ture in a tightly stoppered flask with an 8-9% solution of ammonia or methylamine in absolute ethanol containing approximately a 40% excess of amine. After 3 days the mixture was evaporated to dryness *in vacuo* and treated with a small volume of water. The mixture was made strongly basic with 5 *N* NaOH and the insoluble oil was extracted into ethyl acetate or ether. The oil which remained after evaporation *in vacuo* of the organic solvent was either crystallized and purified or converted into the hydrochloride. A portion was also converted into the picrate.

Stereospecific Vinyl Halide Substitution. III. *cis*- and *trans*-Vinylenebis(diphenylarsines) and Their Rhodium Complexes

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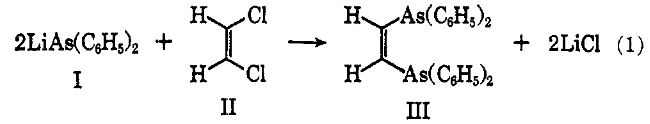
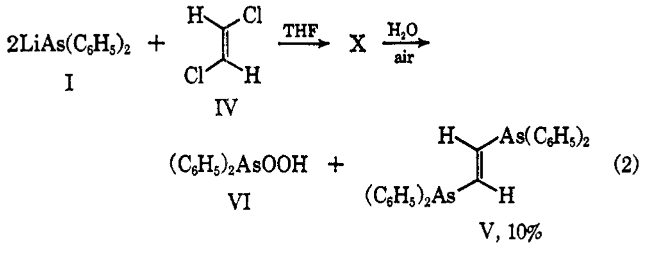
During a study of vinylarsines we reported the stereospecific replacement of the vinyl bromides in the β-bromostyrenes by lithium diphenylarsenide (I).[2] This replacement occurred with retention of configuration.

We wish to report that lithium diphenylarsenide (I) (prepared from triphenylarsine and lithium)[2] reacts with *cis*-1,2-dichloroethene (II), in tetrahydrofuran solution, to give *cis*-vinylenebis(diphenylarsine) (III) in 61% yield (eq 1).


(1)

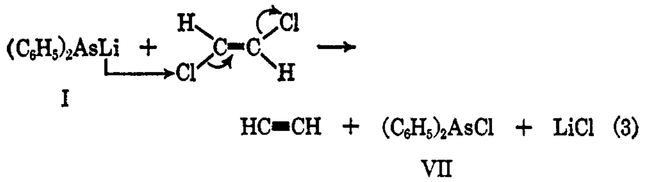
Treatment of I with *trans*-1,2-dichloroethene (IV) under the same conditions produced only 10% of *trans*-vinylenebis(diphenylarsine) (V). The major product isolated was diphenylarsinic acid (VI) (eq 2).


(2)

This is in contrast to the reaction of lithium diphenylphosphide with *cis*- and *trans*-1,2-dichloroethene which leads to *cis*- and *trans*-vinylenebis(diphenylphosphine), respectively, both in excellent yields.[3] Changing the order of addition of reactants did not greatly alter the yields of V and VI.

No *trans*-diarsine (V) was obtained from the reaction of *cis* dichloride (II), and no *cis*-diarsine (III) was obtained from the *trans* dichloride (IV). Therefore an elimination–addition sequence can be excluded since a common intermediate such as acetylene or chloroacetylene would lead to the same product(s) from both isomeric dichlorides. Evidence has been obtained supporting the idea that *trans*-diarsine (V) is stable under the conditions employed. This has been shown by vpc analysis on a 3% SE-30 column at 250° using a flame ionization detector.

It seems that a reaction path lower in activation energy than the halide replacement and leading to diphenylarsenic acid (VI) (or precursor) is possible in the reaction of I with IV. A possible explanation could be halogen–metal interchange, which seems to occur more readily with lithium arsenides than with lithium phosphides. This would be favored with IV (over II) due to the *trans* coplanarity of the halogens in IV and consequent ease of elimination (eq 3).


(3)

Depending on the order of addition of reagents, chlorodiphenylarsine (VII) may or may not react with excess I to give tetraphenyldiarsine (VIII) (eq 4).

$$\underset{\text{VII}}{(C_6H_5)_2AsCl} + \underset{\text{I}}{LiAs(C_6H_5)_2} \longrightarrow \underset{\text{VIII}}{[(C_6H_5)_2As\text{-}]_2} + LiCl \quad (4)$$

Both VII and VIII will react with water and air to produce VI and work is now in progress in an attempt to elucidate the actual pathway by which VI is produced.

An elimination–addition sequence would involve a common intermediate (chloroacetylene) for both the *cis*- and *trans*-dichloroethenes and therefore both reactions would be expected to produce the same or a mixture of isomers. In fact, however, gas chromatographic analysis of the crude reaction mixtures shows that only *one* diarsine is produced from the *cis*-dichloroethene and that it has a distinctly different retention time from the *one* diarsine produced from the *trans*-dichloroethene. Thus the two reactions give different, single products with no mixtures of the two diarsines being found in the same reaction mixture.

Support for the structure assignments III and V as the *cis* and *trans* isomers, respectively, comes from elemental analysis, infrared and proton nmr spectra, and dipole moment measurements. These moments are given in Table I along with those of *cis*- and *trans*-vinylenebis(diphenylphosphine) whose structures have previously been established.[3] From these data, it is clear that the structure assignments made above are the correct ones.

TABLE I
DIPOLE MOMENTS OF
cis- AND *trans*-($(C_6H_5)_2M—CH{=}CH—M(C_6H_5)_2$)

Isomer	M = P	M = As
cis	1.96 D ± 0.21	1.37 D ± 0.09
trans	0.99 D ± 0.09	0.97 D ± 0.09

Further support for these structure assignments comes from the differing behavior of III and V when allowed to react with rhodium dicarbonyl chloride dimer (IX). The reaction of III produces an orange

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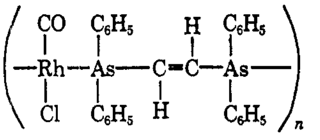
(1) (a) NASA Predoctoral Fellow, 1964–1967; (b) NDEA Predoctoral Fellow, 1966–1968.

(2) A. M. Aguiar and T. G. Archibald, *J. Org. Chem.*, **32**, 2627 (1967).

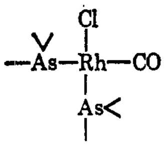
(3) A. M. Aguiar and D. J. Daigle, *J. Amer. Chem. Soc.*, **86**, 2299 (1964).

monomeric complex (X) containing two diarsine moieties and no carbonyl groups which can be readily isolated as the tetrafluoroborate salt from methanol. The complex has an equivalent conductivity of 79.7 ohm^{-1} cm^{-1} in nitromethane solution (10^{-3} M) and is thus a 1:1 electrolyte (typical conductivities for *ca.* 10^{-3} *M* solutions of 1:1 electrolytes in nitromethane are in the range 80–100 ohm^{-1} cm^{-1}).[4-6] It thus appears to be strictly analagous to those complexes formed from IX and ethylenebis(diphenylphosphine)[7] and *cis*-vinylenebis(diphenylphosphine).[3,8] We therefore also formulate X as a square planar complex of Rh(I) containing chelating ligands. This could only be possible if the ligand in the complex were in the *cis* configuration. There is, of course, the possibility that III is a *trans* isomer that has isomerized upon reaction with IX as has been found to occur when the analogous *trans*-vinylenebis(dimethylarsine) is treated with Pd(II).[9] However, we feel that this is quite unlikely since the dipole moment data show that III is undoubtedly the *cis* isomer at the beginning. (See also below.)

By contrast, treatment of V with IX produces a very insoluble yellow complex (XI) containing only *one* diarsine moiety per rhodium. The presence of a strong band in the infrared at 5.04 μ shows that there is still one terminal carbonyl group present. Such behavior is characteristic of the reactions of non-chelating arsines and phosphines with IX, the usual product being *trans*-Rh(CO)ClL$_2$ (L = phosphine or arsine).[10] Thus the production of a carbonyl-containing species strongly suggests that V is not capable of chelating and is therefore most probably the *trans*-diarsine. Since it is bifunctional, it would be expected that both ends would coordinate which would lead to a polymeric complex. This is supported by the extreme insolubility of XI. Furthermore, an analogous complex is formed from IX and the known *trans*-vinylenebis(diphenylphosphine)[3,8] thereby strongly suggesting that V is also a *trans* isomer. The infrared spectrum of (XI) shows, in addition to the strong band at 5.04, a weak shoulder at *ca.* 5.00 μ. We suggest that this is due to a small proportion of *cis* attachment of the diarsine to rhodium in the polymer *viz.*



$$\left(-\underset{\mathrm{Cl}}{\overset{\mathrm{CO}}{\mathrm{Rh}}}-\underset{\mathrm{C_6H_5}}{\overset{\mathrm{C_6H_5}}{\mathrm{As}}}-\underset{\mathrm{H}}{\mathrm{C}}=\overset{\mathrm{H}}{\mathrm{C}}-\underset{\mathrm{C_6H_5}}{\overset{\mathrm{C_6H_5}}{\mathrm{As}}}-\right)_n$$



The complex *cis*-Rh(CO)Cl(P(C$_6$H$_5$)$_3$)$_2$ has recently been reported and it was shown here that the position of the carbonyl band was about 0.05 μ lower than for the *trans* isomer.[11]

When V is treated with IX in methanol in the presence of tetrafluoroborate ion, only the insoluble yellow complex XI is formed and no BF$_4^-$ is incorporated into the complex. Thus under the conditions employed V does not isomerize to a species capable of chelating and hence we conclude that III, which produces a chelate complex, must be the *cis* isomer.

Experimental Section

All reactions involving lithium diphenylarsenide were carried out in dry apparatus under nitrogen. Tetrahydrofuran was dried over calcium hydride and filtered before use. All other chemicals were reagent grade and were used as received. Infrared spectra were obtained on Beckmann IR-5A and IR-8 instruments on potassium bromide pellets and Nujol mulls. Proton nmr spectra were obtained on a Varian A-60 instrument using deuteriochloroform as a solvent and tetramethylsilane as an internal standard. The gas chromatographic studies utilized a Micro-Tek instrument with a 3% SE-30 column and flame-ionization detector. Conductivity measurements were made using a Thomas-Serfass Model RCM15B1 conductivity bridge, and dipole moment measurements were determined on a General Radio 1615-A capacitance bridge, a Balsbaugh 2TN50 cell, and a Bausch and Lomb Modified Abbe-type refractometer on 10^{-3} *M* benzene solutions. Microanalyses were by Galbraith Laboratories, Knoxville, Tenn. All melting points are uncorrected.

Reaction of *cis*-1,2-Dichloroethene.—In a dry apparatus, under nitrogen, was placed 1.2 g (0.0125 mol) of *cis*-1,2-dichloroethene in 40 ml of tetrahydrofuran (THF). A THF solution of lithium diphenylarsenide[2] (25 ml, 0.025 mol) was added slowly. The reaction was very exothermic and immediate decolorization of the arsenide solution occurred upon contact with the halide. When the addition was complete, the slightly yellow solution was allowed to cool. Water (1 ml) was added and an exothermic reaction occurred with complete decolorization of the solution. This hydrolyzed solution was allowed to stand 5 min and the solvent was removed on a rotary evaporator. The resulting oil was extracted with basic water and a solid formed. Filtration and recrystallization from ethanol gave 3.7 g (61%) of *cis*-vinylenebis(diphenylarsine) (III), mp 112–113.

Anal. Calcd for C$_{26}$H$_{22}$As$_2$: C, 64.49; H, 4.55; As, 30.95. Found: C, 64.78; H, 4.62; As, 30.60.

Infrared absorptions (KBr) appeared at 3.3 (w), 6.45 (w), 6.8 (m), 7.0 (m), 7.7 (w), 7.9 (m), 8.45 (w), 8.65 (w), 9.3 (m), 9.4 (m), 9.8 (m), 10.0 (m), 11.05 (w), 13.7 (s), and 14.5 (s) μ.

The 60-MHz proton nmr spectrum of the *cis*-vinylenebis(diphenylarsine) (III) in deuteriochloroform solution showed a phenyl proton signal centered at τ 2.7 and a vinyl proton singlet at 2.55. The relative ratios were 10:1, respectively.

Reaction of *trans*-1,2-Dichloroethene.—To 50 ml of a THF solution of 1.2 g of *trans*-1,2-dichloroethene (0.0125 mol) was added slowly 25 ml of THF solution of the lithium diphenylarsenide (0.025 mol). The reaction was very exothermic and decolorization of the arsenide solution occurred. The solvent was stripped off and the resulting oil was extracted with aqueous base (5% KOH solution). The oil turned into a semisolid, and the water was decanted. Trituration of the semisolid with an ethanol-acetone mixture (6:1) gave a solid which was filtered off. Recrystallization from ethanol gave a 10% yield of *trans*-vinylenebis(diphenylarsine) (V), mp 103–104.

Anal. Calcd for C$_{26}$H$_{22}$As$_2$: C, 64.49; H, 4.55; As, 30.95. Found: C, 64.45; H, 4.65; As, 30.97.

Infrared bands (KBr) were at 3.3 (w), 6.3 (w), 6.8 (m), 7.0 (m), 7.7 (w), 7.95 (w), 8.45 (w), 8.8 (m), 9.3 (m), 9.4 (m), 9.8 (m), 10.0 (m), 10.2 (m), 11.05 (w), 13.7 (s), and 14.5 (s) μ.

The 60-MHz proton nmr spectrum of a deuteriochloroform solution of V showed a phenyl proton signal at τ 2.6, and a vinyl proton singlet at 2.9, with a relative ratio of 10:1.

This compound showed a depressed, mixture melting point with the compound prepared from *cis*-1,2-dichloroethene.

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(10) L. Vallarino, *J. Chem. Soc.*, 2287 (1957).

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Diphenylarsenic acid was obtained in 60% yield by acidification of the alkaline water solution. Infrared and nmr spectra as well as melting point and mixture melting point determinations with an authentic sample were used to establish the identity of this product.

Bis(*cis*-vinylenebis(diphenylarsine))rhodium(I) Tetrafluoroborate Methanol Solvate.—To 0.1 g (0.26 mmol) of $[Rh(CO)_2Cl]_2$ in 15 ml of anhydrous methanol under nitrogen was added 0.5 g (1.04 mmol) of *cis*-$(C_6H_5)_2AsCH{=}CHAs(C_6H_5)_2$ in 10 ml of anhydrous methanol. The yellow orange solution darkened immediately and carbon monoxide was evolved. The solution was refluxed for 5 min and a stoichiometric amount of $NaBF_4$ was added. Upon adding *ca.* 15 ml of diethyl ether and cooling, bright orange crystals of X (0.4 g, 80%) formed. These were filtered off, washed with ether, and dried *in vacuo*, mp 238 dec.

Anal. Calcd for $C_{52}H_{44}As_4RhBF_4 \cdot CH_3OH$: C, 53.47; H, 4.09; As, 25.17; F, 6.38. Found: C, 52.72; H, 4.09; As, 25.74; F, 5.94.

The infrared spectrum (Nujol mull) showed bands due to the diarsine, the BF_4^- ion, and a sharp band of medium intensity at 2.84 μ which can be assigned to the O–H stretching frequency of methanol. No band in the region 4.75–5.60 μ was observed indicating that all the carbonyl groups had been displaced.

Chlorocarbonyl(*trans*-vinylenebis(diphenylarsine))rhodium(I).—Benzene solutions (*ca.* 10 ml each) of 0.1 g (0.26 mmol) of rhodium dicarbonyl chloride dimer and 0.25 g (0.52 mmol) of V were combined at room temperature under nitrogen. Immediate effervescence occurred as carbon monoxide was evolved and the yellow solution became orange. Slow addition of diethyl ether accompanied by mild agitation with a nitrogen stream caused the precipitation of pale yellow microcrystals of XI. These were filtered off, washed well with hot N,N-dimethylformamide, and dried *in vacuo*. The complex decomposes without melting at 235°.

Anal. Calcd for $C_{27}H_{22}As_2OClRh$: C, 49.83; H, 3.41; Cl, 5.45. Found: C, 49.91; H, 3.43; Cl, 5.97.

The infrared spectrum of XI in a Nujol mull showed, in addition to bands due to the diarsine, a strong band at 5.04 with a weak shoulder at 5.00 μ. In addition, the sharp "*trans*" band at 10.2 has shifted to 10.35 μ while becoming weaker and broader.

The complex is extremely insoluble in all common organic solvents thus rendering a molecular weight determination impossible.

Registry No.—III, 15924-20-6; V, 15924-21-7; X, 15956-79-3.

Acknowledgment.—Thanks are extended to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research, and to the National Science Foundation for its contribution toward the cost of the instruments used. We also wish to acknowledge the help of Mr. George Linthicum and of Mr. Jonathan Bullock for obtaining the dipole moment data.

The Thermal Isomerization of Abietic Acid[1a]

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Received August 28, 1967

It has been reported from this laboratory that levopimaric acid,[2] neoabietic acid,[3] and palustric acid,[4] on heating, isomerize to give abietic acid. The reverse reaction, that is, the thermal isomerization of abietic acid to give levopimaric and palustric acids, has not been reported. The isolation of 1% of neoabietic acid from abietic acid which had been heated at 300° for 20 min was noted.[5] It was therefore decided to investigate the isomerization of abietic acid at an elevated temperature to determine its behavior in detail.

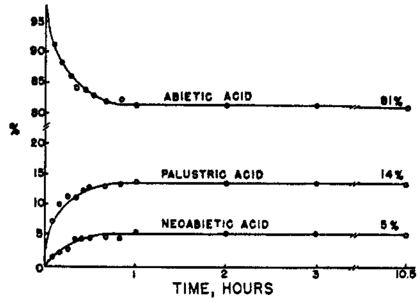

Figure 1.—The isomerization of abietic acid at 200°.

Samples of pure abietic acid were sealed in glass tubes under nitrogen and immersed in a 200° bath. Tubes were removed at intervals and the product analyzed by means of glpc,[6] optical rotation, and ultraviolet absorption spectra. Surprisingly, it was found that abietic acid undergoes a rapid isomerization to give a final equilibrium mixture of 81% abietic, 14% palustric, and 5% neoabietic acid (*cf.* Figure 1.)

Gas–liquid partition chromatography indicated only three peaks in the curve. These peaks were identified by means of relative retention times, infrared and ultraviolet absorption spectra, and optical rotation. The absence of any significant amount of levopimaric acid in the final 81%:14%:5% isomerization mixture was confirmed by the value of the optical rotation of the collected palustric and/or levopimaric peak.[6]

The isomerization of abietic acid was repeated at 180°. The reaction was found to follow first-order kinetics with respect to abietic acid for the first hour of the isomerization; $k = 3.7 \times 10^{-5}\ sec^{-1}$ at 180° ($t_{1/2} = 5.2$ hr).

The isomerization at 200° of palustric, levopimaric, and neoabietic acids was then carried out for the first time to the point at which no further isomerization occurred. It was found that all four (including abietic acid) conjugated dienoic resin acids exhibit the same final distribution of the three resin acids, namely 81% abietic, 14% palustric, and 5% neoabietic acids. This confirms the fact that a true dynamic equilibrium is reached among these three acids at 200°.

The acid isomerization of levopimaric acid[7] and neoabietic acid[8] at room temperature in the presence of mineral acids has been described. The isomerization of the four conjugated dienoic resin acids was repeated in 0.5 *N* ethanolic hydrochloric acid. It was found that all four acids eventually reached the same final distribution of resin acids, namely 93% abietic acid, 4% palustric acid, and 3% neoabietic acid. This confirms

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[1] (a) Presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967. (b) National Academy of Sciences, National Research Council Postdoctoral Fellow. (c) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

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