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.

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The Thermal Isomerization of Abietic Acid[1a]

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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.

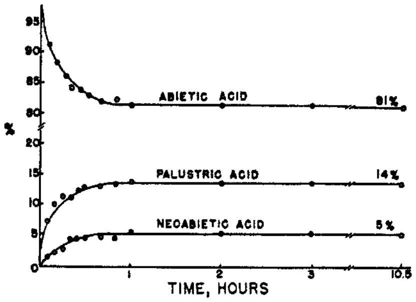

Figure 1.—The isomerization of abietic acid at 200°.

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; $k = 3.7 \times 10^{-5}\ \text{sec}^{-1}$ 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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the fact that a dynamic equilibrium is reached in this system involving abietic, palustric, and neoabietic acids. The isomerization at 200° probably involves catalysis by the carboxylic acid group. The difference in temperature (25 *vs.* 200°) and environment probably accounts for the difference in the composition of the final equilibrium mixtures. The palustric acid peak was again collected, and, based on the observed rotation, it would appear that not more than a trace of levopimaric acid is present in the final equilibrium mixture. Previous workers[7] employing a partition chromatographic analytical method at room temperature reported values of 93% abietic, 4% palustric, and 2% neoabietic acids for the acid isomerization of abietic acid under the same conditions.

The acid-induced equilibria of the four conjugated dienoic resin acids probably involve a common carbonium ion.[8,9] The results of the isomerization experiments show an interesting difference in what might be expected in terms of thermodynamic stabilities.

It is interesting to note that the half-lives of the four conjugated dienoic resin acids at 200° correlate with the absorptivity of the resin acids ($t_{1/2}$, min; absorption at λ_{max}, mμ: levopimaric acid, 15, 19; palustric 40, 31; abietic 75, 77; neoabietic 120, 80). It is generally held that the absorptivity of the resin acids is related to ring strain.

It is of further interest to note that in the case of palustric acid, protonation must occur from the α side exclusively at C-9 or else a 9-β-H abietic and neoabietic acid would be formed. No appreciable amounts of any unknown peaks were observed in the glpc analyses.

Experimental Section

All optical rotations were determined in 95% ethanol at *c* 1.

Thermal Reactions.—About 0.2 g of each acid was placed in a glass Carius tube. The air in each tube was replaced with nitrogen. The tubes were then sealed under vacuum, submerged in an oil bath, and heated at 200°.

Isomerization of Abietic Acid at 200°.—The change in acid composition with time is plotted in Figure 1. Only three peaks were observed in the glpc analysis through 10.5 hr (no disproportionation observed). These were identified as methyl abietate, palustrate, and neoabietate by means of relative retention times, infrared and ultraviolet absorption spectra, and optical rotation. The value for the methyl palustrate peak was $[\alpha]^{25}\text{D}$ +65.2 (theory +68.4).

Isomerization of Abietic Acid in the Presence of Potassium Hydroxide at 200°.—Abietic acid was dissolved in methanol containing potassium hydroxide (1:0.05 mole ratio). The solvent was removed under vacuum. The residual solid was heated at 200° in the usual manner. The system reached the equilibrium distribution in about 8 hr.

Isomerization of Palustric, Levopimaric, and Neoabietic Acids at 200°.—A final equilibrium distribution of 81% abietic, 14% palustric, and 5% neoabietic acid was obtained in all cases. Essentially no disproportionation was observed at the end of 21.5 hr in the case of neoabietic and levopimaric acids. A total of 6.1% of resin acids other than abietic, palustric, and neoabietic acids were observed to be present at the end of 24 hr in the case of palustric acid.

Acid Isomerization of Abietic, Levopimaric, Palustric, and Neoabietic Acids.—A 1% solution of each of the four conjugated dienoic resin acids was made in a 0.5 *N* ethanolic solution of hydrochloric acid. Aliquots were removed periodically and poured into water. The resin acids were immediately extracted with ether, the ether was stripped off (quantitative yield), and the residue was analyzed. The methyl palustrate peak exhibited $[\alpha]^{25}\text{D}$ +67.7° (theory for methyl palustrate is $[\alpha]^{25}\text{D}$ +68.4°). The final equilibrium distribution for all four acids (50 hr at room temperature) was 93% abietic, 4% palustric, and 3% neoabietic acids. No disproportionation was observed in any of the four acids.

Registry No.—Abietic acid, 514-10-3.

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Oxidation of 3β-Acetoxy-14α-methyl-5α-cholest-7-ene[1]

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The susceptibility of 3β-acetoxy-14α-methyl-5α-cholest-7-ene (I) to oxidation by chromium trioxide has already been noted, and this property was used as a means of removing olefin I from a reaction mixture.[2] At the time oxidation was performed on a microscale, and the products were not further investigated. Recently, it became necessary to review the reaction in more detail, and one of the products has now been found to arise by an unusual allylic oxidation.

Small-scale studies showed that oxidation (room temperature) of olefin I with chromium trioxide in aqueous acetic acid was essentially complete in 1 hr. When the reaction was carried out on a larger scale, thin layer chromatography (tlc) of the crude product showed three main spots. Preparative tlc (on silica) led to three crystalline products, each of which was subjected to further purification by the same technique. The main product was the expected 7,11-dione II.[3] A thin band close to the leading edge of the diketone (II) zone provided saturated ketone III,[4] and a third zone gave a new compound which showed an infrared band at 1670 cm^{-1}, typical of an α,β-unsaturated ketone. The latter substance was not Δ^8-7-ketone IV as anticipated. This possibility was eliminated by comparison with an authentic sample, synthesized by Jones oxidation of 8α,9α-epoxy 7α-alcohol Va to ketone Vb followed by treatment with zinc in acetic acid.[5]

A rotatory dispersion curve of the new ketone exhibited a positive Cotton effect in methanol, and in petroleum ether solution showed all the fine structure associated with a Δ^7-6-keto system[6] (Figure 1). The ultraviolet absorption curve showed a maximum at 245

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[1] (a) Steroids and Related Natural Products. XLV. For part XLIV, see T. R. Kasturi, G. R. Pettit, and K. A. Jaeggi, *Chem. Commun.*, 644 (1967). (b) The present contribution was supported by Public Health Service Research Grant 1 RO1 CA-10115-01 from the National Cancer Institute and by National Science Foundation Grant No. GB-4939.

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