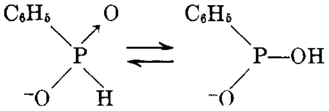
absorption bands at the appropriate frequencies. In this investigation, direct observation of the absorption at these P–H and P–D stretching frequencies in sodium phenylphosphinate was used as a qualitative measure of the exchange taking place in the phosphinic acid system. A more precise measure of the rate of exchange was obtained by following the increase in the intensity of the absorption at the O–H stretching frequency in deuterium oxide solutions containing the acid or its salt.

Since, in common with the majority of kinetic studies which have been made on hydrogen isotope exchange reactions, simultaneous exchange reactions can take place at points in the molecule which are not involved in the reaction of interest, the data are often at best interpreted on the basis of fractional exchange times, and only qualitative conclusions can be made regarding the mechanisms of the reactions involved.[21] This has been done in the present study. In place of more accurate assay methods, the use of the infrared spectrometer in this work not only has given information of sufficient accuracy but also has confirmed and, to a certain extent, identified the competing exchange reactions.

Aside from the interesting possibility of ring deuteration, several conclusions can be drawn from the results which are qualitatively in agreement with the previous work on the phosphonate.[1] There is the hint that perhaps the mechanisms suggested for the ester would also hold for the acid system. Two important points, however, are quite clear: (a) the exchange is catalyzed by both acids and bases, and (b) termolecular mechanisms involving both acids and bases are not important. The latter conclusion is established by the nearly complete absence of catalysis by the constituents of neutral buffers.[22] Since exchange is negligible over a period as long as 6 weeks in neutral or near-neutral aqueous solutions, it also may be concluded that the ionization constant for the P–H bond in this molecule must be exceedingly small. By the same token the postulation of an uncatalyzed equilibrium between the tautomers



does not appear to be well-founded. The findings that the amount of exchange in neutral solution is of the same order of magnitude as that found in acetone serves to place an upper limit on the rate of formation of enolic form in aqueous solutions of sodium phenylphosphinate. Schwarzenbach and Wittwer,[23] using a bromometric technique, found that a 10% aqueous solution of acetone contains about 10^{-4}% enol, but did not estimate a rate of formation.

Earlier work[4–6,8,9] showed that hydrogen isotope exchange took place rapidly with hypophosphorous acid, slowly with phosphorous acid, and was absent in the salts of these acids. It was assumed, but not proved, that exchange was preceded by an acid-catalyzed prototropic transformation to the enolic forms. The independence of the rate of exchange on the concentration of the attacking reagent was not established in any of these reports, and in the present work there is only an indication of such independence. It is of interest, however, that exchange in the phenylphosphinic acid system more closely resembles that of hypophosphorous acid than it does phosphorous acid, and, in fact, most closely resembles that of the dialkyl phosphonates reported previously.[1]

Acknowledgment.—Grateful acknowledgment is made to Dr. Ronald E. Kagarise, Dr. L. B. Lockhart, Jr., and Mr. L. W. Daasch of the Physical Chemistry Branch of the Naval Research Laboratory for many stimulating discussions regarding this problem.

[21] S. Z. Roginsky, "Theoretical Principles of Isotope Methods for Investigation of Chemical Reactions," AEC Translation 2873, Academy of Sciences U.S.S.R. Press, Moscow, 1956, p. 191.

[22] C. G. Swain, *J. Am. Chem. Soc.*, **72**, 4578 (1950).

[23] G. Schwarzenbach and C. Wittwer, *Helv. Chim. Acta*, **30**, 669 (1947).

Structure and Stereochemistry of Diels–Alder Adducts of Levopimaric Acid

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Levopimaric acid or rosin reacted with β-propiolactone and acrylic acid to form adducts, two of which have been isolated in pure form and are related to the adducts previously obtained with acrylonitrile. Structures of these substances and of the adducts formed with methyl acrylate and fumaric acid have been established.

Diene reactions of abietic-type resin acids with fumaric acid[6] and acrylonitrile[7] have been reported earlier from this laboratory, but structures of the products were left uncertain. In this paper we report the reaction of levopimaric acid or rosin with β-propiolactone, acrylic acid, and methyl acrylate. Structures of the major products as well as those of the adducts reported earlier[6,7] have been determined. In the special case of the adducts, levopimaric acid and acrylonitrile, our conclusions based on chemical evidence do not support the preference expressed by other workers on n.m.r. spectroscopic grounds.[8]

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[4] U. S. Public Health Postdoctoral Fellow, 1962–1964.

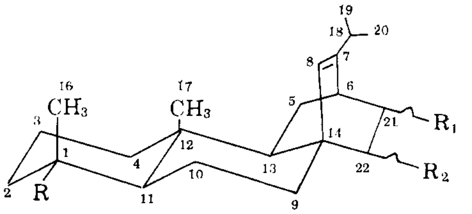
[5] U. S. Public Health Predoctoral Fellow, 1962–1964.

[6] N. J. Halbrook and R. V. Lawrence, *J. Am. Chem. Soc.*, **80**, 368 (1958).

[7] N. J. Halbrook, J. A. Wells, and R. V. Lawrence, *J. Org. Chem.*, **26**, 2641 (1961).

[8] W. L. Meyer and R. W. Huffman, *Tetrahedron Letters*, **16**, 691 (1962).

Reaction of levopimaric acid with 50% excess β-propiolactone at 225° for 4 hr. resulted in 7% of isomerized levopimaric acid and 93% of mixed adduct from which the major component I, $[\alpha]^{25}D$ +25.8°, was separated as a carbon tetrachloride solvate[9] in 57% yield. Partition chromatography of the soluble residue resulted in isolation of 17% of resin acids, 36% of a second adduct II, $[\alpha]^{25}D$ +68.2°, and 47% of a mixture III, $[\alpha]^{25}D$ 0°.



I, R = COOH; R_1 = H_2; R_2 = *endo*-COOH
II, R = COOH; R_1 = H_2; R_2 = *exo*-COOH
III, R = COOH; R_1 = mixed *endo,exo*-COOH; R_2 = H_2
VII, R = COOH; R_1 = H_2; R_2 = *endo*-$COOCH_3$
VIII, R = $COOCH_3$; R_1 = H_2; R_2 = *endo*-$COOCH_3$
IX, R = $COOCH_3$; R_1 = H_2; R_2 = *exo*-$COOCH_3$
X, R = COOH; R_1 = H_2; R_2 = *endo*-CN
XI, R = COOH; R_1 = H_2; R_2 = *exo*-CN
XII, R = $COOCH_3$; R_1 = H_2; R_2 = *endo*-CN
XIII, R = $COOCH_3$; R_1 = H_2; R_2 = *exo*-CN
XIV, R = COOH; R_1 = *endo*-CN; R_2 = H_2
XV, R = COOH; R_1 = *endo*-COOH; R_2 = *exo*-COOH
XVI, R = COOH; R_1 = *exo*-COOH; R_2 = *endo*-COOH
XVII, R = COOH; R_1 = *endo*-COOH; R_2 = *endo*-COOH
XX, R = CH_2OH; R_1 = H_2; R_2 = *endo*-CH_2OH
XXI, R = CH_2OH; R_1 = H_2; R_2 = *exo*-CH_2OH

Gum rosin on reaction with β-propiolactone gave yields of crude adducts equal to those expected on the basis of abietic-type resin acids present in the gum. Extraction with sodium bicarbonate solution and crystallization from carbon tetrachloride gave 30% of I. Crystallization of the residue from alcohol–water furnished 9.7% of II; the noncrystalline adducts III amounted to 18.3%. Reaction of rosin with acrylic acid afforded a mixture of approximately the same composition as that obtained with β-propiolactone.

Structures were assigned to these substances on the basis of the following evidence. I and II were partially interconvertible thermally, with I predominating and with no evidence of III, and are, therefore, epimers. Similarly, heating of the mixture III did not give any of isomer I. III is a mixture of two products differing from I and II and must, therefore, be a mixture of the epimers at C-21.

The possibility that a retrodiene reaction occurred during epimerization of I and II is disproved by the fact that no formation of III took place during the epimerization, and heating the mixture III did not give isomer I. The Diels–Alder reaction gave mixtures of I, II, and III, while a retrodiene reaction should have given the same mixtures. Further evidence against a reversal of the Diels–Alder reaction is provided by the results obtained on hydrolysis of XII and XIII; finally the heating of isomer I with fumaric acid, a more reactive dienophile, gave no detectable amount of fumaropimaric acid.

Lithium aluminum hydride reduction of I and II afforded different diols. Oxidation of I with dilute alkaline permanganate furnished a lactone IV (positive tetranitromethane test) whose infrared spectrum exhibited a strong band at 1770 cm.$^{-1}$ (γ-lactone), but no absorption at 890 cm.$^{-1}$, characteristic of an isopropenyl group. Treatment of I with formic acid–perchloric acid gave a saturated substance (V) which was also a γ-lactone (infrared band at 1770 cm.$^{-1}$).

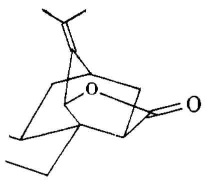
Comparison of the n.m.r. spectra of I, II, IV, and V (Table I) with those of related compounds[13] demonstrates a shift of the H-8 signal of IV and V to higher field. This and its multiplicity (singlet in IV, doublet in V) indicate that the signal is associated with the lactone function which must, therefore, be closed to C-8. The downfield shift of the signals associated with the now vinylic C-19 and C-20 methyl groups required by formula IV are observed.

TABLE I

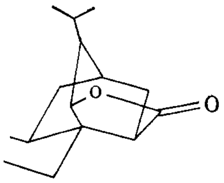
SELECTED N.M.R. PEAKS[a]

	Assignments[b]			
Compound	C-17	C-16	H-8[c]	Isopropyl methyls[c]
I	0.67	1.36	5.54	1.09 d (7)
II	0.69	1.38	5.58	1.04 d (7)
IV	0.71	1.19	5.00	1.77, 1.72
V	0.97	1.20	4.59 d (6)	0.97 d (9)
VII	0.63	1.17	5.38	1.06 d (7)
VIII	0.62	1.15	5.38	1.06 d (7)

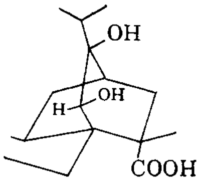
[a] In p.p.m. [b] See Experimental for details. [c] d = doublet; *J* values are in parentheses in c.p.s.



IV



V



VI

The facile formation of IV and V necessitates assignment of the *endo* configuration at C-22 to I. By contrast, II on alkaline permanganate oxidation furnished a dihydroxydicarboxylic acid VI which gave a negative tetranitromethane test. Since II is partially convertible to I, it represents the less stable C-22 *exo* isomer. We assume that approach of the oxidizing agent is less hindered from the α side of II, and that the two hydroxy groups of VI probably possess the configuration indicated in the formula.

The stereochemistry expressed in formula V is that expected from *trans*-diaxial lactone ring closure (although this would require double bond protonation from the more hindered side), as well as from thermodynamic considerations if a free carbonium ion were involved. A Drieding model of the C-7 epimer suggests the presence of large repulsive forces between the isopropyl and the C-17 methyl group. Support for this formulation is found in the H-8 coupling constant; the value, *J* = 6 c.p.s., is closer to that expected

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[9] Maleopimaric acid[10] (both carboxyl groups *endo*[11]) also forms a carbon tetrachloride solvate as does the isomer of fumaropimaric acid, [α] +42.5°,[12] in which the C-22 carboxyl is *endo* (*vide infra*).

[10] R. V. Lawrence and O. S. Eckhardt, U. S. Patent 2,628,226 (Feb. 10, 1953).

[11] L. H. Zalkow, R. A. Ford, and J. P. Kutney, *J. Org. Chem.*, **27**, 3535 (1962).

[12] N. J. Halbrook, unpublished.

[13] W. A. Ayer, C. E. McDonald, and J. B. Stothers, *Can. J. Chem.*, **41**, 1113 (1963).

from V (dihedral angle about 15°) than from its C-7 epimer (approximate dihedral angle 100°).

The infrared spectrum of the noncrystalline adduct mixture III was not significantly different from that of I or II, although the rotation and the n.m.r. spectrum indicated the presence of different components. This was confirmed by gas chromatography of the dimethyl esters. III was separated into two components with retention times of 5.90 and 6.95 min., whereas the methyl esters of I and II had retention times of 5.95 and 4.90 min., respectively. This leads to the conclusion that III is a mixture of the two epimeric C-21 carboxylic acids, since it is possible to form only four isomers by an approach of the dienophile to the α face of levopimaric acid.[8]

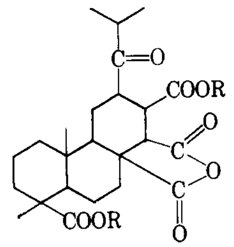
Condensation of levopimaric acid with methyl acrylate at 85° furnished in 90% yield[14] a crystalline isomer (VII) whose structure was established by conversion to the dimethyl ester of I (VIII), and hydrolysis with 10% sodium hydroxide solution to I.

The two acrylonitrile adducts X and XI reported earlier[7] furnished two different methyl esters (XII and XIII). A more convenient route to these compounds involved methylation of the crude mixture of adducts and separation by crystallization. Attempts to hydrolyze the nitrile function of either isomer with acid or with hydrogen peroxide were unsuccessful. Under the relatively drastic conditions required by base-catalyzed hydrolysis (potassium hydroxide in ethylene glycol at 170°), either isomer yielded a mixture of I and II. This demonstrated the point of attachment of the cyanide function as C-22, but does not permit assignment of *endo* or *exo* configuration to either isomer. Meyer and Huffman[8] suggested XI and XIV as the most likely formulas for the two acrylonitrile adducts.

Arbuzov and Khismatullina[15] reported the formation in low yield of an adduct from methyl acrylate and the crude resin acids of *Pinus maritima*. Saponification yielded material whose physical properties show it to be an isomer or isomer mixture differing from the substances reported in this paper.

Fumaropimaric acid,[6] the major Diels–Alder adduct of the abietic-type acids with fumaric acid, may be XV or XVI. Its thermal isomerization[6] to maleopimaric acid, recently shown to be XVII,[11,13,16] although tending to favor XV, might conceivably involve a retrodiene reaction. The following transformation conclusively establishes its structure as XV.

Ozonolysis of fumaropimaric acid in methyl alcohol solution at −70° followed by hypohalite decomposition of the ozonide[17] afforded in 70% yield the keto diacid anhydride XVIII. The dimethyl ester XIX had infrared bands at 1855 and 1790 (succinic anhydride), 1740 (double intensity, carbomethoxy groups), and 1715 cm.$^{-1}$ (ketone). Its n.m.r. spectrum exhibited methyl singlets at 1.11, 1.13 (angular methyls), 3.65, and 3.70 (carbomethoxy groups), and two superimposed methyl doublets at 1.01 p.p.m. (J = 7 c.p.s., isopropyl group), but no low-field protons. The formation of a succinic anhydride with these characteristics is only possible if fumaropimaric acid has structure XV.



XVIII, R = H
XIX, R = CH_3

Experimental[18a]

β-Propiolactone Adduct of Levopimaric Acid.—Levopimaric acid, $[\alpha]^{25}D$ −267.5°, was prepared according to the procedure of Harris and Sanderson.[19] A mixture of 30.2 g. (0.10 mole) of levopimaric acid and 10.8 g. (0.15 mole) of β-propiolactone was heated at 225° in an oil bath with stirring under nitrogen for 3 hr. The resinous mass was cooled, dissolved in ether, and filtered to remove any polymer formed by excess β-propiolactone. The ether solution was washed with water. Evaporation of the ether and drying at 0.5-mm. pressure for 3 hr. and 100° gave 37.4 g. (100%) of the crude product, neut. equiv. 193, $[\alpha]^{25}D$ +23.4°. The ultraviolet spectrum had λ_{max}^{EtOH} 242 mμ (α = 5.2)[18b] indicating the presence of some unchanged isomerized levopimaric acid.

Separation of Adduct I.—A 10.0-g. portion of the product was dissolved in ether, carbon tetrachloride was added, and the ether was removed by warming. The carbon tetrachloride adduct which formed was dried at 150° and 0.5 mm. for 4 hr., yielding 5.7 g. (57%) of crude product, $[\alpha]^{25}D$ +24.8°, neut. equiv. 187.0°. Two crystallizations from benzene and drying as above gave the analytical sample, $[\alpha]^{25}D$ +25.8°, m.p. 222–222.5°.

Anal. Calcd. for $C_{23}H_{34}O_4$: C, 73.76; H, 9.15; neut. equiv., 187.3. Found: C, 73.53; H, 9.10; neut. equiv., 187.3.

Treatment of I with ethereal diazomethane gave the dimethyl ester VIII whose preparation and properties are described subsequently. On gas chromatography it gave a single peak, retention time 5.95 min.

Chromatographic Separation of the Products of the Carbon Tetrachloride Filtrate.—The carbon tetrachloride filtrate was evaporated and dried at 0.5 mm. and 100° to yield 4.20 g. of resin, neut. equiv. 203.0, $[\alpha]D$ +20.7. This resin was separated into three components by means of a partition chromatography column similar to that described by Ramsey.[20] The column was packed with 50 g. of silicic acid which had been mixed with 35 ml. of (80:20) methanol–water. The eluting solvents were prepared by saturating isooctane and 50:50 isooctane–toluene with the methanol–water mixture. The first and second peaks which were eluted at 50 and 80 ml. with the isooctane contained 11.4% and 38.3% of the acids based on titration with alkali. The third fraction was stripped from the column with toluene and contained 49.3% of the acids placed on the column. The acids of each peak were extracted from the isooctane as their sodium salts, acidified with 1 N hydrochloric acid, and taken in ether. The ether was washed, evaporated, and the samples were dried for 3 hr. at 0.5 mm.

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(14) The high selectivity in this reaction may be a consequence of the relatively low temperature.

(15) B. A. Arbuzov and A. G. Khismatullina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2126 (1959).

(16) W. D. Lloyd and G. W. Hedrick, *J. Org. Chem.*, **26**, 2029 (1961).

(17) L. C. King and H. Farber, Abstracts, 136th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1959, p. 89P; *J. Org. Chem.*, **26**, 326 (1961).

(18) (a) Rotations were determined on 2% solutions in 95% alcohol unless otherwise specified. Infrared spectra were run on Perkin-Elmer Model 21 and Infracord spectrophotometers. All gas chromatograms were obtained at 264° using a $^1/_8$ in. × 5 ft. 5% SE-30 silicone rubber on 60–80-mesh Chromosorb W using helium as the carrier gas and a Wilkins Hi Fi flame ionization detector. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., or by Dr. F. Pascher, Bonn, Germany. Nuclear magnetic resonance spectra were run in deuteriochloroform or pyridine solutions on an A-60 spectrometer purchased with the aid of a grant from the National Science Foundation. The internal standard used was 3% tetramethylsilane. I and II were run in pyridine because of their insolubility in deuteriochloroform. Product names are used purely for information and do not constitute an endorsement of those named over any other. (b) α = absorptivity = ϵ/mol. wt.

(19) G. C. Harris and T. F. Sanderson, *J. Am. Chem. Soc.*, **70**, 334 (1948).

(20) L. L. Ramsey and W. J. Patterson, *J. Assoc. Offic. Agr. Chemists*, **31**, 139 (1948).

Rosin Acids.—The acids eluted in the first peak were recovered in 84% yield, calculated as rosin acids, and had neut. equiv. 295.0, $[\alpha]^{25}\mathrm{D}$ $-16.5°$. The ultraviolet spectrum had $\lambda_{\max}^{\mathrm{EtOH}}$ 242 mμ (α = 48.4) and 252 mμ (α = 55.2) characteristic of a mixture of abietic and neoabietic acids.

Adduct II.—The acids eluted in the second peak were recovered in 89.5% yield, calculated as the adduct, and had neut. equiv. 201.0, $[\alpha]^{25}\mathrm{D}$ $+51.9°$. The adduct was recrystallized from methanol–water and dried at 0.5 mm. and 100°, to give a 78% yield based on the acids in the peak by titration, and had neut. equiv. 187.9, m.p. 268–269°, $[\alpha]^{25}\mathrm{D}$ $+68.1°$.

Anal. Calcd. for $C_{23}H_{34}O_4$: C, 73.76; H, 9.15. Found: C, 73.68; H, 9.05.

The dimethyl ester IX was prepared by treatment of 0.5 g. of II with ethereal diazomethane. The product gradually crystallized on scratching. It was purified by chromatography over alumina (solvent and eluent, pentane) and recrystallized from methanol–water, yielding 0.475 g., m.p. 70–71° (depressed on admixture of VIII); $[\alpha]^{25}\mathrm{D}$ $+80.2°$; infrared band at 1730 cm.$^{-1}$; n.m.r. signals at 5.47 (s, H-8)$^{\mathrm{D}}$, 3.68 (s, 3p, $-OCH_3$), 3.65 (s, 3p, $-OCH_3$), 1.13 (s, 3p, C–16 methyl), 1.01 (doublet, J = 7 c.p.s., 6p, C–19 and C–20 methyls), and 0.06 p.p.m. (s, 3p, C–17 methyl). The dimethyl ester gave a single peak on the gas chromatography with retention time of 4.90 min.

Anal. Calcd. for $C_{25}H_{38}O_4$: C, 74.59; H, 9.52. Found: C, 74.62; H, 9.68.

Adduct III.—The acids stripped from the column were recovered in 94% yield, calculated as the adduct from titration data, and had neut. equiv. 201.5, $[\alpha]^{25}\mathrm{D}$ 0°, m.p. 134–138°. The material was converted to the cyclohexylamine salt in acetone. Removal of the solvent and drying at room temperature *in vacuo* over sodium sulfate furnished glassy material which was suspended in ether and washed with 1 N hydrochloric acid. The ether solution was washed with water, dried over sodium sulfate, and evaporated to dryness. The residue was dried at 100° (0.5 mm.), 57.0% yield, $[\alpha]^{25}\mathrm{D}$ 0°, m.p. 136–140°.

Anal. Calcd. for $C_{23}H_{34}O_4$: C, 73.76; H, 9.15; neut. equiv., 187.3. Found: C, 73.70; H, 9.37; neut. equiv., 188.5.

Treatment of III with ethereal diazomethane gave a mixture of dimethyl esters which was noncrystalline and had a double gas chromatogram peak at 5.90 and 6.95 min. Because of its noncrystalline nature, this material was not separated into the two components.

β-Propiolactone Adduct of Gum Rosin.—WW gum rosin, wt. 2225 g. containing approximately 1305 g. (4.35 moles) of abietic-type acids, was heated at 225° with slow stirring, and 482 g. (6.80 mole) of practical grade β-propiolactone was added during 1 hr. Heating at 225° was continued for 4 hr. A 1.6% loss occurred. The product was grade WW on the rosin scale, and had neut. equiv. 240, m.p. 128–134°. The modified rosin (100 g.) was dissolved in 500 ml. of ether, from which the adduct acids were extracted with 5% sodium bicarbonate. The sodium bicarbonate solution was acidified to pH 3 with dilute hydrochloric acid and extracted with ether. The ether solution was washed with water, dried over sodium sulfate, and evaporated. The residue was dried at 100° (0.5 mm.) for 3 hr. and weighed 60.0 g., neut. equiv. 194.2, $[\alpha]^{25}\mathrm{D}$ $+19.3°$.

The crude adduct was refluxed in carbon tetrachloride. The carbon tetrachloride adduct which formed on cooling was dried at 100° (0.5 mm.) for 3 hr to give 30.0 g. of acid I, neut. equiv. 191.3, $[\alpha]^{25}\mathrm{D}$ $+24.1$. Recrystallization from benzene gave the analytical sample, neut. equiv. 188.0, m.p. 218–222.5°, $[\alpha]^{25}\mathrm{D}$ $+25.8°$. Admixture with I gave no depression in the melting point.

The carbon tetrachloride liquors were diluted with isooctane to incipient cloudiness and filtered to remove oxidized material. Cooling of the filtrate furnished crystals which were recrystallized from alcohol–water and dried at 100° (0.5 mm.) for 3 hr., yielding 9.67 g., m.p. 264–265°, $[\alpha]^{25}\mathrm{D}$ $+68.2°$. Admixture with II gave no melting point depression.

The mother liquors were evaporated and the residue was dried at 100° (0.5 mm.) for 3 hr. to give 18.3 g. of adduct, m.p. 130–134°, neut. equiv. 192.1, $[\alpha]^{25}\mathrm{D}$ $+8.43°$. There was no appreciable difference between the infrared spectrum of this noncrystalline β-propiolactone adduct of rosin acids and adduct I. The noncrystalline solid was not further examined.

Adduct of Rosin and Acrylic Acid.—An adduct was prepared as described in the procedure for rosin and β-propiolactone. A 50.0-g. sample of this modification was subjected to the recovery and drying procedures as described above for recovery of adducts I and II. Adducts I and II were obtained in approximately the same yield. No attempt was made to recover the noncrystalline adducts.

Oxidation of I and II with Alkaline Permanganate. Preparation of IV and VI.—Adduct I, 3.78 g. (0.02 equiv.), was dissolved in 25 ml. of water containing 0.80 g. of sodium hydroxide. The solution was cooled to 20° and added to a cold solution of 1.58 g. (3 equiv. of oxidizing agent) of potassium permanganate in 75 ml. of water. The reactants were stored in a refrigerator overnight. The precipitated manganese dioxide was removed, and the filtrate was acidified (pH 3) with dilute hydrochloric acid. The precipitated lactone was collected by filtration and dissolved in 15 ml. of ether. The ether was washed with water and dried over sodium sulfate. Carbon tetrachloride was added and the ether was removed by warming. The unchanged acid crystallized from the carbon tetrachloride. The carbon tetrachloride liquors were concentrated, and the residue was dried under vacuum. Crystallization from acetonitrile gave 3.10 g., 82% yield, of lactone IV, $[\alpha]^{25}\mathrm{D}$ $-92.3°$, m.p. 257–258°. Recrystallization from acetone–water and drying at 0.5 mm. and 100° gave the analytical sample, m.p. 257–258°, $[\alpha]^{25}\mathrm{D}$ $-92.4°$, positive tetranitromethane test, $\nu_{\max}^{\mathrm{mull}}$ 1770 cm.$^{-1}$.

Anal. Calcd. for $C_{23}H_{32}O_4$: C, 74.16; H, 8.66; neut. equiv., 374.5. Found: C, 73.95; H, 8.92; neut. equiv., 374.5.

Adduct II was oxidized as described above for the oxidation of I. A 1.88-g. (0.005 mole) sample was used. Evaporation of the ether solution gave a white powder which was recrystallized from 50:50 toluene–isooctane; the yield of VI was 81.5%, $[\alpha]^{25}\mathrm{D}$ $+74.0°$, neut. equiv. 198.6. Recrystallization from toluene gave the analytical sample, m.p. 180–184° dec., $[\alpha]^{25}\mathrm{D}$ $+78.0$, negative tetranitromethane test.

Anal. Calcd. for $C_{23}H_{36}O_6$: C, 67.62; H, 8.87; neut. equiv., 204.2. Found: C, 67.86; H, 8.69; neut. equiv., 203.8.

The noncrystalline dimethyl ester was prepared using diazomethane, $\nu_{\max}^{\mathrm{CCl_4}}$ 3492 (O–H) cm.$^{-1}$.

Lactonization of Adduct I.—A suspension of 1.0 g. of diacid I in 10 ml. of formic acid containing 1 ml. of perchloric acid was refluxed for 24 hr. On cooling there precipitated 0.54 g. of lactone V, m.p. 240–248°. Dilution of the filtrate with water resulted in the recovery of 0.43 g. of I. Chromatography of crude V over silicic acid furnished 0.47 g. of V in the benzene–ether fractions. Crystallization from ether–petroleum ether (b.p. 30–60°) gave white needles, m.p. 271–273°, $[\alpha]^{25}\mathrm{D}$ $+33.5°$, infrared bands at 1770 (γ-lactone) and 1700 cm.$^{-1}$ (carboxyl).

Anal. Calcd. for $C_{23}H_{34}O_4$: C, 73.76; H, 9.15; O, 17.09. Found: C, 73.98; H, 9.24; O, 16.50.

Reduction of I and II with Lithium Aluminum Hydride. Preparation of XX and XXI.—A solution of 1.25 g. (0.003 mole) of I in 50 ml. of ether was added to an ether solution containing 3.40 g. (0.92 mole) of lithium aluminum hydride. After refluxing for 4 hr., the excess lithium aluminum hydride was destroyed with water and 20% sodium hydroxide. The ether layer was separated and the precipitate was washed with ether. The ether solution was washed, dried over sodium sulfate, and concentrated to give 1.10 g. (96%) of XX as needles, m.p. 163–165°. Recrystallization from acetone and drying at 100° (0.5 mm.) for 3 hr. gave the analytical sample, m.p. 166–167°, $[\alpha]^{25}\mathrm{D}$ 0°, positive tetranitromethane test, $\nu_{\max}^{\mathrm{mull}}$ 3290 cm.$^{-1}$.

Anal Calcd. for $C_{23}H_{38}O_2$: C, 79.71; H, 11.05. Found: C, 79.62; H, 10.91.

Adduct II was reduced in the same manner. A 0.75-g. (0.002 mole) sample was used. The alcohol was obtained on evaporation of the ether as a powder, and had a 0.651-g. (94%) yield of XXI, m.p. 122–124°, $[\alpha]^{25}\mathrm{D}$ $+84.5°$. Recrystallization from hexane and drying at 180° (0.5 mm.) for 3 hr. gave the analytical sample, m.p. 125–126.5°, $[\alpha]^{25}\mathrm{D}$ $+86.0°$, positive tetranitromethane test, $\nu_{\max}^{\mathrm{mull}}$ 3290 cm.$^{-1}$.

Anal. Calcd. for $C_{23}H_{38}O_2$: C, 79.71; H, 11.05. Found: C, 79.75; H, 11.11.

Isomerization of I and II.—Adduct I (2.22 g.) was heated at 250° for 2 hr., and the product was dissolved in ether. Carbon tetrachloride was added and the ether was removed by warming. The unchanged isomer was recovered as the carbon tetrachloride adduct in a 1.27-g. yield. The carbon tetrachloride liquors were extracted with 5% sodium bicarbonate solution. The bicarbonate solution was acidified and extracted with ether. The ether was washed with water, dried over sodium sulfate, evaporated, and dried at 100° (0.5 mm.) for 3 hr., yielding 0.325 g. of the diastereoisomer, $[\alpha]^{25}\mathrm{D}$ $+ 50.1°$. Recrystallization from alcohol–

water gave adduct II, $[\alpha]^{25}\text{D}$ +68.2°, m.p. 268–269°, neut. equiv. 188.0. Admixture with II gave no melting point depression.

Adduct II (0.55 g.) was heated for 2 hr. at 250°, and the products were recovered as above. A 57% yield of I was obtained, neut. equiv. 187.8, m.p. 218–218.5. Admixture with I gave no melting point depression. Adduct II was recovered in 22% yield from the carbon tetrachloride liquors. Adduct mixture III was heated at 225–230° for 4 hr. and dissolved in 5 ml. of carbon tetrachloride. The insoluble carbon tetrachloride addition product of I was not obtained.

Attempted Dienophile Exchange.—A mixture of 3.74 g. (0.01 mole) of I was heated under nitrogen with 2.32 g. (0.02 mole) of fumaric acid at 250° for 1 hr. The mixture was dissolved in ether, and unchanged fumaric acid was removed by filtration and washing. No fumaropimaric acid could be detected in the reaction mixture.

Methyl Acrylate Adduct of Levopimaric Acid.—A solution of 10.0 g. of levopimaric acid in 20 ml. of methyl acrylate was refluxed for 8 hr. and allowed to stand at ambient temperature overnight. Excess methyl acrylate was removed by steam distillation. The residue, 12.8 g., m.p. 107–134°, was recrystallized from methanol, yielding 9.8 g. of VII, m.p. 161–162°, $[\alpha]^{25}\text{D}$ +19.5°, infrared bands at 1725 (ester) and 1690 cm.$^{-1}$ (carboxyl). A second crop, 1.7 g., m.p. 154–158°, was obtained from the mother liquors; the total yield was 90%.

Anal. Calcd. for $C_{24}H_{36}O_4$: C, 74.19; H, 9.34; O, 16.47. Found: C, 74.47; H, 9.52; O, 16.26.

The dimethyl ester VIII was prepared by treatment of 1 g. of VII with ethereal diazomethane. Evaporation of the solvent furnished a colorless oil which was taken up in hot methanol, treated with decolorizing charcoal, and diluted with water to incipient cloudiness. Upon cooling, an oil separated which crystallized on scratching, yielding 0.95 g., m.p. 68–69°, $[\alpha]^{25}\text{D}$ + 17.5°, infrared band at 1725 cm.$^{-1}$ (ester). The substance was homogeneous on a thin layer chromatogram and also was prepared by esterification of I.

Anal. Calcd. for $C_{25}H_{38}O_4$: C, 74.59; H, 9.52; O, 15.90. Found: C, 74.43; H, 9.48; O, 16.35

Hydrolysis of 10 g. of VII by refluxing with 100 ml. of 10% sodium hydroxide solution for 24 hr. followed by acidification and recrystallization from benzene furnished 8.9 g. of I, m.p. 223–225°, $[\alpha]^{25}\text{D}$ +27.5°. The infrared and n.m.r. spectra were superimposable with the levopimaric acid β-propiolactone adduct and reesterification furnished VIII.

Anal. Calcd. for $C_{23}H_{34}O_4$: C, 73.76; H, 9.15; O, 17.09. Found: C, 73.43; H, 9.24; O, 17.17.

Acrylonitrile Adducts of Levopimaric Acid.—The crude adduct mixture prepared by the method of Halbrook, Wells, and Lawrence[7] was esterified with ethereal diazomethane. One gram of the mixture was chromatographed over 50 g. of alumina (Alcoa F-20). Benzene–petroleum ether (b.p. 30–60°, 1:1) eluted 0.39 g. of an oil which was dissolved in methanol. Water was added to incipient cloudiness whereupon one ester nitrile (XII or XIII) separated. Recrystallization furnished material, m.p. 120–121°; $[\alpha]^{25}\text{D}$ +84°; infrared bands at 2230 (-CN) and 1725 cm.$^{-1}$ (ester); n.m.r. signals at 5.42 (H-8), 3.68 (methoxyl), 1.16 (C-16 methyl), 1.03 (doublets, J = 7 c.p.s., isopropyl methyls), and 0.61 p.p.m. (C-17 methyl). This ester also was prepared by direct methylation of the acrylonitrile adduct, m.p. 191°, $[\alpha]^{25}\text{D}$ +88°.[7]

Anal. Calcd. for $C_{24}H_{35}NO_2$: C, 78.00; H, 9.55; N, 3.79; O, 8.66. Found: C, 78.10; H, 9.57; N, 3.95; O, 8.87.

Benzene–petroleum ether (3:1) eluted 0.47 g. of solid, m.p. 132–149°, which was recrystallized from methanol, m.p. 174–176°; $[\alpha]^{25}\text{D}$ 0°; infrared bands at 2230 (-CN) and 1720 cm.$^{-1}$ (ester); n.m.r. signals at 5.52 (H-8), 3.67 (methoxyl), 1.17 (C-16 methyl), 1.06 (doublet, J = 7, c.p.s., isopropyl methyls), and 0.62 p.p.m. (C-17 methyl). This substance could be obtained also from the acrylonitrile adduct, m.p. 182°, $[\alpha]^{25}\text{D}$ 0°.[7]

Anal. Calcd. for $C_{24}H_{35}NO_2$: C, 78.00; H, 9.55; O, 8.66. Found: C, 78.14; H, 9.44; O, 9.04.

For separation of larger quantities of the two ester nitriles, fractional crystallization was more convenient. Five grams of the ester nitrile mixture was dissolved in a minimum of boiling ether. Chilling produced 1.96 g. of the higher melting isomer, m.p. 174–176°. Concentration of the mother liquor furnished 0.67 g. of additional material. Evaporation of the mother liquor gave 2.28 g. of a somewhat impure lower melting isomer; several recrystallizations from methanol were required to raise the melting point to 120–121°.

Hydrolysis of XII and XIII.—A mixture of 1.5 g. of the isomer, m.p. 120–121°, and 3 g. of potassium hydroxide in 25 ml. of ethylene glycol was refluxed in a copper flask. Evolution of ammonia continued for 70 hr. The mixture was poured into ice–hydrochloric acid, yielding 1.46 g., m.p. 164–203°. Purification as described for the β-propiolactone adducts provided 0.72 g. of cubes, m.p. 222–224°, and 0.64 g. of needles, m.p. 267–269°, which were identical with adducts I and II.

Hydrolysis of 3 g. of the isomer, m.p. 174–176°, in the same manner furnished 3.12 g. of crude diacids, m.p. 171–196°, which were separated into 1.73 g. of adduct I and 1.25 g. of adduct II.

Ozonolysis of Fumaropimaric Acid.—A solution of 6 g. of fumaropimaric acid, m.p. 293–295° (sinters at 180°),[6] in 100 ml. of methanol was ozonized at −70° until the blue color of excess ozone was present. It was then added rapidly, with stirring, to an ice-cold solution prepared from 70 ml. of Clorox, 300 ml. of water, 100 ml. of methanol, and 200 g. of ice to which concentrated hydrochloric acid had been added until the green color of free chlorine appeared. Reaction was almost instantaneous, product XVIII separating as a white precipitate which was filtered after a few minutes and dried, yielding 4.5 g. (70%), m.p. 254–259° dec. Purification was difficult owing to limited solubility; the analytical sample, m.p. 267–269° dec., was prepared by allowing a saturated ethyl acetate solution to evaporate slowly.

Anal. Calcd. for $C_{24}H_{32}O_8$: C, 64.27; H, 7.19; O, 28.54. Found: C, 64.02; H, 7.27; O, 29.05.

The dimethyl ester XIX was prepared from 4 g. of XVIII with excess diazomethane in ether. After 15 min. excess diazomethane was destroyed with acetic acid; the solution was washed with dilute sodium bicarbonate solution, dried, and evaporated; and the residue was recrystallized from ethanol to yield 2.69 g., m.p. 222–224°; infrared bands at 1855, 1790, 1740, and 1715 cm.$^{-1}$.

Anal. Calcd. for $C_{26}H_{36}O_8$: C, 65.53; H, 7.61; O, 26.86. Found: C, 65.39; H, 7.73; O, 27.11.