unimportant. For example, although series V and series VI (Table I) both have the same cross-sectional diameters in the planar zigzag conformation, the minimum anchor length is 10 for the latter and 9 for the former. This may be due to a change in the I effect resulting from an increase in the number of fluorine atoms in the molecule from 7 to 11.

Several methods have been previously employed to determine the relative stabilities of the urea inclusion compounds of a homologous series: the dissociation constant at a fixed temperature,[7] the measured heats of formation[2,8] for the inclusion compound, and the use of the dissociation temperatures of the inclusion compounds.[9] A fourth method which was used in our laboratory involves the use of x-ray powder diffraction data. In this and earlier[3] research it was noted (Table II) that the shortest and next to the shortest homologue which showed the characteristic interplanar spacings for complexes also showed spacings for dissociated tetragonal urea. Urea spacings were relatively stronger for the complex of the shorter homologue. Complexes of still higher homologues than these two give characteristic spacings for complex only.

Fluorinated esters containing a sufficiently long unbranched unfluorinated segment can form a urea complex. This generalization can be safely extended to molecules other than esters, *e.g.*, alcohols, acids, amines, etc., so long as the functional group does not increase the maximum cross-sectional diameter of the planar zigzag conformation beyond 6 Å.

The properties of the urea complexes of the fluorinated esters are similar to those of the unfluorinated complexes. The former have transition points[9] and x-ray powder diffraction patterns characteristic of the urea complexes of unfluorinated compounds. Both are made and decomposed in the same manner. No fluorinated ester with an anchor length of less than 7 (see Table I) formed a complex.

The applications which may be made of this technique are essentially the same as for the urea complexes of unfluorinated molecules. These applications (separation, purification, characterization, and storage) have been listed in detail elsewhere.[10]

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[CONTRIBUTION FROM THE NAVAL STORES RESEARCH STATION][1]

Preparation and Some Reactions of the Vinyl Ester of Maleopimaric Acid

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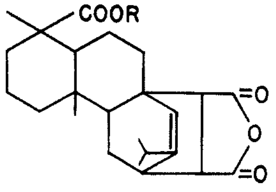
Received December 31, 1959

Maleopimaric acid has been vinylated. The vinyl ester has been characterized, its reactions with alcohols and cyclohexylamine have been delineated and it has been copolymerized with vinyl acetate and vinyl chloride.

Levopimaric acid, a constituent of gum oleoresin, condenses at room temperature with maleic anhydride to form the Diels-Alder addition compound[2] maleopimaric acid, 6,14-dihydrolevopimaric acid-6,14-*endo*-α,β-succinic anhydride (I). Most of the resin acids in conventional rosin react with maleic anhydride under vigorous conditions to form I.[3] There are no recorded preparations of the vinyl ester of this acid.

I R = H
II R = Vinyl
III R = Ethyl



Vinyl esters of the resin acids in rosin have been reported by Reppe.[4] Robinson[5] has prepared the vinyl esters of disproportioned and catalytically reduced rosin. Schildknecht,[6] however, states

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(2) (a) R. G. R. Bacon and L. Ruzicka, *Chem. & Ind. (London)*, 546 (1936). (b) H. Wienhaus and W. Sandermann, *Ber.*, **69**, 2202 (1936).

(3) V. M. Loeblich, D. E. Baldwin, and R. V. Lawrence, *J. Am. Chem. Soc.*, **77**, 2823 (1955).

(4) Walter Reppe (to I. G. Farbenindustrie, AKF.), U. S. Patent **2,066,075**, Dec. 29, 1936.

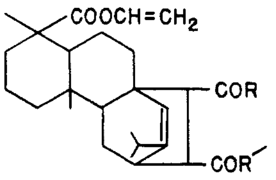
(5) J. C. Robinson, Jr. (to Hercules Powder Co.), U. S. Patent **2,615,012**, Oct. 21, 1952.

(6) C. E. Schildknecht, *Vinyl and Related Polymers*, John Wiley & Son, Inc., New York, N. Y., 1952, Chap. 5, p. 385

that high polymers have not been prepared from vinyl esters of this type. Since I is one of the few pure and cheap compounds derivable from rosin, it was of interest to determine whether the carboxyl group could be vinylated without affecting the anhydride group and further to determine whether the vinyl ester would polymerize upon initiation with a free radical catalyst.

Maleopimaric acid (I) was vinylated by the vinyl interchange reaction of Adelman[7] using vinyl acetate and a mercuric sulfate catalyst in 88% yield without affecting the anhydride group. The product, vinyl maleopimarate (II), was characterized by conversion to ethyl maleopimarate (III), a known compound,[8] by catalytic reduction.

The vinyl ester (II) was characterized further by opening the anhydride ring either with ethyl alcohol to yield a mixed ester (IV) or with cyclohexylamine to yield the cyclohexylamine salt of a cyclohexylamide (V). In both cases the vinyl group was unaffected and it was not possible to determine the direction in which the anhydride ring was opened. The ester (IV) lost ethanol and reverted to II at about 100°. Attempts to prepare dibutyl esters of II were unsuccessful using either acidic or basic catalysts. After one mole of butyl alcohol had been added to the anhydride linkage, transesterification of the vinyl group proved to be more facile than esterification of the free carboxylic acid group.



IV R = OH R = OC$_2$H$_5$
or
R′ = OC$_2$H$_5$ R′ = OH
V R = C$_6$H$_{11}$NH— R = [C$_6$H$_{11}$NH$_3$]$^{+-}$O—
or
R′ = [C$_6$H$_{11}$NH$_3$]$^{+-}$O— R′ = C$_6$H$_{11}$NH—

The homopolymerization of II with benzoyl peroxide in benzene or ethyl acetate solution gave a high-melting, brittle powder which was not a high polymer. Copolymerization with vinyl acetate (Table I) in ethyl acetate using benzoyl peroxide initiator gave polymers which were soluble and colorless, with film-forming properties. The melting points and brittlenesses of the copolymers increased and the intrinsic viscosities decreased as the amount of II in the copolymers increased. The vinyl maleopimarate (II) content of each copolymer was calculated from its carbon analysis and is given in Table II with the elemental analysis and vinyl maleopimarate content of the monomer charge. In all cases the copolymer contained a higher percentage of II than the monomer mixture.

TABLE I

COPOLYMERIZATION OF VINYL MALEOPIMARATE AND VINYL ACETATE AT APPROXIMATELY 80°

Number	Charge[a] Ethyl acetate, ml.	Vinyl maleopimarate, g.	Vinyl acetate, g.	Softening point, °C	Conversion, %	Intrinsic Viscosity
1	40	0	20	65	40	.577
2	40	2	20	70	70	.281
3	40	10	20	100	39	.178
4	20	10	10	110	38	.120
5	20	10	0	250	12	...

[a] Reaction time 16 hr.; initiator, 0.1 g. benzoyl peroxide per charge.

TABLE II

VINYL MALEOPIMARATE CONTENT OF VINYL MALEOPIMARATE–VINYL ACETATE COPOLYMERS AND MONOMER MIXTURES

Polymer No.	Elemental Analysis %, C	%, H	Wt. % of Vinyl Maleopimarate Monomer	Polymer
2	57.88	7.29	9.1	11.9
3	62.93	7.56	33.3	40.9
4	66.51	7.78	50.0	67.3

The copolymers of II with vinyl chloride (Table III) were slightly discolored, brittle and soluble powders. The melting points increased and the conversions decreased with increasing concentrations of II. The vinyl maleopimarate (II) content of each copolymer was calculated from its chlorine analysis and is given in Table IV with the chlorine analysis and vinyl maleopimarate content of the monomer charge. The copolymer compositions approximated those of the monomer mixtures.

TABLE III

COPOLYMERIZATION OF VINYL MALEOPIMARATE AND VINYL CHLORIDE AT 60°

Polymer No.	Charge[a] Vinyl maleopimarate, g.	Vinyl chloride, g.	Conversion, %	Softening Point, °C.
6	0	20	61	85–90
7	3	17	35	100–110
8	10	10	13	110–120

[a] Reaction time, 24 hr.; solvent, 20 ml., tetrahydrofuran per charge; initiator, 0.2 g. benzoyl peroxide per charge.

TABLE IV

VINYL MALEOPIMARATE CONTENT OF VINYL MALEOPIMARATE–VINYL CHLORIDE COPOLYMERS AND MONOMER MIXTURES

Polymer No.	Chlorine Analysis, % Cl	Wt. % of Vinyl Maleopimarate Monomer	Polymer
7	49.07	15	15.6
8	29.89	50	47.3

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EXPERIMENTAL

Vinyl maleopimarate (II). The ester (II) was prepared by the method of Adelman[7] using vinyl acetate and mercuric acetate–sulfuric acid catalyst. Deviations from this procedure were in the amount of vinyl acetate used and in isolation method. Maleopimaric acid (I), $[\alpha]^{22}_{D}$ −24.1 (10% in acetone) m.p. 225–228° (200 g., 0.5 mole), was allowed to react with 880 ml. (9.5 moles) of vinyl acetate. After addition of the catalyst and 4 or 5 hr. agitation at 20°, I went into solution and colorless II started to crystallize. After standing 2 or more days, sodium acetate was added. Yields of 60% were obtainable by filtering at this point. The vinyl acetate was removed by stripping *in vacuo* and the pot residue treated with Norite in hot acetone (600 ml.). After the solution was filtered to remove the charcoal and cooled, the product crystallized in colorless plates. The solid was isolated by filtration and a second crop of crystals was obtained by allowing some of the acetone to evaporate. Recrystallization of the combined solids from acetone gave 187.5 g. (88%) of II, m.p. 164–165:5°, $[\alpha]^{24}_{D}$ −37.6 (5% in chloroform).

Anal. Calcd. for $C_{26}H_{34}O_5$: C, 73.21; H, 8.04; hydrogenation equiv., 426.5; neut. equiv., 213.3 (in acetone), 426.5 (in ethanol). Found: C, 73.19; H, 8.19; hydrogenation equiv. (5% palladium on carbon in acetic acid), 431; neut. equiv., 213.2 (in acetone), 426.0 (in ethanol). Mercury less than 1 part per million.[9]

The reduced vinyl ester (5% palladium on carbon in glacial acetic acid) was identical with the ethyl maleopimarate of Graff.[8]

Reactions of vinyl maleopimarate (II). An ethanolic solution of II was refluxed for 1 hr. in the presence of an equimolar amount of anhydrous sodium carbonate; after filtration to remove sodium bicarbonate and concentration, a sodium salt was obtained. Titration with standard acid to a phenol red end-point and extraction with ether gave a quantitative yield of IV. The product started to melt at 60° and finally melted at 98.5°, resolidified and melted again at 164–165.5°.

Anal. Calcd. for $C_{28}H_{40}O_6$: C, 71.16; H, 8.53; hydrogenation equiv., 472.6; neut. equiv., 472.6. Found: C, 71.86; H, 8.36; hydrogenation equiv. (5% palladium on carbon in acetic acid) 472; neut. equiv. 472.0.

A sample of IV heated overnight at 56° under vacuum did not change. However at 110°, II was obtained, m.p. 164–165.5°, neut. equiv. 426.6 (in ethanol).

Refluxing ethyl alcohol was saturated with II, filtered and cooled; IV crystallized in 70% yield.

A toluene solution of II was refluxed with 2 equivalents of *n*-butyl alcohol in a flask equipped with a Dean-Stark decanter; the top of the condenser was vented through a trap containing Tollens reagent. After several hours of refluxing, no water had collected in the trap. The evolution of a minor amount of acetaldehyde was apparent from the precipitation of silver in the Tollens reagent. The mixture was allowed to cool, 2 g. of *p*-toluenesulfonic acid was added and heating was resumed. Under these conditions acetaldehyde was eliminated rapidly. No water was liberated. Identical results were obtained when chloroform was the solvent (64°). In a similar reaction using octadecanol and xylene (pot temperature 150°) with a little metallic sodium as a catalyst, no water formed. However, acetaldehyde was again liberated.

A solution of II (12.78 g., 0.03 mole) in 200 ml. of diethyl ether was treated with cyclohexylamine (8.94 g., 0.09 mole). A solid separated, which was washed with hexane to remove excess amine. Analytical data indicated that this was the cyclohexylamine salt of a cyclohexylamide (V), m.p. 139–140°.

Anal. Calcd. for $C_{38}H_{60}N_2O_5$: N, 4.48; hydrogenation equiv., 624.9; neut. equiv., 624.9. Found: N (Kjeldahl), 4.48; hydrogenation equiv. (5% palladium on carbon in acetic acid), 631; neut. equiv. (in acetone with cresol red indicator), 624.0.

Polymerization. These polymerizations were conducted in 16 oz. snap-cap bottles sealed with neoprene gaskets. The charges are given in Tables I and III. The vinyl acetate copolymers were heated without shaking on the steam bath and the vinyl chloride copolymers were prepared in a constant temperature bath. The vinyl acetate and vinyl chloride copolymers were isolated by pouring into a large volume of ether and reprecipitated, respectively, from benzene or tetrahydrofuran with pentane.

Acknowledgment. The authors wish to express their appreciation to Mr. L. E. Brown and Mrs. A. F. Cuculla, Southern Utilization Research and Development Division, New Orleans, La., for carbon and hydrogen analyses; to Mr. L. E. Brown for mercury determinations, and to Mr. M. Stark, Jr., for intrinsic viscosity determinations.

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(9) Fritz Feigl, *Qualitative Analysis by Spot Tests*, 3rd Ed., Elsevier Publishing Co., New York, N. Y., 1946, p. 49.