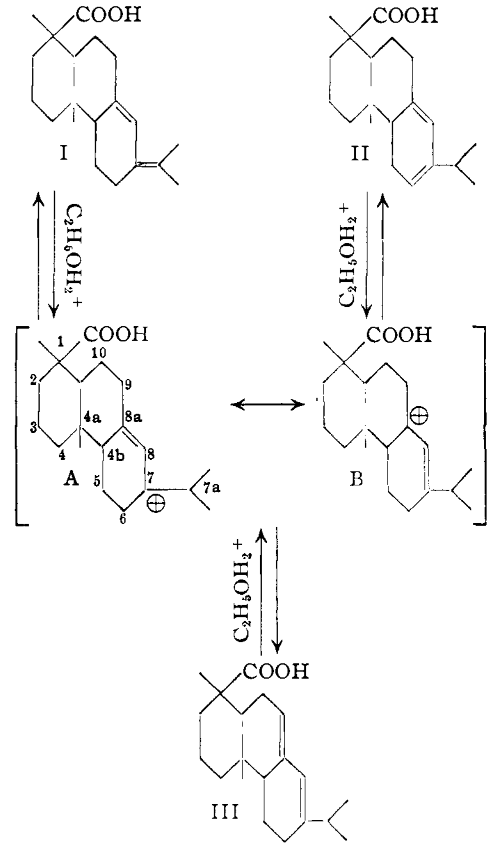

Form A can lose its charge by expulsion of a proton from either position 6 or 7a. If this expulsion occurs at position 6, levopimaric acid is regenerated, and if it occurs at 7a, neoabietic acid is regenerated. In neither case does isomerization result. On the other hand, form B can lose its charge by expelling a proton at position 9 or 4b. When position 9 is involved, the result is the formation of abietic acid (III) but if 4b were involved, a new resin acid would be formed. No evidence has been found for the existence of such a new resin acid, and since conjugation between two rings seems to be favored over conjugation within one ring, it is assumed that expulsion of a proton from position 9 is favored. The fact that the final equilibrium mixture contains over 90% abietic acid as shown by the ultraviolet absorption spectra is in agreement with this assumption.

Acknowledgment.—The authors wish to express their thanks to Dr. George C. Harris of these laboratories who supplied the neoabietic acid used during the course of this research.

Summary

Neoabietic acid is converted by ethanolic solutions of strong acids into a mixture consisting chiefly of abietic acid but containing small amounts of levopimaric acid. Ultraviolet absorption spectra afford no indication of the presence of neoabietic or levopimaric acid in the reaction mixture.

The isomerization of neoabietic acid in ethanol appears to be catalyzed exclusively by the solvated proton. Assuming complete dissociation of hydrogen chloride and hydrogen bromide at concentrations of 0.01 to 0.1 mole/liter the catalytic coefficient of the reaction (in liters mole^{-1} min.$^{-1}$) is given by the expression $k_{C_2H_5OH_2^+} = 6.3 \times 10^{14}\ e^{-21,450/RT}$. Small amounts of water in the medium seriously inhibit the reaction.

Data obtained by measurement of the velocity of isomerization at various concentrations of the strong acids, hydrogen chloride and hydrogen bromide, are in good agreement with the Brönsted theory of primary electrolyte effects. The two sulfonic acids seem to be incompletely dissociated in ethanol at the concentration employed in these experiments.

Wilmington 99, Delaware Received August 4, 1949

[Contribution from the Institute of Polymer Research, Polytechnic Institute of Brooklyn]

The Preparation of *p*-Acyloxystyrenes[1]

By C. G. Overberger, Evelyn J. Luhrs and P. K. Chien

We have undertaken the preparation of monomers[2] that contain straight-chain alkyl groups which when polymerized give a polymer with this alkyl group in the side chain. In particular, the formation of crystallites[3] in such a side chain and the influence of this crystallization on the polymer properties are of special interest.

This paper will describe a convenient preparation of some *p*-acyloxystyrenes (II) in which R is a straight-chain alkyl group. The procedure is outlined below. With the exception of R = CH_3, the substituted cinnamic acids (I) and the styrenes have not been previously described. *p*-Acetoxystyrene[4] has previously been prepared by dehydroacetylation of the diacetate of *p*-hydroxyphenylmethylcarbinol and by the dehydration[5] of *p*-(α-hydroxyethyl)-phenyl acetate. The method used, the decarboxylation of a

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(1) A portion of theses by Evelyn Luhrs and P. K. Chien submitted to the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Master of Science.

(2) Overberger and Roberts, This Journal, 71, 3618 (1949).

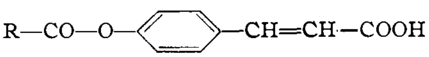
(3) Kaufman, Sacher, Alfrey and Fankuchen, *ibid.*, 70, 3146 (1948).

(4) Alderman and Hanford, U. S. Patent 2,276,138, March, 1942.

(5) Emerson, Heyd, Lucas, Cook, Owens and Shortridge, This Journal, 68, 1665 (1946).

TABLE I

p-ACYLOXYCINNAMIC ACIDS,

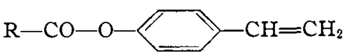


R	Yield,[b] %	Recryst. solvent	M. p.,[d] °C.		Carbon, %[e] Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Neut. equiv. Calcd.	Neut. equiv. Found
CH_3[a]	38	Water	205.5–206		64.07	64.15	4.89	5.09	206	206
C_2H_5	70	Alcohol–water	181–183		65.44	65.21	5.50	5.76	220	220
C_3H_7	64	Alcohol–water	163–164	185–186	66.65	66.91	6.03	6.24	234	232
C_5H_{11}	85	Alcohol–water	149.7–150.7	175.6–177.6	68.68	68.72	6.92	6.95	262	260
C_7H_{15}	78	Alcohol–water	149–153	177–181	70.32	70.42	7.64	7.68	290	289
$C_{11}H_{23}$	88[c]	1:1 Benzene–methanol	159–160	164–167	72.84	72.45	8.73	8.86	346	346
$C_{15}H_{31}$	90[c]	3:1 Benzene–methanol	160–161	165–167	74.40	74.71	9.49	9.54	402	402

[a] Prepared by Perkin procedure, ref. 8. [b] Yield of purified product. [c] Yield after one recrystallization. [d] All melting points are corrected. The first melting point indicates the formation of the cloudy melt (liquid crystal); the second, the formation of clear liquid. [e] Analyses by Mr. H. S. Clark, Mr. Ralph Schachat and Mr. Pao-Tung Huang.

TABLE II

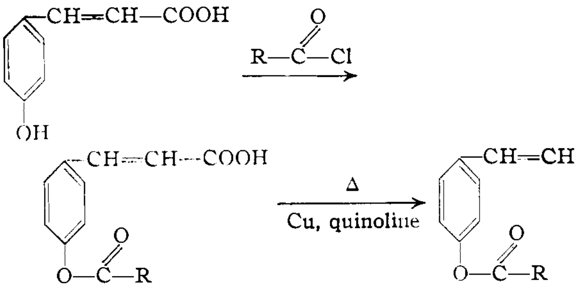
p-ACYLOXYSTYRENE,



R	B. p., °C.	Mm.	Yield, %	$n^{25}D$	d^{25}_4	Molecular refraction Calcd.	Molecular refraction Found	Formula	Carbon,[d] % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
CH_3[a]	80	1.5	37[c]	1.5397	1.0548	46.28	48.22	$C_{10}H_{10}O_2$	74.05	73.79	5.98	5.98
C_2H_5	85–86.5	1	50[c]	1.5303	1.0402	50.88	52.35	$C_{11}H_{12}O_2$	74.99	74.62	6.87	6.88
n-C_3H_7	95–96	2	34[c]	1.5238	1.0156	55.48	57.30	$C_{12}H_{14}O_2$	75.76	76.03	7.42	7.41
n-C_5H_{11}	112–113	1.5	43[c]	1.5146	0.9880	64.69	66.60	$C_{14}H_{18}O_2$	77.03	76.86	8.31	8.41
n-C_7H_{15}	129–130	2.0	31[c]	1.5074	0.9670	73.90	75.84	$C_{16}H_{22}O_2$	78.01	77.87	9.00	9.12
n-$C_{11}H_{23}$	M. p. 44–45[b]		77	....	....	...	...	$C_{20}H_{30}O_2$	79.42	79.46	10.00	9.99
n-$C_{15}H_{31}$	M. p. 59–60		70	....	....	...	...	$C_{24}H_{38}O_2$	80.39	80.26	10.68	10.79

[a] Ref. 5 reported b. p. 83–86° (2 mm.), $n^{25}D$ 1.5368, d^{25}_4 1.0586. Ref. 6 reported b. p. 100–105° (4 mm.), $n^{25}D$ 1.5356, d^{25}_{25} 1.065. [b] All m. p.'s are corrected. [c] Yields of refractionated product. [d] Analysis by Mr. H. S. Clark, Mr. Ralph Schachat and Mr. Pao-Tung Huang.

substituted cinnamic acid, is essentially that of Walling and Wolfstirn[6,7] who prepared monohalo- and methoxystyrenes.



I II

When R = CH_3, the acetylated derivative of the cinnamic acid was obtained directly by the use of the Perkin procedure[8] instead of the usual Döbner modification of the Perkin reaction,[9] the procedure by which the *p*-hydroxycinnamic acid was best prepared.

The substituted cinnamic acid intermediates all contract from 10 to 20° below the melting point. In addition, with the exception of R = CH_3 and C_2H_5, they show anomalies on melting due to the formation of liquid crystals.[10] This is indicated in Table I by the two melting points recorded. Compounds exhibiting this anomaly tend to preserve a pseudocrystalline structure above the melting point which is stable as a cloudy melt between this temperature and that at which a clear isotropic liquid is formed. The melting points of these cinnamic acids appeared to pass through a minimum at R = C_6H_{13}, C_8H_{17}.

Small amounts of crystalline by-products were obtained in the preparation of *p*-butyroxy and *p*-caproxycinnamic acids. Analyses of these high melting by-products indicate that they are the esterified products obtained from the acyloxycinnamic acids and *p*-hydroxycinnamic acid.

Decarboxylation of the resulting cinnamic acids gave the corresponding styrenes which are described in Table II. As expected, considerable molecular exaltation was exhibited by these styrenes.

Experimental[11]

***p*-Acyloxycinnamic Acids.**—*p*-Hydroxycinnamic acid was prepared by the procedure of Vorsatz[10] except that piperidine was replaced by aniline. From 81 ml. (1 mole) of purified pyridine, 52 g. (0.5 mole) of purified malonic

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(6) For previous examples in the literature of this general decarboxylation procedure see Walling and Wolfstirn, THIS JOURNAL, 69, 852 (1947).

(7) Wiley and Hobson, *ibid.*, **71**, 2429 (1949).

(8) v. Konek and Pacsu, *Ber.*, **51**, 855 (1918). These investigators reported no yield or melting point for this compound prepared by the Perkin procedure, since they converted the crude product to the hydroxy acid. Likewise, Tiemann and Herzfeld (*ibid.*, **10**, 63 (1877)) prepared *p*-acetoxycinnamic acid from the sodium salt of *p*-hydroxybenzaldehyde, acetic anhydride and sodium acetate, but reported no yield.

(9) Vorsatz, *J. prakt. Chem.*, [2] **145**, 265 (1936).

(10) For a discussion of this phenomenon see Bernal and Wooster, "Ann. Repts. on Progress Chem. (Chem. Soc. London)", **28**, 280 (1931). Mark, "Physical Chemistry of High Polymeric Systems," Interscience Publishers, Inc., New York, N. Y., 1940, p. 205.

(11) All melting points are corrected.

acid, 2 ml. of aniline and 61 g. (0.5 mole) of recrystallized *p*-hydroxybenzaldehyde, there was obtained after three recrystallizations from water, 57 g. (70%), m. p. 210.5-211 (206°, 52%[8]), (207°, 33%[12a]), (62%, no m. p.[12b]), (206°, 70%[12c]), (206°, 80%[12d]), (no m. p., 80% crude yield[12e]).

The acid chlorides were prepared according to the procedure described for the preparation of *n*-butyryl chloride (thionyl chloride) by Helfrich and Schaefer[13] (R = n-C_3H_7, n-C_5H_{11}, n-C_7H_{15}) or by the procedure described by Hickenbottom[14] using phosphorus trichloride (R = C_2H_5, n-$C_{11}H_{23}$, n-$C_{15}H_{31}$)and were purified by distillation.

The *p*-acyloxycinnamic acids were prepared by esterification of *p*-hydroxycinnamic acid by the method described by Ullman and Nadai.[15]

The reaction mixture was added to a dilute sulfuric acid solution and either a solid or a heavy oil precipitated. The heavy oils soon solidified on standing. This product was then purified by recrystallization, the first recrystallization being carried out with the addition of Norite. For example, from 41.6 ml. (0.3 mole) of caproyl chloride and 25.5 g. (0.155 mole) of *p*-hydroxycinnamic acid in 175 ml. of dry pyridine, there was obtained 66.8 g. (85%) of a white crystalline solid, m. p. 149.7-150.7°, 175.6-177.6°. These *p*-acyloxycinnamic acids are described in Table I.

p-Acetoxycinnamic acid was prepared by the Perkin procedure according to the method described by v. Konek and Pacsu (38%).[8]

Isolation of By-Products in the Preparation of *p*-Acyloxycinnamic Acids.—On effecting solution of the crude *p*-butyroxycinnamic acid in absolute ethanol, there was obtained a small quantity of a white crystalline material, more insoluble than the main product, m. p. 210.5-211.5°. This may be the product resulting from the esterification of *p*-butyroxycinnamic acid by *p*-hydroxycinnamic acid.

Anal. Calcd. for $C_{22}H_{20}O_6$: C, 69.46; H, 5.31. Found: C, 69.45; H, 5.29.

In a similar way a white crystalline by-product was obtained from *p*-caproxycinnamic acid, m. p. 193.5-194.5°.

Anal. Calcd. for $C_{24}H_{24}O_6$: C, 70.57; H, 5.92. Found: C, 70.54; H, 5.85.

***p*-Acyloxystyrenes.**—The decarboxylation procedure was similar to that described by Walling and Wolfstirn[7] with the following modifications. This procedure was used to prepare all the styrenes except R = $C_{15}H_{31}$. *p*-*t*-Butylcatechol was used as the inhibitor. The period of decarboxylation as determined by carbon dioxide evolution (gas buret and lime water) required about forty minutes. Decarboxylation usually started between 140 and 180° (maximum rate of decarboxylation was reached about 205-210°) and continued as the temperature was raised to the boiling point of quinoline. The colorless liquid styrenes were purified by several distillations from modified Claisen flasks. A typical experiment employed 10 g. of a *p*-acyloxycinnamic acid, 30 g. of quinoline, 1 g. of copper powder and a small amount of *p*-*t*-butylcatechol. When R = $C_{11}H_{23}$, the initial distillation gave a fraction, b. p. 144-157° (1 mm.), which solidified. Four recrystallizations from 95% methanol gave the desired product. This procedure gave a lower yield for R = $C_{11}H_{23}$ than that reported in Table II.

An alternate procedure was used in the preparation of the solid styrenes, R = $C_{11}H_{23}$, $C_{15}H_{31}$ (Table II). The reaction mixture after decarboxylation was separated from the copper powder by filtration. Ether was added to the filtrate and the ether solution treated as described in reference 7, except that additional acidic washes were used. After removal of the ether, the styrenes were recrystallized from 95% methanol. Four or five recrystallizations were necessary in order to obtain an analytical sample.

The use of copper powder in nitrobenzene or aqueous mineral acid to effect the decarboxylation was unsuccessful.

Summary

The preparation and properties of six new *p*-acyloxycinnamic acids and six new *p*-acyloxystyrenes are described.

BROOKLYN, NEW YORK RECEIVED SEPTEMBER 2, 1949

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(12) (a) Kurien, Pandya and Surange, *J. Indian Chem. Soc.*, **11**, 823 (1934); (b) Posner, *J. prakt. Chem.*, (2) **82**, 425 (1910); (c) Eigel, *ibid.*, **20**, 2527 (1887); (d) Zincke and Leisse, *Ann.*, **322**, 220 (1902); (e) Sonn, *Ber.*, **46**, 4050 (1913).

(13) Helfrich and Schaefer, "Organic Syntheses," Vol. 9, John Wiley and Sons, Inc., New York, N. Y., 1929, p. 32.

(14) Hickenbottom, "Reactions of Organic Compounds," Longmans, Green and Co., 1946, p. 195.

(15) Ullman and Nadai, *Ber.*, **41**, 1870 (1908); see also Einhorn, *Ann.*, **301**, 95 (1898).

[CONTRIBUTION FROM THE IOWA AGRICULTURAL EXPERIMENT STATION]

Studies on the Schardinger Dextrins. III. Redistribution Reactions of *Macerans* Amylase[1]

BY ETHELDA NORBERG[2] AND DEXTER FRENCH

The formation of Schardinger dextrins from starch and linear glucosidic dextrins has been attributed to a type of "glucosidic exchange" action.[3] Here, *macerans* amylase is apparently capable of bringing about the exchange of the energy from one α-1,4-glucosidic bond in a linear chain to another new α-1,4-glucosidic bond in a cyclic dextrin. This action has been found to be reversible.[4] *Macerans* amylase has been shown to be capable of transforming purified cyclic dextrins into longer linear molecules in the presence of suitable cosubstrates, such as glucose, maltose, α-methyl glucoside, sucrose, cellobiose, and maltobionic acid.

The studies reported here have shown that the glucosidic exchange action of *macerans* amylase is not limited to reactions involving cyclic dextrin molecules. In the presence of the *macerans* enzyme, linear dextrins are also capable of entering into reaction with each other, which effects redistribution of the available glucose residues among

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(2) A portion of the thesis submitted to the Graduate School, Iowa State College, by Ethelda Norberg in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1949. Present address: Biochemical Division, Medical School, University of California, Berkeley 4, California.

(3) Cori, *Federation Proc.*, **4**, 226 (1945).

(4) French, Pazur, Levine and Norberg, THIS JOURNAL, **70**, 3145 (1948).