and its chlorination products were analyzed by direct sampling of the reaction mixtures on to the GLC column. Penyl phenyl ether and its chlorination products were separated from the surfactants which interfered with the GLC analysis by adding to the reaction mixture pentane (10 mL) followed by 33% w/v aqueous calcium chloride solution. The solution was mixed vigorously and the pentane layer separated and concentrated under a stream of nitrogen. The extraction procedure and the GLC analyses were all calibrated with authentic samples.

Energies of the Stilbenes and Stilbene Dibromides

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The enthalpy difference of the stilbenes is of the interest in connection with the much-studied[1,2] mechanism of photochemical interconversion of the two stereoisomers; it also has a bearing (see below) on the mechanism of bromine elimination from the corresponding dibromides.[3] Interpretation of the latter reaction also depends crucially on a knowledge of the conformational equilibria in the two dibromides (vide infra). This note deals with these two problems.

The standard free-energy difference $\Delta G°$ of the stilbenes has been determined in a hydrocarbon solvent at 27 °C, by equilibration, to amount to 3.7 ± 0.1 kcal/mol (15.5 ± 0.4 kJ/mol),[4] the trans isomer being the more stable one. Through determination of the dependence of the equilibrium composition on temperature, $\Delta H°$ (in toluene) was estimated to be 2.3 ± 0.3 kcal/mol (9.6 ± 1.3 kJ/mol); however, because of the one-sideness of the equilibrium and the corresponding small changes of $\Delta G°$ over a relatively large range (−30 to +90 °C) of temperature, the accuracy of this value is subject to question. Unfortunately a rather discrepant value of 5.7 ± 0.2 kcal/mol (23.9 ± 0.8 kJ/mol) was found from differences in heat of hydrogenation,[5] a method which, at first sight, would seem to be more accurate, since it is more direct and the number whose difference is taken are not large. A priori, however, it is not clear which of the two values is closer to the true one.

The heats of the combustion of the stilbenes were determined[6] a number of years ago and are 7401.1 ± 0.7 kJ/mol (1768.0 ± 0.2 kcal/mol) for the cis isomer and 7361.1 ± 0.5 kJ/mol (1758.5 ± 0.1 kcal/mol) for the trans
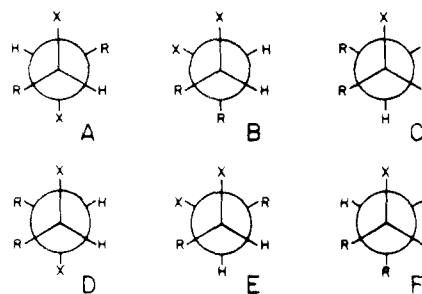
isomer. Since *trans*-stilbene was burned as a solid and cis–stilbene as a liquid, these values are not directly comparable and could not, at the time, be used to compute the heat of isomerization. However, since then the increments needed to convert these data to the gas phase have been reported: the heat of vaporization of the cis isomer is 15.8 ± 0.3 kcal/mol (66.1 ± 1.3 kJ/mol),[7] and the heat of sublimation of the trans isomer is 95.4 ± 3.0 kJ/mol (22.8 ± 0.7 kcal/mol).[8] With these additional data one can compute the heats of combustion of the stilbenes in the vapor phase to be 7467.2 ± 1.5 kJ/mol (1783.8 ± 0.4 kcal/mol) for the cis isomer and 7456.5 ± 3.0 kJ/mol (1781.3 ± 0.7 kcal/mol) for the trans isomer. The difference, 10.7 ± 3.4 kJ/mol (2.5 ± 0.8 kcal/mol), represents the heat of isomerization, in good agreement with the value obtained from the temperature dependence of equilibrium and in disagreement with the hydrogenation value. The lower value ($\Delta H° = 2.3 ± 0.3$ kcal/mol, 9.6 ± 1.3 kJ/mol) may therefore be accepted as the correct one.

The mechanism of elimination of the stilbene dibromides with iodide ion to give stilbenes, iodine, and bromide has been studied by Miller and co-workers.[3,9,10] The experimental facts are as follows: (1) The reaction is quite stereospecific[11] in most solvents (methanol being an exception),[9,10] the meso dibromide giving only *trans*-stilbene and the *dl* dibromide giving 88–96% *cis*-stilbene, suggesting that the elimination is largely anti. From this it might be assumed that the major course of the *dl* dibromide elimination with iodide proceeds by the same mechanism as the elimination from the meso dibromide, whatever that mechanism may be.[10] (2) The meso dibromide reacts 323 times as fast as the *dl* one in DMF at 36 °C,[3] implying a difference in activation energy of 3.5 kcal/mol (14.8 kJ/mol). (3) The equilibrium constant for the meso and *dl* dibromides in benzene is 3.0 at 80 °C, implying a $\Delta G°$ of 0.77 kcal/mol (3.2 kJ/mol) favoring the meso isomer.[12] (4) *trans*-Stilbene is more stable (vide supra) than *cis*-stilbene by $\Delta G° = 3.7$ kcal/mol (15.5 kJ/mol) at 27 °C (hydrocarbon solvent).

From these data it was concluded[10] that, since the energy differences between the starting materials were small but those between the products much larger, the large difference in activation energy—which was nearly the same as the difference in product free energy—suggested that the transition state in this reaction was product-like. However, this conclusion must be accepted with some caution, as will be explained in the sequel.

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According to the Winstein–Holness equation,[13-15] the rate constant of reaction of a conformationally heterogeneous system is equal to the sum of the rate constants for reaction of the individual conformers weighted by their mole fractions. Thus for *meso-* and *dl*-dibromostilbene (Scheme I) $k_{ept.}^{trans} = n_A k_A + n_B k_B + n_C k_C$, and similarly for the cis isomer $k_{ept.}^{cis} = n_D k_D + n_E k_E + n_F k_F$. If one assumes that only anti elimination proceeds at an appreciable rate,[16] $k_B = k_C = k_E = k_F = 0$: hence $k_{ept.}^{trans} = n_A k_A$, $k_{ept}^{cis} = k_D n_D$, and $(k_{trans}/k_{cis})_{ept.} = k_A n_A / k_D n_D$. The assertion that this ratio, found experimentally to be 323, is a measure of transition-state energies for reaction of these trans and cis isomers disregards the weighting factors n_A and n_D. In principle it might be possible that $k_A = k_D$ provided $n_A = 323 n_D$; in fact, if $n_A > 323 n_D$, $k_A < k_D$; thus to assert that the near equality of the difference in activation energy and the difference in product energy suggests a product-like transition state is risky; an alternative possibility is that the reactive conformation is much more populated in the starting meso dibromide than in the *dl* one, in which case the rate constants might differ little and might not reflect product stability at all. We shall now examine this possibility.

To estimate the conformational composition of *meso-* and *dl*-stilbene dibromide, we used the dipole moment date—meso, 0.4–0.9 D, and *dl*, 2.81 D—reported many years ago by Weissberger.[17] In addition we measured the proton–proton coupling constants in these compounds using the signals of the ^{13}C satellites:[18] meso, 11.3 Hz in CDCl₃; *dl*, 8.6 Hz in CDCl₃, 9.6 Hz in CD₃OD, 10.0 Hz in (CD₃)₂CO; 10.3 Hz in Me₂SO-d₆.

For the meso isomer, conformation A and the enantiomeric conformers B and C must be considered. A will have a dipole moment near zero (a small moment might be induced by libration about the equilibrium position). For B/C, if one takes the bond moment for C–CHBr–C to be 2.03 D,[19] one calculates a Br/Br gauche moment of 3.3 D.[20] If one now assumes a value of 0.45 D for the Ph–C bond dipole,[22] the calculated dipole moment for B and C is 3.0 D. If one then calculates the conformational composition to give a measured dipole moment as low as 0.4 D or as high as 0.9 D (vide supra) using the formula $\mu^2 = n_A \mu_A^2 + n_B \mu_B^2 + n_C \mu_C^2$ ($\mu_A = 0$, $\mu_B = \mu_C$, $n_B = n_C$, $n_A + n_B + n_C = 1$) one obtains n_A, the mole fraction of conformer A in the meso isomer, to be between 91% and 98%. In other words, virtually all of the meso isomer is in the anti conformation A. Since the H/H coupling constant of the meso isomer is found to be 11.3 Hz and the calculated coupling constant of B and C, according to the Altona equation,[23] is ca, 2.5 Hz, one calculates a coupling constant

for conformer A of 11.5–12.2 Hz (we are assuming that the conformer distribution in CDCl₃ is about the same as in CCl₄).

The calculation for the *dl* isomer is somewhat less certain. With the limits of the $J_{H/H}^{anti} = J_{H/H}^F$ (assumed $= J_{H/H}^A$) just given, and assuming $J_{H/H}^E = J_{H/H}^D = 2.5$ Hz (the calculated[23] values are 3.2 Hz for E and 2.0 Hz for F) one obtains $n_F = 0.63$–0.68 in CDCl₃. (Using the full range of J_{gauche} from 2–3.2 Hz broadens this range to 0.58–0.69.)

With these figures in hand, one can now compute n_D after calculating $\mu_D = 0.7$ D, $\mu_E = 3.3$ D, and $\mu_F = 2.6$ D. Since $\mu^2 = n_D \mu_D^2 + n_E \mu_E^2 + n_F \mu_F^2$, $n_F = 0.65$, and $n_D + n_E = 0.35$, one obtains $n_D = 0.03$ and $n_E = 0.32$; in other words, only about 3% of the *dl* molecules are in the "reactive" Br/Br_anti conformation D.[24,25]

When one passes from solvent CDCl₃ to solvent CD₃OD, this percentage evidently diminishes further; in any case, the value of the H/H coupling constant increases from 8.6 to 9.6, meaning that the proportion of conformer F increases from 63–68% to 74–79% (or 71–80% if the full range of $J_{H/H}^{gauche}$ is used). The higher dielectric constant of methanol (32.6 at 25 °C) compared to chloroform (4.7) should favor the higher dipole conformers E and F over the lower dipole one, D. That this in fact happens suggest that n_D must be nonnegligible in chloroform (vide supra); the fact that the observed coupling constant increases even further in Me₂SO (see below) suggests qualitatively that even in methanol $n_D \neq 0$. A quantitative calculation is unfortunately not possible because the dipole moment in methanol is unknown (and cannot be measured because the solvent is itself quite polar). However, assuming that the ratio n_D/n_E can be no larger in the more polar methanol than in the less polar chloroform, and with $n_D + n_E \leq 0.29$, the *maximum* reasonable value for n_D in methanol is 0.11.

The situation is even more extreme in DMF. The coupling constant in Me₂SO (10.3 Hz) is probably representative of the conformational situation in DMF as well. It indicates that 79–87% of the *dl* isomer is in conformation F. With the arguments given above for n_D/n_E, n_D must be between 0 and 0.08, which, according to the Winstein–Holness equation, would account for a rate factor of at least 13 and probably much more as between k_{meso} and k_{dl} in anti elimination. Of the total measured rate ratio of 323 in DMF[3] a substantial fraction is thus due to the fact that the *dl* isomer is largely not in the conformation (D) appropriate for antiperiplanar elimination. At most a factor of 25 but probably much less is due to an intrinsically lower rate constant of conformer D of the *dl* compared to A of the meso isomer. This factor is probably due, as Miller et al. have postulated,[10] to the fact that the transition state resembles the product and that some of the greater (stabilizing) π-orbital overlap in *trans*-stilbene compared to *cis*-stilbene is already seen in the transition state leading from the meso dibromide to the *trans*-olefin. However, considering that $\Delta G°$ for the stilbenes is 3.7 kcal/mol, the rate factor, if this energy difference were fully expressed in the transition state, would be over 400 at 36 °C. Thus, in fact a relatively small fraction of this energy difference appears in the transition states for antiperiplanar elimination from conformers A and D. Also,

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(20) The minimum possible value for the Br/Br gauche bond moment is 3.2 D since a lesser value cannot account for the 2.81 D moment of the *dl* dibromide even if n_D, the mole fraction of D in Scheme I, is zero (cf. ref 24). The maximum reasonable value is 3.55 D, the dipole moment of 2α,3β-dibromo-*trans*-decalin.[21]

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(24) The calculation is not very sensitive to the value of n_F. Varying n_F from 0.58 to 0.69 changes n_D from 0.06 to 0.01. If one tries to assume lower values for $\mu_{Br/Br}$ (see ref 20) one finds that the lowest possible value compatible with $\mu_{dl} = 2.81$ D and taking the minimum value of 0.58 for n_F is 3.2 D ($\mu_D = 0.7$ D, $\mu_E = 3.2$ D, $\mu_F = 2.5$ D, $n_D = 0$, $n_E = 0.42$).

(25) If one uses a larger value for the Br/Br–gauche moment, this percentage will increase. In the extreme, assuming $\mu_E = 3.55$ D, $\mu_D = 0.75$ D, $\mu_F = 2.8$ D, and $n_F = 0.58$, one obtains $n_D = 0.16$ and $n_E = 0.26$.

the reason for the lesser rate ratio k_{meso}/k_{dl} (elimination) in methanol[3,10] (40) and in acetone$_3$ (23) compared to DMF may lie in the larger population of conformer D in the less polar solvents methanol and acetone as compared to the more polar DMF.

Experimental Section

The *meso* and *dl* pair isomers of 1,2-dibromo-1,2-diphenyl-ethane were prepared as previously described; meso, mp 249–251 °C (lit.[26] 254–255 °C dec); *dl*, mp 108–109 °C (lit.[27] mp 110–111 °C). The reported $^3J_{H/H}$ couplings were obtained in either a WP-200-SY (Department de Química Orgánica, Universidad Autónoma de Madrid, Spain) or a WM-250 (UNC) Bruker instrument from the ^{1}H-NMR spectra, looking at the ^{13}C satellites of the ^{12}CH signal centered at 5.48 (CDCl), 5.69 (CD$_3$OD), 5.87 (acetone-d_6) or 6.10 (Me$_2$SO-d_6) ppm for the *dl* pair and 5.48 (CDCl$_3$) ppm for the *meso* isomer. The distance in Hz between the two observed doublets flanking the normal, intense signal was identical, within the experimental error, with the $^1J_{C-H}$ coupling (ca. 156.5 Hz for both isomers) observed in the proton coupled ^{13}C spectra (CDCl$_3$) for the CHBrCHBr carbon signal 56.2 ppm for the *meso* isomer and at 59.1 ppm for the *dl* pair.

Registry No. *trans*-Stilbene, 103-30-0; *meso*-α,α'-dibromo-bibenzyl, 13440-24-9; (±)-α,α'-dibromobibenzyl, 13027-48-0.

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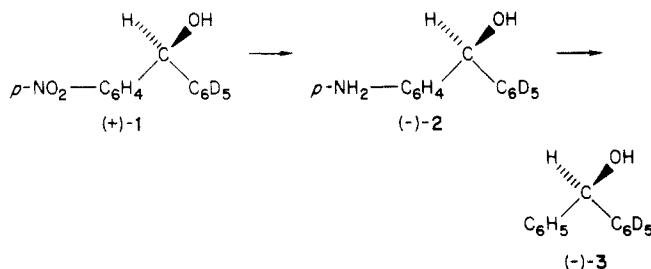

Configuration of Some Para-Substituted Benzhydrols

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The preparation of optically active benzhydrol-2,3,4,5,6,-d_5 (3, phenyl(perdeuteriophenyl)carbinol, $[\alpha]^{20}_D$-0.85° (c 16, CHCl$_3$) from resolved (+)-4'-nitro-benzhydrol-2,3,4,5,6-d_5 (1) via the corresponding (–)-4'-amino compound (2) was reported recently.[2] The con-

figurations of the compounds in this series (1 → 2 → 3) were tentatively assigned by application of the Horeau method[3] to 1. Treatment of either (+)-1 or the corresponding nondeuteriated compound[4] with excess *dl*-α-

phenylbutyric anhydride gave recovered (+)-α-phenyl-butyric acid (optical yield of 4.3–4.5%).

According to the empirical model developed by Horeau,[3] when (+)-α-phenylbutyric acid is recovered from this kinetic resolution, the configuration of the optically active carbinol is represented by 4.
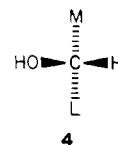
Without prior knowledge, one would make the reasonable assumption that the *p*-nitrophenyl group would be the L (larger) group and phenyl the M (medium) group. It would also be reasonable to assume that this steric difference might not be very great because the difference in bulk is at the para position considerably removed from the chiral center. However, recent studies by Guetté and co-workers[5,6] convincingly demonstrate that for *p*-Me, *p*-Br, *p*-OMe, and *p*-CF$_3$ benzhydrols, Horeau's method predicts the correct absolute configuration *when the para-substituted phenyl ring is designated M and the unsubstituted phenyl group is designated L!* This conclusion is based on a direct chemical correlation of the (+)-*p*-bromo- and (–)-*p*-methylbenzhydrols to (S)-(+)-mandelic acid.[5] Interpreting our results in light of Guetté's studies, we tentatively predict the absolute configurations as shown in 1 → 2 → 3. We felt, however, that these assignments should be confirmed by a direct correlation.

Based on the ruthenium dioxide oxidation of an aromatic system as applied by Nakagawa and co-workers,[7] we studied the oxidation of (–)-*p*-acetamidobenzhydrol acetate.[8] *p*-Nitrobenzhydrol was resolved as previously reported[2,9,10] and the (+)-isomer 5 reduced (10% Pd/C) to the (–)-amine 6 that was converted to the diacetate (–)-7.
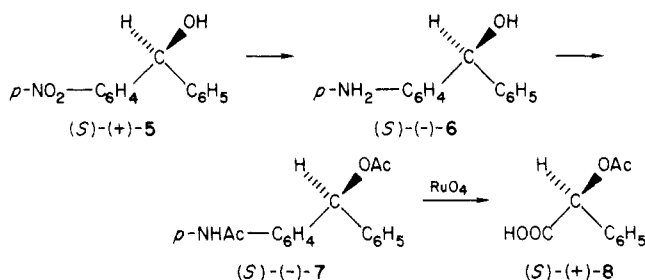
This was oxidized (RuO$_2$ + NaIO$_4$) to give (after exacting chromatographic purification) (S)-(+)-O-acetylmandelic acid (8 18% yield) which was identical (IR, NMR, mass spectrum, mixture melting point, and optical rotation) with an authentic sample. Since the chiral center is not dis-

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(4) The configuration of (+)-1, $[\alpha]^{20}_D$ +77.4° (c 2, CHCl$_3$), and the corresponding (+)-nondeuteriated compound,[5,6] $[\alpha]^{20}_D$ +78.2° (c 2, CHCl$_3$), are obviously the same since deuteriation would affect the rotation in the order of 1° out of a total of 77°.
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