purified by streaking an ether solution on Eastman chromagram sheet and using benzene–hexane (90:10) as the solvent system. Compound **4** appeared as an orange band with R_f 0.85. Compound **5** was a colorless band, visible under ultraviolet light, with R_f 0.077. Shiny red crystals of **4** melted at 140–141° when the sample was placed in the Mel-Temp melting point apparatus at 120° and heated 2 deg/min. The infrared spectrum of a KBr disk showed a maximum at 1745 cm^{-1}. The ultraviolet–visible spectrum in $HOCH_2CH_2OCH_3$ showed maxima at 449 mμ (ϵ 513), 348 (346–350) (1.98×10^4), 238 (2.48×10^4), and a shoulder at 255 (1.89×10^4).

Anal. Calcd for $C_{27}O_{20}O_2N_2$: C, 80.19; H, 4.95; N, 6.93. Found: C, 80.06; H, 4.98; N, 7.27.

Preliminary studies of the rearrangement at 101.5 ± 0.1° in $HOCH_2CH_2OCH_3$ were followed by changes in absorption at 350 mμ. Light absorption of **4** [4] and **5** [5] at this wavelength followed Beer's law. The absorption of light by **4** and **5** (ϵ_5^{350} 1.43×10^4) at this wavelength was additive. The expression for [4] was $\epsilon_4^{350}[4] + \epsilon_5^{350}[C_0 - [4]] = OD_{obsd}$. The first-order rate constant was estimated to be 1.11×10^{-4} sec^{-1}. The rearrangement product was shown to be identical with **5** by a mixture melting point and similarity in the spectrum.

Registry No.—**4a**, 13144-85-9; **5**, 13144-86-0.

Acknowledgment.—We are grateful to the Research Corp., to the City College General Faculty Committee on Research, and to the NSF Undergraduate Student Participation Program for partial support.

Retention of Configuration in Nucleophilic Vinylic Halide Substitution. II. Stereospecific Preparation of Vinylarsines

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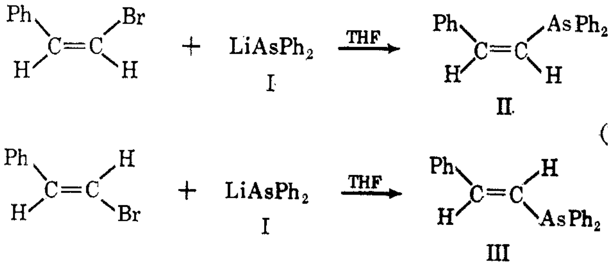
Received February 7, 1967

In a study of nucleophilic vinylic halide substitution, we have reported the stereospecific replacement of bromine in the β-bromostyrenes by lithium diphenylphosphide.[2,3] This reaction was shown to occur with retention of configuration leading to the production of stereochemically pure β-styryldiphenylphosphines, having the same configuration as the starting halide.[3]

Extension of this work has shown that lithium diphenylarsenide (I) also reacts in the same manner to give stereochemically pure β-styryldiphenylarsines, retaining the configuration of the starting halide (eq 1).



(1)

Reaction of the β-bromostyrenes with the mixture of lithium diphenylarsenide and phenyllithium, obtained by the lithium cleavage of triphenylarsine, led to a complex mixture of products.

We have described a convenient preparation of phenyllithium free tetrahydrofuran (THF) solutions of lithium diphenylphosphide from triphenylphosphine and lithium.[4] In an analogous manner, a tetrahydrofuran solution of I was prepared from triphenylarsine and lithium metal, followed by treatment with an equimolar amount of *t*-butyl chloride (eq 2).

$$Ph_3As + 2Li \xrightarrow{THF} \underset{I}{Ph_2AsLi} + PhLi \qquad (2)$$

$$PhLi + (CH_3)_3CCl \xrightarrow{THF} PhH + (CH_3)_2C{=}CH_2 + LiCl$$

The reaction of I with *cis*-β-bromostyrene gave *cis*-β-styryldiphenylarsine (II), isolated in 61% yield, mp 91–92°.

The reaction of I with commercial *trans*-β-bromostyrene gave *trans*-β-styryldiphenylarsine (III), isolated in 70% yield, bp 187–189° (0.25 mm).

Reaction of excess I with either II or III caused no isomerization, nor addition to give phenylethylenebis(diphenylarsine). Complete isomerization of II to III occurred with a small amount of PCl_5 in refluxing benzene after 10 hr, as shown by gas chromatographic analysis.

The 60-Mc nuclear magnetic resonance (nmr) spectrum of II in $DCCl_3$ solution shows a phenyl complex at τ 2.65 and one-half of the AB vinyl proton signal at τ 3.36 (J = 12 cps). The other half of this vinyl signal is hidden under the phenyl complex as indicated by the relative ratios of 16:1. The spectrum of III shows only a complex centered at τ 2.70. The coupling constants for vinyl proton signals found by Cullen, *et al.*,[5] for $Me_2AsCH{=}CHCF_3$ were J_{cis} = 13 cps and J_{trans} = 18 cps. Comparison of these values with the coupling constant (J = 12 cps) found for II indicate it to be the *cis* isomer.

The stereochemical purity of the β-styryldiphenylarsines was verified by gas chromatographic analysis on a $^1/_8$ in. × 4 ft, 3% SE 30 column at 200°. Neither II nor III isomerized under these conditions. The reaction of I with pure *cis*-β-bromostyrene gave only II. Reaction of I with commercial *trans*-β-bromostyrene (containing 10% of the *cis* isomer) gave II and III in a ratio of 1:10.

Although other nucleophilic vinylic halide substitutions with retention of configuration are known,[2,3,6-9] this is the first instance where a metalloorgano arsenide has been the nucleophile.

Experimental Section

General Procedure.—All reactions, unless otherwise stated, were run under nitrogen in a dry, three-neck, 500-ml flask fitted with dropping funnel, gas inlet tube, condenser, gas outlet tube, and magnetic stirrer. Proton nmr spectra were taken on a Varian nmr spectrometer, Model A-60, using a tetramethylsilane standard (τ 10.0). All of the gas–liquid partition chromatography was done on a Microtech Model DSS instrument, having a flame ionization detector, using a $^1/_8$ in. × 4 or 10 ft column (3% SE

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30 on Chromosorb). Normal column temperatures for arsine chromatographic analysis were 200–215° with inlet and detector blocks at least 50° higher.

The lithium diphenylarsenide was prepared in 0.1-mole quantities and diluted to 100-ml solutions in THF. Reactions employed aliquots of this quantity. Care was taken to dry all reagents before reaction. The THF was dried over calcium hydride and filtered before use.

Preparation of Phenyllithium-Free Lithium Diphenylarsenide (I).—Triphenylarsine (30.6 g, 0.1 mole) was dissolved in 70 ml of THF (calcium hydride dried) and placed in a flask under nitrogen. Lithium metal rod (1.4 g, 0.02 mole) was washed with ether, pounded flat, cut into small squares, and added to the stirred arsine solution. After a 5-min induction period, the solution turned deep red (transient greenish yellow). As the reaction proceeded, the color darkened and enough heat was generated to cause the THF to come to reflux. After 20 min, the reaction began to subside. The mixture was allowed to cool to ambient temperature and stirred for 2 hr. The dark blackish red solution was transferred, under nitrogen, to a dropping funnel and the excess lithium was left in the funnel as the red solution was added to a clean setup. Since lithium is less dense than the solution, the separation was easily accomplished. To this solution 9.2 g (0.1 mole) of *t*-butyl chloride, in 25 ml of THF, was added slowly. Cooling was required to keep the solution near room temperature. When the addition was complete and no further gas was evolved, the color lightened to a yellower red. This solution was then transferred to a clean dropping funnel, diluted to 100 ml, and used as the stock solution for all reactions. It should be used within 12 hr to obtain good yields.

Preparation of *cis*-β-Styryldiphenylarsine (II).—In a dry setup was placed 1.83 g (0.01 mole) of *cis*-β-bromostyrene in 20 ml of THF. Lithium diphenylarsenide solution was decolorized immediately upon contact with the halide and the reaction was very exothermic. Upon completion of the addition, the solution was allowed to cool and the THF was removed with a rotary evaporator. The resulting oil was shaken with weakly basic water (approximately 5% KOH). After several minutes the oil solidified and was filtered. The resulting *cis*-β-styryldiphenylarsine was recrystallized from ethanol, yield 2.1 g (63.2%), mp 91–92°.

Anal. Calcd for $C_{20}H_{17}As$: C, 72.28; H, 5.14; As, 22.58. Found: C, 72.02; H, 5.23; As, 22.75.

The proton nmr spectrum of a deuteriochloroform solution of the *cis*-β-styryldiphenylarsine showed a complex phenyl proton signal centered at τ 2.65 and one-half of an AB vinyl proton signal, a doublet, J = 12 cps, at τ 3.5.

Preparation of *trans*-β-Styryldiphenylarsine (III).—In a dry setup, lithium diphenylarsenide solution, 25 ml (0.025 mole), was added slowly to 4.3 g (0.025 mole) of *trans*-β-bromostyrene (Eastman, contains 10% of *cis* isomer) in 25 ml of THF. The reaction was very exothermic and the arsenide was immediately decolorized upon contact with the halide. When the addition was complete, the solution was allowed to cool, the solvent was stripped off, and the resulting oil was distilled under vacuum. A small amount of unreacted *trans*-β-bromostyrene was recovered as forerun. The product, *trans*-β-styryldiphenylarsine, was collected (bp 187–189° at 0.25 mm), yield 5.9 g (71.3%). The proton nmr spectrum of a deuteriochloroform solution of III showed a complex proton signal at τ 2.7.

Gas Chromatographic Analysis of *cis*- and *trans*-β-Styryldiphenylarsines.—The isolated *cis*- and *trans*-β-styryldiphenylarsines were found to pass unisomerized through a $^1/_8$ in. × 4 ft, 3% SE 30 column at 200° with retention times of 1–1.5 min. The difference in retention times between the two isomers was sufficient to allow their separation and positive identification. A reaction mixture of 0.9 g (0.005 mole) of *cis*-β-bromostyrene and 5 ml (0.005 mole) of lithium diphenylarsenide in 10 ml of THF was prepared in a septum-topped bottle by the use of syringes. A similar solution, employing commercial *trans*-β-bromostyrene instead of the *cis* isomer was also prepared. The *cis* mixture showed only a single peak (aside from a small peak identified as unreacted triphenylarsine) which had a retention time identical with that of the isolated *cis*-β-styryldiphenylarsine. The *trans* mixture showed two peaks (beside the triphenylarsine peak). The ratio of the shorter retention time peak (identical with the isolated *cis* isomer) to the longer retention time peak (identical with the isolated *trans* isomer) was found to be 1:10 by mechanical integration. The commercial *trans*-β-bromostyrene was shown to contain 10% *cis* isomer.

Isomerization of *cis*- to *trans*-β-Styryldiphenylarsine. A. Butyllithium.—A solution of approximately 0.5 g of *cis*-β-styryldiphenylarsine in 20 ml of THF was treated with 20 ml of a 15% solution of butyllithium in hexane at reflux for 2 hr. The mixture was allowed to stand under nitrogen for 24 hr and analyzed by vapor–liquid preparative chromatography at 200°. There was no *trans* isomer present.

B. Phosphorus Trichloride.—In a similar reaction, the *cis*-arsine was refluxed with 2 g of phosphorus trichloride in 200 ml of THF. No isomerization occurred as shown by gas chromatography.

C. Phosphorus Pentachloride.—To a solution of approximately 0.5 g of *cis*-β-styryldiphenylarsine in 20 ml of THF, approximately 0.1 g of phosphorus pentachloride was added. The solution was refluxed for 2 hr. Gas chromatographic analysis at 200° showed only the *trans* isomer to be present.

Attempted Addition of Lithium Diphenylarsenide to the Styrylarsines.—To 0.5 g (0.0015 mole) of *cis*-β-styryldiphenylarsine in 20 ml of THF was added 5 ml (0.005 mole) of lithium diphenylarsenide. This solution was allowed to stand for 24 hr. Gas chromatographic analysis of the crude reaction mixture showed only the *cis* isomer to be present. Evaporation of the solvent and extraction of the semisolid with basic water (5% KOH) gave a solid identical with starting material as shown by mixture melting point determinations. The proton nmr spectrum of a deuteriochloroform solution of the crude solid before recrystallization showed no methylene or methyne proton signals, which would have indicated the presence of small amounts of phenylethylenebis(diphenylarsine).

Registry No.—I, 1013-87-2; II, 13084-50-9; III, 13084-51-0.

Acknowledgments.—This work was done under Grant No. 2326-A1,4 from the Petroleum Research Fund of the American Chemical Society.

Rearrangements of a 2-Vinylaziridine

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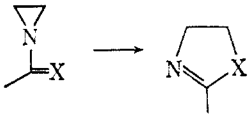
Received February 28, 1967

Aziridines possessing unsaturated substituents on nitrogen readily undergo ring expansion to 1-azacyclopentene derivatives.[1,2] Formally analogous to the vinylcyclopropane–cyclopentene isomerization, these rearrangements have been effected by nucleophiles, acids, and heat. It was of interest to determine whether similar processes would occur in the 2-vinylaziridine system.



X = C<, O, S, N—

The model compound I was prepared by photolysis of the *p*-bromophenyl azide–isoprene adduct, a method that has been previously described.[3] On heating in xylene solution, I was converted in high yield to an isomeric compound (II). The infrared spectrum of the

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