but no rearrangement to isobutylbenzene (2) (or other isomers[7,8]).

It is interesting to consider the reaction pathways by which 2-phenyl-2-^{14}C-butane (1) may be converted into four different kinds of products (1i, 1e, 2, and 3, Scheme I). Isomerization to 2-phenyl-3-^{14}C-butane (1i) and to isobutylbenzene (2) may both involve the intermediate secondary carbonium ion 4. On the basis of stability of the carbonium ions produced, competition between the phenyl and methyl shifts would be expected to be in favor of the latter, since the charge on 5 may be delocalized by the benzene ring. The experimental observation that the isotopic isomerization ($1 \rightleftarrows 1i$) reaches equilibrium under conditions that produce no *sec*-butylbenzene–isobutylbenzene isomerization ($1 \rightleftarrows 2$) seems to indicate that participation of the phenyl group in the 1,2 shift is a more important factor than the stabilization of the ion 5.

The fact that the production of 3 and benzene by disproportion is an even more facile reaction than the isotopic isomerization may be rationalized, however, on the basis that the tertiary benzylic carbonium ion 6 is formed much more readily than the aliphatic secondary ion 4,[9] and the disproportionation proceeds by the Pines–Streitwieser alkylation–dealkylation mechanism.[10] This explanation is consistent also with the observation[4] that racemization of optically active 2-phenylpentane by aluminum chloride is much more rapid than isomerization to 3-phenylpentane. Although our 2-phenyl-2-^{14}C-butane was not optically active, racemization of asymmetric molecules would undoubtedly follow the pathway $1 \rightleftarrows 6 \rightleftarrows 1e$, which involves the same intermediate (6) required for the disproportionation.[11]

Experimental Section

Synthesis of 2-Phenyl-2-^{14}C-butane (1).—The radioactive title compound was synthesized by methods described previously. $C_6H_5{}^{14}COCH_3$ was prepared from $CH_3{}^{14}CO_2Na$, benzene, and $AlCl_3$;[8a] treatment of $C_6H_5{}^{14}COCH_3$ with ethylmagnesium bromide was followed by catalytic reduction of the crude product to give 1.[8b,c] This product (and the 2-phenylbutane recovered after reaction with $AlCl_3$) was converted into *p*-nitrobenzoic acid by reaction with concentrated nitric acid (reflux, 24 hr). The crude *p*-nitrobenzoic acid was purified by dissolving it in aqueous NaOH solution, extracting nonacidic organic impurities into ether, and reprecipitating the *p*-nitrobenzoic acid by the addtion of concentrated HCl. It was recrystallized from aqueous ethanol and sublimed under reduced pressure; radioassay was carried out by wet combustion to CO_2, which was counted on a vibrating-reed electrometer.[8a]

Reaction of 2-Phenyl-2-^{14}C-butane with Aluminum Halides.—Details of six experiments are given in Table I. The reaction mixtures were stirred with Teflon-covered magnetic stirring bars, decomposed with crushed ice and HCl, and worked up by addition of ether and extraction in the usual way.[8] *sec*-Butylbenzene (2-phenylbutane) was recovered by fractional distillation; vpc showed it to be free of *n*-butyl- and *t*-butylbenzene isomers; and it indicated the absence of isobutylbenzene.[12] Disproportionation to benzene and di-*sec*-butylbenzene in even the lowest temperature reactions was demonstrated, both by vpc and by the fractional distillations of the reaction mixtures. The amount of *sec*-butylbenzene recovered ranged from 30% at 25° to 60% at −14°.

Registry No.—1, 17398-79-7.

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[7] Skeletal rearrangements to isobutyl-, *t*-butyl-, or *n*-butylbenzene would have been detected by vpc or ir analysis.[8] Rearrangement to 2-phenyl-1- or -4-^{14}C-butane is unlikely on the basis of requiring primary carbonium ion intermediates and also because a loss of more than 50% of the ^{14}C from the 2 position would probably have been observed in the 25° experiments.

[8] (a) R. M. Roberts and J. E. Douglass, *J. Org. Chem.*, **28**, 1225 (1963); (b) R. M. Roberts, G. A. Ropp, and O. K. Neville, *J. Amer. Chem. Soc.*, **77**, 1764 (1955); (c) R. M. Roberts and S. G. Brandenberger, *ibid.*, **79**, 5484 (1957).

[9] The intermediate ion **4** may not only be produced directly from **1** by intermolecular hydride abstraction as shown in Scheme I, but also from **6** by intramolecular hydride shift. It is probably impossible to distinguish experimentally between these alternatives, and actually it is likely that **4** is produced in both ways. The rationalization of the relative ease of formation of products **1i**, **1e**, **2**, and **3** on the basis of the stability of the intermediates **4** and **6** has the same relevance whether **4** is formed directly from **1** or indirectly *via* **6**.

[10] (a) H. Pines and J. T. Arrigo, *J. Amer. Chem. Soc.*, **80**, 4369 (1958); (b) A. Streitwieser, Jr., and L. Reif, *ibid.*, **86**, 1988 (1964).

[11] By analogy with the behavior of 2-phenylpentane,[4] racemization of optically active 2-phenylbutane would be expected to be still faster than disproportionation.

[12] Analysis of the butylbenzenes by vpc and ir is described by R. M. Roberts and D. Shiengthong, *J. Amer. Chem. Soc.*, **82**, 732 (1960).

The Solvent Isotope Effect in the Acid-Catalyzed Isomerization of *cis*-Stilbenes[1,2]

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It has been pointed out several times in recent years that deuterium isotope effects should vary with structure in a rational manner, reaching a maximum in situations where the hydrogen isotope is symmetrically disposed in the transition state. Westheimer has presented these concepts in more quantitative terms.[5] He assumes that A–H and B react to form A and B–H by way of a linear transition state A–H–B, and finds that the isotope effect is at a maximum when k_1 is equal to k_2, where k_1 and k_2 represent the stretching force constants of the A–H and H–B bonds in the transition state.

Bell and Goodall,[6] in a particularly careful study have observed that the deuterium isotope effect is at a maximum for the ionization of deuterated nitroparaffins when the proton transfer is between two acid–base systems of approximately equal p*K*. The recent study by Goodall and Long[7] has likewise shown that a very similar result obtains in the reverse reaction involving deuterated acids in deuterated medium.

In recent studies from these laboratories we have examined in some detail the mechanism of the acid-catalyzed isomerization of a group of substituted *cis*-stilbenes.[8] As the rate-limiting step was shown to be the initial proton transfer from the acidic medium to the organic substrate, this series of compounds represents a useful group in which to examine the variation of the solvent isotope effect as a function of structure.

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[2] A portion of this work has been reported in a preliminary communication: D. S. Noyce, D. R. Hartter, and F. B. Miles, *J. Amer. Chem. Soc.*, **86**, 3584 (1964).

[3] Shell Fellow in Chemistry, 1963–1964.

[4] National Science Foundation Cooperative Fellow, 1962–1964.

[5] F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

[6] R. P. Bell and D. M. Goodall, *Proc. Roy. Soc., Ser. A*, **294**, 273 (1966).

[7] D. M. Goodall and F. A. Long, *J. Amer. Chem. Soc.*, **90**, 239 (1968).

[8] D. S. Noyce, D. R. Hartter, and F. B. Miles, *ibid.*, **90**, 4633 (1968).

We have measured the solvent isotope effect on the rate of isomerization of ten substituted *cis*-stilbenes. The results are tabulated in Tables I and II. Table I gives the results of the rate measurements in the deuterated medium, and Table II gives the values of the solvent isotope effect, extrapolated to a common acidity. It is immediately apparent from these results that there is a distinct trend in the magnitude of the solvent isotope effect, tending to higher values as the stability of the resulting carbonium ion is increased by the appropriate interaction with the substituent in the aromatic moiety. In the extreme, *cis*-4,4′-dimethoxystilbene gives a solvent isotope effect of 6.0, whereas *cis*-4-nitrostilbene gives a solvent isotope effect of only 2.9.

TABLE I

RATE OF ISOMERIZATION OF *cis*-STILBENES IN D_2SO_4 AT 25.00°

No.	Compound[a] X	Compound[a] Y	Wt % D_2SO_4[b]	$k \times 10^5$, sec^{-1}	$-D_0$[c]
1	4-Methoxy	4′-Methoxy	39.04	18.5	2.48
			42.44	42.7	2.83
			45.89	105.	3.21
			49.12	274.	3.55
2	4-Methoxy	4′-Methyl	41.83	19.6	2.77
			48.11	100.	3.44
			50.58	202.	3.71
3	4-Methoxy	H	45.16	45.2	3.14
			49.18	110.	3.56
			51.07	167.	3.75
4	4-Methoxy	3′-Nitro	42.43	4.12	2.83
			51.53	46.7	3.83
5	4-Methoxy	4′-Nitro	47.90	13.1	3.42
			51.32	41.2	3.79
			54.27	74.0	4.12
			57.41	262.	4.46
			58.18	251.	4.51
6	4-Methyl	H	55.32	36.5	4.25
			57.64	71.1	4.53
7	4-Methyl	4′-Nitro	54.61	3.16	4.15
			66.39	172.	5.76
8	H	3′-Methoxy	60.27	15.2	4.83
			62.67	49.1	5.18
			64.98	116.	5.54
9	H	4′-Nitro	64.91	7.0	5.53
			67.04	17.8	5.88
			69.90	54.7	6.36

[a] Substituted *cis*-stilbenes $XC_6H_4CH{=}CHC_6H_4Y$. [b] Weight % D_2SO_4 in the final solution, containing 5% ethanol. [c] For definition, see Experimental Section.

TABLE II

VALUES OF THE KINETIC SOLVENT ISOTOPE EFFECT FOR THE ISOMERIZATION OF *cis*-STILBENES $XC_6H_4CH{=}CHC_6H_4Y$

X	Y	$(k_{H_2O}/k_{H_2O})_{-4}$[a]
4-CH_3O	4′-CH_3O	6.0
4-CH_3O	4-CH_3	3.5
4-CH_3O	H	4.2
4-CH_3O	3′-NO_2	3.5
4-CH_3O	4′-NO_2	3.7
4-CH_3	H	2.8
4-CH_3	4′-NO_2	3.5
H	H	2.4[b]
H	3′-CH_3O	2.5
H	4′-NO_2	2.9

[a] Rates compared by extrapolation or interpolation to $H_0 = -4.00$. $H_0 = D_0 = -4.00$ corresponds to 55.25% H_2SO_4 and to 53.21% D_2SO_4, and to mole fraction sulfate = 0.191. [b] Data given in previous paper.[8]

The Hammond postulate[9] states that, if two species differ greatly in stability, the transition state for their interconversion resembles structurally the less stable of the two species. Thus, one would expect the transition state for protonation of stilbene to resemble the product of the protonation reaction, a carbonium ion of the form ArC^+HCH_2Ar'. One can then extend this postulate by saying that as the stability of ArC^+HCH_2–Ar' is increased, one would expect the transition state for protonation of stilbene to resemble this carbonium ion to a lesser and lesser extent. That is, the more stable the carbonium ion is, the stronger one would expect the O–H bond to be and the weaker one would expect the C–H bond to be in the transition state.

A trend in the solvent isotope effects was observed by Noyce, Avarbock, and Reed[10] in the acid-catalyzed *cis–trans* isomerization of cinnamic acids. The kinetic solvent isotope effect for isomerization of *cis*-*p*-methoxycinnamic acid is 4.5 while for *cis*-cinnamic acid it is 3.8. This, then, is a case in which proton transfer is more than "half complete" at the transition state.[11]

An example of the opposite trend is shown in the data of Kuivila and Nahabedian[12] in the study of the acid-catalyzed protodeboronation of areneboronic acids.

The trends observed in the present study, though clear, also show that there are additional factors involved, which prelude a complete analysis of the present situation.

In recent study by Schubert, Lamm, and Keeffe,[13] similar perturbations were observed in the hydration of substituted styrenes.

Experimental Section

The preparation of all compounds used in the present study has been reported previously.[8] For studies of the rate of isomerization in deuterated media a 5-ml aliquot of the desired *cis*-stilbene in ordinary ethanol was diluted with deuteriosulfuric acid in D_2O (99.8% *d*) to 100 ml. The titer of the final solution is that given in Tables I and II. The proton pool is thus about 99% *d*. Kinetics were followed by observing the appearance of the absorption band for the *trans* isomer.

Högfeldt and Bigeleisen[14] have concluded that $H_0 = D_0$ at the same molarity of acid. As the molar volumes of H_2O and H_2SO_4 are nearly equal to the molar volumes of D_2O and D_2SO_4, respectively,[15] we have made comparisons at the same mole fraction sulfate, and assumed that $D_0 \equiv H_0$ under these conditions.

Registry No.—Table I: 1, 2510-75-0; 2, 17555-94-1; 3, 1657-53-0; 4, 17555-96-3; 5, 4648-14-0; 6, 1657-45-0; 7, 17556-09-1; 8, 14168-83-3; 9, 6624-53-9.

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[9] G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

[10] D. S. Noyce, H. S. Avarbock, and W. L. Reed, *ibid.*, **84**, 1647 (1962).

[11] Westheimer[6] points out the difficulty with the idea of "partial bond breaking" in the transition state, and that of more direct concern is the relationship of k_1 to k_2, the force constants for the A–H and H–B bonds in the transition state. Nevertheless the descriptive phrase is useful.

[12] H. G. Kuivila and K. V. Nahabedian, *ibid.*, **83**, 2159, 2164 (1961); K. V. Nahabedian and N. G. Kuivila, *ibid.*, **83**, 2167 (1961).

[13] W. M. Schubert, B. Lamm, and J. R. Keeffe, *ibid.*, **86**, 4727 (1964).

[14] E. Högfeldt and J. Bigeleisen, *ibid.*, **82**, 15 (1960).

[15] R. H. Flowers, R. J. Gillespie, J. V. Oubridge, and C. Solomons, *J. Chem. Soc.*, 667 (1958).