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Electrophilic Substitution at Saturated Carbon. XXIII. Stereochemical Stability of Allylic and Vinyl Anions[1]

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The potassium *tert*-butoxide catalyzed isomerization and hydrogen-isotope exchange reactions of *cis*- and *trans*-α-methylstilbene and α-benzylstyrene, and of *cis*- and *trans*-stilbene, have been studied in *tert*-butyl alcohol and *tert*-butyl alcohol-O-*d*. The kinetics of deuterium incorporation and of isomerization of *cis*- and *trans*-α-methylstilbene and α-benzylstyrene into one another can be made most internally consistent with a mechanism which involves noninterconverting *cis*- and *trans*-allylic anions as intermediates. The equilbrium constants for interconversions of the three olefins were determined, and the kinetic and thermodynamic data are most consistent with one another on the basis of this same mechanism. The allylic rearrangement of α-benzylstyrene into *cis*-α-methylstilbene was shown to proceed with 55% intramolecularity, and into *trans*-α-methylstilbene with 36% intramolecularity. A solvent kinetic isotope effect of $(CH_3)_3COD/(CH_3)_3COH \sim 2$ was observed for these isomerizations. The rearrangements were shown to proceed considerably faster (factors of 20 to 2000) than either exchange or isomerization of *cis*- and *trans*-stilbene. For *cis*-stilbene, the following rate factors (per hydrogen) were observed: vinyl exchange/isomerization ~ 2500; vinyl exchange/aryl exchange ~ 100. For *trans*-stilbene, vinyl exchange/aryl exchange ~ 7. Vinyl exchange in *cis*-stilbene exceeded that in *trans*-stilbene by a factor of ~10. Aryl exchange in *trans*-stilbene exceeded that in *cis*-stilbene by a factor of ~2. It was concluded that the vinyl anion of *cis*-stilbene exhibits considerable stereochemical stability, and that the transition state for its formation involves charge delocalization into the attached benzene ring.

Four fundamental problems of carbanion chemistry meet in the present study, each of which can be defined in terms of a question. (1) Can appropriately substituted open-chain allylic anions exist as discrete geometric isomers (*cis* and *trans*) which are chemically distinguishable? (2) What structural features control the amount of intramolecularity in base-catalyzed allylic proton transfers? (3) What is the stereochemical course of base-catalyzed hydrogen–deuterium exchange of vinyl hydrogen in geometric isomers? (4) What are the relative kinetic acidities of aryl and vinyl hydrogens in the stilbenes?

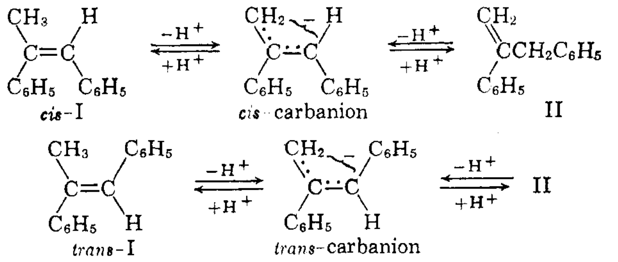
Simple Hückel molecular orbital calculations on the allylic system itself predict the same delocalization energy (0.828β) for the carbonium ion, the radical, and the carbanion.[2] Evidence for the stereochemical stability in a geometric sense of the allylic carbonium ion and radical have appeared in the literature. Thus the allylic butenyl[3] and 1,2-diphenylpropenyl[4] cations exhibit geometric isomerism, as does the allylic butenyl radical.[5] To our knowledge, evidence of this sort has not been published for allylic carbanions, although the related question of the configurational stability of allylic organometallic compounds has received some attention.[6]

The discovery that base-catalyzed proton transfers in allylic rearrangements can proceed intramolecularly[7] was enriched by the knowledge that the degree of intramolecularity is very much a function of substrate, medium, and catalyst structures.[8]

Implicit in a study of the base-catalyzed rearrangement of 1-halo-2,2-diphenylethylenes is the inference that such substrates undergo vinyl exchange of their vinyl hydrogens concurrent with rearrangement but without isomerization.[9]

To our knowledge, no assessment has been made of the relative kinetic acidities of aryl and α-styryl protons.

The present study was designed to obtain information bearing on the above questions. The three olefins, *cis*-α-methylstilbene (*cis*-I), *trans*-α-methylstilbene (*trans*-I), and α-benzylstyrene (II) were selected for these reasons: (1) Together these olefins form a system possibly interlinked by allylic anions which would exhibit *cis–trans* isomerism. (2) The olefins lend themselves to study of base-catalyzed intramolecular proton transfers. (3) The olefins are acidic enough to undergo hydrogen isotope exchange and isomerization with potassium *tert*-butoxide in *tert*-butyl alcohol at reasonable temperatures, and mixtures of the olefins can be readily analyzed by vapor phase chromatographic (v.p.c.) techniques. The isomeric stilbenes (*cis*-III and *trans*-III) were used to study the questions of the stereochemical stability of the vinyl anion formed by hydrogen abstraction, and the relative acidities of vinyl and aryl protons. Results from the stilbene



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(2) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 40.

(3) W. G. Young, S. H. Sharman, and S. Winstein, *J. Am. Chem. Soc.*, **82**, 1376 (1960).

(4) J. H. Brewster and H. O. Bayer, *J. Org. Chem.*, **29**, 105 (1964).

(5) C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961).

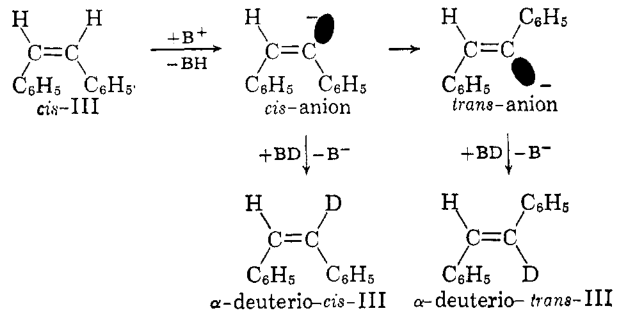
(6) (a) R. H. De Wolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956); (b) P. D. Sleezer, S. Winstein, and W. G. Young, *J. Am. Chem. Soc.*, **85**, 1890 (1963); (c) E. J. Lanpher, *ibid.*, **79**, 5578 (1957); (d) W. O. Haag and H. Pines, *ibid.*, **82**, 387 (1960).

(7) D. J. Cram and R. T. Uyeda, *ibid.*, **84**, 4358 (1962).

(8) (a) S. Bank, C. A. Rowe, and A. Schriescheim, *ibid.*, **85**, 2115 (1963); (b) C. Bergson and A. Weidler, *Acta Chem. Scand.*, **17**, 862, 1798 (1963); (c) W. von E. Doering and P. P. Gaspar, *J. Am. Chem. Soc.*, **85**, 3043 (1963); (d) D. J. Cram and R. T. Uyeda, *ibid.*, **86**, 5466 (1964).

(9) (a) D. Y. Curtin, E. W. Flynn, and R. F. Nystrom, *ibid.*, **80**, 4599 (1958); (b) J. G. Pritchard and A. A. Bothner-By, *J. Phys. Chem.*, **64**, 1271 (1960).

system served as controls for the experiments in the α-methylstilbene system.



Methods and Results

Preparation of the five olefins employed in this investigation is described in the Experimental. The isomerizations of *cis*- and *trans*-α-methylstilbene (*cis* and *trans*-I) and of α-benzylstyrene (II) were studied in *tert*-butyl alcohol 0.284 *N* in potassium *tert*-butoxide at 50.10 and 75.10°, and at 74.99–116° in *tert*-butyl alcohol-O-*d* with potassium *tert*-butoxide ranging in concentration from 0.255 to 0.408 *N*. Compositions of the olefinic mixtures were determined by vapor phase chromatography (v.p.c.) as described in the Experimental. A weight balance conducted on a run (19 of Table V) with II as substrate, which was carried further than any of the kinetic runs, provided a 90% accounting of starting materials. Therefore, all composition calculations were made with the assumption that the 3 olefinic peaks in the v.p.c. represented the total material. An error analysis is found in the Experimental.

Since the equilibrium mixture of *cis*- and *trans*-I and of II highly favored *trans*-I, the kinetics of isomerization of *cis*-I and II could be easily followed during the first part of their disappearance. Good first-order rate constants were calculated from 9 or 10 points taken during the first 10% of the isomerization of *cis*-I, and during the first two half-lives of isomerization of α-benzylstyrene (II). The least-squares method, using the IBM 7090 computer, was employed in obtaining the rate constants and their standard deviations. In these kinetic runs, the base concentrations varied from 0.255 to 0.284 *N*, and second-order rate constants were calculated assuming that the reaction was first order catalytic in base.[10] Table I records the conditions and results. Footnote *d* of this table records the activation parameters calculated from runs 2–5. In run 5 of Table I, α-benzylstyrene was isomerized under similar conditions in *tert*-butyl alcohol-O-*d*, and k_2 determined.

Table II records the ratios *trans*-I/*cis*-I produced in runs 3 and 4 at various conversions, the % reaction varying between 1 and 62. The fact that this ratio remained essentially constant (11 ± 0.7%) over the range indicates that α-benzylstyrene (II) isomerizes under conditions which leave *cis*- and *trans*-I untouched. Preliminary experiments established that *trans*-I isomerized slower than *cis*-I, and comparison of the rate constants of runs 1, 3, and 4 indicates that II isomerizes faster than *cis*-I by a factor of about 125.

TABLE I

KINETICS OF ISOMERIZATION OF *cis*-α-METHYLSTILBENE (*cis*-I) AND α-BENZYLSTYRENE (II) IN *tert*-BUTYL ALCOHOL–POTASSIUM *tert*-BUTOXIDE

	Substrate		Base			
Run	Nature	Concn., *M*	concn., *M*	*T*, °C.[a]	No. of points	$k_2 \times 10^6$, l./mole sec.[b]
1	*cis*-I	0.15	0.284	75.10	10[c]	0.80 ± 5.4%
2[d]	II	.12	.284	50.10	10[e]	6.8 ± 3.3%
3[d]	II	.15	.284	75.10	9[e]	103 ± 3.2%
4[d]	II	.13	.284	75.10	9[e]	97 ± 3.7%
5[f]	II	.113	.255	74.99	5[e]	186 ± 2.0%

[a] °C. ± 0.05°. [b] Slope and % standard deviation was computed by the least squares method. The second-order rate constants were calculated from the observed first-order rate constants assuming the reaction to be first order catalytic in potassium *tert*-butoxide concentration. [c] Points were taken during the first 10% isomerization. [d] Activation parameters were calculated from the runs: E_a, 24.10 kcal./mole, ΔF^*, 26.7 kcal./mole at 63°, ΔH^*, 23 kcal./mole, ΔS^* −10 ± 4 e.u. [e] Points were taken over two half-lives of the isomerization. [f] Run was made in *tert*-butyl alcohol-O-*d*, 0.99 atom of deuterium per molecule (combustion and falling drop method).

TABLE II

RATIOS OF *trans*- TO *cis*-α-METHYLSTILBENE (*trans*-I/*cis*-I) PRODUCED IN ISOMERIZATION OF α-BENZYLSTYRENE (II) IN *tert*-BUTYL ALCOHOL–0.284 *M* IN POTASSIUM *tert*-BUTOXIDE AT 75.10 ± 0.05°[a]

Run 3		Run 4	
Reaction, %	*trans*-I/*cis*-I ± mean deviation	Reaction, %	*trans*-I/*cis*-I ± mean deviation
10.63	9.6 ± 0.3	1.26	4.7 ± 1.0
21.24	11.0 ± .8	4.59	9.0 ± 2.0
24.22	10.5 ± .2	8.57	12.0 ± 0.5
30.88	10.7 ± .2	13.22	9.4 ± .3
39.48	11.8 ± .2	18.61	10.6 ± .2
46.74	11.7 ± .6	23.09	11.3 ± .9
51.88	11.5 ± .1	27.14	11.1 ± .4
54.99	11.9 ± .1	27.70	10.8 ± .3
61.56	12.3 ± .4	32.15	11.2 ± .2

Average 11.0 ± 0.7%

[a] See Table I for substrate concentrations.

In Table III are presented the percentages of II produced (total olefin = 100%) when *cis*-I (run 1) and *trans*-I (run 6) were carried through 10 and 4% loss of starting material, respectively. As *cis*-I dis-

TABLE III

PERCENTAGE OF α-BENZYLSTRYRENE (II) IN TOTAL OLEFIN OBTAINED FROM ISOMERIZATION OF *cis*- AND *trans*-α-METHYLSTILBENE (*cis*- AND *trans*-I) IN *tert*-BUTYL ALCOHOL 0.284 *M* IN POTASSIUM *tert*-BUTOXIDE AT 75.10 ± 0.05°

Run 1 (*cis*-I as substrate)[a]		Run 6 (*trans*-I as substrate)[b,c]	
Reaction, %	% II	Reaction, %	% II
1.28	0.20	0.56	0.26
1.51	.37	.72	.44
1.93	.65	.89	.66
2.62	.80	1.44	1.22
3.16	.80	2.91	2.44
3.98	.86	3.29	2.52
5.19	.88	3.66	2.48
7.73	1.04	3.88	2.80
9.06	1.00	4.34	2.61
10.02	1.22		

[a] Substrate concentration, 0.15 *M*. [b] Substrate concentration, 0.21 *M*. [c] Estimated second-order rate constant for *trans*-I isomerization is $k_2 = 2.5 \pm 1.4 \times 10^{-6}$ l./mole sec. This compares to $k_2 = 2.2 \times 10^{-6}$ calculated from equilibrium data (Table IV), collapse ratios, and k_2 for *cis*-I (Table I).

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(10) D. J. Cram, B. Rickborn, C. A. Kingsbury, and P. Haberfield [*J. Am. Chem. Soc.*, **83**, 3678 (1961)] found that in the potassium *tert*-butoxide catalyzed racemization of (+)-2-methyl-3-phenylpropionitrile in *tert*-butyl alcohol, over a range of base concentrations from 0.0016 to 0.439 *M* and water concentrations from less than 0.003 to 0.01 *M*, k_2 varied by only a factor of about 3.

TABLE IV

PERCENTAGES OF *cis*- AND *trans*-α-METHYLSTILBENES (*cis*- AND *trans*-I) AND α-BENZYLSTYRENE (II) IN EQUILIBRIUM MIXTURES PRODUCED BY ACID- AND BASE-CATALYZED ISOMERIZATION OF EACH OLEFIN

	Substrate			Catalyst						
Run	Nature	Concn., *M*	Solvent	Nature	Concn., *M*	*T*, °C.	Time, hr.	% *cis*-I	% *trans*-I	% II
7	*cis*-I	0.10	$(CH_3)_3COH$	$(CH_3)_3COK$	0.586	75.10	1600[a]	19.9	78.1	2.03
8	*trans*-I	.10	$(CH_3)_3COH$	$(CH_3)_3COK$	.586	75.10	1600[a]	19.2	79.0	1.83
9	II	.10	$(CH_3)_3COH$	$(CH_3)_3COK$	.586	75.10	1600[a]	19.3	78.8	1.92
		Average ± mean deviation: 19.5 ± 0.3% *cis*-I, 78.6 ± 0.4% *trans*-I, 1.92 ± 0.07% II								
10	*cis*-I	0.10	CH_3CO_2H[b]	p-$CH_3C_6H_4SO_3H$	0.02	116	24	21.4	74.2	4.4
11	*trans*-I	0.10	CH_3CO_2H[b]	p-$CH_3C_6H_4SO_3H$	0.02	116	24	21.3	76.2	2.5

[a] Tubes were first kept at 100° for 7 days, and the remainder of the time at 75.10°. [b] 90% acetic acid, 10% acetic anhydride by volume.

TABLE V

RESULTS OF POTASSIUM *tert*-BUTOXIDE CATALYZED HYDROGEN–DEUTERIUM EXCHANGE BETWEEN *cis*- AND *trans*-α-METHYLSTILBENE (*cis*- AND *trans*-I), α-BENZYLSTYRENE (II), AND *tert*-BUTYL ALCOHOL-O-*d*[a]

						Products							
						cis-I			*trans*-I			II	
	Substrate						Atoms D in			Atoms D in			
Run	Nature	Concn., *M*	Base concn., *M*	*T*, °C.	Time, min.	%	Vinyl	Methyl	%	Vinyl	Methyl	%	Atom D
12	*cis*-I	0.50	0.408	116[b]	480	43.3	0.23[c]	1.65[c]	56.6	0.44[c]	2.55[c]	0.2	...
13	*trans*-I	.53	.408	116[b]	45	1.7	...	...	95.8	.12[c]	1.27[c]	2.5	...
14	*trans*-I	.50	.408	116[b]	160	4.4	...	...	94.3	.02[c]	1.77[c]	1.3	...
15	*trans*-I	.50	.408	116[b]	480	9.2	...	...	90.5	.24[c]	2.29[c]	0.3	...
16	II	.30	.510	75.1[d]	110	3.0	...	...	36.5	.0[c]	0.63[c]	60.5	0.046[e]
17	II	.53	.255	75.1[d]	121	2.3	...	...	26.5	0.651[e]		71.2	.024[e]
18	II	.53	.255	75.1[d]	220	3.7	...	...	42.2	0.666[e]		54.1	.043[e]
19	II	.53	.259	75.1[d]	400	5.4	0.452[e]		64.8	0.014[f]	0.726[f]	29.8	.087[e]
20	*cis*-I	.51	.259	75.1[d]	400	99.2	0.024[e]		0.3	...	...	0.5	...
21	*trans*-I	.52	.259	75.1[d]	400	0.04	...	...	98.6	0.224[e]		1.4	...

[a] 0.99 atom of deuterium per molecule by combustion and falling drop method. [b] ±2°. [c] Total deuterium content determined by combustion and falling drop method. Distribution of deuterium between vinyl and methyl positions determined by n.m.r. analysis with acenaphthene as internal standard. Total deuterium by two methods agrees within 0.15 atom of deuterium per molecule except in run 12, where combustion method is 0.30 atom of deuterium lower than n.m.r. method. [d] ±0.05°. [e] Total deuterium content determined by combustion and falling drop method. [f] Olefin was submitted to ozonolysis, and the fragments submitted to deuterium analysis by combustion and falling drop method. Permanganate oxidation of the same olefin gave benzoic acid, which was similarly analysed for deuterium.

appeared in run 1, the % of II in the mixture increased slowly, reaching 1.22% at 10.02% loss of *cis*-I. As *trans*-I disappeared in run 6, the % of II in the mixture increased faster, and reached a maximum of 2.80% when 3.88% of *trans*-I had been isomerized. The amount of II in the mixture then decreased to about 2% as equilibrium was approached (see below).

Table IV records the results of potassium *tert*-butoxide catalyzed (0.586 *M*) equilibration of *cis*-I, *trans*-I, and II in *tert*-butyl alcohol at 75° (runs 7, 8, and 9). Starting with any of the 3 olefins, a mixture of 19.5 ± 0.3% *cis*-I, 78.6 ± 0.4% *trans*-I, and 1.92 ± 0.07% II was produced. Others[11] equilibrated these 3 olefins with potassium *tert*-butoxide in refluxing xylene, and obtained results in rough agreement with ours (21.0% *cis*-I, 76.6% *trans*-I, and 2.4%-II at 139°).

Since these values disagreed markedly with those obtained in a previous investigation[12] in which *cis*- and *trans*-I were equilibrated with *p*-toluenesulfonic acid in acetic acid at 75°, *cis*- and *trans*-I were equilibrated in glacial acetic acid 0.02 *M* in *p*-toluenesulfonic acid at 116°, and the products analyzed (runs 10 and 11 of Table IV). The results are suprisingly close to those obtained in the above base-catalyzed equilibrium (note the difference in temperature and solvent), and differ from those obtained previously.[12] The earlier study was made before v.p.c. was available, and the amounts of *cis*-I and *trans*-I in the mixtures were estimated with ultraviolet spectroscopic techniques. The presence of α-benzylstyrene in the mixture (not recognized) and incomplete isomerization produced the erroneous analytical results.[13]

Results of potassium *tert*-butoxide catalyzed isomerization and isotopic exchange of *cis*-I, *trans*-I, and II in *tert*-butyl alcohol-O-*d* are found in Table V. In runs 12–21, the total amounts of deuterium incorporated into unrearranged recovered olefin were determined by the combustion and falling drop method.[14] In runs 12 (*cis*-I) and 16–18 (II), the amounts of deuterium incorporated into rearranged *trans*-I were also determined by the same method.[14] The total deuterium incorporation was also roughly determined with nuclear magnetic resonance techniques in runs 12–16 (see Experimental), and the two methods gave results in general agreement with one another. The nuclear magnetic resonance spectra also provided the distribution of deuterium between the vinyl and methyl positions of *cis*- and *trans*-I in the products from runs 12–16. In run 19 with II as starting material, the *trans*-I produced was ozonized, and the fragments were reduced to give benzyl alcohol and 1-phenylethanol. These alcohols were separated by v.p.c. and analyzed by the combustion and falling drop method.[14] The *trans*-I product of run 19 was also submitted to permanganate oxidation to benzoic acid, which was submitted to deuterium analysis.[14] The latter experiment

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(11) A. Zwierzak and H. Pines, *J. Org. Chem.*, **27**, 4084 (1962).

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

(13) The general conclusions of this earlier investigation are not altered by this experimental error.

(14) These analyses were performed by J. Nemeth of Urbana, Ill.

TABLE VI

RESULTS OF POTASSIUM *tert*-BUTOXIDE CATALYZED ISOMERIZATION AND HYDROGEN–DEUTERIUM EXCHANGE OF *cis*- AND *trans*-STILBENE (*cis*-III AND *trans*-III) IN *tert*-BUTYL ALCOHOL-O-*d*[a]

						Product					
						cis-III			*trans*-III		
	Substrate		Base				Atoms D in			Atoms D in	
Run	Nature	Concn., M	concn., M	T, °C.	Time, hr.	%	Vinyl[b]	Phenyl[b]	%	Vinyl[b]	Phenyl[b]
22	*cis*-III	0.67	0.255	146[c]	36.7	99	1.42	0.116	1	..	..
23	*trans*-III	.22	.513	220[d]	23	..	..	...		1.34	6.8[e]
24	*trans*-III	.22	.513	146[c]	23	..	..	...		0.30	0.23
25	*trans*-III	.22	.513	100[c]	23	..	..	...		0.007	0.005

[a] 0.99 atom of deuterium per molecule by combustion and falling drop method. [b] Olefin was analyzed for deuterium by combustion and falling drop method; then the material was oxidized to benzoic acid, which in turn was analyzed for deuterium by combustion and falling drop method. [c] ±0.5°. [d] +2°. [e] In this run, the stilbene was in isotopic equilibrium with the solvent (68% of a deuterium atom per position).

indicated that no aryl hydrogens had exchanged. In all of these runs, the concentration of substrate (0.255 to 0.510) was low compared to the deuterium pool (~10 M), and exchange was not carried far enough to dilute seriously the deuterium pool with protium except in runs 12 and 15, when at the end of the run, the pool approached 10% protium.

Table VI reports the results of potassium *tert*-butoxide catalyzed hydrogen–deuterium exchange of *cis*- and *trans*-stilbene (*cis*-III and *trans*-III) with *tert*-butyl alcohol-O-*d*. The products were recovered, and the total deuterium present analyzed by the combustion and falling drop method.[14] These olefins were then oxidized to benzoic acid, and the amount of deuterium was again determined by the same method.[14] The relative amounts of deuterium in the vinyl and phenyl portions of the molecule were calculated by difference. In run 23, *trans*-III was brought into isotopic equilibrium with the solvent (68% of a deuterium atom per position), and in run 25, *trans*-III hardly underwent exchange. In runs 22 and 24, exchange proceeded to an extent which did not seriously dilute the solvent deuterium pool with protium, and yet far enough to allow the relative rates of vinyl exchange and isomerization, and of vinyl and aryl exchange, to be estimated.

Intramolecularity of the Allylic Rearrangement.—In runs 17, 18, and 19 (Table V), α-benzylstyrene (II) was converted to *cis*- and *trans*-I in deuterated *tert*-butyl alcohol. The fact that *cis*- and *trans*-I contained substantially less than one atom of deuterium per molecule indicates that at least part of this isomerization occurred intramolecularly. However, in these runs, the number of atoms of deuterium per molecule in the products increased with the length of time of the run from a limiting value which reflected the true intramolecularity of the rearrangement.

As controls, *cis*- and *trans*-I were submitted to the conditions of the isomerization reactions, and the amounts of deuterium incorporated into nonisomerized material were determined (runs 20 and 21 of Table V). These values were then used to correct the values for intramolecularity obtained when II was isomerized. The mathematical treatment is given in Appendix I, and the results are presented in Table VII.

TABLE VII

INTRAMOLECULARITY IN CONVERSION OF α-BENZYLSTYRENE (II) TO *cis*-α-METHYLSTILBENE (*cis*-I) AND *trans*-α-METHYLSTILBENE (*trans*-I)

	Intramolecularity to give	
Run	*cis*-I, %	*trans*-I, %
17	..	35.8
18	..	36.2
19	54.9	34.6

The three values obtained for the intramolecularity for production of *trans*-I agree well with one another although the reaction times differed by a factor of greater than 3. Thus any error introduced by not correcting for introduction of deuterium into the starting material II before rearrangement is negligible. Further support of this conclusion is found in the low level of deuterium found in II recovered from runs 17, 18, and 19 (0.024, 0.043, and 0.087 atom of deuterium per molecule, respectively).

Appendix I. Calculation of Isotopic Exchange Correction Applied to Intramolecularity of the Isomerization Reaction.—If the first-order irreversible formation of products (T, C) from starting material (B) is assumed, the time-average fraction of products are $\bar{T}$ and $\bar{C}$. For the reaction scheme

$$\mathrm{T} \xleftarrow{k_\mathrm{T}} \mathrm{B} \xrightarrow{k_\mathrm{C}} \mathrm{C}$$

$$\bar{T} = \frac{1}{r}\left(\frac{k_\mathrm{T}}{k_\mathrm{T} + k_\mathrm{C}}\right)\int_0^r (1 - e^{-(k_\mathrm{T} + k_\mathrm{C})t})\mathrm{d}t$$

where r = total reaction time and t = time vector. Solution of the last equation gives (1) where f = fraction of B consumed. Thus, the correction to be subtracted from the observed atoms of deuterium per

$$\bar{T} = \left(\frac{k_\mathrm{T}}{k_\mathrm{T} + k_\mathrm{C}}\right)\left(1 - \frac{f}{(k_\mathrm{T} + k_\mathrm{C})r}\right) \quad (1)$$

molecule in product T at total time r is

$$\text{correction} = \frac{(\text{atoms of D/molecule introduced in control run})r\bar{T}}{(\text{time in control run})}$$

This correction is applied to the results of runs 17, 18, and 19 as follows.

Run 17: Isomerization of II (B) to *trans*-I (T).—Since the disappearance of B (II) is approximated as a first-order irreversible process

$$\frac{B}{B_0} = e^{-(k_\mathrm{T} + k_\mathrm{C})r} = 0.712$$

and

$$(k_\mathrm{T} + k_\mathrm{C})r = \ln 0.712 = 0.340$$

The time-average fraction of T produced in run 17 is

$$\bar{T} = \frac{k_T}{k_T + k_C}\left(1 - \frac{0.288}{0.340}\right)$$

From Table II, $k_T/k_C = 11.0$; thus $\bar{T} = 0.140$

correction =

$$\frac{0.224 \times 121 \times 0.140}{400} = 0.0095 \text{ atom of D/molecule}$$

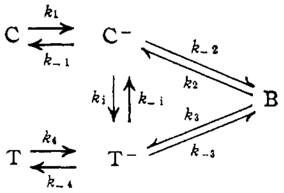
corrected % intermolecularity = $100 \times (0.651 - 0.009) = 64.2\%$

% intramolecularity = 35.8%

Similar corrections were calculated for the isomerization of II to *trans*-I in runs 18 and 19, and II to *cis*-I in run 19.

Models for Allylic Anions.—In the base-catalyzed conversion of α-benzylstyrene (II) to *cis*- and *trans*-α-methylstilbene (*cis*- and *trans*-I), and in the reverse reaction, the possibility exists that the intermediate allylic anions exhibit geometric isomerism. In this connection, the compatibility of the data with two general mechanisms will be examined. In one of these mechanisms, noninterconverting *cis*- and *trans*-allylic anions are treated as intermediates. In the other, rapidly equilibrating *cis* and *trans* anions are considered as intermediates. Each of these two mechanisms are regarded as limiting cases of a more general mechanism embodied in model I. In this and subsequent formulations, the symbol C is used for *cis*-I, C^- for the *cis*-carbanion, T for *trans*-I, T^- for the *trans*-carbanion, and B for α-benzylstyrene. The steady-state approximation is applied to the carbanionic intermediates, whose lives must be extremely short in the proton-donating *tert*-butyl alcohol.

Model I



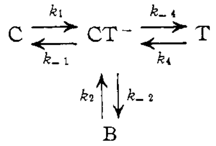
Model I reduces to model II in the limit where k_{-1} and $k_{-2} >> k_i$, and where k_{-3} and $k_{-4} >> k_{-i}$

Model II

$$C \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C^- \underset{k_2}{\overset{k_{-2}}{\rightleftarrows}} B \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} T^- \underset{k_4}{\overset{k_{-4}}{\rightleftarrows}} T$$

Model I condenses to model III in the limit where $k_i >> k_{-1}$ and k_{-2}, and where $k_{-i} >> k_{-3}$ and k_{-4}. No differentiation is made in this model between two rapidly equilibrating or a single anionic intermediate. The symbol CT^- is used to designate both possibilities.

Model III



In the next sections, the consistency between the data and the mechanisms of models II and III will be examined. Two approaches are used. In the first, the kinetic data will be applied to each model, and equilibrium constants between C and B calculated. These calculated values will then be compared with the experimentally determined values. In the second approach, model II is subjected to a detailed kinetic analysis through use of an IBM 7090 computer, and calculated and observed results are compared.

Collapse Ratios of *cis*- and *trans*-Carbanions.—As part of the calculation of the equilibrium constant between C and B from kinetic data and model II, the collapse ratios for $C^-(k_{-1}/k_{-2})$ and $T^-(k_{-4}/k_{-3})$ are computed. In this connection, it is assumed that the intramolecularity for each geometric carbanion is a property of the anion, and is independent of the olefin from which it was formed and to which it collapses.

The collapse ratio for C^-(*cis*-carbanion) was obtained by allowing C(*cis*-I) to isomerize in *tert*-butyl alcohol-O-*d* (run 20, Table V). The rate of deuterium incorporation into C after correction for intramolecularity was taken as a measure of the rate of collapse of C^- to C; *i.e.*, $k_1k_{-1}/(k_{-1} + k_{-2})$. The rate of isomerization of C to B (α-benzylstyrene) was taken as a measure of the rate of collapse of C^- to B; *i.e.*, $k_1k_{-2}/(k_{-1} + k_{-2})$. The ratio of these two rates equals k_{-1}/k_{-2}, and was calculated to be 6.5 (see Appendix II).

The collapse ratio for T^-(*trans*-carbanion) was obtained by allowing B to isomerize in *tert*-butyl alcohol-O-*d* (run 17, Table V). The rate of deuterium incorporation into the starting material (B) after correction for further reaction and for intramolecularity was taken as a measure of collapse of carbanion to C; *i.e.*, $k_3k_{-3}/(k_{-3} + k_{-4})$. The rate of isomerization of B was taken as a measure of collapse of T^- to form T; *i.e.*, $k_3k_{-4}/(k_{-3} + k_{-4})$. The ratio of these two rates equals k_{-4}/k_{-3}, and was calculated to be 8.8 (see Appendix II). In the latter calculation it was demonstrated that a kinetic isotope effect of 5 for the rate of isomerization of protio- *vs.* deuterio-B would have only a trivial effect on k_{-4}/k_{-3} values.

Appendix II. Calculation of Collapse Ratios. For *cis*-Carbanion C^-.—Of the three olefins, C is the slowest reacting isomer (see Table III). However, B reacts to give primarily T, as is shown by the fact that T/C = 11 for the first 60% of isomerization of B (see Table II). For this reason, and the observed cleanly first-order kinetics for the isomerization of C (run 1 of Table I), it is safe to conclude that for low conversions of C an insignificant amount of C is regenerated from B or T. Thus, for low conversions of C, model II simplifies to eq. 2. This equation can be modified to eq. 3, which distinguishes between C (unreacted *cis*-I) and C*(*cis*-I produced by collapse of C^- back to C). Since only 0.8% conversion of *cis*-I was observed in run 20, further reaction of C* can be neglected.

$$C \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C^- \xrightarrow{k_{-2}} B + T \tag{2}$$

$$C \xrightarrow{k_x} C^* \qquad k_x = (k_1k_{-1})/(k_{-1} + k_{-2}) \tag{3}$$

$$C \xrightarrow{k_y} B + T \qquad k_y = (k_1k_{-2})/(k_{-1} + k_{-2})$$

For a system of parallel first-order reactions as exemplified by 3, eq. 4 applies.[15] The intramolecularity of the process C → C* should be the same (54.9%) as for the process B → C if the mechanism of model II is assumed. Thus, for the results of run 20, B + T = 0.5 + 0.3% = 0.8%, and C* = 2.4% × 0.992/0.451 = 5.3%. These values applied to eq. 4 give $k_x/k_y = k_{-1}/k_{-2} = 6.5$, which is the collapse ratio of C^- in model II.

$$(k_x/k_y) = C^*/(B + T) \qquad (4)$$

Collapse of *trans*-Carbanion T^-.—The results of runs 1–6 indicate that the rate of isomerization of B (α-benzylstyrene) is about 40 times faster than T (*trans*-I) and 125 faster than C (*cis*-I). These data, coupled with a comparison of the results of runs 17–21, indicate that T and C once formed do not react further appreciably in either exchange or isomerization during the first half-life of isomerization of B. The data of Table II indicate that B produced T/C = 11 over one half-life of B. Thus, $T/C \sim T^-/C^- \sim 11$, and the deuterium uptake by B or T attributed to C^- during the first half-life of B is negligible. These conditions reduce model I to eq. 5.

$$\mathrm{B} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \mathrm{T}^- \xrightarrow{k_{-4}} \mathrm{T} \qquad (5)$$

The term B* is used to distinguish original B from that material regenerated from B^-, and eq. 6 can be written.

$$\mathrm{B} \xrightarrow{k_a} \mathrm{T} \qquad k_a = (k_3k_{-4})/(k_{-3} + k_{-4})$$

$$\mathrm{B} \xrightarrow{k_b} \mathrm{B}^* \xrightarrow{k_c} \mathrm{T} \quad k_b = (k_3k_{-3})/(k_{-3} + k_{-4}) \qquad (6)$$

The B* is composed of both protio- and monodeuterio-α-benzylstyrene (B) with the proportion of each determined by the intramolecularity of the collapse reaction. The intramolecularity of B → B* is assumed to be the same as B → T(35.5%) and, therefore, $k_{-4}/k_{-3} = k_a/k_b$.

In the differential equations associated with (6) and their solutions (eq. 7–9), B, B^*, and T refer to the concentration of these species at time t, and B_0 refers to the initial concentration of B. Dividing eq. 9

$$\mathrm{d}B/\mathrm{d}t = -(k_a + k_b)B$$

$$\mathrm{d}B^*/\mathrm{d}t = k_bB - k_cB^*$$

$$\mathrm{d}T/\mathrm{d}t = k_aB + k_cB^*$$

$$B = B_0e^{-(k_a + k_b)t} \qquad (7)$$

$$B^* = \frac{B_0k_b}{k_c - (k_a + k_b)}\,[e^{-(k_a + k_b)t} - e^{-k_ct}] \qquad (8)$$

$$T = \frac{B_0}{k_c - (k_a + k_b)}\,[k_c - (k_a + k_b) + (k_a - k_c)e^{-(k_a + k_b)t} + k_be^{-k_ct}] \qquad (9)$$

by 8 gives eq. 10, which is used along with the results of runs 17 or 18 of Table V to evaluate k_a/k_b.

$$\frac{T}{B^*} = \frac{k_c - (k_a + k_b) + (k_a - k_c)e^{-(k_a + k_b)t} + k_be^{-k_c}}{k_b(e^{-(k_a + k_b)t} - e^{k_ct})} \qquad (10)$$

From run 17, %T = 26.5, %B* = (71.2 × 0.024)/0.645 = 2.6, and %B = 71.2 − 2.6 = 68.6. From eq. 7, $B/B_0 = e^{-(k_a + k_b)t} = 0.686$.

The exact value of k_a/k_b can be determined only if the kinetic isotope effect associated with rearrangement of deuterated and nondeuterated B* is known. However, the following calculations demonstrate that the value of k_a/k_b is insensitive to the isotope effect.

If $k_H/k_D = 5$, then $k_c/k_a = [0.355 + 0.645(1 + 1/5)/2] = 0.75$, and eq. 10 becomes eq. 11. Values of k_a/k_b can be extracted from eq. 11 only by the method

$$\frac{k_a}{k_b} = \frac{11.2e^{-0.75k_at} - 8.00}{0.0785} \qquad (11)$$

of successive approximations. If k_a/k_b is assumed equal to 9.1, then $k_a + k_b = 1.10k_a$, $e^{-(k_a + k_b)t} = e^{-1.10k_at} = 0.686$, and $e^{-0.75k_at} = 0.775$, and from eq. 11, $k_a/k_b = 8.7$. Similarly, if k_a/k_b is assumed equal to 8.9, eq. 11 yields $k_a/k_b = 9.0$, and further refinement is pointless.

If $k_H/k_D = 1$, then $k_a = k_c$, and eq. 8 reduces to $e^{-k_at} = 0.714$. Since $e^{-(k_a + k_b)t} = 0.686$, then e^{-k_bt} 0.961 and $k_a/k_b = 8.6$.

Similar calculations applied to run 18 of Table V yield $k_a/k_b = 8.5$ for a kinetic isotope effect of 1 and 9.1 for a kinetic isotope effect of 5. These calculations indicate that the kinetic isotope effect has little effect on the collapse ratio k_a/k_b (or k_{-4}/k_{-3}) and the average value of 8.8 for the collapse ratio will be adopted.

Calculations of Equilibrium Constants by Application of Kinetic Data to the Two Mechanisms for Isomerization.—The equilibrium constant $(B/C)_e$ was calculated by application of the rate data of runs 1, 3, and 4 of Table I and the product ratio data of Table II to model II. Application of the same data to model III provided a second and widely different value for $(B/C)_e$. Comparison of each of these two values with the experimentally determined value for the equilibrium constant from Table IV indicates good agreement between the value found and that calculated based on model II, but a decided lack of agreement between the observed value and that calculated based on model III. Table VIII records the values. The data strongly support the mechanism which involves noninterconverting *cis*- and *trans*-allylic anions as intermediates in the isomerization. The details of the calculations are found in Appendix III.

TABLE VIII

VALUES FOR THE EQUILIBRIUM CONSTANT FOR EQUILIBRIUM BETWEEN α-BENZYLSTYRENE (B) AND *cis*-α-METHYLSTILBENE (C)

	$(B/C)_e$
Calcd. from model II	10.3 ± 1.5
Calcd. from model III	102 ± 15
Obsd. experimentally	10.1 ± 0.5

Appendix III. Calculations of Equilibrium Constants for Equilibrium between α-Benzylstyrene (B) and *cis*-α-Methylstilbene (C). Model II.—Equations 12 and 13 for the initial rate constants for isomerization of *cis*-I (C) and II (B) can be obtained from the differential rate equations

$$k_C{}^0 = \frac{k_1k_{-2}}{k_{-1} + k_{-2}} \qquad (12)$$

$$k_B{}^0 = \frac{k_2k_{-1}}{k_{-1} + k_{-2}} + \frac{k_3k_{-4}}{k_{-3} + k_{-4}} \qquad (13)$$

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(15) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 147.

Similarly, eq. 14 expresses the ratio T/C produced by B as t approaches zero, and 15 the ratio of C/B at equilibrium.

$$\left(\frac{T}{C}\right)_{t \to 0} = \frac{k_3k_{-4}/(k_{-3} + k_{-4})}{k_2k_{-1}/(k_{-1} + k_{-2})} \qquad (14)$$

$$\left(\frac{C}{B}\right)_{\mathrm{e}} = \frac{k_{-1}k_2}{k_1k_{-2}} \qquad (15)$$

From Table II, $(T/C)_{t \to 0} = 11.0 \pm 0.7$, and application of this value to eq. 14 gives 16. Combination of 16 with 13 produces 17 which, when divided by eq. 12, gives 18.

$$\frac{k_4k_{-4}}{k_{-3} + k_{-4}} = 11.0\frac{k_2k_{-1}}{k_{-1} + k_{-2}} \qquad (16)$$

$$k_{\mathrm{B}}{}^0 = 12.0\frac{k_2k_{-1}}{(k_{-1} + k_{-2})} \qquad (17)$$

$$\frac{k_{\mathrm{B}}{}^0}{k_{\mathrm{C}}{}^0} = \frac{12.0k_2k_{-1}/(k_{-1} + k_{-2})}{k_1k_{-2}/(k_{-1} + k_{-2})} = 12.0\frac{k_2k_{-1}}{k_1k_{-2}} \qquad (18)$$

From the values for the rate constants of runs 1, 3, and 4 in Table I, $k_{\mathrm{B}}{}^0/k_{\mathrm{C}}{}^0 = 125 \pm 11.0$, and application of this value in eq. 15 and 18 gives 19.

$$(C/B)_{\mathrm{e}} = (k_{-1}k_2/k_1k_{-2}) = 10.3 \pm 1.5 \qquad (19)$$

Model III.—In terms of this model, the initial rate constants for isomerization of B and C are expressed by eq. 20 and 21. In addition, eq. 22 expresses the ratio T/C produced from B as t approaches 0, and eq. 23 the ratio $(C/B)_{\mathrm{e}}$.

$$k_{\mathrm{C}}{}^0 = \frac{k_1(k_{-2} + k_{-4})}{k_{-1} + k_{-2} + k_{-4}} \qquad (20)$$

$$k_{\mathrm{B}}{}^0 = \frac{k_2(k_{-1} + k_{-4})}{k_{-1} + k_{-2} + k_{-4}} \qquad (21)$$

$$(T/C)_{t \to 0} = (k_{-4}/k_{-1}) \qquad (22)$$

$$(C/B)_{\mathrm{e}} = (k_2k_{-1}/k_1k_{-2}) \qquad (23)$$

Dividing eq. 21 by 20 gives eq. 24. From Table II, the ratio of T to C produced from B as time approached zero was $(T/C)_{t \to 0} = 11.0 \pm 0.7$, and substitution of this value in eq. 22 gives $k_{-4} = 11.0k_{-1}$. The collapse ratio for the carbanionic intermediate T^- to T and B was calculated in Appendix II. The assumptions made in calculating this ratio apply equally well to models II and III. In terms of model III, the collapse ratio can be expressed as $k_{-4}/k_{-2} = 8.8$, or $k_{-4} = 8.8k_{-2}$. Appropriate substitution of the above values for k_{-4} in eq. 24 gives 25.

$$\frac{k_{\mathrm{B}}{}^0}{k_{\mathrm{C}}{}^0} = \frac{k_2(k_{-1} + k_{-4})}{k_1(k_{-2} + k_{-4})} \qquad (24)$$

$$\frac{k_{\mathrm{B}}{}^0}{k_{\mathrm{C}}{}^0} = \frac{k_2(k_{-1} + 11.0k_{-1})}{k_1(k_{-2} + 8.8k_{-2})} = \frac{12.0k_2k_{-1}}{9.8k_{-2}k_1} \qquad (25)$$

From the values for the rate constants of runs 1, 3, and 4 in Table I, $k_{\mathrm{B}}{}^0/k_{\mathrm{C}}{}^0 = 125 \pm 11.0$, and this value in eq. 23 and 25 gives 26.

$$\left(\frac{C}{B}\right)_{\mathrm{e}} = \frac{k_2k_{-1}}{k_1k_{-2}} = 102 \pm 15 \qquad (26)$$

Refinement of Mechanistic Model Involving Discrete *cis*- and *trans*-Carbanion Intermediates (Model II) by Computer Analysis.—The striking agreement between the equilibrium constant for *cis*-I and II observed and that calculated from kinetic data applied to mechanistic model II encouraged a more thorough analysis of this mechanism through computer analysis. Model II can be simplified kinetically to either model IIa or model IIb by application of a steady-state approximation to the *cis*- and *trans*-allylic anions, C^- and T^-. Models IIa and IIb are treated in turn, and in each the starting substrate is designated as X.

Model II
$$C \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C^- \underset{k_{-2}}{\overset{k_2}{\leftrightarrows}} B \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} T^- \underset{k_{-4}}{\overset{k_4}{\leftrightarrows}} T$$

Model IIa
$$X \underset{k_{\mathrm{e}}}{\overset{k_{\mathrm{d}}}{\rightleftarrows}} Y \underset{k_{\mathrm{g}}}{\overset{k_{\mathrm{f}}}{\leftrightarrows}} Z$$

Model IIb
$$X \underset{k_{\mathrm{n}}}{\overset{k_{\mathrm{m}}}{\rightleftarrows}} Y$$

$$X \underset{k_{\mathrm{p}}}{\overset{k_{\mathrm{o}}}{\rightleftarrows}} Z$$

Model IIa.—An exact mathematical solution has been obtained for this kinetic model by two sets of authors.[16] The equations of Lowry and John were adapted to a computer program. The isomerizations of both *cis*-I and *trans*-I were treated by assigning rate constant values to k_{d}, k_{e}, k_{f}, and k_{g} which simulated actual experiment. For *cis*-I isomerization, the rate constant assignments in terms of model IIa are $k_{\mathrm{d}} = 0.008$, $k_{\mathrm{e}} = 0.083$, $k_{\mathrm{f}} = 0.0244$, and $k_{\mathrm{g}} = 0.917$. For *trans*-I isomerization, the assignments are $k_{\mathrm{d}} = 0.0244$, $k_{\mathrm{e}} = 0.917$, $k_{\mathrm{f}} = 0.008$, and $k_{\mathrm{g}} = 0.083$. The relationship between k_{e} and k_{g} is based on the data of Table II. The relative values of the rate constants for isomerization of *cis*-I and α-benzylstyrene (II) were assigned on the basis of runs 1, 3, and 4 of Table I. The relative values of the rate constants for isomerization of *trans*-I and II were based on the equilibrium data of Table IV coupled with the previously assigned rate constants.

TABLE IX

RESULTS OF COMPUTER CALCULATIONS OF RATIOS OF INSTANTANEOUS TO INITIAL FIRST-ORDER RATE CONSTANTS FOR DISAPPEARANCE OF *cis*- AND *trans*-α-METHYLSTILBENE (*cis*-I AND *trans*-I) BASED ON MODEL Ia

Starting materials					
cis-α-Methylstilbene			*trans*-α-Methylstilbene		
% reaction	k_i/k_0[a]	% Y	% reaction	k_i/k_0[a]	% Y
0.0	1.0	0.0	0.0	1.0	0.0
1.0	0.94	0.58	0.3	0.89	0.29
2.0	0.92	0.75	0.5	0.81	0.49
3.0	0.91	0.80	0.7	0.74	0.68
5.0	0.91	0.85	1.0	0.63	0.97
7.0	0.90	0.88	1.5	0.46	1.43
10.0	0.89	0.93	2.0	0.29	1.86
15.0	0.88	1.01	2.5	0.16	2.19
20.0	0.86	1.09	3.0	0.09	2.34
30.0	0.81	1.25	3.5[b]	0.08	2.36
40.0	0.75	1.41	4.0	0.08	2.36

[a] k_i refers to the instantaneous first-order rate constant, and k_0 to the first-order rate constant at zero time. [b] At 96.5% *trans*-I, the maximum in the % Y occurs (2.36%).

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(16) (a) T. M. Lowry and W. T. John, *J. Chem. Soc.*, 2634 (1910); (b) ref. 15, p. 162.

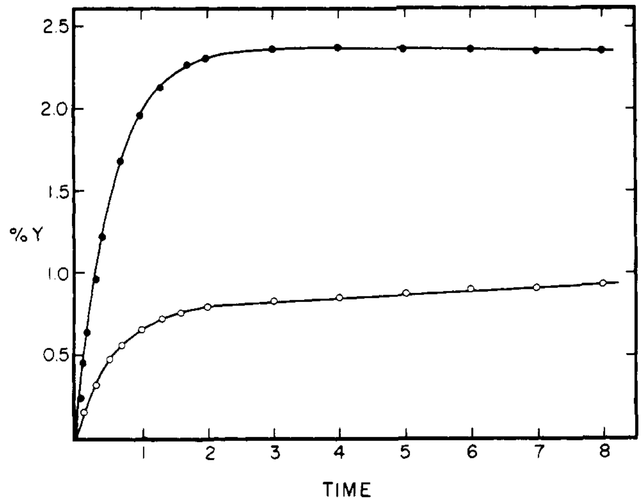

Fig. 1.—Plots of computer-simulated isomerizations of *cis*-α-methylstilbene (*cis*-I) and *trans*-α-methylstilbene (*trans*-I) based on model IIa. Solid circles trace plot of % Y produced by *trans*-I against time. Open circles trace plot of % Y produced by *cis*-I against time.

The values of the fractions of X, Y, and Z present, and the instantaneous first-order rate constants for isomerization of X(k_i), were calculated for predetermined values of t. Table IX records the values of the k_i/k_0 ratio (k_0 = first-order rate constant at t = 0) which correspond to given % reactions for *cis*-I and for *trans*-I. The data indicate that for the first 10% of isomerization of *cis*-I, reasonable first-order behavior is expected (as was observed), but that the rate constant obtained is about 9% low. However, *trans*-II is expected to show a rapid drift in rate, as was also observed.

Table IX also contains the values of the % Y produced which correspond to given % reactions of *cis*-I and *trans*-I. Figure 1 contains plots of the % Y produced against time in the computer-simulated isomerizations of *cis*-I and *trans*-I. Figure 2 contains plots of time against the % II actually observed in the isomerization of *cis*-I and *trans*-I. The curve shapes in Fig. 1 and 2 closely resemble one another. The agreement between experiment and model II is striking, particularly in view of the fact that the isomerization reactions were carried only a short way. Particularly noteworthy is the fact that a maximum occurs in the computer-simulated plot of Fig. 1 at 3.5% isomerization of *trans*-I, at which point % Y = 2.36. In the experimental plot of Fig. 2, a similar maximum is found after 3.8% isomerization of *trans*-I, at which point % II = 2.76.

TABLE X

COMPARISON OF COMPUTER-CALCULATED (MODEL IIa) AND OBSERVED PERCENTAGE OF *trans*-α-METHYLSTILBENE (*trans*-I) PRODUCED AS A FUNCTION OF PERCENTAGE ISOMERIZATION OF *cis*-α-METHYLSTILBENE (*cis*-I)

	% *trans* I	
Reaction, %	Obsd.	Calcd.
1.28	1.08	0.64
1.51	1.14	0.82
1.93	1.28	1.20
2.62	1.82	1.80
3.16	2.36	2.35
3.98	3.12	3.11
5.19	4.31	4.33

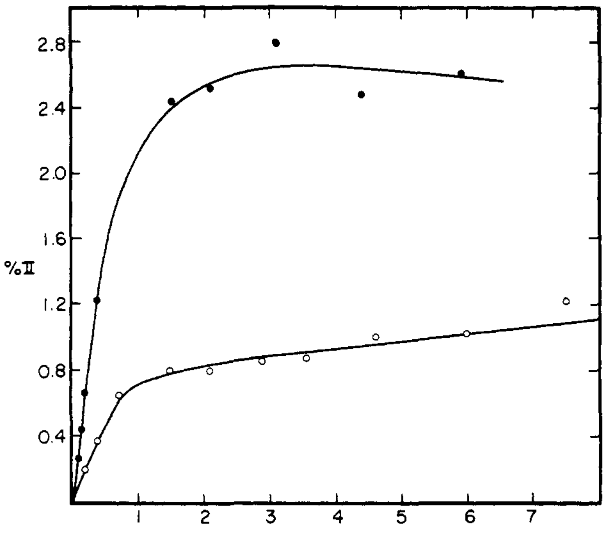

Fig. 2.—Plots of observed isomerizations of *cis*-α-methylstilbene (*cis*-I) and *trans*-α-methylstilbene (*trans*-I). Solid circles trace plot of % α-benzylstyrene (% II) produced by *trans*-I against time. Open circles trace plot of % II produced by *cis*-I against time.

Table X records a comparison of the computer-calculated (model IIa) and observed % *trans*-I produced as *cis*-I is isomerized. Again, agreement is remarkably good between the results and the mechanism embodied in model II. The only deviation between observed and calculated values occurs at 1.28% reaction when the accuracy of determination of *trans*-I and II in the mixture was low.

Model IIb.—With the techniques described in Frost and Pearson[16b] and Benson,[17] the differential equations corresponding to model IIb were solved to produce eq. 27, 28, and 29. In these equations X, Y, and Z represent the concentrations of these species at time t, and X_0 is the concentration of X at zero time. Furthermore, $\lambda_2 = (\sigma + R)/2$ and $\lambda_3 = (\sigma - R)/2$, where $\sigma = k_m + k_n + k_\sigma + k_p$, and $R = [\sigma^2 - 4(k_nk_p + k_mk_p + k_\sigma k_n)]^{1/2}$.

$$X = X_0\left[\frac{k_nk_p}{\lambda_2\lambda_3} + \frac{(k_p - \lambda_2)(k_n - \lambda_2)}{\lambda_2(\lambda_2 - \lambda_3)}e^{-\lambda_2 t} + \frac{(k_m - \lambda_3)(k_n - \lambda_3)}{\lambda_3(\lambda_3 - \lambda_2)}e^{-\lambda_3 t}\right] \quad (27)$$

$$Y = X_0\left[\frac{k_mk_p}{\lambda_2\lambda_3} + \frac{k_m(k_p - \lambda_2)}{\lambda_2(\lambda_2 - \lambda_3)}e^{-\lambda_2 t} + \frac{k_m(k_p - \lambda_3)}{\lambda_3(\lambda_3 - \lambda_2)}e^{-\lambda_3 t}\right] \quad (28)$$

$$Z = X_0\left[\frac{k_\sigma k_n}{\lambda_2\lambda_3} + \frac{k_\sigma(k_n - \lambda_2)}{\lambda_2(\lambda_2 - \lambda_3)}e^{-\lambda_2 t} + \frac{k_\sigma(k_n - \lambda_3)}{\lambda_3(\lambda_3 - \lambda_2)}e^{-\lambda_3 t}\right] \quad (29)$$

Equations 27–29 were programmed to yield values of X, Y, Z, Z/Y, and the instantaneous first-order rate constants for isomerization of $X(k_i)$ for appropriate values of t. The values for the rate constants were the same as those used in model IIa. Table XI records

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[17] S. W. Benson, "Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 39.

Table XI

Results of Computer Calculations of Ratios of Instantaneous to Initial First-Order Rate Constants for Disappearance of α-Benzylstyrene (II) and Ratios of *trans*- to *cis*-α-Methylstilbene (*trans*-I/*cis*-I) Predicted Based on Model IIb

Reaction, %	k_i/k_0[a]	*trans*-I/*cis*-I predicted	Reaction, %	k_i/k_0[a]	*trans*-I/*cis*-I predicted
0.0	1.00	. .	40.0	0.99	11.2
1.0	1.00	11.2	50.0	.98	11.1
5.0	1.00	11.2	60.0	.97	11.1
10.0	1.00	11.2	70.0	.95	11.1
20.0	1.00	11.2	80.0	.92	11.0
30.0	1.00	11.2	90.0	.81	10.9

[a] k_i refers to instantaneous first-order rate constant, and k_0 to the first-order rate constant at zero time.

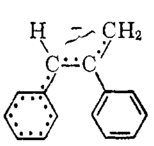
the values of k_i/k_0 (k_0 is k_i at zero time) and *trans*-I/*cis*-I predicted by the computer-simulated isomerization of α-benzylstyrene (II) based on model IIb. The near constancy of the *calculated* values for k_i/k_0 over the first 60% of the isomerization corroborates the good first-order kinetics *observed* for isomerization of II through 60% conversion. The constancy of the *calculated* values of the ratio *trans*-I/*cis*-I over 60% of the isomerization of II corroborates the constancy *observed* experimentally over the first 60% of conversion. The computer produced a value of 11.2 for this ratio, whereas 11.0 was observed experimentally (see Table II). Again, dramatic agreement between experiment and predictions based on model II are in evidence.

Discussion

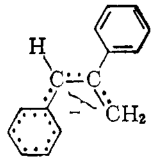
In this section, the following topics will be discussed in turn: (1) geometric stability of the allylic anions; (2) collapse preferences of the allylic anions; (3) intramolecularity in the allylic rearrangement; (4) geometric stability of vinyl anions, and relative kinetic acidity of allyl, vinyl, and aryl hydrogens; (5) solvent isotope effects on isomerization.

Geometric Stability of Allylic Anions.—In previous sections, strong evidence was presented that *cis*-α-methylstilbene (*cis*-I) and α-benzylstyrene (II) under the influence of base isomerize into one another and undergo isotopic hydrogen exchange with solvent through a *cis*-carbanion. Likewise, *trans*-α-methylstilbene (*trans*-I) and II isomerize into one another and undergo isotopic hydrogen exchange with solvent through a *trans*-carbanion. These two allylic ions are geometric isomers of one another, and they collapse to their respective olefins without undergoing appreciable interconversion. Thus interconversion of *cis*-I and *trans*-I occurs mainly through II.

The collapse of *cis*-carbanion favors *cis*-I over II by a factor of 6.5, whereas the collapse of *trans*-carbanion favors *trans*-I over II by a factor of 8.8. In the isomerization of II, the ratio, *trans*-I/*cis*-I = 11, is maintained over much of the reaction. These values indicate that the transition state for the production of *trans*-carbanion is more stable than that for production of *cis*-carbanion, and suggest that the *trans*-allylic anion is more stable than the *cis*-allylic anion. This conclusion is compatible with what might be expected on structural grounds. In the *cis*-carbanion, coplanarity of the directly conjugated benzene ring and the allylic π-system is sterically inhibited more than in the *trans*-carbanion. Hence, negative charge should be more delocalized in the *trans*-carbanion, and that anion should be the more stable.



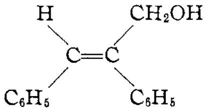
cis-allylic anion,
more strictly hindered,
less stable



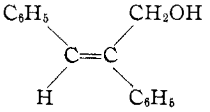
trans-allylic anion,
less strictly hindered,
more stable

The isomerization and exchange reactions were conducted in *tert*-butyl alcohol with potassium *tert*-butoxide as catalyst. In this nondissociating medium, the carbanions were undoubtedly part of an ion-pair. Delocalization of negative charge in the *trans*-carbanide ion-pair would not involve as much charge separation as in the more elongated *cis*-carbanion, and this effect also probably contributes to the greater stability of the *trans*-carbanion.

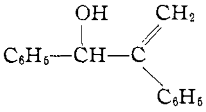
Interesting results have been reported[4] in what can be considered as a carbonium ion analog of the system of the present investigation. The carbonium ions were generated from alcohols IV–VI, and were subsequently reduced to *cis*- and *trans*-I and II with chloroaluminum hydrides. The *cis*-carbonium ion largely retained its geometrical integrity, but the *trans*-carbonium ion retained only part of its integrity. This result contrasts with those obtained with the carbanions of the present investigation. The reasons for this difference are not clear, but might be associated with the large differences in lifetime of the two kinds of charged species. In the carbanion study, proton capture was probably extremely rapid, and the carbanion lifetime very short. In the carbonium ion study, hydride ion capture was probably much slower, and the carbonium ion lifetime much greater.



IV



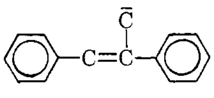
V



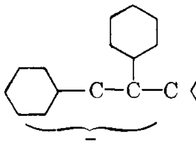
VI

Collapse Preferences of the Allylic Anions.—At equilibrium, *cis*-I predominated over II by a factor of about 10 (Table IV). The collapse ratio of the *cis*-carbanion favored *cis*-I over II by a factor of 6.5. Thus, proton capture occurred at that center (methylene group) which led to the thermodynamically more stable product. A similar relationship is observed in the *trans* system. At equilibrium, *trans*-I predominated over II by a factor of about 40 (Table IV), and the collapse ratio of *trans*-carbanion favored *trans*-I by a factor of 8.8 Again, the more thermodynamically stable olefin is preferentially produced in the kinetically controlled process.

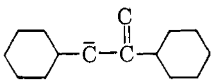
For comparative purposes, simple Hückel molecular orbital calculations were made for the 1,2-diphenylallylic anion in which charge is delocalized (VIII) and on its localized counterparts VII and IX. The total π-energies were calculated for the localized forms by summation of the π-energies of the component systems. The π-energy for VII was obtained from the π-energy of stilbene and of a carbon p-orbital containing two electrons. Similarly, the π-energy of IX was obtained from that of styrene, benzene, and a carbon p-orbital containing two electrons. The delocalization energies (D.E.) are the difference between the total π-energies of the delocalized structure and the localized structures VII and IX. The results are tabulated. The delocalization energies can be expressed in kcal./mole assuming a conversion factor of β = 20 kcal./mole.[18]



VII



VIII

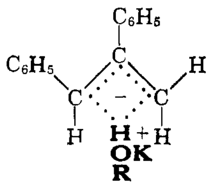


IX

The direction of the difference in delocalization energies favors collapse to the α-methylstilbenes as is experimentally observed. However, the energy difference of 9 kcal./mole predicts a collapse ratio of about 10^5, whereas 10^1 is observed. Apparently the transition states for proton capture have only a small amount of localized character, but enough to favor strongly the α-methylstilbenes from a product point of view. This result is expected, since the proton capture reaction is undoubtedly strongly exothermic.

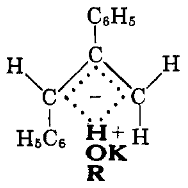
Intramolecularity in the Allylic Rearrangement.—For the base-catalyzed isomerization of α-benzylstyrene (II) in *tert*-butyl alcohol-O-*d*, the intramolecularity observed in the production of *cis*-I was 55%, and of *trans*-I was 36% (see Table VII). These values are similar to those observed in the isomerization of 3-phenyl-1-butene to *cis*-2-phenyl-2-butene in the same medium (51% intramolecularity).[8d] In dimethoxyethane–*tert*-butyl alcohol-O-*d*–potassium *tert*-butoxide, 3-phenyl-1-butene gave *cis*- and *trans*-2-phenyl-2-butene with essentially the same intramolecularity (50%).[8d] Evidence was also gathered that, in nondissociating solvents, collapse of the hydrogen-bonded carbanion occurred mainly from the face of the anion from which the hydrogen was abstracted. This effect was interpreted as reflecting the tendency of the system not to produce a "product-separated" potassium alkoxide ion-pair in a solvent of low dielectric constant.

The question arises as to why the 2-phenylbutyl system gives the same intramolecularity in producing its geometric isomers, but the system at hand gives different intramolecularities in generating its geometric species. This difference in behavior is attributed to the larger difference in steric compression in the *cis*- and *trans*-carbanions of the α-methylstilbene system as compared to the difference in steric compression in the *cis*- and *trans*-carbanions of the 2-phenyl-2-butene system. The phenyl–phenyl interactions in the carbanion of *cis*-I are greater than the methylene–phenyl interactions in the carbanion of *trans*-I. Thus the *cis*-carbanion is expected to be more puckered, and the π-electron cloud more concentrated, on the face of the anion that is hydrogen bonded and close to the potassium ion. As a result, the *cis*-carbanion should have a stronger hydrogen bond than the *trans*-carbanion, and should favor the intramolecular process. The isomeric hydrogen-bonded carbanions are formulated as X and XI.



X

cis-potassium carbanide ion-pair, more puckered, more strongly hydrogen bonded, favors intramolecularity



XI

trans-potassium carbanide ion-pair, less puckered, less strongly hydrogen bonded, favors intermolecularity

Geometric Stability of Vinyl Anions, and Relative Kinetic Acidities of Allyl, Vinyl, and Aryl Anions.—The rates of potassium *tert*-butoxide catalyzed isomerization and exchange of *cis*- and *trans*-stilbenes (*cis*- and *trans*-III) in *tert*-butyl alcohol-O-*d* were measured for several reasons: (1) The stilbene system provided a control for the α-methylstilbene system with respect to possible exchange at the vinyl position, and to possible *cis–trans* isomerization through vinyl anionic intermediates. (2) The relative rates of isotopic exchange and isomerization of the stilbene system provide a means of assessing the geometric stability and shape of the vinyl anion. (3) The stilbene system provides a means of determining the relative kinetic acidity of its vinyl and aryl hydrogens. The relevant rate data corrected to a common temperature are recorded in Table XII.

Table XII

Comparison of Second-Order Rate Constants[a] Corrected to 116°[b] for Isomerization of *cis*-α-Methylstilbene (*cis*-I) and *cis*-Stilbene (*cis*-III), and Hydrogen–Deuterium Exchange of *cis*- and *trans*-Stilbene (*cis*-III and *trans*-III) in *tert*-Butyl Alcohol–Potassium *tert*-Butoxide

		$k_2 \times 10^8$, l./mole sec.		
			Exchange[c]	
Run	Substrate	Isomerization	Phenyl	Vinyl
12	*cis*-I	7100	. . .	. . .
22	*cis*-III	0.14	3.6	360
24	*trans*-III	. . .	5.4	38

[a] One-point rate constants calculated assuming a first-order catalytic dependence upon potassium *tert*-butoxide. [b] From the results of runs 24 and 25 (Table VI), an Arrhenius activation energy of 25 kcal./mole for vinyl exchange was calculated, and used to correct the rates in runs 22 and 24 from 146 to 116°. [c] Rate constants are per exchangeable position. The two vinyl groups of *cis*- and *trans*-III are the same, and the 10 protons of the two phenyl groups are assumed to exchange at the same rate.

These data indicate that *cis*-I isomerizes 20 times as fast as *cis*-III undergoes isotopic exchange. The inductive effect of the methyl group in *cis*-I probably reduces the rate of vinyl exchange for the substance several powers of ten below what is observed for *cis*-III. Since *cis*-I was the slowest of the three isomeric olefins to isomerize, it is safe to conclude that vinyl exchange played no role in any of the reactions of this investigation involving *cis*-I, *trans*-I, or II. Since vinyl exchange in *cis*-III was faster than aryl exchange by two powers of ten, it is also safe to conclude that aryl exchange played no role in any of the reactions of this investigation involving *cis*-I, *trans*-I, or II. The same conclusion was reached from the lack of

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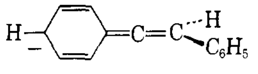
[18] J. D. Roberts, "Notes on Molecular Orbital Calculations," W. A. Benjamin, Inc., New York, N. Y., 1962, p. 101.

deuterium in the benzoic acid obtained by oxidation of the *trans*-I produced in run 19. Since vinyl exchange in *cis*-III was faster than isomerization by more than three powers of ten, isomerization of *cis*- to *trans*-I (or the reverse reaction) through vinyl carbanions as intermediates could not have contributed to the observed isomerization rates.

Isotopic exchange of *cis*-stilbene (*cis*-III) through an addition–elimination mechanism involving a mole of *tert*-butyl alcohol-O-*d* is shown to be untenable by the results of Curtin and Kellom.[19] These authors demonstrated that potassium *tert*-butoxide catalyzed elimination of 1,2-diphenylethyl 2,4,6-triethylbenzoate gave exclusively *trans*-stilbene. In the present investigation, had isotopic exchange of *cis*-III occurred by an addition–elimination mechanism, the rates of exchange and isomerization would have been the same, or at least close to one another. The data of Table XII indicate that *cis*-III underwent isotopic exchange over three powers of ten faster than it underwent isomerization to *trans*-III.

Clearly, isotopic exchange of *cis*-stilbene at the vinyl position involves the vinyl anion as an intermediate. The high rate of exchange compared to isomerization of *cis*-III indicates that the anion has considerable geometric stability. The geometric stability of vinyl anions has been studied by others in connection with vinyl organometallic compounds[20] and decarboxylation reactions.[21]

In the stilbene system, the vinyl anion can be pictured as involving considerable delocalization of charge into one of the benzene rings. In the extreme, an allenic type of geometry can be visualized (XIII). If such a geometry applied to the stilbene system, isotopic exchange without isomerization of *cis*-stilbene would have to depend on geometric factors involving the counter-ion of the ion-pair and the solvation shell. That such factors play an important role in determining the stereochemical fate of saturated carbanions has been amply demonstrated.[22]



XIII

Vinyl exchange occurs one power of ten faster for *cis*-stilbene than for *trans*-stilbene (see Table XII). This fact suggests that overlap is not negligible between the orbital of the vinyl anion and the π-system of the attached benzene ring. The interference between the two benzene rings in *cis*-stilbene places these rings in a geometry which is much more favorable for such overlap than the more planar *trans*-stilbene system. Such overlap should accelerate the rate of proton abstraction, and therefore exchange.

Solvent Isotope Effects on Proton Abstraction.—A solvent isotope effect on the rate of isomerism of II is visible in the results of runs 3, 4, and 5 (Table I). Isomerization of II proceeded faster by a factor of about 2 in deuterated as compared to nondeuterated *tert*-butyl alcohol. Similar medium isotope effects have been observed for base-catalyzed allylic rearrangement of the 2-phenylbutenyl system in alcoholic solvents,[8d] and in other studies involving base-catalyzed rearrangement of 1-halo-2,2-diphenylethylenes[9b] and hydrogen–deuterium exchange of monohydrofluorocarbon.[23]

The cause of the solvent isotope effect in the alcoholic systems can be pictured in two ways. The first involves greater solvation of anions in the protio than in the deuterio medium and the ground state anion being more solvated than the transition state anion. The second involves greater solvation of anions in the deuterio than the protio medium and the transition state anion being more solvated than the ground state anion. Since charge is more dispersed in the transition state than the ground state, solvation of the ground state should be the more important of the two. Thus *tert*-butyl alcohol-O-*h* would seem to solvate anions more than *tert*-butyl alcohol-O-*d* (see ref. 8d for more discussion and references).

Experimental

Preparation of *cis*- and *trans*-α-Methylstilbenes (*cis*-I and *trans*-I).—A mixture of diastereomeric 1,2-diphenyl-1-propanols was prepared[24] in 59% yield, b.p. 123–126° (1.4 mm.). This mixture was converted to its corresponding bromides (procedure "C"),[25] and the relatively insoluble *erythro*-bromide was isolated by crystallization from ether (14% yield, m.p. 148–155°). The residual mixture of *threo*- and *erythro*-bromides (200 g. of material obtained in 74% yield) was suspended in 80 ml. of N,N-dimethylformamide. To this mixture was added 165 ml. of a near-saturated solution of lithium bromide in the same solvent. Potassium carbonate (catalytic amount) was added, and the mixture was stirred at 25° for about 3 days. The heavy precipitate of *erythro*-bromide was collected. To the filtrate was added potassium carbonate, and the mixture was again stirred for 4 days. The additional solid *erythro*-bromide that separated was collected, and all samples of *erythro*-bromide were combined to give 144 g. (77%), m.p. 168–170°.

This material was converted to *cis*-α-methylstilbene,[26] which was finally purified by chromatography on an activity 1 alumina column, with a 20:1 alumina–substrate ratio and ether–pentane as eluting agent. From 150 g. of neutral material obtained from the elimination reaction, 25 g. of *cis*-I was obtained which by v.p.c. was shown to contain less than 0.1% *trans*-I. Recrystallization of this material from pentane gave *cis*-I, m.p. 47–48°, which by v.p.c. was shown to contain less than 0.05% *trans*-I.

To 53 g. of a mixture of the *cis*- and *trans*-I obtained by preparation of pure *cis*-I was added 100 ml. of freshly distilled dimethyl sulfoxide (Baker analyzed grade) and 10 g. of potassium *tert*-butoxide in 100 ml. of dimethyl sulfoxide. An additional 100 ml. of solvent was added. The very dark brown-green solution was stirred for 5 min., and 10 ml. of water was added, which discharged the color. Addition of 100 ml. of water deposited an oil which immediately crystallized. The mixture was shaken with a mixture of pentane and water, the organic layer was washed with water, with 3 *N* hydrochloric acid, again with water, and was dried, and evaporated. The residue was recrystallized 4 times from ether–pentane to give *trans*-I, m.p. 79.0–79.5° (35% yield), which contained less than 0.025% of other olefins (*cis*-I or II) as shown by v.p.c. (see later section).

N,N-Dimethyl-α,β-diphenylpropionamide.—Crude α,β-diphenylpropionic acid[27] (obtained in 67% yield), 237 g., was mixed with 300 g. of thionyl chloride (Eastman White Label), and the solution was refluxed for 1 hr. The excess thionyl chloride was evaporated at 20 mm., and the residue was dissolved in 200 ml. of ether. Into this solution was bubbled an excess of dimethylamine. The slurry was shaken with ether–water, the

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[19] D. Y. Curtin and D. B. Kellom, *J. Am. Chem. Soc.*, **75**, 6011 (1953).

[20] (a) D. Y. Curtin and E. E. Haris, *ibid.*, **73**, 2716 (1951); (b) E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2078 (1951); (c) D. Y. Curtin and J. W. Crump, *J. Am. Chem. Soc.*, **80**, 1922 (1958).

[21] D. Jambotkar and R. Ketcham, *J. Org. Chem.*, **28**, 2182 (1963).

[22] For example, D. J. Cram, *Pure Appl. Chem.*, 155 (1963).

[23] S. Andreades, *J. Am. Chem. Soc.*, **86**, 2003 (1964).

[24] D. J. Cram and F. A. Abd Elhafez, *ibid.*, **74**, 5828 (1952).

[25] D. J. Cram and F. A. Abd Elhafez, *ibid.*, **75**, 339 (1953).

[26] D. J. Cram and F. A. Abd Elhafez, *ibid.*, **74**, 5851 (1952).

[27] C. R. Hauser and W. R. Dunnavant, *Org. Syn.*, **40**, 38 (1960).

ether layer was washed with 3 *N* hydrochloric acid, 3 *N* sodium hydroxide, twice with water, dried, and the solvent was evaporated to give 201 g. (79%) of crude amide.

The amide was used after one recrystallization from ether. A sample was recrystallized 3 times to constant melting point, 87.5°. *Anal.* Calcd. for $C_{17}H_{19}NO$: C, 80.57; H, 7.56. Found: C, 80.78; H, 7.86.

1-Dimethylamino-2,3-diphenylpropane.—To 100 g. of lithium aluminum hydride in ether at about 10° was added 201 g. of crude N,N-dimethyl-α,β-diphenylpropionamide in ether. The mixture was stirred at reflux for 14 hr., and the excess lithium aluminum hydride was decomposed with ethyl acetate followed by water and dilute phosphoric acid. To the resulting mixture was added 10 *N* sodium hydroxide until precipitation was complete. The precipitate was dissolved in a minimum of 6 *N* sodium hydroxide solution (~12 l.), and the basic aqueous phase was extracted twice with ether. The organic layers were combined, washed with water, and dried. The solvent was evaporated, and the residual oil was distilled through a spinning band column, b.p. 128° at 1.5 mm., $n^{25}\mathrm{D}$ 1.5469, wt. 158 g. (84%) of amine. *Anal.* Calcd. for $C_{17}H_{21}N$: C, 85.30; H, 8.84. Found: C, 85.11; H, 8.54.

α-Benzylstyrene (II).—A mixture of 43 g. of 30% hydrogen peroxide and 50 g. of 1-dimethylamino-2,3-diphenylpropane was stirred past homogeneity (18 hr.). Excess hydrogen peroxide was decomposed with beef liver catalase, and the water was removed by lyophilization. The resulting viscous oil was dissolved in 200 ml. of tetrahydrofuran freshly distilled from lithium aluminum hydride, and 50 g. of Molecular Sieves (Linde Co.) was added.[28] The progress of the reaction at 25° was followed with nuclear magnetic resonance spectra of 0.2-ml. samples withdrawn, at appropriate times. After 37 hr., the peaks attributed to the amine oxide methyl groups had been reduced to one-third of their initial size. The reaction mixture was heated an additional 24 hr. at 50° after which the spectra indicated the absence of starting material. The Molecular Sieves were collected and washed twice with ether. The combined filtrates were washed with water, with 3 *N* hydrochloric acid, with 3 *N* sodium hydroxide, and again with water. The solution was dried, evaporated, and the residual oil was distilled through a spinning band column, b.p. 81–83° at 0.12 mm. (lit.[29] 164–166° (14 mm.)), to give 29 g. (72%) of α-benzylstyrene (II), $n^{25}\mathrm{D}$ 1.5894 (lit.[30] $n^{20}\mathrm{D}$ 1.5903). In v.p.c., only one component could be detected. *Anal.* Calcd. for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.78; H, 7.05.

***cis*- and *trans*-Stilbene.**—The *cis* isomer was prepared by reported procedures,[31] and was purified by distillation through a spinning band column (b.p. 89° (0.7 mm.), lit.[31] 95–97° (1 mm.)) to yield olefin, $n^{25.5}\mathrm{D}$ 1.6192, lit.[9] $n^{25}\mathrm{D}$ 1.6183–1.6193.° Analysis of this material by v.p.c. (see later section) indicated the presence of 0.53% *trans* isomer.

The *trans*-stilbene employed was Eastman White Label quality (m.p. 123–24°, lit.[32] 124°). Analysis by v.p.c. indicated about 4% *cis* isomer. Analysis (v.p.c.) of the *trans* isomer submitted to deuterium analysis indicated less than 1% of the *cis* isomer.

Base-Catalyzed Equilibrium of *cis*- and *trans*-α-Methylstilbene and α-Benzylstyrene.—To a weighed amount of olefin in a cleaned dried test tube that had been flushed with nitrogen was added an aliquot of standardized 0.586 *N* potassium *tert*-butoxide in *tert*-butyl alcohol. The tubes were sealed under nitrogen at Dry Ice–acetone temperature. Upon warming to 25°, clear, colorless solutions were obtained. The tubes were placed in a 100° bath for 7 days and then in a bath at 75.10 ± 0.05° for 2 months. Product was isolated and analyzed as in the kinetic runs.

Acid-Catalyzed Equilibration of *cis*- and *trans*-α-Methylstilbene and α-Benzylstyrene.—The method previously reported was closely followed except that the sample size of the stilbenes was reduced to 0.25 g. Analyses of the resulting mixtures were performed on a 0.25 in. by 6 ft. v.p.c. column of 10% Carbowax 30M on 60/80 firebrick.

Solvents and Solutions.—The *tert*-butyl alcohol-O-*d* was prepared as previously reported,[33] calcium oxide being used for the final drying, and the final distillation was onto predried Molecular Sieves. Deuterium analysis by the combustion and falling drop method[14] gave 0.997 atom of deuterium per molecule. Protio-*tert*-butyl alcohol (Eastman White Label) was distilled from Molecular Sieves (Linde Co.) onto Molecular Sieves. Solutions of potassium *tert*-butoxide in *tert*-butyl alcohol and *tert*-butyl alcohol-O-*d* were prepared by dissolving weighed, clean potassium metal directly in solvent at 25° under an atmosphere of purified nitrogen. The solution was stored under nitrogen. The base concentration was determined by withdrawing 1- or 2-ml. samples of solution, adding water, and titrating the resulting solution with 0.05 *N* sulfuric acid to the methyl orange–brom cresol green end point. Titration of the solutions used in the kinetic runs before the first and after the last run gave the same titer.

Typical Procedure for a Kinetic Run.—A weighed amount (~0.25 g.) of substrate was introduced into a pear-shaped flask that had been well flushed with oxygen-free, dry nitrogen. The standard base solution (~10 ml.) was added through a pipet at ambient temperature. The flask was immediately stoppered, swirled, and placed in a constant temperature bath (zero time). When solids were used, zero time was taken at the moment of complete solution, about 1 min. after immersion.

At appropriate times, sample was removed with a syringe, the flask being kept open a minimum amount of time. The syringe was rapidly emptied into a 125-ml. separatory funnel containing 50 ml. of water. The total time elapsed from the opening of the flask to the emptying of the syringe was about 0.2 min. The water layer was shaken with 50 ml. of pentane, and the pentane layer was washed with water three times and dried. The pentane was slowly evaporated through a Vigreux column. Just before v.p.c. analysis, the residue was dissolved in a minimum of ether, and the totally dissolved sample was submitted to v.p.c. analysis.

In run 6 (*trans*-I as substrate), which extended over the longest period of time, an aliquot of the reaction solution was titrated for base before the first (0.281 *N*) and after the last sample (0.282 *N*) was taken.

Typical Procedure for an Isotopic Exchange Run.—All reaction vessels and tubes were treated with hot chromic acid, rinsed with water, dilute ammonium hydroxide, several times with distilled water, and dried at 130°. The olefin was weighed into the reaction tube which was flushed thoroughly but gently with oxygen-free, dry nitrogen. An aliquot of standard base solution was added with a pipet, the tube was restoppered, cooled to −78°, and sealed. The tubes were then warmed until the medium melted, shaken, and submerged in a constant temperature bath.

In runs 12–15, the tubes were suspended in the vapor of refluxing glacial acetic acid. The temperature gradient over the length of the tubes was about 4°, and the average temperature was recorded. Runs 16–21 were conducted in a constant temperature bath. At the end of the reaction period, the tube was removed, cooled immediately to −78°, and opened. The contents were transferred to a separatory funnel and shaken with equal volumes of pentane and water. The pentane layer was washed with water (3 times), dried, and evaporated slowly through a Vigreux column to dryness. The residue was dissolved in a minimum of fresh ether totally transferred to a sample vial, and the solution analyzed by v.p.c. (see later section).

In runs 12–16, the olefins were separated on a preparative column of 5% silicone nitrile oil on 30/60 Chromosorb W. The effluent material from the preparative column was finally purified by alumina chromatography. In runs 17–19 and 22, a preparative column of 17% silicone nitrile oil (XF-1150) on 60/80 firebrick was employed, followed by sublimation or distillation of the effluent olefins. In runs 20, 21, and 23–25, the olefins were purified by sublimation only. A bath temperature of 65° at 0.3 mm. was used for *trans*-I, of 45° at 0.3 mm. for *cis*-I, and II was distilled at a bath temperature of 120–130° at 0.4 mm. After purification, the samples were submitted for deuterium analysis by the combustion and falling drop method.[14] In run 19, the total olefins obtained after preparative v.p.c. represented a 90% recovery of material.

Isotopic Exchange of *cis* and *trans*-Stilbene (*cis*-III and *trans*-III).—The procedure resembled that employed for the other olefins except in runs 22–24, where Claisen tubes were sealed under vacuum and about two-thirds submerged in a bath at the temperature reported (Table VI). When *trans*-stilbene (Eastman White Label) was used, ether was used as the extraction solvent,

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[28] This procedure is similar to that of D. J. Cram and M. R. V. Sayhun, *J. Am. Chem. Soc.*, **85**, 1263 (1963). Removal of the water destroys the hydrogen bonds to the oxide, raises the energy of the ground state, and increases the rate of reaction as well as the yield.

[29] P. Ramart and P. Amagat, *Ann. chim.*, [10] **8**, 309 (1927).

[30] J. V. Braun, J. Seeman, and A. Schultheiss, *Ber.*, **55**, 3803 (1922).

[31] R. E. Buckles and N. G. Wheeler, *Org. Syn.*, **33**, 88 (1953).

[32] "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, Vol. 42, 1960–1961, p. 1227.

[33] D. J. Cram and B. Rickborn, *J. Am. Chem. Soc.*, **83**, 2178 (1961).

and the extraction residues were sublimed at a bath temperature of 75° (0.1 mm.). When *cis*-stilbene was employed, the material from extraction was distilled at a bath temperature of 110–120° at 0.1 mm.

The oxidations of the products from the exchange runs to benzoic acid were conducted as follows. From 150 to 300 mg. of *cis*- or *trans*-III was dissolved in a mixture of 20 ml. of *tert*-butyl alcohol and 10 ml. of water, heated to reflux, and crystalline potassium permanganate was added until a pink color persisted. The solution was held at reflux for an additional 15 min., cooled, and sodium bisulfite was added until a colorless solution was obtained. The precipitate was removed by filtration through Celite, and the clear filtrate was evaporated to dryness on a rotatory evaporator. The residue was dissolved in a minimum of water, washed with ether, acidified with 3 *N* hydrochloric acid, and extracted continuously with ether. The ether layer was evaporated, and the residual benzoic acid was sublimed at 80° (0.1 mm.) and submitted for deuterium analysis by combustion and falling drop method.[14] An 80% yield of benzoic acid was obtained from *trans*-III, and 65% from *cis*-III.

Ozonolysis of *trans*-α-Methylstilbene from Run 19.—Ozone-enriched oxygen was bubbled into a solution of 1.06 g. of *trans*-α-methylstilbene (*trans*-I) in 25 ml. of cyclohexane at 0° until thin layer chromatography (0.25 mm. silica gel G plate with 2% methanol–pentane as developer and iodine as detector) indicated absence of olefin. The volume of cyclohexane had diminished to about 10 ml. Ether (25 ml.) was added, followed by slow addition of 1.0 g. of lithium aluminum hydride. The reaction mixture was stirred an additional 4 hr., and a saturated solution of sodium sulfate in water was added dropwise until no more hydrogen was evolved. The ether layer was decanted, and the precipitate was re-extracted with ether. The combined ether layers were washed once with water, once with 10% sodium bicarbonate, three times with water, and dried. The ether was evaporated, and the residual oil was distilled (bath temperature 125–140°) to give 0.896 g. of a clear oil. The mixture was analyzed by v.p.c. (0.25 in. × 6 ft. column of 20% 30M Carbowax on 60/80 firebrick), and found to contain 35% benzyl alcohol, 37% α-methylbenzyl alcohol, 1.3% acetophenone, 0.1% benzaldehyde, and 13% cyclohexane. The alcohols were each produced in 55% yield. This mixture was separated by preparative v.p.c. on a column of 20% 30M Carbowax on 60/80 firebrick. The samples were immediately distilled and sealed in an ampoule to avoid air oxidation. Oxidation of a 0.203-g. sample of *trans*-I by the procedure given for *cis*- and *trans*-stilbene yielded 0.144 g. (57%) of benzoic acid.

Analytical Method and Error Analysis.—All v.p.c. analyses were performed on a 9-ft. × 0.25-in. column of 20% silicone nitrile gum (XE-60) on 60/80 mesh firebrick (column 200°, inlet 280°, detector 300°, helium flow rate 30 ml./min.). Sample sizes from 1–10 μl. of solution yielded about 1500 theoretical plates for the column. The peaks had little tailing and came at 21 min. (*cis*-I), 28 min. (II), and 42 min. (*trans*-I). In the analyses for *cis*- and *trans*-stilbene mixtures, the retention times were 20 and 54 min., respectively.

For the 3 peaks of the α-methylstilbene system, the absolute mean deviation was about ±0.05% in the range 0–10%, and increased to ±0.20% in the range 10–70%. These reproducibility values were obtained as the result of three v.p.c. analyses per sample in runs 3 and 4. The accuracy of the analyses was tested with a known mixture and is reported in Table XIII.

TABLE XIII

ACCURACY OF V.P.C. ANALYSES

	cis-I	*trans*-I	II
Weight, %	7.42	63.08	29.49
Area, %	7.38 ± 0.09	63.9 ± 0.4	28.8 ± 0.3
Deviation, %	−0.5	+1.1	−2.3

Deuterium analyses[14] run on compounds containing less than 0.20 atom/mole-% excess deuterium were run against a standard protio sample, and were reproducible to within ±0.02 atom % excess deuterium. Deuterium analyses by n.m.r. in carbon tetrachloride were run with the maximum expanded field. The integrated peak area of the methylene hydrogens of a weighed acenaphthene internal standards was compared with that of the methyl or vinyl hydrogens of a weighed, purified sample of olefin. The % mean deviation in repeated integrations was 5% of total hydrogen. By "mean deviation" is meant the average of the absolute deviations of the values from the mean. Error estimates in calculations are by the method of total differentials.[34]

(34) L. L. Smail, "Analytical Geometry and Calculations," Appleton-Century-Crofts, New York, N. Y., 1953, p. 544.

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Electrophilic Substitution at Saturated Carbon. XXIV. Trifluoromethyl as a Carbanion-Stabilizing Group[1]

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Two systems have been prepared for study of the stereochemical course of the base-catalyzed hydrogen–deuterium exchange at carbon attached to a trifluoromethyl group. Optically active 2-methyl-3-phenyl-1,1,1-trifluoropropane (I), and the same compound deuterated in the 2-position, and optically active 2-phenyl-1,1,1-trifluorobutane (II), and its deuterated counterpart (2-position), were examined. In *tert*-butyl alcohol-O-*d* at 124°, (+)-I-*h* was found to undergo elimination reaction to the exclusion of isotopic exchange. The initially formed 1,1-difluoro-2-methyl-3-phenylpropene underwent a base-catalyzed allylic rearrangement to give a 6.5 to 1 mixture of *trans*- to *cis*-3,3-difluoro-2-methyl-1-phenylpropene (*trans*- to *cis*-III), which were identified by their spectral properties. The base-catalyzed elimination reaction exhibited a kinetic isotope effect of 1.2, a fact which suggests a carbanion intermediate for the reaction. The 2-phenyl-1,1,1-trifluorobutane system (II) also underwent elimination to give 1,1-difluoro-2-phenyl-1-butene (IV) and its polymers. However, hydrogen–deuterium exchange also occurred, but at a much slower rate. In *tert*-butyl alcohol–potassium *tert*-butoxide, and in ethanol–potassium ethoxide, isotopic exchange went with total racemization (k_e/k_α, the ratio of the rate constant for exchange to the rate constant for racemization, was equal to unity). In methanol–potassium methoxide, or methanol–lithium methoxide, isotopic exchange went with net inversion (k_e/k_α ranged from 0.60 to 0.84, depending on whether the substrate or the solvent was deuterium labeled). This result is interpreted in terms of an asymmetrically solvated symmetrical and dissociated carbanion.

In previous investigations, the stereochemistry of the base-catalyzed hydrogen–deuterium exchange of a number of α-substituted α-phenylethyl or α-phenylpropyl systems has been examined by measuring the value of k_e/k_α ratios, where k_e is the rate constant for exchange and k_α the rate constant for racemization. The substituents examined were ethyl,[2a] methoxy,[2a]

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(2) (a) D. J. Cram, C. A. Kingsbury, and B. Rickborn, *J. Am. Chem. Soc.*, **83**, 3688 (1961); (b) D. J. Cram, B. Rickborn, C. A. Kingsbury, and P. Haberfield, *ibid.*, **83**, 3678 (1961); (c) D. J. Cram and L. Gosser, *ibid.*, **86**, 5457 (1964).