in an oven, was sufficient to produce a pure product.

Anal. Calcd.: N, 4.6; neut. equiv., 151. Found: N, 4.4; neut. equiv., 151.

As check on the synthetic utility of the various "new" solvents mentioned above, a preparation of dichloroacetyl-L-leucine was made in each. The yield in *p*-dioxane was 73%, 56% in anhydrous tetrahydrofuran, 40% in acetoacetic ester, and 33% in 2,4-pentandione. In each case the product was identified by its melting point, 120–122°,[8] and reactions were conducted at room temperature. As judged by the complete solution of the amino acid, reaction in tetrahydrofuran was over in just 10 min. and within 0.5 hr. in the other solvents. Removal of the solvent left a yellow oil which was induced to crystallize by the addition of benzene aided by deep-freeze temperatures. Pure product was then obtained merely by washing the crystals with benzene. However, removal of tetrahydrofuran yielded crystals immediately; these were recrystallized from acetone–heptane.

Notes

Vinylic Halide Displacement by Metallo Organophosphides. Preparation of *trans*-β-Styryldiphenylphosphine Oxide and Sulfide

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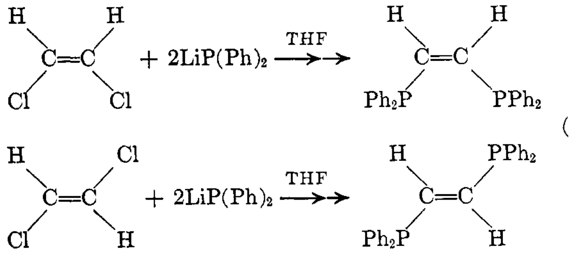
The stereospecific substitution of the vinyl halides in *cis*- and *trans*-1,2-dichloroethenes by diphenylphosphorus employing lithium diphenylphosphide was reported recently (eq. 1).[1] Although these results remove an elimination–addition sequence from consideration as a mechanistic explanation, little else can be concluded about the path of reaction.



(1)

In order to obtain more information on the stereospecific replacement of vinylic halogen by diphenylphosphorus we have examined the reaction of β-bromostyrene with lithium diphenylphosphide in tetrahydrofuran (THF).

Commercially obtained (Eastman) β-bromostyrene has been shown to consist of at least 90% *trans* isomer.[2] Using gas chromatography, infrared, and n.m.r. spectroscopy we have obtained similar results with the Eastman sample of β-bromostyrene used in this work.[2-4] Seyferth has shown that isomerization of either isomer does not occur to any appreciable extent at 140–160° on a cyanoethylsilicone column.[2] Grovenstein has demonstrated that the *trans* isomer is not changed after 4 hr. at 115° nor upon moderate exposure to diffuse daylight or artificial illumination.[3] Cristol has shown that *cis*-β-bromostyrene can be prepared in refluxing acetone containing sodium bicarbonate.[5] The equilibrium ratio is known to be *ca.* 90% *trans* and 10% *cis.*[6]

No noticeable change of isomer ratio occurred after refluxing in tetrahydrofuran containing lithium halide salts. It can reasonably be assumed that the β-bromostyrene used in this work consisted of at least 90% *trans* isomer and that little or no isomerization occurred prior to reaction with lithium diphenylphosphide in tetrahydrofuran. Following rapid exothermic reaction of these reagents and oxidation using 1% hydrogen peroxide, *trans*-β-styryldiphenylphosphine oxide (I) was isolated as the major component. The structure of I was established by chemical analysis, infrared and p.m.r. spectra, hydrogenation to β-phenylethyldiphenylphosphine oxide (II, prepared unequivocally from β-chloroethylbenzene and lithium diphenylphosphide), and synthesis from 2-bromo-2-phenylethyldiphenylphosphine oxide (III, prepared from II and N-bromosuccinimide, eq. 2). Aside from the expected bands for a vinylphenylphosphine oxide, the infrared spectrum of a potassium bromide pellet of I also exhibited bands at 10.0 (m) and 10.1 (m) μ which are indicative of a *trans* structure. Bromination of II to III rather than to 1-bromo-β-phenylethyldiphenylphosphine oxide is expected by the general theory of allylic halogenation[7] and supported by the fact that identical conditions failed to brominate ethylenebis(diphenyl-

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(1) A. M. Aguiar and D. Daigle, *J. Am. Chem. Soc.*, **86**, 2299 (1964).

(2) D. Seyferth, L. G. Vaughan, and R. Suzuki, *J. Organometal. Chem.*, **1**, 437 (1964).

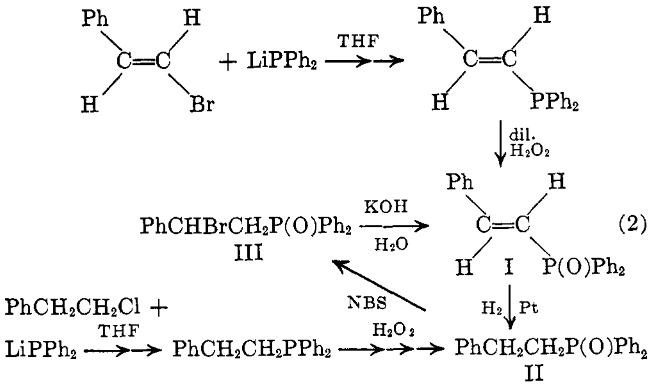
(3) E. Grovenstein, Jr., and D. E. Lee, *J. Am. Chem. Soc.*, **75**, 2645 (1953).

(4) A private communication from the manufacturers, Synfleur Scientific Laboratories, Inc., of Monticello, N. Y., stated that the sample (P283) was made "in the usual manner by the decarboxylation of bromocinnamic acid and it contains approximately 5 to 10% of the *cis* isomer with the balance being the *trans* isomer."

(5) S. J. Cristol and W. P. Norris, *J. Am. Chem. Soc.*, **75**, 2645 (1953).

(6) C. Dufraisse, *Compt. rend.*, **172**, 67 (1921).

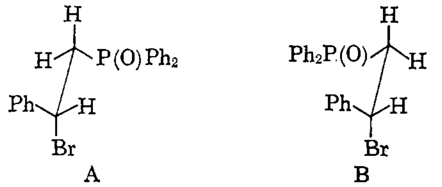
(7) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 381.



phosphine) dioxide, as well as by the p.m.r. spectrum of III. Horner reported the allylic bromination of diphenylbenzylphosphine oxide using similar conditions.[8]

If the dehydrohalogenation of III to I is assumed to proceed *via* a conformation of III in which the elements of hydrogen bromide are axial and coplanar, two such conformations present themselves for each enantiomorph[9] (Chart I). Dehydrohalogenation *via* conformation A leads to *trans*-β-styryldiphenylphosphine oxide (I) while similar elimination *via* B gives rise to the *cis* isomer. Owing to the "eclipsing effect" in the transition state of the β elimination *via* conformation B, the rate of dehydrohalogenation *via* A should be faster and thus the product should be largely the *trans* isomer I.[9]

CHART I



A B

Treatment of the unisolated precursor to I, β-styryldiphenylphosphine, with thiophosphoryl chloride produced compound IV, a β-styryldiphenylphosphine sulfide (eq. 3).

$$PhCH{:}CH_2PPh_2 + PSCl_3 \longrightarrow \underset{IV}{PhCH{:}CH_2P(S)Ph_2} \quad (3)$$

Thiophosphoryl chloride has been found to convert either *cis*- or *trans*-1,2-vinylenebis(diphenylphosphine) to *trans*-1,2-vinylenebis(diphenylphosphine) disulfide, whereas sulfur has led to the corresponding disulfides with no stereomutation.[10] This would indicate that sulfide IV has a *trans* structure. The infrared spectrum of IV, like that of I, showed bands at 10.0 (m) and 10.1 (m) μ, indicative of a *trans* structure. P.m.r. spectra of deuteriochloroform solutions of IV were quite similar to the spectrum of I under similar conditions, but with shifts to slightly lower field strength as expected.[11] Although oxidation of IV with 30% hydrogen peroxide in glacial acetic acid produced I, this fact can only be used to support the *trans* structure of I and not the *trans* structure of IV. This is true because we have found that identical conditions convert both *cis*- and *trans*-1,2-vinylenebis(diphenylphosphine) disulfide to *trans*-1,2-vinylenebis(diphenylphosphine) dioxide.[11]

Since oxidation by dilute aqueous peroxide of *cis*- and *trans*-1,2-vinylenebis(diphenylphosphine) to the corresponding dioxides occurs under conditions identical with those employed in the conversion of the unisolated β-styryldiphenylphosphine to I, which has been shown to have a *trans* configuration, it may be reasonably assumed that the unisolated β-styryldiphenylphosphine has a *trans* configuration. Oxidation of pure *cis*-β-styryldiphenylphosphine to *cis* oxide under identical conditions would show this conclusively. Synthesis of the *cis* isomer is now underway.

There still remains the possibility of isomerization of initially produced *cis*-β-styryldiphenylphosphine under reaction conditions and prior to derivatization. This seems unlikely in view of the reported stereospecificity reported for the reaction of *cis*- and *trans*-1,2-dichloroethenes under identical conditions.[1] If the assumption is made that *cis*-β-styryldiphenylphosphine is unstable toward isomerization under reaction conditions encountered in this work, equilibration of *cis* and *trans* isomers would be expected to occur.

Gas chromatographic analysis of the initially obtained crude I, using a 6 ft. × $^1/_8$ in. 3% SE-52 column at 270° and a flame-ionization detector, showed only one major component aside from small amounts of triphenylphosphine and triphenylphosphine oxide. Since this technique has been found capable of differentiating between isomeric diphenyltolylphosphine oxides,[12] it is reasonable to assume that the presence of any α-styrylphosphine oxide would have been detected.

Until *cis*-β-styryldiphenylphosphine and its oxide are synthesized and found to be stable to isomerization and separable from the *trans* isomers under the gas chromatographic conditions employed, it will not be possible to exclude the presence of these isomers in the crude reaction mixture.

Experimental

***trans*-β-Styryldiphenylphosphine Oxide (I).**—A solution of 18.3 g (0.10 mole) of β-bromostyrene (Eastman) in 50 ml. of tetrahydrofuran was added dropwise to a rapidly stirring, refluxing solution of lithium diphenylphosphide (prepared from 26.2 g. (0.10 mole) of triphenylphosphine by lithium cleavage)[13] in 150 ml. of tetrahydrofuran under a prepurified nitrogen atmosphere over a period of 10 min. The red color of the phosphide was completely discharged toward the end of the addition. After refluxing for 15 min. longer, the tetrahydrofuran was distilled off under nitrogen and the remaining mass was added to 300 ml. of aqueous 1% hydrogen peroxide. After the mixture returned to room temperature a white precipitate had formed. The suspension was filtered after standing overnight. Only 0.25 g. of diphenylphosphinic acid was obtained by acidification and concentration of the alkaline aqueous filtrate. After air drying the solid weighed 30.0 g. Dissolution in acetone and water followed by addition of 3% hydrogen peroxide produced slight warming. After most of the acetone had been allowed to evaporate, water was added. The solid thus produced was filtered off and dried in the oven at 100° for 3 hr. It now weighed 28 g. Continuous extraction with warm cyclohexane in a Soxhlet apparatus led to the precipitation of white crystals of relatively

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(8) L. Horner, H. Hoffmann, H. Ertel, and G. Klahre, *Tetrahedron Letters*, **No. 1**, 9 (1961).

(9) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, pp. 489.

(10) A. M. Aguiar and D. Daigle, *J. Am. Chem. Soc.*, **86**, 5354 (1964).

(11) A. M. Aguiar and D. Daigle, unpublished work.

(12) A. M. Aguiar, H. J. Greenberg, and K. E. Rubenstein, *J. Org. Chem.*, **28**, 2091 (1963).

(13) A. M. Aguiar, J. Beisler, and A. Mills, *ibid.*, **27**, 1001 (1962).

pure I from the hot cyclohexane. Very little material was left in the thimble. Filtration of the cyclohexane suspension at room temperature led to the recovery of 24 g. of I which, after recrystallization from ethanol–water, had m.p. 168–169°.

Anal. Calcd. for $C_{20}H_{17}OP$: C, 78.93; H, 5.63; P, 10.17. Found: C, 78.66; H, 5.49; P, 10.18.

The infrared spectrum of a potassium bromide pellet of this material showed peaks at 3.28 (s), 3.32 (s), 6.21 (m), 6.38 (s), 6.75 (s), 6.96 (m), 7.6 (s), 8.1 (s), and 8.5 (w) with shoulders at 8.32 (s), 8.4 (m), 8.45 (w) and 8.6 (m), and also at 8.9 (m), 9.1 (m), 9.35 (s), 9.7 (s), 10.0 (m), 10.1 (m), 10.85 (s), 11.7 (s), 11.85 (s), 11.95 (s), 12.3 (m), 13.3 (s), 13.4 (s), 13.5 (s), 13.9 (m), 14.3 (s), and 14.5 (s) μ.

The proton magnetic resonance of a deuteriochloroform solution of I showed a broad phenyl proton complex centered at δ 7.5 = p.p.m. along with two small peaks at 6.5 and 6.85 and two larger ones at 6.8 and 7.2, the last overlapping the phenyl protons and making accurate area-ratio determinations impossible. No other bands were present between these and the resonance peak of the tetramethylsilane used as a standard.

Using triphenylphosphine, triphenylphosphine oxide, and pure I as standards, methanol solutions of samples from all of the stages of isolation indicated above were analyzed by gas chromatography. A 6 ft. × $^1/_8$ in. column packed with 3% SE-52 silicone oil on Chromosorb W at 270° was employed for this. A flame-ionization detector employing nitrogen at 30 p.s.i. as the carrier gas completed the system. In all cases only one major peak was obtained. The more impure fractions showed two other, much smaller peaks, shown to be triphenylphosphine and its oxide which undoubtedly arise from incomplete cleavage in the initial production of the lithium diphenylphosphide.[13]

β-Phenylethyldiphenylphosphine Oxide (II).—A solution of 7.0 g. (0.05 mole) of β-chloroethylbenzene (Eastman) in 150 ml. of tetrahydrofuran was added dropwise to a rapidly stirring, refluxing solution of lithium diphenylphosphide, prepared from 13.1 g. (0.05 mole) of triphenylphosphine, under a prepurified nitrogen atmosphere over a period of 10 min. The tetrahydrofuran was distilled off and the residue was dissolved in acetone. Addition of 3% hydrogen peroxide followed by overnight stirring and dilution with water yielded white crystals. After filtration only 0.25 g. of diphenylphosphinic acid could be obtained by acidification of the filtrate. The residual solid weighed 12.8 g. after air drying. Three recrystallizations from cyclohexane gave material with m.p. 102–103°.

Anal. Calcd. for $C_{20}H_{19}OP$: C, 78.5; H, 6.21; P, 10.11. Found: C, 76.94; H, 6.41; P, 9.79.

The infrared spectrum of a potassium bromide pellet of this material showed peaks at 3.4 (s), 6.1 (s), 6.25 (s), 6.3 (s), 6.7 (s), 6.99 (m), 7.19 (s), 7.5 (s), 7.65 (s), 7.9 (s), 8.25 (s), 8.31 (s), and 8.55 (s), with shoulders at 8.39 (s) and 8.41 (m), and also at 8.95 (m), 9.1 (m), 9.4 (s), 9.8 (s), 10.0 (s), 10.09 (s), 10.7 (s), 11.6 (s), 12.1 (s), 12.81 (m), 13.15 (s), 13.4 (s), 13.6 (s), 13.97 (m), 14.15 (s), 14.35 (s) μ.

A deuteriochloroform solution of this material gave a p.m.r. spectrum containing a phenyl proton complex centered at about δ = 7.7, a fairly sharp second phenyl proton peak at 7.23, and a broad multiplet extending between 2.3 and 3.2 p.p.m., in the ratio of 2.5:1.25:1, indicating that the first set can be assigned to the two phenyls bonded to the phosphorus, the second peak to the phenyl of the styryl group, and the last set to the methylene protons.

Hydrogenation of β-Styryldiphenylphosphine Oxide to β-Phenylethyldiphenylphosphine Oxide.—A solution of β-styryldiphenylphosphine oxide in absolute ethanol containing platinum (20% on carbon) was placed under 2000-p.s.i. hydrogen pressure in a rocker bomb hydrogenator and heated to 80° for 24 hr. Filtration of the catalyst and evaporation of the solvent left a crude solid. The product thus obtained, after recrystallization from ethanol–water, showed a melting point and infrared and p.m.r. spectra identical with that of the β-phenylethyldiphenylphosphine oxide prepared above. Mixture melting points of these two materials showed no depression.

2-Bromo-β-phenylethyldiphenylphosphine Oxide (III).—A solution of 4.0 g. (0.0131 mole) of β-phenylethyldiphenylphosphine oxide in 250 ml. of carbon tetrachloride was placed under a nitrogen atmosphere and 2.33 g. (0.0131 mole) of N-bromosuccinimide was added. After refluxing for 3.5 hr., the solid floating on the orange solution was filtered off. The solution was stripped of solvent leaving a white solid which melted at 130–140° after drying. This solid weighed 1.0 g. (1.1 g. theory). After recrystallization from hexane, the material had m.p. 147–148°.

Anal. Calcd. for $C_{20}H_{18}BrOP$: C, 62.34; H, 4.68; P, 8.05; Br, 20.78. Found: C, 62.02; H, 4.69; P, 7.78; Br, 21.14.

The infrared spectrum of a potassium bromide pellet of this material showed peaks at 3.29 (s), 3.4 (s), 3.45 (s), 6.3 (s), 6.78 (s), 6.9 (s), 7.0 (m), 7.05 (s), 7.53 (s), 8.0 (m), and 8.4 (w), with shoulders at 8.35 (m), 8.49 (w) and 8.6 (m), and also at 8.79 (s), 8.99 (m), 9.65 (s), 9.8 (s), 10.05 (s), 10.95 (s), 11.4 (m), 12.95 (s), 13.5 (s), and with a shoulder at 13.6 (w), 13.98 (m), 14.53 (w), 15.0 (s), and 15.7 (s) μ.

A deuteriochloroform solution of III showed a phenyl proton complex centered at δ = 7.4, an ill-defined quartet centered at 5.62 with coupling constant of about 8 c.p.s., and an uneven quintet centered at 3.4 p.p.m., in the ratio of 15:1:2, respectively.

Dehydrohalogenation of 2-Bromo-β-phenylethyldiphenylphosphine Oxide to *trans*-β-Styryldiphenylphosphine Oxide.—To a solution of 0.56 g. of potassium hydroxide (0.10 mole) in 70 ml. of 95% ethanol was added 1.5 g. (0.0039 mole) of 2-bromo-β-phenylethyldiphenylphosphine oxide; the solution was refluxed for 2 hr. on a steam bath. After this was cooled to room temperature, the solid precipitate was filtered off. This material was water soluble and was discarded. The ethanolic solution was allowed to evaporate to dryness. The 1.1 g. of solid thus obtained had m.p. 160–164°. After recrystallization from ethanol–water, it melted at 168–169°. Mixture melting points with I showed no depression. The infrared and p.m.r. spectra were identical with those of I.

***trans*-β-Styryldiphenylphosphine Sulfide** (IV).—The procedure described above for the preparation of β-styryldiphenylphosphine oxide was followed up to, but did not include, the distillation of the tetrahydrofuran. To the tetrahydrofuran reaction solution was added 4.25 g. (0.025 mole) of thiophosphoryl chloride. The preparation employed 0.025 mole of triphenylphosphine and β-bromostyrene. After the very exothermic reaction subsided, the yellow solution was refluxed for 20 min., cooled, and added to water. The yellow sirup thus produced was made solid by trituration with 95% ethanol. The crude solid weighed 7.3 g. (90%). After recrystallization from hexane, the material had m.p. 106.5–107.5°.

Anal. Calcd. for $C_{20}H_{18}PS$: C, 74.77; H, 5.61; P, 9.66; S, 9.97. Found: C, 74.99; H, 5.35; P, 9.36; S, 10.53.

The infrared spectrum of a potassium bromide pellet of this material showed peaks at 3.28 (s), 6.23 (m), 6.35 (s), 6.75 (s), 6.99 (m), 7.5 (s), 7.65 (s), 8.18 (s), 8.4 (s), 8.5 (s), 8.65 (s), 9.0 (m), 9.1 (m), 9.75 (s), 10.02 (m), 10.12 (m), 11.85 (m), 12.25 (m), 12.4 (m), 13.25 (w), 13.5 (w), 13.95 (m), 14.1 (w), and 15.0 (s) μ.

A deuteriochloroform solution of IV gave a p.m.r. spectrum showing the phenyl protons centered at δ = 7.5 p.p.m. and a set of four peaks in the same order and magnitude as found in I but shifted to lower field strength by 5 c.p.s. As in I, the overlap with the phenyl protons made it impossible to determine accurately an area ratio.

Oxidation of *trans*-β-Styryldiphenylphosphine Sulfide to *trans*-Styryldiphenylphosphine Oxide.—A solution of 0.5 g. (0.00157 mole) of IV in glacial acetic acid was treated with 30% hydrogen peroxide and heated to a boil. After standing at room temperature overnight, crystals were obtained, which were shown by melting point, mixture melting point, and infrared and p.m.r. spectra to be I.

Acknowledgment.—This work was carried out under a grant from the Petroleum Research Fund of the American Chemical Society. All of the p.m.r. spectra were obtained by Mr. Gordon Boudreaux of the Cotton Physical Properties Division of U. S. Southern Regional Utilization and Research Laboratories at New Orleans, Louisiana. The gas chromatographic analysis was carried out with the help of Mrs. V. Cirino of the same laboratories.