

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY AND THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Elimination and Replacement Reactions of *dl-erythro-* and *dl-threo-*2-Deutero-1,2-diphenylethanol and Derivatives^{1,2}BY DAVID Y. CURTIN³ AND DAVID B. KELLOM

RECEIVED JULY 13, 1953

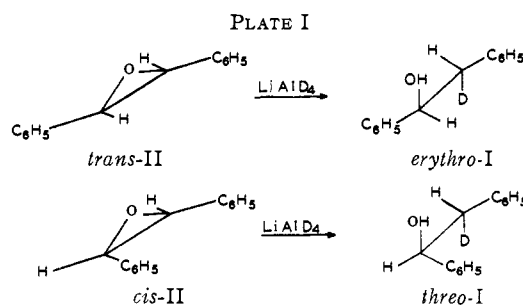
dl-erythro- and *dl-threo-*2-deutero-1,2-diphenylethanol have been prepared by the reaction of *dl-trans-* and *cis-*stilbene oxide, respectively, with lithium aluminum deuteride. The two triethyl benzoates of the above alcohols were found to undergo a stereospecific *trans* elimination on treatment with potassium *t*-butoxide to give *trans*-stilbene which in one case had retained the deuterium but in the other lost it. Pyrolysis of the two esters led to a somewhat less stereospecific *cis* elimination. Unlike the triethyl benzoate, the acetate underwent a predominately *cis* elimination with potassium amide. A special cyclic mechanism is proposed. A difference in the degree of specificity of the reactions of the *erythro-* and *threo-*isomers has been explained in terms of the isotope effect. The reaction of *dl-erythro-* and *threo-*2-deutero-1,2-diphenylethanol with hydrogen bromide at -80° or with thionyl chloride was found to lead to halide with some 90% retention of configuration and 10% inversion (or 80% retention and 20% racemization). The thermal elimination of the two bromides prepared above occurred preferentially in a *cis* fashion.

A number of stereoisomers have been prepared which owed their separate existence to the substitution of one or more hydrogens by deuterium.⁴⁻¹² Only recently has it been possible to distinguish between such isomers by physical or chemical means. Thus Raman and infrared spectra have been used to distinguish between *meso-* and *dl-*1,2-dibromo-1,2-dideuteroethane^{5,6} and between *cis-* and *trans-*1,2-dideuteroethylenes.⁷ A single enantiomorph of 2,3-dideutero-*trans*-menthane,⁸ α -deuteroethylbenzene⁹ and 1-deutero-1-butanol¹⁰ has been obtained and shown to have optical activity. The two enantiomorphous α,α -dideuterocitric acids have been prepared and shown to be optically active and chemically distinguishable by the stereospecific action of an enzyme.¹¹ More recently, *d-* and *l-* α -deuteroethanol have been obtained and distinguished by their behavior in enzymatic reactions.¹²

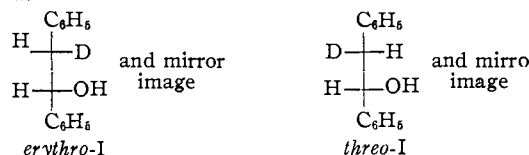
Differences in chemical behavior of the diastereoisomers mentioned above toward symmetric reagents have been reported in only one case. This was the study of the debromination of *meso-* and *dl-*1,2-dibromo-1,2-dideuteroethane¹³ with zinc, magnesium and sodium.¹⁴ Not only did the work provide a means for establishing the stereochemistry

of these elimination reactions, but the reaction with zinc or magnesium could be used to relate the configurations of such dihalides to the corresponding olefins, the stereochemical course of this reaction having been established in other systems.¹⁵

The present work was undertaken to study further the preparation and reactions of diastereoisomers which differed in the positions of hydrogen and deuterium. As the starting point, *dl-erythro-* and *dl-threo-*2-deutero-1,2-diphenylethanol (*erythro-* and *threo-*I)¹⁶ were prepared from *trans-* and *cis-*stilbene oxide (*trans-* and *cis-*II), respectively, by treatment with lithium aluminum deuteride. The deuterium analyses of the products were in each case in agreement with that of a monodeutero compound.



The opening of other epoxides with lithium aluminum hydride has been shown to proceed with inversion of configuration.¹⁷ On this basis the tentative assignments of configuration to the isomers of I have been made. These assignments are strengthened by the results to be reported below. It is believed, further, that the lithium aluminum deuteride reactions were highly stereospecific. Such specificity has been observed in the

(15) W. G. Young, Z. Jasaitis and L. Levanas, *ibid.*, **59**, 404 (1937).(16) The designations "*erythro-* and *threo-*" will be used as indicated below.

(17) See W. G. Brown in "Organic Reactions," Vol. VI, edited by Roger Adams, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 478.

(1) Taken in part from the dissertation submitted by David B. Kellom in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

(2) Presented at the 122nd Meeting of the American Chemical Society at Atlantic City, N. J., Sept. 16, 1952.

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(4) See R. L. Shriner, R. Adams and C. S. Marvel in Gilman's "Organic Chemistry," Vol. 1, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 302, for a discussion of the earlier work.

(5) M. de Hemptinne in "Contribution a l'Étude de la Structure Moleculaire," Desoer, Liege, 1947, p. 150.

(6) H. J. Bernstein, A. D. E. Pullin, B. S. Rabinovitch and N. R. Larson, *J. Chem. Phys.*, **20**, 1227 (1952).(7) R. L. Arnett and B. L. Crawford, Jr., *ibid.*, **18**, 118 (1950).(8) E. R. Alexander and A. L. Pinkus, *THIS JOURNAL*, **71**, 1786 (1949).(9) E. L. Eliel, *ibid.*, **71**, 3970 (1949).(10) A. Streitwieser, Jr., *ibid.*, **75**, 5014 (1953).(11) C. Martius and G. Schorre, *Ann.*, **570**, 140 (1950).(12) F. Loewus, F. H. Westheimer and B. Vennesland, *THIS JOURNAL*, **75**, 5018 (1953).(13) The isomers were not obtained free from each other. The authors worked with two mixtures, one containing 95% *meso-* and 5% *dl-* and the other containing 50% *meso-* and 50% *dl-*.(14) W. M. Schubert, B. S. Rabinovitch, N. R. Larson and V. A. Sims, *THIS JOURNAL*, **74**, 4590 (1952)

reaction of D-(+)-*trans*-2,3-epoxybutane with lithium aluminum hydride which gave D-(-)-2-butanol of 99% optical purity.¹⁸

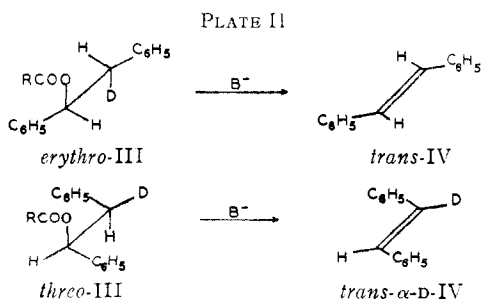
Base-catalyzed *trans* Elimination Reactions of Esters.—In order to confirm the configurations and stereochemical purity of *erythro*- and *threo*-I, it was desired to examine first an elimination reaction of high stereospecificity and known stereochemistry. A further requirement was that it should be possible to relate the configurations of the substances studied to the alcohols (*erythro*- and *threo*-I) from which they were to be prepared.

It was at first hoped that the *p*-toluenesulfonate esters might be suitable for this purpose since it had been shown that such compounds, which could be prepared from the corresponding alcohols without change of configuration, underwent *trans* elimination with ethoxide ion with a high degree of specificity.¹⁹ Because of difficulty encountered in the purification of the tosylates, however, a search was made for some more satisfactory ester.

The benzoate of 2-phenylethanol has been shown to undergo a cleavage to 2-phenylethanol and benzamide rather than elimination on treatment with potassium amide in liquid ammonia. This competing reaction had been suppressed however in favor of the desired elimination reaction when the mesitoate ester was employed.²⁰ *erythro*- and *threo*-I were therefore converted to their 2,4,6-triethyl benzoates (*erythro*- and *threo*-III).²¹ It was found that each gave the desired elimination reaction to the *trans*-stilbenes (*trans*-IV and *trans*- α -D-IV) when treated with potassium amide in liquid ammonia for 1 minute.

It was anticipated as discussed below that *trans*- rather than *cis*-stilbenes would be formed almost exclusively because of the considerably higher energy required for the transition state with the two phenyls *cis* to each other.

If the elimination were to occur in a *trans* fashion and with the two phenyls *trans*, *erythro*-III should give *trans*-IV with no deuterium while *threo*-III should give *trans*- α -D-IV.



It was in fact found that *threo*-III formed *trans*-stilbene in which $98.6 \pm 1.8\%$ of the deuterium was retained. *erythro*-III, however, lost only $66.3 \pm 0.6\%$ of its deuterium in the conversion to *trans*-stilbene. It seemed possible that the considerable lack of specificity observed in this latter case might

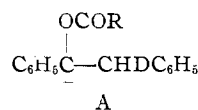
(18) P. J. Leroux and H. J. Lucas, *THIS JOURNAL*, **73**, 41 (1951).

(19) See for example D. J. Cram, *ibid.*, **74**, 2149 (1952).

(20) C. R. Hauser, J. C. Shivers and P. K. Skell, *ibid.*, **67**, 409 (1945).

(21) The triethylbenzoates rather than the mesitoates were utilized because triethylbenzoic acid happened to be more readily available.

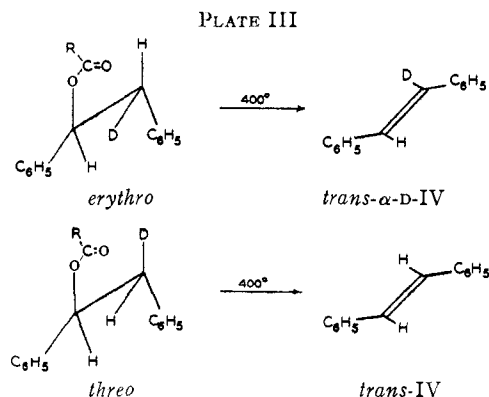
be due to a competing reaction in which *erythro*- and *threo*-III prior to elimination were being interconverted by amide ion (possibly by way of the anion A). Since base-catalyzed eliminations in which deuterium is removed are slower than those



involving removal of hydrogen²² the *trans* elimination of *erythro*-III should be slower than that of *threo*-III and, therefore, more seriously disturbed by a competing epimerization, the rate of which should be independent of the relative positions of deuterium and hydrogen.

This analysis of the problem suggested that a weaker base might slow down the isomerization more rapidly than the elimination and thus give rise to a greater degree of specificity. Such was found to be the case. When potassium *t*-butoxide was employed as the base, *erythro*-III gave *trans*-stilbene with $100.8 \pm 1.8\%$ retention of deuterium and *threo*-III was converted to *trans*-stilbene with $92.7 \pm 0.4\%$ loss of its deuterium. It is likely that the 7% retention of deuterium in the reaction of *threo*-III is due to the same type of competing reaction as that postulated in the amide ion-catalyzed elimination discussed previously. An alternative explanation, that *threo*-III was contaminated by appreciable quantities of the *erythro*-isomer, is rendered unlikely by the results on ester pyrolysis reported below.

Ester Pyrolysis.—Since the formation of olefins by the thermal decomposition of esters has been shown in a number of cases to occur in a *cis* fashion,²³ the thermal decomposition of esters of I was examined. In this case it was expected that *erythro*-III would give *trans*-stilbene with retention of the deuterium atom while *threo*-III should lose its deuterium during the elimination.



The results of the pyrolysis of *erythro*- and *threo*-III as well as the corresponding acetates and benzoates of I are given in Table I.

It is seen that the results are qualitatively those to be expected, but that again the reactions in which the carbon-deuterium bond is broken are considerably less stereospecific than those in which the

(22) See V. J. Shiner, Jr., *THIS JOURNAL*, **74**, 5285 (1952).

(23) (a) D. H. R. Barton, *J. Chem. Soc.*, 2174 (1949); (b) E. R. Alexander and A. Mudrak, *THIS JOURNAL*, **72**, 1810, 3194 (1950).

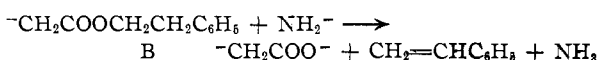
TABLE I
 ESTER PYROLYSIS AT 400°^a

Ester of I	Deuterium retained in the thermal conversion to <i>trans</i> -stilbene, %	
	<i>erythro</i>	<i>threo</i>
2,4,6-Triethylbenzoate (III)	97.0 ± 1.8	17.5 ± 0.6
Benzoate	98.8 ± 1.8	18.3 ± 0.6
Acetate (V)	95.6 ± 1.7	26.4 ± 0.6

^a Since the stilbenes are known to undergo decomposition above 300° (G. B. Kistiakowsky and R. W. Smith, *THIS JOURNAL*, **56**, 638 (1934); D. C. Downing and G. F. Wright, *ibid.*, **68**, 141 (1946)) and thermal isomerization in the presence of organic acids (W. J. Taylor and A. R. Murray, *J. Chem. Soc.*, 2078 (1938)), the quantitative interpretation of the data is subject to some uncertainty.

carbon-hydrogen bond is cleaved. The fact that the less specific reactions in the thermal elimination are those of the *threo*-series while the less specific in the base-catalyzed reactions were those of the *erythro* appears to exclude the possibility considered above that the deviation from specificity of the reactions could be due to stereochemical inhomogeneity of the starting materials employed.

Base-catalyzed *cis* Elimination of Acetates.—It was found by Hauser, Shivers and Skell²⁰ that while 2-phenylethyl benzoate reacted with potassium amide to form benzamide and 2-phenylethanol, the acetate under similar conditions gave styrene and, further, that 1,2-diphenylethyl acetate gave *trans*-stilbene. They suggested that the difference between the benzoate and acetate was due to the fact that the acetate reacted by way of an anion B not possible with the benzoate and that styrene formation involved the reaction of B with a second amide ion.



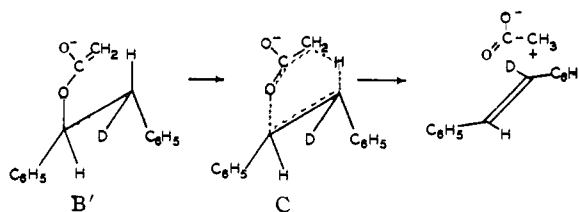
Because the possibility of a cyclic elimination of B had not been rigorously excluded, the reactions of *erythro*- and *threo*-2-deutero-1,2-diphenylethyl acetate (*erythro*- and *threo*-V) with potassium amide under the conditions used by Hauser, Shivers and Skell were examined. The *trans*-stilbene formed from *erythro*-V, instead of having lost most of the deuterium as in the reaction of the *erythro*-2,4,6-triethylbenzoate, retained 90.7 ± 1.7% of the deuterium. With the *threo*-isomer, instead of the retention of all of the deuterium as in the reaction of *threo*-III, 42.3 ± 1.0% of the deuterium was lost.²⁴

Although it is apparent that one reaction was much less clean-cut than the other, it seems clear that the sterically favored course of elimination of the acetate is *cis*—the reverse of the situation with the triethylbenzoate. The most likely explanation appears to be that an anion B', like that postulated by Hauser, Shivers and Skell as an intermediate, undergoes elimination through a cyclic transition state C.²⁵

(24) It is perhaps significant that the reaction of the *threo*-acetate with potassium amide gave only a 35% yield of *trans*-stilbene, about half that obtained with the *erythro*-acetate and in all other reactions studied. In an attempt to improve this yield it was found that potassium *t*-butoxide, a weaker base than potassium amide, gave the alcohol rather than *trans*-stilbene.

(25) This cyclic process was considered by Hauser (ref. 18, Note 7, p. 410) and rejected because excess amide ion was required to convert 2-phenylethyl acetate to styrene. Since it is not clear to what extent the behavior of 1,2-diphenylethyl acetate parallels that of 2-

PLATE IV



Magnitude of the Isotope Effect and Degree of Stereospecificity.—In each of the eliminations discussed above, it is apparent that two factors are operative: one, the isotope effect and the other, the "stereochemical specificity" which would persist in the absence of the isotope effect. In the elimination of one diastereoisomeric racemate these operate in the same direction while in the reaction of the other they are opposed. The result is that neither reaction gives a true measure of the degree of stereochemical specificity of such an elimination. However, the two results taken together can be used to calculate both the isotope effect and the degree of stereochemical specificity by the following method.

If it is assumed, for example, that *erythro*-III can, on pyrolysis, undergo a kinetically first-order²⁶ stereospecific *cis* elimination to give α -deutero-*trans*-stilbene at a rate k_1 or a competing first-order elimination²⁷ to give undeuterated *trans*-stilbene at a rate k_2 the ratio k_1/k_2 is measured directly by the fraction of the deuterium originally present in the ester which is retained in the product, *trans*-stilbene. Similarly a ratio k'_1/k'_2 , can be measured from the reaction of *threo*-III. If it is considered that k_1/k_2 is the product of the factor S (a measure of stereospecificity in the absence of the isotope effect) and I (the isotopic discrimination in the absence of a steric effect), then

$$k_1/k_2 = SI \text{ and } k'_1/k'_2 = S/I$$

from which it follows that

$$S = (k_1/k_2)(k'_1/k'_2)$$

and

$$I = (k_1/k_2)/(k'_1/k'_2)$$

In the case of III

$$k_1/k_2 = 97/3 = 32$$

and

$$k'_1/k'_2 = 82/18 = 4.7$$

from which it can be concluded that

$$S = 12 \text{ and } I = 2.6$$

The results of similar calculations for several of the reactions studied are summarized in Table II. Unfortunately the accuracy of the analytical data did not permit significant calculations to be made for every reaction.

phenylethyl acetate and, furthermore, the effect of initial concentration of amide ion on the products has been so little investigated, we have used the simple description of the reaction given above with the reservation that a thorough kinetic study might require significant modification.

(26) D. W. Vanas and W. D. Waters, *THIS JOURNAL*, **70**, 4035 (1948); C. E. Rudy, Jr., and P. Fugassi, *J. Phys. Colloid Chem.*, **52**, 357 (1948).

(27) This may occur by direct *trans* elimination, by a process involving epimerization to *threo*-III followed by *cis* elimination or by isomerization of initially formed *cis*-stilbene.

It will be noted that the values for S in the pyrolytic reactions are of the same order of magnitude as the value of 12 calculated from the data of Alexander and Mudrak^{25b} on the pyrolysis of *cis*- and *trans*-2-phenylcyclohexyl acetate. Further the value for I in these reactions is in good agreement with the theoretical value of 2.7 for 400°.²³

While the accuracy of these data is not great, the fact that S and I have reasonable orders of magnitude confirms this analysis. Certainly the values of S are more reliable measures of the degree of stereospecificity of these reactions than are the gain or loss of deuterium during elimination of either the *erythro*- or *threo*-racemate.

TABLE II
ISOTOPE AND STERIC EFFECT

Reaction ^a	k_1/k_2	k'_1/k'_2	S	I
2,4,6-Triethylbenzoate, Δ	32 \pm 19	5 \pm 2	12 \pm 6	2.6 \pm 0.9
Acetate, Δ	22 \pm 8	2.8 \pm 0.7	8 \pm 2.5	2.8 \pm 0.6
Acetate, KNH ₂	10 \pm 2	0.73 \pm 0.02	2.7 \pm 0.5	3.7 \pm 0.3

^a The pyrolyses were carried out at 400 \pm 10°, the reactions with potassium amide at -33°.

Magnitude of the *cis* Effect²⁹ of Phenyl in Elimination Reactions.—In connection with other work on steric effects it was of interest to know the relative rates at which *cis*- and *trans*-stilbene are formed in elimination reactions of compounds derived from I. Reliable data are not easy to obtain since the amount of *cis*-stilbene formed is small and therefore difficult to measure accurately.

In this and in similar cases the isotope effect provides a potentially valuable tool since *erythro*-III has a deuterium atom so placed that the rate of *trans* elimination to give *trans*-stilbene is depressed by the isotope effect which is here estimated from the work of Shiner²² to be a factor of 7. Thus, the relative amount of *cis*-stilbene is magnified by this factor and therefore can be more accurately determined.

The elimination reaction of *erythro*-III was therefore reexamined and found to give 95% of *trans*-stilbenes (consisting as shown previously of a mixture of 7% α -deutero-*trans*-IV and 88% undeuterated *trans*-IV) and 5% of *cis*-IV (presumably α -deuterated). It is seen that the ratio of rates of formation of *trans*- and *cis*-IV in the absence of the isotope effect is given by

$$k_t/k_o = 88/5 \times 7 = 130$$

Thus, the steric retardation which results from forcing two phenyls next to each other in this elimination amounts to a factor of about 10². Since the free energy difference between the two transition states in elimination and that between the two products, *cis*- and *trans*-IV, bear some resemblance to each other it is of interest to compare what data are available on the stilbenes. Although no direct measure of the equilibrium constant has been possi-

(28) H. Eyring and A. Sherman, *J. Chem. Phys.*, **1**, 345 (1933).

(29) The term "*cis* effect" is used here to refer to the total destabilization of the transition state leading to *cis*-stilbene as compared to that leading to *trans*. The effect is no doubt a composite one including such factors as steric strain, steric inhibition of resonance, dipole interactions and selective restriction of motion in one isomer (D. Y. Curtin, Abstracts, Thirteenth National Organic Chemistry Symposium, Ann Arbor, Michigan, June, 1953, p. 40).

ble because of the very small amount of *cis*-IV at equilibrium,³⁰ ΔH for the equilibrium *cis*-IV \rightleftharpoons *trans*-IV has been calculated from the heats of hydrogenation to be about -5.7 kcal./mole.³¹ If this difference appeared in the difference in the free energies of activation it would amount to a factor of 10⁴ in rate. It is quite reasonable that the *cis* effect should be smaller in the transition state leading to *cis*-IV than it is in *cis*-IV since the phenyls are closer to each other in the latter.

It is of interest to compare the above results with the value of 6 for the ratio of *trans*- to *cis*-2-butene obtained by the elimination reaction in aqueous ethanol of 2-chlorobutane.³² Although the latter value is subject to some uncertainty since it was obtained before the present spectral methods of analysis became available, it seems clear that the steric effect of two methyls is of a different order of magnitude from that of two phenyls in depressing the rate of formation of the *cis* isomer.

Steric Course of the Reaction of 1,2-Diphenylethanol with Hydrogen Bromide.—The reaction of 1-phenylethanol with hydrogen bromide was reported by Levene and Rothen to proceed at -80° with predominant retention of configuration.³³ By making an estimate of the specific rotation of pure active 1-phenylethyl bromide it was concluded that the retention was essentially complete. More recently, Gerrard³⁴ has reported the preparation of 1-phenylethyl bromide with twice the rotation assumed by Levene and Rothen to be that of the pure substance.

The difficulty in demonstrating that a halide is completely resolved leads to uncertainty as to the degree of retention of configuration. The study of the replacement reactions of *erythro*- and *threo*-I, however, is free from such uncertainty since advantage may be taken of the stereospecific *trans* elimination of halides³⁵ to determine the nature of the products of replacement. Thus, if hydrogen bromide reacts with *erythro*-I with retention of configuration (Path A), treatment of the bromide with sodium ethoxide should give as the product of a *trans* elimination, *trans*-IV which does not contain deuterium. But should the reaction involve inversion (Path B), the *trans*-IV formed by a basic elimination reaction should contain deuterium.

The bromide prepared from *erythro*-I by treating the alcohol in a pentane slurry with anhydrous hydrogen bromide at -78°, gave on treatment with sodium ethoxide *trans*-IV with a loss of 87% of the deuterium, whereas the bromide prepared similarly from *threo*-I gave *trans*-IV with retention of 89% of the deuterium. Thus, in each case the bromide was formed with about 85-90% retention of configuration and 10-15% inversion (*or*, alternatively, 70-80% retention and 20-30% racemization). When the reaction was carried out at 0° in benzene

(30) Table I, note (a).

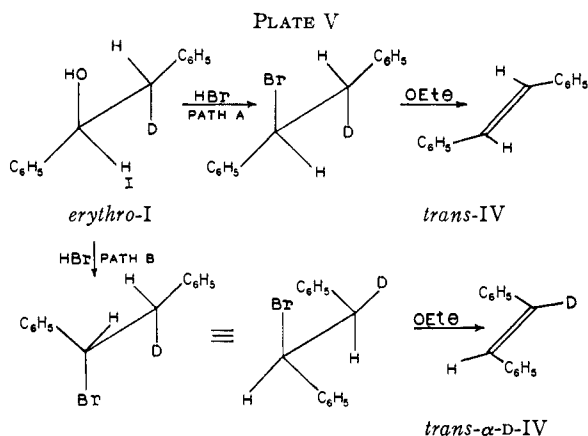
(31) R. B. Williams, *This Journal*, **64**, 1395 (1942).

(32) H. J. Lucas, T. P. Simpson and J. M. Carter, *ibid.*, **47**, 1462 (1925). This value seems to be an upper limit and the correct value may be less than 1 (compare M. L. Dhar, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2058 (1948)).

(33) P. A. Levene and A. Rothen, *J. Biol. Chem.*, **127**, 237 (1939); see also C. L. Arens, *J. Chem. Soc.*, 236 (1941).

(34) W. Gerrard, *ibid.*, 741 (1946).

(35) S. J. Cristol, *This Journal*, **69**, 338 (1947).



there was approximately 75% retention of configuration with 25% inversion (or 50% retention and 50% racemization).

The reaction of (+)-1,2-diphenylethanol with hydrogen bromide at 0° had been found to give (-)-1,2-diphenylethyl bromide accompanied by an unknown amount of racemization.³⁶ Since similar bromides have been shown to have the same sign of rotation as their configurationally related alcohols³⁷ it seems likely that the reaction of Wallis and Adams (which apparently differed from ours in that no solvent was used) proceeded with predominate inversion. It may be noted that the use of deuterium together with a knowledge of the stereochemistry of the elimination reaction provides a method for relating the absolute configurations of alcohols and halides.

Reaction of 1-Phenylethanol with Thionyl Chloride.—The reaction of thionyl chloride with alcohols has been found under certain conditions to lead to reaction with retention of configuration.³⁸ Since, as in the case of the hydrogen bromide reaction just discussed, a knowledge of the extent of retention or racemization during replacement ordinarily demands that the rotation of optically pure halide be known, it was of interest to examine the reaction of thionyl chloride with I. It was found by the method employed in the previous section that the product was formed with about 90% retention of configuration and 10% inversion (or 80% retention and 20% racemization).³⁹

Thermal Elimination of Halides.—A number of halides have been shown by Barton⁴⁰ to undergo a thermal unimolecular elimination in the vapor

(36) E. S. Wallis and F. H. Adams, *ibid.*, **55**, 3838 (1933).

(37) See P. Brewster, F. Hiron, E. D. Hughes, C. K. Ingold and P. A. D. S. Rao, *Nature*, **166**, 179 (1950).

(38) (a) A. McKenzie and G. W. Clough, *J. Chem. Soc.*, 687 (1913); (b) P. A. Levene and L. A. Mikeska, *J. Biol. Chem.*, **75**, 587 (1927); (c) see E. S. Lewis and C. E. Boozer, *THIS JOURNAL*, **74**, 308 (1952), and D. J. Cram, *ibid.*, **75**, 332 (1953), for most recent work and other references.

(39) From the previous data on the reaction of 1-phenylethyl alcohol with thionyl chloride it may be calculated that there was approximately 70% retention and 27% inversion or 40% retention and 60% racemization^{33a-35b} if $[\alpha]_D$ for completely resolved chloride is taken to be about $\times \pm 110^\circ$. We are indebted to Dr. Ernest Eliel for pointing out evidence for this estimate.

These results, like those of the present work, were obtained with the reaction in excess thionyl chloride as solvent. It has been observed^{39a, 39d} that the optical course of the reaction is very sensitive to change in solvent, even with solvents which are supposedly "inert."

(40) D. H. R. Barton, *J. Chem. Soc.*, 2174 (1949).

phase and it was pointed out that such a reaction might be expected to proceed through a *cis* four-centered transition state. It was of interest, therefore, to examine the thermal elimination of *erythro*- and *threo*-2-deutero-1,2-diphenylethyl bromide and chloride.

The *erythro*- and *threo*-bromides obtained from the hydrogen bromide reaction described above were heated for one minute at 400° and an analysis of the *trans*-stilbene formed indicated that *cis* elimination had predominated by a factor of about 2 and the isotope effect amounted to 1.4. A detailed interpretation of this reaction is subject to difficulties due to the possible occurrence of isomerization of the starting material and/or products during reaction at the temperatures employed as well as to the possibility of decomposition by a non-specific free radical process.⁴¹ It seems clear, however, that the *cis* path is preferred.

When heated under reflux, the *erythro*- and *threo*-chloride each gave the same mixture (73% deuterated *trans*-stilbene and 27% undeuterated). This suggests that each isomer reacted by a mechanism in which only isotopic discrimination (a factor of 2.7) was operative.

The infrared absorption spectra showed some points of unusual interest. The deuterated alcohols (*erythro*- and *threo*-I) have spectra which differ markedly in the finger-print region both from the undeuterated alcohol and from each other (Fig. 1).

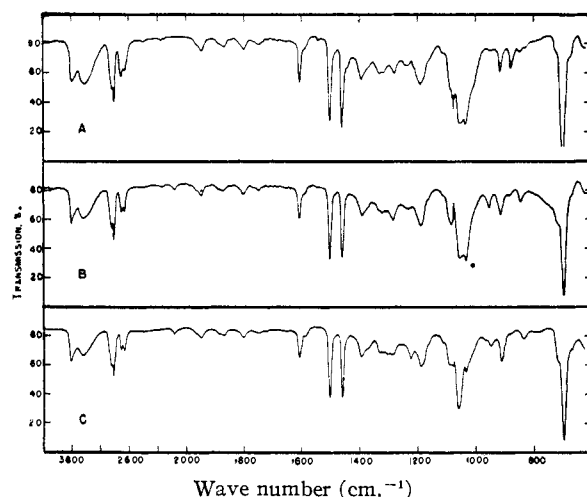


Fig. 1.—Infrared absorption spectra of: A, commercial 1,2-diphenylethanol; B, *erythro*-I; C, *threo*-I (8.6% solutions in carbon tetrachloride).

The location of the C-D stretching frequency (2030–2350 cm^{-1})⁴² has been found to be at $2160 \pm 5 \text{ cm}^{-1}$ for *erythro*-I and for its acetate, benzoate and triethylbenzoate. The corresponding members of the *threo*-series all had absorption at $2175 \pm 5 \text{ cm}^{-1}$ (cf. Fig. 2, curves A, B and C).

It was of interest also that the strong band at 970 cm^{-1} , which is present in *trans*-stilbene (Fig. 2, curve D) and which is associated with the *trans*

(41) D. H. R. Barton and P. F. Onyon, *THIS JOURNAL*, **72**, 988 (1950).

(42) H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangle, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 43.

—CH=CH— grouping, is absent in α -deutero-*trans*-stilbene (Fig. 2, curve E) and that the latter has its C—D absorption at 2230 cm^{-1} .

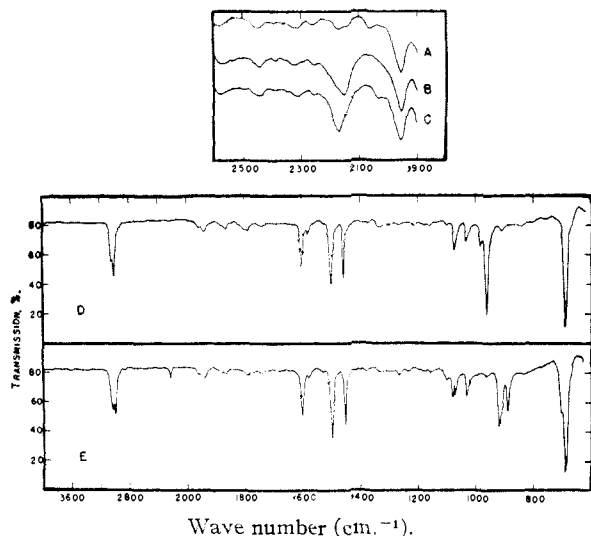


Fig. 2.—Infrared spectra of: A, 1,2-diphenylethyl acetate; B, *erythro*-V; C, *threo*-V (all as pure liquid); D, *trans*-IV; E, *trans*- α -D-IV. (6.4% solutions in carbon tetrachloride.)

Experimental⁴³

Deuterium Analysis.—The deuterium content was determined by combustion of the organic compounds and analysis by the falling drop method of the water produced.⁴⁴ The errors were computed as standard deviations.⁴⁵ Deuterium analyses are given in Tables III and IV.

Preparation of *cis*-Stilbene (*cis*-IV).⁴⁶—The decarboxylation of α -phenyleinamic acid with copper chromite catalyst in quinoline gave *cis*-IV, b.p. 100–102° (1.2 mm.), 85–86° (0.2 mm.), n_D^{20} 1.6188, in an average yield of 72%. The ultraviolet spectrum of the colorless liquid was almost identical with that reported by Solmsen.⁴⁷

Preparation of *cis*-Stilbene Oxide (*cis*-II).—To a solution of 22.2 g. (0.124 mole) of *cis*-IV in 55 ml. of dry benzene was added 17.8 g. (0.130 mole) of perbenzoic acid⁴⁸ in 375 ml. of benzene. After complete reaction the yellow solution was washed with 5% sodium bicarbonate solution, water and dried with anhydrous sodium sulfate. Removal of the solvent under reduced pressure gave a yellow oil which was dissolved in hot 70% aqueous ethanol and then cooled. Recrystallization of the solid from the same solvent gave 12.6 g. (52%) of *cis*-II as fine white needles, m.p. 37.0–37.5° (lit. 40°, 49°, 42°⁵⁰).

Preparation of *trans*-Stilbene Oxide (*trans*-II).—*trans*-IV (Eastman White Label, recrystallized, m.p. 123.0–124.0°) was treated with perbenzoic acid in a manner similar to that for *cis*-IV. After two recrystallizations from 70% aqueous

ethanol, *trans*-II was obtained in 55% yield, m.p. 69.0–69.5° (lit. 69–70°).⁵⁰

Preparation of *erythro*- and *threo*-2-Deutero-1,2-diphenylethanol (*erythro*- and *threo*-I).—To 5.03 g. (0.120 mole) of lithium aluminum deuteride of 96% isotopic purity⁵¹ in 200 ml. of dry ether was added 21.0 g. of *cis*- or *trans*-II in 100 ml. of ether over a period of 35 minutes.

The gray mixture was stirred at 20° for 15 minutes, at reflux for 30 minutes and again at 20° for 75 minutes. Hydrolysis of the complex formed, extraction with ether and removal of the ether gave a white solid (17.5 g.) after recrystallization from heptane.

This solid when obtained from *cis*-II was *threo*-I, m.p. 64.4–65.4°. However, the solid obtained from *trans*-II was a mixture, m.p. 48–62°, of *erythro*-I and unreacted *trans*-II. Separation was achieved by chromatography on 500 g. of Mallinckrodt aluminum hydroxide which had been activated at 350–400° for several hours. *trans*-II was removed from the column with hexane and amounted to 2.3 g., m.p. 67.4–68.6°. *erythro*-I, m.p. 64.4–65.4° (13.0 g. or 68% based on unrecovered starting material), was then recovered by elution with benzene containing a small amount of absolute ethanol. A mixed m.p. with commercial 1,2-diphenylethanol showed no depression.

The reaction of *trans*-II (1.96 g., 0.010 mole) with lithium aluminum hydride (0.420 g., 0.011 mole) in 43 ml. of ether gave 1.43 g. (72%) of 1,2-diphenylethanol, m.p. 64.4–65.4°, the infrared spectrum of which was identical with that of commercial 1,2-diphenylethanol (Fig. 1, curve A).

1,2-Diphenylethyl 2,4,6-Triethylbenzoate and Triethylbenzoates (*erythro*- and *threo*-III) of *erythro*- and *threo*-I.—The alcohol (1.81 g., 9.14 mmoles) was heated under reflux with 2.06 g. (9.17 mmoles) of 2,4,6-triethylbenzoyl chloride⁵² in 5 ml. of dry benzene for 3 hours. The clear solution was then poured into 40 ml. of hexane, the solution washed with water, 5% potassium carbonate and again with water, dried and evaporated to give 3.13 g. of an oil which slowly crystallized. Recrystallization of the solid from 10 ml. of heptane gave 2.42 g. (69%) of the triethylbenzoate ester, m.p. 76–78°. Recrystallization from 95% ethanol gave m.p. 77–77.6°. The analysis of the undeuterated ester is reported below.

Anal. Calcd. for $\text{C}_{27}\text{H}_{30}\text{O}_2$: C, 83.9; H, 7.8. Found: C, 84.3; H, 7.9.

Benzoates of 1,2-diphenylethanol and *erythro*- and *threo*-I were prepared in 70% yield by the reaction of the alcohol with benzoyl chloride in pyridine.⁵³

1,2-Diphenylethyl 3,5-dinitrobenzoate was prepared from 1,2-diphenylethanol and 3,5-dinitrobenzoyl chloride in pyridine. After recrystallization from chloroform it had m.p. 190–191°.

Anal. Calcd. for $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_6$: C, 64.3; H, 4.1; N, 7.1. Found: C, 64.2; H, 4.2; N, 7.2.

1,2-Diphenylethyl Acetate and Acetates (*erythro*- and *threo*-V) of *erythro*- and *threo*-I were prepared in 77–87% yield by treatment of the alcohol with acetic anhydride and fused sodium acetate at 100° for 3 hours. The products were colorless oils, b.p. 121–123 (0.8 mm.), n_D^{20} 1.5500, n_D^{20} 1.5478.

Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_2$: C, 80.0; H, 6.7; sapon. equiv., 240. Found: C, 80.2; H, 6.8; sapon. equiv., 240 \pm 6.

Reaction of *erythro*- and *threo*-I Triethylbenzoates (*erythro*- and *threo*-III) with Potassium Amide.—About 15 ml. of liquid ammonia was distilled from sodium into a three-necked 100-ml. flask cooled in a Dry Ice–chloroform-bath. Potassium (0.894 g., 0.0288 g. atom) was added together with a small crystal of hydrated ferric nitrate. The mixture was stirred until the blue color disappeared. Then the cooling bath was removed and 5 minutes later a solution of 685 mg. (1.78 mmoles) of *erythro*- or *threo*-III in 5 ml. of anhydrous ether was rapidly added. After 1 minute 1.22 g. (0.0288 mole) of ammonium chloride and 10 ml. of water were added.

The mixture was stirred for 10 minutes at room tempera-

(51) Obtained from Metal Hydrides, Inc., Beverly, Massachusetts, on allocation from the Atomic Energy Commission.

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(43) All melting points are corrected. The microanalyses were performed by Miss E. Davis, Mrs. E. Fett and Mrs. K. Pih of the Micro-analytical Laboratory, University of Illinois. The infrared spectra were obtained by Miss H. Miklas and Mrs. R. F. Hill using a Perkin-Elmer Double Beam Infrared Spectrophotometer, Model 21, with (0.1 mm.) sodium chloride cells. The ultraviolet spectra were obtained by Mr. H. Burch and Mrs. B. Burnett using a Carey Recording Spectrophotometer, Model 11.

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TABLE III
 BASE-CATALYZED ELIMINATIONS

Compound ^a	Base	Time, min.	G. atom D/mole starting material	Yield, <i>trans</i> -stilbene, %	G. atom D/mole stilbene
<i>erythro</i> -I 2,4,6-Triethylbenzoate	KNH ₂	1	1.028 ± 0.015 ^b	69	0.334 ± 0.004
<i>threo</i> -I 2,4,6-Triethylbenzoate	KNH ₂	1	1.028 ± .015 ^b	67	.978 ± .013
<i>erythro</i> -I 2,4,6-Triethylbenzoate	KOBu- <i>t</i>	90	1.028 ± .015 ^b	69	.072 ± .004
<i>threo</i> -I 2,4,6-Triethylbenzoate	KOBu- <i>t</i>	90	1.028 ± .015 ^b	59	1.000 ± .013
<i>erythro</i> -I Acetate	KNH ₂	1	0.976 ± .013	76	0.898 ± .012
<i>threo</i> -I Acetate	KNH ₂	1	.995 ± .013	30	.572 ± .006
<i>erythro</i> -I Bromide ^c	NaOEt	30	.978 ± .012	82	.132 ± .005
<i>erythro</i> -I Bromide ^d	NaOEt	30	.920 ± .012	78	.263 ± .005
<i>threo</i> -I Bromide ^e	NaOEt	30	.991 ± .013	84	.887 ± .011
<i>threo</i> -I Bromide ^f	NaOEt	30	.998 ± .013	81	.800 ± .010
<i>erythro</i> -I Chloride ^g	NaOEt	180	71	.211 ± .005
<i>threo</i> -I Chloride ^h	NaOEt	180	76	.908 ± .012

^a The substances in this column were all prepared from *erythro*-I, m.p. 64.4–65.4° containing 0.990 ± 0.013 g. atom D/mole or *threo*-I, m.p. 64.4–65.5° containing 0.992 ± 0.013 g. atom D/mole. ^b *threo*-I (0.992 ± 0.013 g. atom D/mole) gave *threo*-I benzoate with 1.037 ± 0.013 g. atom D/mole which when hydrolyzed back gave *threo*-I with 0.978 ± 0.013 g. atom/mole. It seems likely therefore that the slightly high D analyses peculiar to the aromatic esters in this table are due to a small systematic error in the analytical method or to a small amount of contamination of ester with *erythro*- or *threo*-I. For this reason in the calculations of loss of deuterium from the triethylbenzoates, the values for the alcohols rather than the ester have been taken as the initial amount of deuterium present. ^c From *erythro*-I suspended in pentane and hydrogen bromide at -78°. ^d From *erythro*-I in benzene and hydrogen bromide at 0°. ^e From *threo*-I suspended in pentane and hydrogen bromide at -78°. ^f From *threo*-I in benzene and hydrogen bromide at 0°. ^g From *erythro*-I and thionyl chloride. ^h From *threo*-I and thionyl chloride.

ture, diluted with another 10 ml. of water and warmed on the steam-bath for 10 minutes. Then the reddish-brown mixture was extracted with benzene. The extract was washed with water, dilute hydrochloric acid and again with water. Removal of the solvent gave a white solid which was recrystallized from 5 ml. of 95% ethanol to give *trans*-IV, m.p. 123–124°.

From the aqueous solution, 70% of 2,4,6-triethylbenzoic acid, m.p. 114–115°, was recovered.

Under the conditions used above, 1,2-diphenylethyl benzoate gave a 64% yield of 1,2-diphenylethanol, m.p. 62–64°, while 1,2-diphenylethyl 3,5-dinitrobenzoate gave a 25% yield of crude 3,5-dinitrobenzamide, m.p. 177–179°, and 37% of 1,2-diphenylethanol, m.p. 63.4–165.2°. No *trans*-IV could be found.

Reaction of 1,2-Diphenylethyl 2,4,6-Triethylbenzoate and *erythro*- and *threo*-III with Potassium *t*-Butoxide.—To 10 ml. of a 1.3 *N* solution of potassium *t*-butoxide in absolute *t*-butyl alcohol was added 457 mg. (1.18 mmoles) of 1,2-diphenylethyl 2,4,6-triethylbenzoate. After refluxing for 1.5 hours, the mixture was poured into 75 ml. of water. The insoluble material was recrystallized from 95% ethanol giving 139 mg. of *trans*-IV, m.p. 123.0–124.0°.

The cloudy filtrate was extracted with benzene. After washing with water, the extract was evaporated to dryness and the residue dissolved in 95% ethanol. Ultraviolet analysis of this solution indicated the presence of 4.6 mg. of *cis*-IV and 53 mg. of *trans*-IV giving a total yield of 197 mg. (93%) of IV from the reaction, 2% of the product being the *cis*-olefin.

The procedures used to obtain the data in Table III for *erythro*- and *threo*-III were identical, except that no ultraviolet analysis was carried out. The reaction of *erythro*-III repeated under the same conditions was found with the use of ultraviolet analysis as above to lead to an 89% yield of stilbenes of which 5% was *cis*.

Reaction of Acetates (*erythro*- and *threo*-V) with Potassium Amide.—To a solution of potassium amide prepared from 0.853 g. (0.0218 g. atom) of potassium and 12 ml. of liquid ammonia was added 0.469 g. (1.95 mmoles) of *threo*-V dissolved in 4 ml. of ether. Again after 1 minute the base was destroyed.

Evaporation of the solvent from the benzene extract gave 454 g. of a semi-solid residue which was dissolved in 6 ml. of hot 95% ethanol. On cooling 103 mg. (30%) of *trans*-I, m.p. 122.0–123.5°, was obtained.

The light yellow liquid residue, 300 mg., which remained after evaporation of the alcohol, was shown by the infrared spectrum to be largely unreacted *threo*-V. A slight -OH absorption indicated only a small amount of *threo*-I or residual traces of solvent. Saponification of this residue with

1 *N* alcoholic sodium hydroxide gave 239 mg. of a semi-solid which was dissolved in 6 ml. of hot heptane. This solution on cooling gave 148 g. of *threo*-I, m.p. 64.3–65.0°. Deuterium analysis: 1.029 ± 0.013 g. atom D/mole. Evaporation of the heptane gave 72 mg. of a yellow solid, m.p. 60–88°, which was identified by ultraviolet analysis as a mixture of 19 mg. of *trans*-IV, 7 mg. of *cis*-IV with the remainder being presumably *threo*-I.

Therefore this reaction of *threo*-V with potassium amide gave 122 mg. (35%) of *trans*-IV, 7 mg. (2%) of *cis*-IV and 235 mg. (50%) of unreacted *threo*-V isolated as the alcohol. A similar yield of *trans*-IV was obtained in a duplicate experiment.

erythro-V under the conditions above gave a 76% yield of *trans*-IV, m.p. 123–124°, and no unreacted starting material or *cis*-IV was observed.

When 1,2-diphenylethyl acetate (0.243 g., 1.01 moles) was treated with 5 ml. of 1.3 *N* potassium *t*-butoxide in anhydrous *t*-butyl alcohol under reflux for 30 minutes and the mixture poured into water, 0.138 g. (71%) of 1,2-diphenylethanol, m.p. 64.7–65.2°, was obtained and there was no evidence of *trans*-IV.

Reaction of 1,2-Diphenylethanol and *erythro*- and *threo*-I with Hydrogen Bromide. (a) At -78°.—A slurry of 1.00 g. (5.05 mmoles) of the alcohol in 25 ml. of pentane was cooled in a Dry Ice-acetone-bath and anhydrous hydrogen bromide bubbled through the cold solution for 1 hour. The mixture was removed from the bath and allowed to warm to room temperature in 10 minutes while dry nitrogen was swept through the flask. Then the slightly cloudy solution was poured into water, the organic layer separated, washed thoroughly with water, once with 5% sodium carbonate solution and again with water.

Evaporation of the solvent after drying the solution with anhydrous magnesium sulfate gave 1.18 g. of a slightly cloudy liquid. Since the bromide decomposed on distillation even in vacuum, the product could be purified only by filtration through a small amount of charcoal held on a sintered glass funnel. The bromide was obtained in 70–80% yield as a clear liquid, *n*_D²⁰ 1.6019.

Anal. Calcd. for C₁₄H₁₃Br: C, 64.4; H, 5.0; sapon. equiv., 261. Found: C, 64.5; H, 5.1; sapon. equiv., 260 ± 1.

(b) At 0° in Benzene.—A solution of 1.00 g. (5.05 mmoles) of the alcohol in 15 ml. of anhydrous benzene was cooled in an ice-bath until the solvent began to crystallize. Then a stream of anhydrous hydrogen bromide was bubbled through the cold solution for 20 minutes with occasional shaking. After removal of most of the excess hydrogen bromide by evacuation of the flask with a water pump, the

TABLE IV
 THERMAL ELIMINATIONS

Compound ^a	Time, min.	Temp., °C.	G. atom D/mole starting material	Yield of <i>trans</i> -stilbene, %	G. atom D/mole stilbene
<i>erythro</i> -I 2,4,6-Triethylbenzoate	2	400	1.028 ± 0.015 ^b	58	0.960 ± 0.012
<i>threo</i> -I 2,4,6-Triethylbenzoate	2	400	1.028 ± .015 ^b	52	.174 ± .005
<i>erythro</i> -I Benzoate	2	400	1.023 ± .013 ^b	69	.978 ± .013
<i>threo</i> -I Benzoate	2	400	1.037 ± .013 ^b	56	.181 ± .005
<i>erythro</i> -I Acetate	10	400	0.976 ± .013	74	.946 ± .012
<i>threo</i> -I Acetate	10	400	.995 ± .013	61	.262 ± .005
<i>erythro</i> -I Bromide ^c	1	420	.978 ± .012	67	.720 ± .010
<i>erythro</i> -I Bromide ^d	1	420	.920 ± .012	43	.705 ± .008
<i>threo</i> -I Bromide ^e	1	420	.991 ± .013	60	.545 ± .006
<i>threo</i> -I Bromide ^f	1	420	.998 ± .013	72	.565 ± .007
<i>erythro</i> -I Chloride ^g	2	Reflux	39	.728 ± .010
<i>threo</i> -I Chloride ^h	2	Reflux	42	.723 ± .010

^a The substances in this column were prepared from *erythro*-I, m.p. 64.4–65.4°, containing 0.990 ± 0.013 g. atom D/mole or *threo*-I m.p. 64.4–65.5°, containing 0.992 ± 0.013 g. atom D/mole. ^b Calculation of loss of deuterium based on alcohol rather than this value. ^c From *erythro*-I suspended in pentane and hydrogen bromide at –78°. ^d From *erythro*-I in benzene and hydrogen bromide at 0°. ^e From *threo*-I suspended in pentane and hydrogen bromide at –78°. ^f From *threo*-I in benzene and hydrogen bromide at 0°. ^g From *erythro*-I and thionyl chloride. ^h From *threo*-I and thionyl chloride.

benzene solution was washed with water, 5% sodium bicarbonate solution and again with water. The solvent was removed in a stream of dry air after the solution had been dried with anhydrous sodium sulfate leaving a cloudy light yellow residue which was filtered through charcoal to give a 70–80% yield of a clear straw colored liquid, n_D^{20} 1.6020.

Anal. Calcd. for C₁₄H₁₈Br: C, 64.4; H, 5.0; sapon. equiv., 261. Found: C, 65.3; H, 5.1; sapon. equiv., 256 ± 3. From these results the bromide was about 97% pure.

Reaction of 1,2-Diphenylethanol and *erythro*- and *threo*-I with Thionyl Chloride.—To 15 ml. of purified thionyl chloride⁶⁴ cooled in an ice-bath was added in small portions 4.90 g. (0.025 mole) of the alcohol. The clear yellow solution was warmed at 35–40° for 1.5 hours while a dry stream of nitrogen was bubbled through the solution. Then the excess thionyl chloride was removed under reduced pressure and the light brown residue diluted with 50 ml. of heptane. This solution was washed with water, dilute sodium hydroxide and again with water before drying with anhydrous magnesium sulfate. After filtering the solution, the solvent was evaporated in a stream of dry air. The crude light yellow residue was purified by filtering through charcoal since it could not be distilled without decomposition. The yield was 4.37 g. (82%), n_D^{20} 1.5850.

Anal. Calcd. for C₁₄H₁₈Cl: C, 77.6; H, 6.1; Cl, 16.4. Found: C, 79.3; H, 6.4; Cl, 14.9. The liquid was therefore only about 92% chloride.

Reaction of the Halides with Sodium Ethoxide.—The bromides (250 mg.) prepared from *erythro*- and *threo*-I were

treated for 30 minutes with 20 ml. of 2 *N* sodium ethoxide in absolute ethanol under reflux. The *trans*-IV in every case melted with a range of not more than 1.2° at an initial temperature of 121.8–123°.

The chlorides were treated similarly except that the reaction time was 3 hours.

The thermal eliminations were carried out by heating the halide or ester in a test-tube in a Wood's metal-bath under the conditions of time and temperature specified in Table IV. After extraction of the acid with potassium carbonate the *trans*-IV, purified by crystallization, in every case melted with a range of not more than 1.2°, at an initial temperature of 122.5–123°.

Stability of *cis*-IV. (a) Toward Potassium Amide.—To a solution of potassium amide prepared from 0.714 g. (0.0183 g. atom) of potassium and 10 ml. of liquid ammonia was added 167 mg. of *cis*-IV dissolved in 4 ml. of dry toluene. One minute after the addition, the base was destroyed and the products isolated as above. Ultraviolet analysis of the liquid residue (139 mg.) obtained by evaporation of the benzene indicated that about 9% *trans*-IV was present. Therefore potassium amide is a strong enough base in liquid ammonia to cause partial isomerization of *cis*-IV.

(b) Toward Potassium *t*-Butoxide.—A sample of *cis*-IV refluxed for 1.5 hours with a 1.3 *N* solution of potassium *t*-butoxide in absolute *t*-butyl alcohol showed no isomerization observable with ultraviolet analysis.

(c) Toward Sodium Ethoxide.—A sample of *cis*-IV refluxed for 30 minutes with a 1.9 *N* solution of sodium ethoxide in absolute ethanol showed no isomerization detectable by ultraviolet analysis.

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