of the 3-phenylpentane–*trans*-propenylbenzene mixture was added to a clean, dry 5-ml pear-shaped flask that had been thoroughly swept with nitrogen and capped with a stopper fitted with a Teflon sleeve, stopcock, and serum cap. Two other flasks were similarly charged with equivalent portions of the *cis*-propenylbenzene–3-phenylpentane mixture and of allylbenzene. The three flasks were placed in the 25° bath and after a few minutes, 1.0-ml portions of the dimethyl sulfoxide–potassium *t*-butoxide solutions were transferred to each by means of a 2.0-ml syringe. The flasks were swirled and let stand for *ca.* 30 min., at which time 0.25-ml aliquots were withdrawn from each flask and subjected to procedure C isolation. The vpc analyses appear in the tables. Each aliquot appeared homogeneous and was colored a deep green; the color was discharged upon quenching. Each sample showed several new high-boiling peaks, together totaling no more than 1–2% of the total area of the olefin peaks. The major impurity gave a retention time of *ca.* 2.5 relative to that of *trans*-propenylbenzene. A very small (*ca.* 0.1% or less) peak appeared some 96 min after sample injection. In each analysis this peg was allowed to appear in order to secure a steady base line throughout the next analysis. The ratio of total olefins to internal standard in the run originating from *trans*-propenylbenzene was 2.34 (the original molar ratio was 2.07). Similarly, from *cis*-propenylbenzene, a ratio of 2.92 *vs.* that of 2.55 was observed.

Kinetic Runs. Allylbenzene at 25° in *t*-Butyl Alcohol. The mixture of allylbenzene and 3-phenylpentane, 272 mg (1.42 mmoles of allylbenzene), was weighed out in a clean, dry 50-ml pear-shaped flask. The flask was placed in the 25° bath and swept with purified nitrogen. A solution of potassium *t*-butoxide in *t*-butyl alcohol was equilibrated in the 25° bath, and, with a clean and dry pipet, 15 ml of the solution was transferred to the reaction flask. After the flask was swept with nitrogen for a few seconds, it was capped with a stopper fitted with a Teflon sleeve, stopcock, and serum cap. The flask was then swirled vigorously (initial swirling denoted time zero) and let stand in the bath. Immediately after swirling, a portion of the reaction mixture was withdrawn; titration gave 0.416 *M* base. At appropriate times *ca.* 1-ml aliquots of the reaction solution were removed and subjected to isolation procedure A. The ratio of total olefins to internal standard remained constant throughout the run at close to the orginal value of 2.00.

Allylbenzene at 25° in *t*-Butyl Alcohol-O-*d*. The procedure employed was identical with that for allylbenzene in protio solvent at 25° with the following exceptions. The weight of substrate mixture used was 88.6 mg which corresponded to 0.46 mmole of olefin; 5.0 ml of potassium *t*-butoxide–*t*-butyl alcohol-O-*d* (0.99 atom of deuterium per molecule) was added. A 1.00-ml aliquot gave 0.394 *M* for base concentration. The volumes of the aliquots were 0.25 ml and the isolation procedure employed was procedure B. The ratios of olefins to internal standard remained constant throughout the run.

***cis*-Propenylbenzene at 97.7° in *t*-Butyl Alcohol.** A portion of the standard *cis*-propenylbenzene–3-phenylpentane mixture, 37.9 mg, or 0.216 mmole of olefin, was added to a clean, dry 5-ml pear-shaped flask that had been thoroughly swept with purified nitrogen. To the flask was added 2.00 ml of *t*-butyl alcohol, 0.390 *M* in potassium *t*-butoxide. The flask was again swept with purified nitrogen; the top was then quickly plugged with a serum cap and the flask swirled. During this time a large-bore hypodermic needle had been fitted to the nitrogen line and, with a fast stream of nitrogen passing through it, the needle was inserted into a clean, dry 6-mm tube that had been closed off at one end and constricted to facilitate sealing. After the nitrogen had passed through the tube for a few minutes, the needle was removed and the tube quickly plugged with a serum cap. In this manner five more tubes were purged with nitrogen. With the aid of a clean, dry hypodermic needle and a 0.5-ml syringe, *ca.* 0.25 ml of the substrate–base solution prepared above was withdrawn from the flask and quickly transferred to tube. Each of the six tubes was so loaded; in each transfer the needle was inserted and withdrawn through the serum cap of the flask, but, in order to reduce transfer time, the serum cap on each tube was momentarily removed when the syringe needle was inserted. Each of the tubes was then placed on the vacuum line, frozen in a Dry Ice–acetone bath, opened to vacuum, and sealed. The tubes were thawed and shaken, and five of the six were placed in the constant-temperature bath. The sixth was opened and subjected to isolation by procedure B. Analysis of this tube by vpc established that no isomerization had occurred during the above operations. At appropriate times a tube was removed, cooled to room temperature, and opened and the contents subjected to isolation by procedure B. The vpc analyses are presented in the tables. The ratios of total moles of olefin to moles of internal standard averaged 2.81 instead of the expected 2.55. The large (±0.12) and random scatter among the five points, as well as the fact that in the duplicate run in deuterated solvent the ratios averaged to the predicted number with little scatter, suggests that the discrepancy (amounting to loss of *ca.* 9% of 3-phenylpentane) was a function of the manner in which the tubes were prepared in this run.

***cis*-Propenylbenzene at 97.7° in *t*-Butyl Alcohol-O-*d*.** This run was conducted in a manner identical with the corresponding run in protio solvent with only the following exceptions. The weight of substrate was 38.9 mg, or 0.220 mmole, of olefin; the base concentration was 0.398 *M*. The average of the ratio of total moles of olefin to moles of 3-phenylpentane for the four points was 2.56 (±0.04) which is identical with the theoretical value of 2.55.

Allylbenzene at 97.8°. A tube of *ca.* 2-ml capacity and fitted with a 14/38 joint was cleaned, dried, flushed with purified nitrogen, and stoppered with a serum cap. The cap was wired in place and *ca.* 0.5 ml of *t*-butyl alcohol, 0.39 *M* in potassium *t*-butoxide, was transferred to the tube with a clean, dry syringe. The tube was placed in the constant-temperature bath, swirled, positioned so that only the serum cap was above the oil level, and allowed to equilibrate for *ca.* 10 min. Allylbenzene, *ca.* 5 mg, was withdrawn with a microsyringe and injected directly into the hot solution through the serum cap. The tube was swirled and, 1 min after the olefin had been added, quickly removed from the bath, opened, and directly poured into a centrifuge tube loaded with the mixture for isolation by procedure B. Analysis by vpc showed 33.4 ± 0.1% reaction with a *trans*-propenylbenzene to *cis*-propenylbenzene ratio of 9.0 (±0.1).

Preparative Isomerizations of the Olefins in Potassium *t*-Butoxide–*t*-Butyl Alcohol-O-*d*. Allylbenzene at 25°. Allylbenzene, 0.588 g, was added to a ground-glass-stoppered 50-ml flask that had been swept with purified nitrogen. This flask and a second that contained the solvent–base solution were placed in the 25° bath for *ca.* 15 min. Each flask was flushed with purified nitrogen and 25.0 ml of the basic solution was added to the flask containing the olefin. This latter flask was momentarily flushed with nitrogen, then stoppered with a glass stopper fitted with a Teflon sleeve, shaken, and allowed to stand for 35.9 hr. The flask was opened, a 0.1-ml aliquot removed for vpc analysis (procedure B), a 1.00-ml aliquot removed for titration, and the remainder of the reaction solution poured into a separatory funnel that contained 300 ml of water, 30 ml of saturated brine, and 200 ml of pentane. The mixture was shaken and separated; the aqueous phase was washed with a 200-ml portion of pentane. The pentane phases were combined and washed with single 200-ml portions of water and brine, dried, and filtered into a 1000-ml round-bottomed flask. The 1.00-ml aliquot was added to 15 ml of water and titrated to give 0.394 *M* base. The aqueous solution was then poured into a separatory funnel and the titration flask washed with 25 ml of pentane and 10 ml of water. The washings were added to the separatory funnel, the mixture shaken and separated, and the aqueous phase washed with 20 ml of pentane. The pentane phases were combined and washed with single 20-ml portions of 1 *M* sodium hydroxide, water, and brine. The pentane layer was then dried, filtered, and added to the dried pentane solution of the major portion of the reaction mixture. Most of the pentane was then evaporated on the steam bath through a 30-in. Vigreux column. The residue was transferred to a tared 50-ml flask and further evaporated under reduced pressure. A portion of the remaining 0.88 g of solution was transferred to an nmr tube for preliminary analysis. The benzyl and terminal vinyl protons of allylbenzene were well separated from the protons of the propenylbenzene isomers and pentane, but the low concentration of allylbenzene precluded precise integration. The solution was washed from the nmr tube into the original 50-ml flask. A small portion (*ca.* 10–15 mg of olefins) of the resulting solution was removed for experimentation with mass spectral analysis, and the remainder was subjected to preparative vpc (column B, 88°, 11 psi). The recovered allylbenzene, 60 mg, was washed from the collector with a small portion of spectral grade carbon tetrachloride and filtered through a plug of anhydrous magnesium sulfate into an nmr tube. An additional few drops of carbon tetrachloride were used to rinse the magnesium sulfate plug and were added to the tube. The nmr spectrum (20%) showed no extraneous peaks; a spectrum (19%) of unreacted allylbenzene was used for comparison of peak ratios. After nmr analyses, both tubes were sealed under vacuum and submitted for total deuterium analyses. The reacted allylbenzene (in carbon tetrachloride solution) showed 1.85 atom % excess deuterium; the protio solution gave 0.04 (compared to benzoic acid).

The collected *trans*-propenylbenzene, 0.319 g, was filtered through a 5-g plug of silica gel and flash distilled. Part of the distillate was diluted with carbon tetrachloride; nmr analysis of the resulting solution (24%) was compared to a 23% solution of protio olefin. The remainder of the distillate was submitted for total deuterium analysis. The pertinent vpc, nmr, and deuterium analysis data for this experiment appear in the Results section.

***cis*-Propenylbenzene at 97.7°.** The olefin, 0.226 g, was added to a clean, dry 18 × 150 mm test tube that had been constricted to facilitate sealing and swept thoroughly with pure nitrogen. The tube was again swept briefly with purified nitrogen and capped with a serum cap. With a clean, dry 10-ml syringe that had been purged with nitrogen, 10.0 ml of *t*-butyl alcohol-O-*d* (0.99 atom of deuterium per molecule), 0.394 *M* in potassium *t*-butoxide, was added to the tube. The tube was immediately fixed on the vacuum line; the contents was frozen with a Dry Ice–acetone bath and exposed to vacuum, and the tube was sealed. The contents was thawed in the constant-temperature bath; when all solid had melted the tube was shaken thoroughly and totally immersed in the bath, and the timer was started. After 90 min the tube was removed from the oil bath and immersed in a 600-ml beaker filled with water. The outside of the tube was cleaned, the tube opened, and 0.1 ml of the contents was removed and worked up (procedure B) for vpc analysis. The remaining reaction solution was added to a separatory funnel filled with 100 ml of pentane, 150 ml of water, and 15 ml of saturated brine. The isolation procedure was on a scale of one-half of that used in the allylbenzene exchange experiment. The reaction mixture was subjected to preparative vpc (column A, 88°, 10 psi). The recovered starting material, 67 mg, was transferred from the collector to an nmr tube by the method used for starting material in the allylbenzene exchange experiment. The nmr solution (15%) of reacted olefin was integrated against a 15% solution of authentic protio olefin. After nmr analysis the two tubes were sealed and submitted for total deuterium analysis. The pertinent analytical data appear in the Results section.

***trans*-Propenylbenzene at 97.7°.** This experiment was performed in the same way as the above experiment involving *cis*-propenylbenzene. The sample of *trans*-propenylbenzene used (270 mg) contained *ca.* 0.06% *cis*-propenylbenzene and less than 0.01% allylbenzene by vpc analysis. The *t*-butyl alcohol-O-*d* (0.99 atom of deuterium per molecule) contained 0.394 *M* potassium *t*-butoxide. The contents of the tube was melted in the 75° bath, and only when the contents were melted and mixed was the tube immersed in the 97.7° bath for 30 min. Starting material was recovered by preparative vpc (column A, 90°, 10 psi); the 131 mg collected was passed through a 6-g column of silica gel with pentane as eluent and flash distilled at aspirator pressure. The solution prepared for nmr analysis (33%) was integrated against a 33% solution of unreacted olefin. The pertinent analytical data appear in the tables.

Control Runs. Allylbenzene at 25°. Allylbenzene, *ca.* 10 mg, and *t*-butyl alcohol, *ca.* 0.25 ml that had been distilled from molecular sieves, were mixed in a 6-mm o.d. tube that had been swept with purified nitrogen. The tube was sealed under vacuum and placed in the 25° bath for 90 hr. It was then opened and the contents subjected to isolation by procedure B (no added base). Analysis demonstrated the presence of less than 0.2% of either of the propenylbenzenes.

***cis*-Propenylbenzene at 98°.** A mixture of *cis*-propenylbenzene and 3-phenylpentane, *ca.* 3 mg, and *ca.* 0.2 ml of *t*-butyl alcohol that had been distilled from molecular sieves, was placed in a 6-mm tube that had been swept with purified nitrogen. The tube was sealed under vacuum and placed in the 98° bath for 22 hr. The tube was then opened and the contents worked up by procedure B (but with no added base). Analysis showed 4.0% *trans*-propenylbenzene and less than 0.05% allylbenzene. Analysis of the starting mixture showed that less than 0.1% *trans*-propenylbenzene was present. It was not rigorously demonstrated that the 4% of the *trans* isomer did not arise by ionic catalysis from trace amounts of acid introduced in the mixing, sealing, or isolation processes.

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ortho-Substitution Rearrangement of 2- and 4-Substituted Benzyltrimethylammonium Ions Having Functional Substituents[1]

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Abstract: *ortho*-Substitution rearrangements of 2- and 4-substituted benzyltrimethylammonium ions in which the substituent contained a carbinol, amide, ketone, or olefin group were effected by means of potassium amide in liquid ammonia. Generally the reagent reacted initially with an active hydrogen of the substituent to form monoanions, which underwent rearrangement with excess reagent through appropriate dianions. Certain of the rearranged amines from the 4-substituted quaternary ions were further rearranged through their methiodides. An earlier method for preparation of the 4-substituted benzyldimethylamines required for their methiodides was improved and extended. Theoretical and synthetic aspects of the rearrangement are considered.

Ring-substituted benzyltrimethylammonium ions have previously been observed to undergo the *ortho*-substitution rearrangement with sodium amide or potassium amide in liquid ammonia when the 2, 3, or 4 substituent was methyl,[2,3] methoxy,[3] or chloro[3] and the 3 substituent was benzyl,[4] but not when the 2 or 4 substituent was benzyl,[4] the 3 substituent bromo or trifluoromethyl,[3b] and the 4 substituent cyano.[3a] With the possible exception of the 3-benzyl quaternary ion, none of these quaternary ions underwent an initial reaction with the reagent involving the ring substituents and yet exhibited the rearrangement with excess reagent. Recently,[5] however, two such examples were reported.

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[1] Supported by the Army Research Office (Durham) and by the National Science Foundation.

[2] S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **73**, 4122 (1951).

[3] (a) W. Q. Beard, Jr., and C. R. Hauser, *J. Org. Chem.*, **25**, 334 (1960); (b) W. Q. Beard, Jr., D. N. Van Eenam, and C. R. Hauser, *ibid.*, **26**, 2310 (1961).

[4] C. R. Hauser, W. Q. Beard, Jr., and F. N. Jones, *ibid.*, **26**, 4790 (1961).

[5] R. L. Vaulx, G. C. Jones, and C. R. Hauser, *ibid.*, **27**, 4385 (1962).