

studied. We repeated the procedure of the authors and obtained a product with the molecular formula  $C_{12}H_{13}Hg_4NO_3$ . Infrared spectral analysis of this compound indicates the presence of an N-H peak at 3450  $cm^{-1}$  and an acetate peak at 1610  $cm^{-1}$ . The structure of the compound was thus identified as pyrrolyl-2,3,4,5-tetrameric acetate.

**Solvolysis and Reduction.**—When the solution of pyrrolyl-2,3,4,5-tetrameric acetate in acetic acid-toluene (65:35) was treated with ferrocene under comparable conditions as that for phenylmercuric acetate,<sup>2</sup> we observed the characteristic blue color of ferrocenium ion. Pyrrole was formed in 58% yield. Using acetic acid alone as solvent, no pyrrole was obtained from the reaction mixture, but some polymeric substances resulted with unsaturation bands in the 6- $\mu$  region. Further characterization of this substance was not fruitful at this time.

The appearance of blue ferrocenium ion and subsequent detection of pyrrole strongly suggests that there is similarity between this reaction and the reduction of phenylmercuric cation. The absence of pyrrolylmercuric cation does not demercurate to yield the corresponding carbonium ion.<sup>7</sup> The formation of polymeric substances in acetic acid may reflect that the pyrrolyl radical is relatively stable, incapable of abstracting hydrogen from acetic acid. Thus, recombination of radicals leading to polymeric products becomes more important.

The solvolysis and reduction are perhaps stepwise. Simultaneous reduction and demercuration should provide a benzyne type intermediate, for which we have not secured any evidence. Experiments with

(7) F. Jensen and R. Ouellette, *J. Am. Chem. Soc.*, **83**, 4477, 4478 (1961).

polymeric acetates of thiophene and benzene are in progress in this laboratory.

### Experimental Section

**Preparation of Pyrrolyl-2,3,4,5-tetrameric Acetate.**—Mercuric acetate (15 g., 0.042 mole, Merck Co.) was dissolved in 60 ml. of hot water and some red precipitate was filtered immediately. Pyrrole (1.0 g., 0.015 mole, Eastman, freshly distilled, b.p. 130–131°) was added to the freshly filtered solution of mercuric acetate. The mixture was allowed to stand for 1 hr. A white precipitate, 2.9 g. (20%), was collected. It decomposed above 200° with the formation of mercury beads. The analytical sample was obtained by recrystallization from an acetic acid-ethanol mixture.

*Anal.*<sup>8</sup> Calcd. for  $C_{12}H_{13}Hg_4NO_3$ : C, 13.06; H, 1.13; Hg, 72.80; N, 1.27. Found: C, 12.88; H, 1.26; Hg, 72.08; N, 1.27.

Other mole ratios of pyrrole and mercuric acetate were tried in acetic acid as well as water as solvent, but many difficulties were encountered. Using a mole-to-mole ratio of pyrrole and mercuric acetate, a dark blue viscous mess was obtained. When the amount of water was reduced, a gelatinous mixture resulted which made filtration impossible.

**Solvolysis and Reduction of Pyrrolyl-2,3,4,5-tetrameric Acetate.**—To a solution containing 0.2 g. ( $2 \times 10^{-4}$  mole) of pyrrolyltetrameric acetate in 1 ml. of glacial acetic acid with trace amounts of *p*-toluenesulfonic acid (Matheson Coleman and Bell), 0.15 g. ( $8 \times 10^{-4}$  mole) of ferrocene (Aldrich Chemical Co., m.p. 173–174°) in 0.5 ml. of toluene was added. The yellowish reaction mixture turned dark bluish green gradually upon standing at room temperature. At the end of 24 hr., 5  $\mu$ l. of the reaction mixture was analyzed by v.p.c. at 150–155°, with a helium flow rate of 60 cc./min. The yield of pyrrole was 58%. In the blank run, with all the components but ferrocene, under identical conditions, no pyrrole was detected.

The remainder of the reaction mixture was concentrated to almost dryness. A gummy mess resulted. Purification and identification were not successful.

(8) The analysis was performed by Dr. M. S. Nagy of Massachusetts Institute of Technology.

## Stereochemistry of the Additions of Acids to Stilbene and Styrene Oxides<sup>1</sup>

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*threo*-2-Chloro-1,2-diphenylethanol was the main or only product of the reaction of *trans*- and *cis*-stilbene oxide with hydrogen chloride in several different solvents. The *erythro*-chlorohydrin was formed in slight excess only in the reaction of the *trans*-oxide in ether containing water. *trans*-Stilbene oxide was transformed into its *cis* isomer in better than 90% yield by reaction with hydrogen chloride, followed by treatment with alkali. The steric course of the reaction of (+)-styrene oxide with hydrogen chloride to give 2-chloro-2-phenylethanol was found to depend greatly on the solvent, as percentages of inversion ranging from 24% in dioxane to 83% in chloroform were observed. Additions of several organic acids to (+)-styrene oxide in different solvents were also investigated. Absolute configurations were deduced for *threo*-2-chloro-1,2-diphenylethanol, 1,2-diphenylethanol, and 2-chloro-2-phenylethanol.

It appears that, in all known cases, additions of nucleophiles to epoxides in basic or neutral media take place with complete inversion.<sup>2</sup> On the other hand, the stereochemistry of additions which take place in acidic solutions, with formation of glycols, glycol esters, or halohydrins, is much less straightforward and deserves further investigation. While purely aliphatic or cycloaliphatic epoxides open mostly in a *trans* fashion, it is now clear that this does not hold when aryl substitu-

ents are present on the oxirane ring: several recent examples in the literature show that retention, rather than inversion, takes place as a rule in this case.<sup>3</sup>

Apparent exceptions to this rule are the reactions of *cis*- (1) and *trans*-stilbene oxide (4) with hydrogen chloride. According to Reulos and Collin,<sup>4</sup> this reaction, carried out in moist ether, gives the *trans*

(1) Taken in part from the doctoral thesis of P. L. Ferrarini.

(2) For a complete review, see A. Rosowsky, "Heterocyclic Compounds with Three- and Four-Membered Rings," part 1, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p. 1.

(3) (a) J. H. Brewster, *J. Am. Chem. Soc.*, **78**, 4061 (1956); (b) D. Y. Curtin, A. Bradley, and Y. G. Hendrickson, *ibid.*, **78**, 4064 (1956); (c) R. C. Cookson and J. Hudec, *Proc. Chem. Soc.*, 24 (1957); (d) G. Berti and F. Bottari, *J. Org. Chem.*, **25**, 1286 (1960); (e) G. Berti, F. Bottari, and B. Macchia, *Gazz. chim. ital.*, **90**, 1783 (1960); (f) *Tetrahedron*, **20**, 545 (1964).

(4) D. Reulos and C. Collin, *Compt. rend.*, **218**, 795 (1944).

adducts, respectively *threo*- (8) and *erythro*-2-chloro-1,2-diphenylethanol (6). Recently, Letsinger and Morrison<sup>5</sup> reported similar results, although they had to use dry, instead of moist, ether. As we could not explain the reason why 1 and 4 should add hydrogen chloride in a *trans* way and tri- and dichloroacetic acid exclusively in a *cis* way,<sup>3d,e</sup> we decided to investigate further the former reactions, in order to establish whether the type of solvent might have some influence on their steric course. This work was then extended to the study of the stereochemistry of additions of acids to styrene oxide in different solvents.

### Results

On reinvestigating the addition of hydrogen chloride to 1 and 4 we obtained results<sup>6</sup> some of which were in contrast with the previous ones.<sup>4,5</sup> *cis*-Stilbene oxide (1) gave in all solvents which were used (ether, chloroform, benzene, and dioxane) the *trans* adduct 8 as the main product, and small amounts of the *cis* adduct 6 and of carbonylic rearrangement compounds. This is in accordance with the previous reports, although we obtained for 8 a melting point of 57–58°, instead of 47°<sup>4</sup> or 42–43°.<sup>5</sup> The differences in melting point were found to be due to the fact that 8 can exist in two crystalline modifications: a sample of 8, kindly supplied by Dr. Letsinger, melted completely at 44°, but resolidified on seeding with our compound, and melted again at 57–58°. The fact that our product was the pure *threo*-chlorohydrin was confirmed by its almost quantitative transformation into 1 with base.

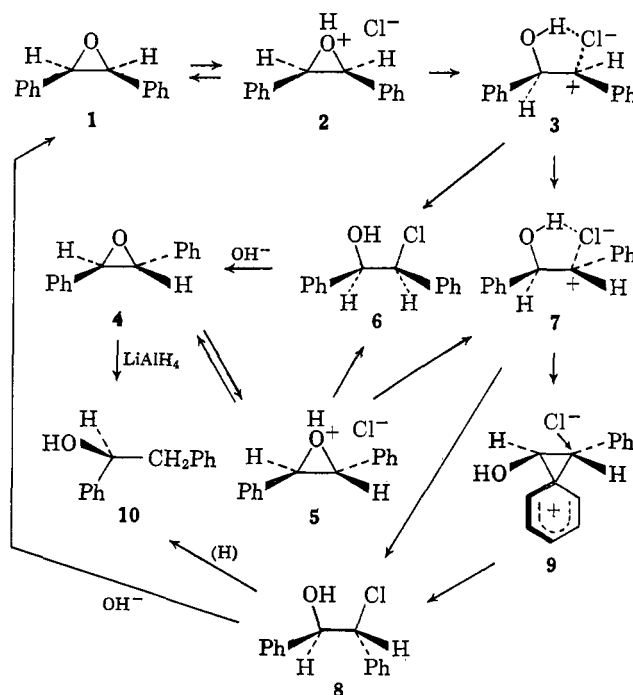
Addition of concentrated aqueous hydrochloric acid to an ether solution of *trans*-stilbene oxide (4)<sup>4</sup> gave a mixture of 6, 8, and some rearrangement product, from which 6, which was in slight excess, could be separated only in low yield by fractional crystallization. When the same reaction was carried out in anhydrous ether, as described by Letsinger and Morrison,<sup>5</sup> we were not able to obtain the 80% yield of the *erythro*-chlorohydrin 6 reported by the previous authors; our crude product was a liquid mixture of 8 and 6, containing a large excess of the *threo* isomer 8, which was isolated pure in 37% yield by fractional crystallization. We are not able to explain the discrepancy between the previous results and ours; 8 is stable in the reaction medium and does not give any of the *erythro* isomer even after several days in ether saturated with hydrogen chloride. The different results could perhaps be due to a particular sensitivity of the steric course of the reaction to small differences in the conditions under which it is carried out, or to impurities.

The *threo*-chlorohydrin was obtained free of its diastereoisomer, in over 90% yield, when the addition of hydrogen chloride to 4 was carried out in benzene or chloroform. This reaction, followed by treatment with base, is a good preparative method for the transformation of *trans*-stilbene oxide into the less easily available *cis*-stilbene oxide, in better than 90% over-all yield. When ethanol, 2-propanol, or tetrahydrofuran were used as solvents, mixtures of 8 and 6 were ob-

tained, which contained large amounts of side products, probably ethers formed by reaction with the solvent.

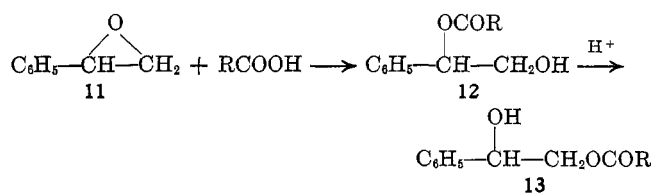
Hydrogen chloride was also added to the (+)-epoxide 4 in benzene. The chlorohydrin 8 was obtained with practically quantitative optical yield, as shown by its catalytic reduction to (+)-1,2-diphenylethanol (10), which was also obtained directly from (+)-4 by reduction with lithium aluminum hydride (see Scheme I). As the absolute configuration of (+)-

SCHEME I



stilbene oxide is that shown in 4,<sup>7</sup> it is possible to assign the configurations shown in 8 and 10 to the chlorohydrin and the alcohol. The crude reaction product of (+)-4 with hydrogen chloride gave on treatment with base essentially pure *cis*-epoxide, exhibiting only a very small rotation which, if due to some (+)-4, would indicate the presence of less than 1% of the *erythro*-chlorohydrin 6 in the initial reaction mixture.

The role of solvent in determining the stereochemistry of epoxide ring opening with acids was further investigated with a simpler compound, optically active styrene oxide (11). Previous work<sup>8</sup> had shown that in the primary process organic acids attack 11 exclusively on the asymmetric carbon atom, to give the  $\alpha$ -monoesters 12, even if the products, after isolation, contained substantial amounts of the rearranged esters 13. The percentages of inversion<sup>9</sup> in the esters obtained



(7) G. Berti, F. Bottari, and B. Macchia, *Farmaco* (Pavia) *Ed. sci.*, **15**, 377 (1960).

(8) (a) G. Berti, F. Bottari, and B. Macchia, *Ann. chim.* (Rome), **62**, 1101 (1962); (b) T. Cohen, M. Dughi, V. A. Notaro, and G. Pinkus, *J. Org. Chem.*, **27**, 814 (1962).

(9) Percentages of inversion are based on the total number of inverted molecules: i.e., 50% inversion = 100% racemization.

(5) R. L. Letsinger and J. D. Morrison, *J. Am. Chem. Soc.*, **85**, 2227 (1963).

(6) For a preliminary report on this part of the present work, see G. Berti, F. Bottari, and B. Macchia, *Chim. ind.* (Milan), **45**, 1527 (1963).

TABLE I  
REACTIONS OF (+)-(*R*)-STYRENE OXIDE WITH ORGANIC ACIDS IN DIFFERENT SOLVENTS

Acid	% inversion in phenyl glycol <sup>a</sup>					Excess acid	THF-H <sub>2</sub> O <sup>b</sup>	H <sub>2</sub> O
	Dioxane	THF	C <sub>6</sub> H <sub>6</sub>	CHCl <sub>3</sub>				
CF <sub>3</sub> COOH	27	<50 <sup>c</sup>	38	43	...	>50 <sup>c</sup>	...	
CCl <sub>3</sub> COOH	...	<50 <sup>c</sup>	40	42	..	>50 <sup>c</sup>	...	
CHCl <sub>2</sub> COOH	...	...	43	45	..	...	...	
CH <sub>2</sub> ClCOOH	...	...	49	53	..	...	...	
HCOOH	...	...	...	..	53	...	...	
CH <sub>3</sub> COOH	...	...	...	...	60	...	...	
H <sub>2</sub> O <sup>+</sup> (HSO <sub>4</sub> <sup>-</sup> )	...	...	..	...	...	...	66 <sup>d</sup>	

<sup>a</sup> See footnote 9. <sup>b</sup> Water (4%) in THF. <sup>c</sup> See Experimental Section. <sup>d</sup> Taken from previous work; see ref. 8a.

with different acids and in different solvents are summarized in Table I. The optical yields were calculated on the basis of the rotation of the phenyl glycol obtained by lithium aluminum hydride reduction of the esters 12 or 13. Although all reactions led to extensive racemization, a certain degree of stereospecificity and dependency on the strength of the acid and on the solvent was observed in all of them.

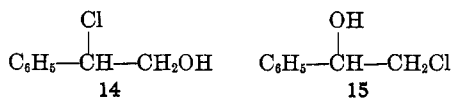
The results of the reaction of 11 with hydrogen chloride are given in Table II. In all cases, as shown by

TABLE II  
REACTIONS OF (+)-(*R*)-STYRENE OXIDE WITH HYDROGEN CHLORIDE

Solvent	-2-Chloro-2-phenylethanol-		Polymeric side products, [α] <sub>D</sub> <sup>20</sup> (CHCl <sub>3</sub> ) <sup>b</sup>
	% yield	% inversion <sup>a</sup>	
Dioxane	47	24	-36
THF	64	37	+44
Benzene	60	59	+64
THF-H <sub>2</sub> O (95:5)	..	~80 <sup>c</sup>	...
CHCl <sub>3</sub> <sup>d</sup>	71	83	+97
CHCl <sub>3</sub> <sup>e</sup>	69	74	+71

<sup>a</sup> See footnote 9. <sup>b</sup> Calculated on the basis of optically pure styrene oxide. <sup>c</sup> See Experimental Section. <sup>d</sup> Anhydrous. <sup>e</sup> Half-saturated with water.

infrared analysis and in accordance with previous results,<sup>10</sup> the product was the chlorohydrin 14, while the isomer 15 was completely absent. Optically active polymers were also formed as side products.



The percentages of inversion are maximum (below 50%) or minimum (above 50%) values, as they were deduced by reconversion of 14 into the epoxide 11 with base; this reaction, however, should give an entirely stereospecific inversion.<sup>11</sup> The absolute configuration of 11 being known,<sup>12</sup> it was possible to assign the (*S*) configuration (18) to (+)-14. The data in Table II show a striking dependency of the stereochemistry of the addition of hydrogen chloride from the type of solvent, with inversion values ranging from 24% in dioxane to 83% in chloroform.

### Discussion

Reactions of epoxides with acids, although they bear some resemblance to electrophilic additions to olefins,

(10) (a) J. R. Clark and M. Pugliese, *J. Org. Chem.*, **24**, 1088 (1959); (b) H. Bodot, E. Dieuzeide, and J. Jullien, *Bull. soc. chim. France*, 1086 (1960).

(11) Reference 2, p. 94.

(12) E. L. Eliel and D. W. Delmonte, *J. Org. Chem.*, **21**, 596 (1956).

may also be considered as nucleophilic displacements of a particular type, in which the leaving group remains in the immediate surroundings of the reaction site and can exert a considerable influence on the steric course of the reaction. The fact that, in all reactions of styrene oxide we have examined, the nucleophile attacks the carbon atom α to the phenyl group seems to imply a considerable cationic character of the transition state, in accordance with what would be expected for S<sub>N</sub>1 or "borderline S<sub>N</sub>2" reactions.<sup>13</sup> It is known<sup>14</sup> that S<sub>N</sub>1 reactions may take place with excess retention, excess inversion, or complete racemization, depending on the type of leaving group, solvent, substituents on the reaction site, and attacking nucleophile. Such a wide range of stereochemical results was observed in the additions described above; the nature of the cationic intermediate and solvation effects can account for many of the results.

The reactions of the stilbene oxides with hydrogen chloride in benzene or chloroform appear to be rather stereoselective, even if not stereospecific, the *threo*-chlorohydrin being the main or only addition product obtained from both diastereoisomers. Tung and Speziale<sup>15</sup> observed the same stereoselectivity, leading to the *threo*-chlorohydrin, in the reactions of both *cis*- and *trans*-*N,N*-diethyl-3-phenylglycidamides with hydrogen chloride in benzene, while in methanol the *trans* isomer gave complete inversion. These reactions were explained with an intramolecular assistance in the transition state by the carbonyl group, which is absent in our epoxides. Apparently, in our case, the higher stability of the *trans*oid cation 7 seems to be of importance for the stereoselectivity in low polarity solvents. The isomerization of the *cis*oid cation 3, formed from the *cis*-epoxide 1, to 7, could explain the similarity in the reaction products obtained from 1 and 4 better than the assumption of a *trans* addition to 1 and a *cis* one to 4. The transformation of 7 into 8 can take place through the phenonium ion 9, or by direct reaction inside the ion pair in a cage of solvent.<sup>3a</sup> In this connection, mention may be made of the fact that recently Dewar<sup>16</sup> has observed a large excess of *cis* addition to phenyl-substituted olefins, some of which could not give phenonium ions.

The behavior of 1 and 4 with hydrogen chloride is partly in contrast with that of the same epoxides with tri-<sup>3d</sup> and dichloroacetic acid<sup>3e</sup> which add in a stereospecific *cis* way also to the *cis* isomer 1; this may be

(13) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 745 (1959).

(14) D. J. Cram, J. L. Mateos, F. Hauck, A. Langemann, K. R. Kopecky, W. D. Nielsen, and J. Allinger, *J. Am. Chem. Soc.*, **81**, 5774 (1959).

(15) C. C. Tung and A. J. Speziale, *J. Org. Chem.*, **28**, 2009 (1963).

(16) J. S. Dewar and R. C. Fahey, *Angew. Chem. Intern. Ed. Engl.*, **3**, 245 (1964).

due to the higher nucleophilicity of the carboxylic anions, which, after the slow protonation step, could attack the *cis* cationoid intermediate, analogous to **3**, before it has passed to the more stable transoid conformation.

The reactions we carried out with styrene oxide gave results differing in part from those obtained with the stilbene oxides. It must be stressed that there is a fundamental difference in the cationoid intermediates formed from the two types of epoxides: while those formed from the stilbene oxides remain asymmetric even after rotation around the  $\alpha,\beta$  bond and may therefore still give a stereoselective reaction, that formed from styrene oxide loses its steric individuality simply by a rotation of  $90^\circ$ , and any step leading to an optically active product must take place before such a rotation.

The reactions of styrene oxide with hydrogen chloride (Table II) show rather different courses in different solvents and must involve several different mechanisms (see Scheme II). Racemization can of

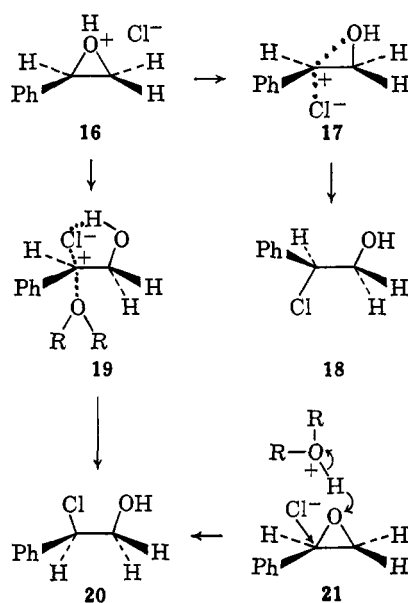
composition of chlorosulfites to chlorides, reported a dependency of the stereochemistry from the solvent, which is at least in part of the same type as that of the reaction of styrene oxide with hydrogen chloride: thus, dioxane gave 95% retention and toluene 95% inversion. Hart and Elia<sup>19</sup> obtained very high retentions in the cleavage of benzhydryl  $\alpha$ -phenethyl ether with hydrogen chloride in toluene, 3-pentanone, and 1-butanol.

Addition of water to tetrahydrofuran caused a drastic change in the steric course of the addition from excess retention to excess inversion, probably because of competitive interference of water with the ion-pair process.

The fact that in low-polarity solvents hydrogen chloride adds to *trans*-stilbene oxide with retention, and to styrene oxide with excess inversion, may perhaps be considered as a proof for the intermediate formation of a phenonium ion (**9**) in the first case; such an intermediate is not possible in the case of styrene oxide.

The data for the additions of organic acids to styrene oxide (Table I) show a low, but definite stereospecificity and some dependence from the strength of the acid and from the solvent. Dioxane is the solvent giving highest retention, as in the reaction with hydrogen chloride. A slight excess of retention was observed for almost all additions carried out in benzene and chloroform, in contrast with the excess inversion obtained with hydrogen chloride; as in the case of the additions to *cis*-stilbene oxide, this points to a situation more favorable for retention when the nucleophile is a carboxylate, instead of a halogen anion. When water was present and when excess acid was the solvent, the products were formed with an excess of inversion, probably because of an increase in dielectric constant, of particularly strong solvation effects, and of the presence of a large excess of reagent molecules.

SCHEME II



course be accounted for by any process taking place after a rotation of at least  $90^\circ$  around the C-C bond, inversion can best be explained with a "borderline  $S_N2$ " mechanism (**17**), while retention is likely to imply a cyclic intermediate similar to **7**.

The reactions conducted in ethers were the only ones that gave excess retention and this may well be accounted for by backside stabilization of the intermediate through nucleophilic solvation as shown in **19**, followed by collapse of the ion pair to **20**. The following could be an alternative explanation: as tetrahydrofuran and dioxane are much stronger bases than epoxides,<sup>17</sup> the former should be protonated preferentially to the latter. Reaction could therefore take place predominantly between the oxonium chloride ion pair and the nonprotonated epoxide, to give directly the noninverted chlorohydrin, as shown in **21**. Boozer and Lewis,<sup>18</sup> for a typical  $S_N1$  reaction, the de-

### Experimental Section

Melting points were determined on a Kofler hot stage and are corrected.

**trans-Stilbene Oxide (4).**—A solution of 5.4 g. of *trans*-stilbene (30 mmoles) in 60 ml. of chloroform was added to a suspension of 7.5 g. (33 mmoles) of 80% *p*-nitroperoxybenzoic acid (Prolabo) in 100 ml. of chloroform; the mixture was left at room temperature for 24 hr. with occasional shaking, filtered, washed with 10% sodium carbonate, and evaporated. The residue was crystallized from petroleum ether (b.p. 30–50°) to give 5.5 g. (93%) of the oxide **4**, m.p. 65–67° (lit.<sup>20</sup> m.p. 69°).

(+)-(R,R)-Stilbene Oxide, m.p. 69–70°,  $[\alpha]_D^{20} +357^\circ$  (c 0.590, benzene), optical purity about 95%, was obtained according to the method of Read and Campbell.<sup>21</sup>

**Reactions of trans-Stilbene Oxide with Hydrogen Chloride. A. In Benzene.**—Dry hydrogen chloride was passed for 10 min. through a solution of 1.00 g. of the oxide **4** in 60 ml. of benzene. The solution was washed with saturated sodium bicarbonate, dried over magnesium sulfate, and evaporated to dryness. The residue, taken up in a little petroleum ether, gave 1.10 g. (93%) of pure *threo*-2-chloro-1,2-diphenylethanol (**8**), m.p. 57–58° (lit. m.p. 47°, 42–43°). A sample of the metastable form, m.p. 42–44°, prepared in Dr. Letsinger's laboratory, was melted on the Kofler apparatus and a seed of our product was added to the melt, which resolidified and melted again at 57–58°. The infrared spectra of Nujol mulls of the two forms showed some differences, particularly in the region between 7.5 and 8.5  $\mu$ , but the spectrum of the mull of the lower melting form became

(17) (a) S. Searles, M. Tamres, and E. R. Lippincott, *J. Am. Chem. Soc.*, **75**, 2775 (1953); (b) M. Brandon, M. Tamres, and S. Searles, Jr., *ibid.*, **82**, 2129 (1960); (c) H. E. Wirth and P. I. Slick, *J. Phys. Chem.*, **66**, 2277 (1962).

(18) C. E. Boozer and E. S. Lewis, *J. Am. Chem. Soc.*, **75**, 3182 (1953).

(19) H. Hart and R. J. Elia, *ibid.*, **83**, 985 (1961).

(20) P. Rabe and J. Hallensleben, *Ber.*, **43**, 884 (1910).

(21) J. Read and I. G. M. Campbell, *J. Chem. Soc.*, 2377 (1930).

identical with that of the higher melting one after a day. Spectra taken on solutions of the two forms in carbon tetrachloride were perfectly identical.

A solution of 1.16 g. (5 mmoles) of **8** in 15 ml. of methanol was treated dropwise with 5.2 ml. of 1 *N* aqueous sodium hydroxide, diluted with water, and extracted with ether. The ether was dried and evaporated, and the residue was crystallized from petroleum ether to give 0.93 g. (95%) of *cis*-stilbene oxide (**1**), m.p. 41–42° (lit.<sup>20</sup> m.p. 42°).

The same reaction, carried out with 0.57 g. of (+)-(*R*:*R*)-stilbene oxide, gave 0.54 g. of (*R*:*R*)-2-chloro-1,2-diphenylethanol, m.p. 66–67°,  $[\alpha]^{20}_D -20.2^\circ$  (*c* 5.2, ethanol), which, on treatment with sodium hydroxide as described above, yielded completely inactive **1**. The residue obtained from the mother liquor (0.11 g.) had  $[\alpha]^{20}_D -15.5^\circ$ , and, on treatment with sodium hydroxide, gave 0.09 g. of a crude stilbene oxide,  $[\alpha]^{20}_D +7^\circ$  (benzene); this rotation, if due to (+)-**4**, would correspond to less than 2% of the latter compound.

**B. In Chloroform.**—A solution of 1.00 g. of **4** in 100 ml. of 0.2 *M* HCl in chloroform, was treated, after 90 min., as described in A, to give 0.90 g. (76%) of **8**, m.p. 57–58°. Evaporation of the filtrate gave 0.21 g. of a residue consisting of **8**, contaminated with a carbonyl compound (band at 5.83  $\mu$ , diphenylacetaldehyde?).

**C. In Dry Ether.**—Dry hydrogen chloride was bubbled for 10 min. through a solution of 0.50 g. of **4** in 50 ml. of dry ether, saturated with hydrogen chloride. After 15 hr. the solution was treated as given in A. The residue of evaporation of the ether was an oil, which, taken up in petroleum ether, gave 0.22 g. (37%) of the *threo*-chlorohydrin **8**, m.p. 56–58°. The mother liquor (0.33 g.) contained the *threo*- and *erythro*-chlorohydrins in a ratio of about 8:2, and some carbonyl-containing material. Analysis of the mixtures of **6** and **8** was based on the comparison of their infrared spectra in carbon tetrachloride solution with those of artificial mixtures of known composition. Although the solution spectra of **6** and **8** are rather similar, it is thus possible to estimate the composition of their mixtures with an accuracy within  $\pm 5\%$ , on the basis of the relative intensities of bands at 9.45 and 9.72  $\mu$ .

The *threo*-chlorohydrin was recovered unchanged after 3 days from a solution in ether saturated with hydrogen chloride.

**D. In Moist Ether.**—A solution of 0.50 g. of **4** in 20 ml. of ether was shaken 2 hr. with 10 ml. of concentrated hydrochloric acid, then washed, dried, and evaporated. The residue, taken up in petroleum ether, gave, after storage at 0°, 70 mg. of *erythro*-2-chloro-1,2-diphenylethanol (**6**), m.p. 76–77°, identical with a sample prepared according to Lutz and co-workers.<sup>22</sup> The noncrystallizable product remaining in the mother liquor was composed of about equal amounts of **6** and **8**, and traces of carbonylic rearrangement products (infrared analysis).

**E. In Other Solvents.**—Addition of hydrogen chloride to **4** in dioxane gave a product composed of about 70% of **8** and 30% of **6**. Reactions carried out in ethanol, 2-propanol, or tetrahydrofuran gave mixtures of **6** and **8** contaminated with large amounts of ethers, as shown by low chlorine contents and broad bands in the 9–10- $\mu$  region.

*cis*-Stilbene oxide (**1**) was prepared in 92% over-all yield by treating the *trans*-oxide with hydrogen chloride in benzene and dehydrohalogenating the total crude halohydrin with sodium hydroxide in methanol, as described above.

**Reactions of *cis*-Stilbene Oxide with Hydrogen Chloride. A. In Benzene.**—The reaction carried out on 0.20 g. of **1** in 15 ml. of benzene, as described for *trans*-stilbene oxide, gave, after crystallization from petroleum ether, 0.15 g. of the *threo*-chlorohydrin **8**, m.p. 57–58°, and 0.07 g. of a noncrystallizable residue, containing about equal amounts of the two chlorohydrins.

**B. In Chloroform.**—The reaction of 1.00 g. of **1** with hydrogen chloride in chloroform gave 0.75 g. (63%) of pure **8** and 0.30 g. of a mixture consisting mostly of **8**, some **6**, and carbonylic by-products.

**C. In Dry Ether.**—The reaction carried out with 0.53 g. of **1** as described for the *trans*-oxide gave 0.32 g. (51%) of pure *threo*-chlorohydrin and 0.25 g. of a mixture of **8** and **6** in a ratio of about 9:1, with carbonylic side products.

**D. In Dioxane.**—The same reaction, carried out in dioxane, produced about 70% of **8** and 30% of **6**.

(+)-(*S*)-1,2-Diphenylethanol (**10**). **A. From **8**.**—A solution

of 0.52 g. of (–)-**8** in 50 ml. of ethanol was shaken with hydrogen in the presence of 0.5 g. of 5% Pd–CaCO<sub>3</sub>. After absorption of the calculated amount of gas, the solution was filtered and evaporated, and the residue was crystallized from petroleum ether to give 0.37 g. of **10**, m.p. 66–67°,  $[\alpha]^{18}_D +55.9^\circ$  (*c* 1.40, ethanol) (lit.<sup>23</sup> m.p. 67°,  $[\alpha]^{25}_D +52.8^\circ$ ).

**B. From **4**.**—A solution of 100 mg. of (+)-**4** in 15 ml. of ether was refluxed 6 hr. with 0.1 g. of lithium aluminum hydride, treated with ethyl acetate, then with saturated potassium sodium tartrate and extracted with ether. Evaporation of the ether and crystallization from petroleum ether gave 60 mg. of **10**, m.p. 65–66°,  $[\alpha]^{18}_D +56.1^\circ$  (*c* 1.00, ethanol).

(+)-(*R*)-Styrene oxide (**11**), b.p. 89–90° (23 mm.),  $n^{20}_D 1.5345$ ,  $d_{20} 1.051$ , was prepared by the previously described method.<sup>24</sup> It had an optical purity of about 95% and the following specific rotations:  $[\alpha]^{20}_D +32.9^\circ$ ,  $[\alpha]^{20}_{435} +37.4^\circ$ ,  $[\alpha]^{20}_{435} +64.2^\circ$  (neat);  $[\alpha]^{18}_D +44.5^\circ$ ,  $[\alpha]^{18}_{545} +50.2^\circ$ ,  $[\alpha]^{18}_{435} +87.7^\circ$  (*c* 1.05, benzene);  $[\alpha]^{18}_D -24.6^\circ$ ,  $[\alpha]^{18}_{545} -28.4^\circ$ ,  $[\alpha]^{18}_{435} -53.4^\circ$  (*c* 1.34, chloroform); and  $[\alpha]^{18}_D +16.9^\circ$  (*c* 1.06, ether).

**Reactions of (+)-(*R*)-Styrene Oxide with Organic Acids.**—

The following example illustrates the general method followed for these reactions. (+)-Styrene oxide (**11**) (100 mg., 0.8 mmole) in 4 ml. of dry dioxane was treated with 4 ml. of 0.25 *N* trifluoroacetic acid in dry dioxane and the volume was brought to 10 ml. The solution, which had  $\alpha_{435} +0.32^\circ$ , was left at room temperature ( $20 \pm 2^\circ$ ), until a constant rotation was reached ( $\alpha_{435} -1.62^\circ$  after 24 hr.). The solution was diluted with ether, washed with saturated sodium bicarbonate solution, and evaporated to dryness; the residue was dissolved in 10 ml. of ether and shaken 1 hr. with 50 mg. of lithium aluminum hydride. Treatment with saturated potassium sodium tartrate solution, followed by extraction with 200 ml. of ether and evaporation of the ether, gave a residue consisting of a mixture of 1-phenylethane-1,2-diol and polymeric side products of reaction of **11** with the acid. Extraction with 5 ml. of water and vacuum evaporation of the extract yielded 60 mg. (52%) of phenyl glycol, m.p. 62–64°,  $[\alpha]^{20}_{435} -38^\circ$  (*c* 1.50, water). As phenyl glycol of the same optical purity as the starting epoxide has  $[\alpha]^{20}_{435} -83^\circ$ , this amounts to 54% racemization or 27% inversion. Addition of periodic acid to the aqueous solution of the glycol produced complete disappearance of optical activity; therefore, no other optically active compound was present besides the glycol.

The other runs were carried out in a similar way and the results are summarized in Table I. The times required to reach optical stability varied from a few minutes for the reactions of trifluoroacetic acid in benzene or chloroform to 4 days for that of mono-chloroacetic acid in benzene. The epoxide **11** was recovered unchanged from a benzene solution containing acetic acid, after storage for 2 months at room temperature.

For the reactions in anhydrous and aqueous tetrahydrofuran it is not possible to give exact data, as some water-soluble optically active impurity (probably a  $\beta$ -hydroxyethyl ether of **11**) was formed as a side product: therefore, the solution of **11** retained some optical activity after treatment with periodic acid. However, subtraction of this residual rotation from the initial value showed that the reaction involved excess retention in the dry and excess inversion in the aqueous solvent.

**Reactions of (+)-(*R*)-Styrene Oxide with Hydrogen Chloride.**

—The following is an example of the general method used in this group of reactions. Pure (+)-(*R*)-styrene oxide (**11**) was diluted with racemic oxide to give a product,  $[\alpha]^{21}_D +5.05^\circ$ ,  $[\alpha]^{21}_{435} +9.96^\circ$  (*c* 7.31, benzene), of 10.8% optical purity, 3.32 g. (27.6 mmoles) of which was dissolved in 20 ml. of dry chloroform, cooled to 0°, and treated with 130 ml. (32.5 mmoles) of equally cooled 0.25 *N* dry hydrogen chloride in chloroform. After 20 min. at room temperature the solution was washed with saturated sodium bicarbonate solution, evaporated, and distilled, to give 3.08 g. (71%) of 2-chloro-2-phenylethanol (**14**): b.p. 97–99° (1.2 mm.);  $n^{20}_D 1.5560$ ;  $\alpha^{22}_D +11.58^\circ$ ,  $\alpha^{22}_{435} +24.32^\circ$  (1 dm., neat);  $[\alpha]^{20}_D +9.63^\circ$ ,  $[\alpha]^{20}_{435} +19.90^\circ$  (*c* 6.40, chloroform), [lit.<sup>10a</sup> b.p. 110–114 (8 mm.),  $n^{20}_D 1.5532$ , for the racemic compound].

Absence of the isomeric chlorohydrin **15** was shown by the absence of a band at 11.45  $\mu$  in the infrared spectrum. Redistillation gave a product showing the same optical rotation values. The residue of the first distillation was a polymer, with  $[\alpha]^{24}_D +10.50^\circ$  (*c* 6.67, chloroform).

A solution of 2.00 g. of the redistilled chlorohydrin in 20 ml.

(22) R. E. Lutz, R. L. Wayland, and H. G. France, *J. Am. Chem. Soc.*, **72**, 5511 (1950).

(23) W. Gerrard and J. Kenyon, *J. Chem. Soc.*, 2564 (1928).

of 2-propanol was titrated with aqueous 1 *N* sodium hydroxide to a stable phenolphthalein end point, diluted with water, and extracted with ether. Evaporation of the ether and distillation gave 1.17 g. (76%) of pure styrene oxide (11): b.p. 79–80° (17 mm.);  $[\alpha]^{17}_D +3.36^\circ$ ,  $[\alpha]^{17}_{435} +6.61^\circ$  (*c* 10.05, benzene).

The styrene oxide obtained in the last reaction had a rotation which was 66% of that of the starting material; this corresponds to 17% inversion and, assuming that the transformation of 14 to 11 takes place with complete inversion, 14 should be formed from 11 with 83% inversion. Furthermore, on the basis of the optical purity of the starting 11, optically pure (+)-(*S*)-2-

chloro-2-phenylethanol (18) should have at least  $\alpha^{25}_D +162.4^\circ$ ,  $\alpha^{25}_{435} +341.1^\circ$  (1 dm., neat);  $[\alpha]^{20}_D +135.1^\circ$ ,  $[\alpha]^{20}_{435} +279.1^\circ$  (chloroform).

The results of all reactions carried out with 11 and hydrogen chloride, in a manner similar to that described above, are summarized in Table II. The percentage of inversion in the reaction carried out in 95:5 tetrahydrofuran-water is somewhat less accurate than the other ones, as the chlorohydrin was contaminated with some 1,4-butanediol and 4-chloro-1-butanol, which were formed by cleavage of solvent molecules and could not be completely eliminated by distillation.

## The Disilylation of Styrene and $\alpha$ -Methylstyrene. The Trapping of Short-Lived Intermediates from Alkali Metals and Aryl Olefins<sup>1</sup>

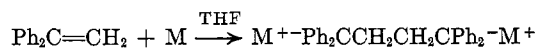
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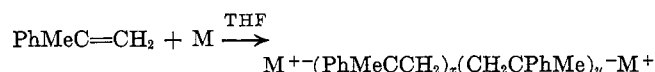
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Monochlorosilanes, an alkali metal, and styrene or  $\alpha$ -methylstyrene in aprotic solvents give disilylalkanes containing one (A) or two (B) reduced olefin units, phenyl-1,2-disilyl ethanes, and 1,4-diphenyl-1,4-disilylbutanes from styrene or 2-phenyl-1,2-disilylpropanes and 2,5-diphenyl-2,5-disilylhexanes from  $\alpha$ -methylstyrene. Lithium naphthalene also serves as a source of alkali metal in this synthesis to give the above products and naphthalene. The ratio of A and B with lithium in tetrahydrofuran (THF) can be altered by varying the ratio of chlorosilane to olefin: 2:1 or higher ratios give high yields of A and equal molar amounts of chlorosilane and olefin give high yields of B. Dimethyldichlorosilane and styrene with lithium in THF give 1,1-dimethyl-2,5-diphenyl-1-silacyclopentane and 1,1-dimethyl-3,4-diphenyl-1-silacyclopentane at chlorosilane to olefin ratios of 1:1 and 2:1, respectively. All structural assignments are confirmed by the  $H^1$  n.m.r. spectra and conversion to known derivatives by alkaline cleavage of benzylic carbon-silicon bonds. These data support a reaction sequence involving the trapping, *via* reaction with a chlorosilane, of organoalkali intermediates from the alkali metal and aryl olefin. In the proposed reaction scheme the monomolecular derivatives (A) and bimolecular derivatives (B) result from the trapping of monomeric and dimeric organoalkali derivatives, respectively.

The preparation of organoalkali reagents *via* the interaction of alkali metals with olefins has been the subject of many excellent reviews<sup>2-4</sup> since its discovery by Schlenk and Bergmann.<sup>5</sup> This reaction provides a convenient source of dimeric organodialkali reagents from 1,1-diaryl olefins and polymeric organodialkali



reagents from the more polymerizable monoaryl olefins, styrene and  $\alpha$ -methylstyrene.<sup>6,7</sup> Even with these latter olefins, high yields of the dimeric organodialkali reagents have been obtained at low temperatures with sodium dispersions.<sup>8</sup>



In all cases the organodialkali reagents represent the reaction products of short-lived monomeric organoalkali reagents, anion radicals, formed *via* electron transfer from the alkali metal to the aryl olefin.<sup>9</sup>

(1) Presented in part before the Organic Section at the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1961.

(2) G. E. Coates, "Organometallic Compounds," Second Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 32–43.

(3) A. J. Birch, *Quart. Rev.* (London), **4**, 69 (1950).

(4) K. N. Campbell and B. K. Campbell, *Chem. Rev.*, **31**, 77 (1942).

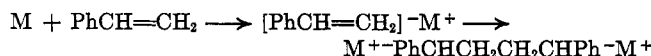
(5) W. Schlenk and E. Bergmann, *Ann. Chem.*, **463**, 1 (1928); *Chem. Abstr.*, **22**, 4493 (1928).

(6) M. Szwarc, M. Levy, and R. Milkovich, *J. Am. Chem. Soc.*, **78**, 2656 (1956).

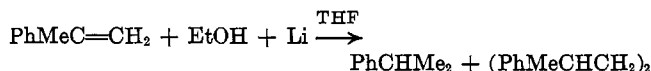
(7) M. Szwarc, *Macromol. Chem.*, **35**, 132 (1960).

(8) C. E. Frank, J. R. Leebrick, L. F. Moormeier, J. A. Scheben, and O. Homberg, *J. Org. Chem.*, **26**, 307 (1961).

(9) For an excellent review of the reactions of anion radicals, see B. J. McClelland, *Chem. Rev.*, **64**, 301 (1964).



Owing to their reactivity, any synthetic procedure utilizing these monomeric or dimeric organoalkali reagents from monoaryl olefins must be based on trapping them as they are formed from the alkali metal and olefin. The chemical reduction of olefins and aromatic compounds<sup>10</sup> represents such a trapping system where these intermediate reagents are protonated by some protic solvent to give either monomolecular or bimolecular products.<sup>11</sup> Trialkylchlorosilanes



and dialkylalkoxychlorosilanes have a high reactivity toward organoalkali reagents and a low reactivity toward alkali metals which are the main requirements for a successful trapping agent. Their utility in the trapping of a minutely low equilibrium concentration of anion radicals has been demonstrated by the synthesis of 3,6-disilyl-1,4-cyclohexadienes from benzene, trimethylchlorosilane, and lithium in THF.<sup>12</sup> The current study demonstrates the utility of these chlorosilanes for the trapping of anionic species from alkali metals and aryl olefins which, in the absence of trapping

(10) For an excellent review of chemical reduction, see H. Smith, "Organic Reactions in Liquid Ammonia," Vol. I, part 2, Interscience Publishers, New York, N. Y., 1963, pp. 151–280.

(11) A 65% yield of the bimolecular reduction product, 2,5-diphenylhexane, is obtained from an equal molar mixture of  $\alpha$ -methylstyrene and ethanol with lithium in THF: D. R. Weyenberg, *J. Org. Chem.*, **30**, 3236 (1965).

(12) D. R. Weyenberg, and L. H. Toporcer, *J. Am. Chem. Soc.*, **84**, 2843 (1962).