lized twice with bone-blacking from ethanol to give 0.25 g. (13% yield) of light yellow, fluffy needles, m. p. 243.5–244.5°. The mixed melting point and ultraviolet absorption spectra proved the product to be identical with the 2-hydroxy-3-methyl-6-methoxyquinoxaline prepared by method A, above.

Preparation of Hinsberg's Mixture of 2-Hydroxy-3-methyl-6-methoxyquinoxaline and 2-Hydroxy-3-methyl-7-methoxyquinoxaline.—A solution of 5.05 g. (0.03 mole) of 3-nitro-4-aminoanisole in 20 ml. of ethanol was reduced with hydrogen over W-2 Raney nickel catalyst at room temperature and pressure until the theoretical amount of hydrogen had been taken up. The alcoholic solution of 3,4-diaminoanisole was filtered into a solution of 2.9 g. (0.033 mole) of pyruvic acid[9] in 10 ml. of ethanol. After the brown solution had been refluxed for thirty minutes, the alcohol was concentrated to a small volume, and the product crystallized out to give 5.05 g. of dark brown material. The product was dissolved in 10 ml. of 5% sodium hydroxide solution, passed through a column of charcoal and Super-cel, and reprecipitated with acetic acid. The light brown product was recrystallized from ethanol to give 3.1 g. (54% yield) of light tan crystals, m. p. 192–193°. The melting point reported by Hinsberg[2] was 197°. (Reference to Fig. 1 shows that a 1:1 mixture of analytical samples of 2-hydroxy-3-methyl-6-methoxyquinoxaline and 2-hydroxy-3-methyl-7-methoxyquinoxaline melted at 193–194°.) This material was exhaustively recrystallized from 95% ethanol to give as the least soluble component 0.1 g. of the amphoteric, light-yellow crystals of 2-hydroxy-3-methyl-6-methoxyquinoxaline, m. p. 241–244°.

Anal. Calcd. for $C_{10}H_{10}O_2N_2$: N, 14.7. Found: N, 14.8.

Mixed melting points proved this material to be identical with the 2-hydroxy-3-methyl-6-methoxyquinoxalines prepared by methods A and B, above.

Absorption Spectra.—The ultraviolet absorption spectra in Fig. 2 were obtained on a Beckman Model DU Quartz Spectrophotometer. All curves were run on analytical material at concentrations of 10 mg./l. of solvent; width of quartz sample cell was 1.003 cm.

Acknowledgment.—The authors are grateful to Dr. J. P. Sickels and Dr. W. H. Steinbach for their kind encouragement and interest.

Summary

Starting with 3-amino-4-nitroanisole and also 3-nitro-4-acetamidoanisole, 2-hydroxy-3-methyl-6-methoxyquinoxaline was prepared by two unequivocal procedures.

2-Hydroxy-3-methyl-7-methoxyquinoxaline was prepared by an unequivocal procedure, starting with 3-nitro-4-aminoanisole.

The product of the direct condensation of 3,4-diaminoanisole with pyruvic acid was shown to be an equimolecular mixture of 2-hydroxy-3-methyl-6-methoxyquinoxaline and 2-hydroxy-3-methyl-7-methoxyquinoxaline.

CORAL CABLES, FLORIDA RECEIVED FEBRUARY 17, 1949

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[9] Pyruvic acid obtained from Paragon Chemical Company was used without further purification.

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Preparation of Some Polymerizable Esters of 10-Hendecenoic (Undecylenic) Acid

BY E. F. JORDAN, JR., AND DANIEL SWERN

As an extension of our work on the relationship between the structure of long-chain unsaturated esters and their polymerizability,[2,3] we have prepared a series of esters of 10-hendecenoic (undecylenic) acid with seven unsaturated alcohols, and have briefly investigated the polymerizability of the more reactive products. A search of the literature revealed that none of the esters we planned to prepare had been described, although the vinyl[4] and allyl[5] esters have been mentioned in patents.

Vinyl 10-hendecenoate was prepared by acidolysis of vinyl acetate with 10-hendecenoic acid in the presence of mercuric acetate and 100% sulfuric acid as catalysts.[2,3,6] The allyl, 2-chloroallyl, crotyl and 3-buten-2-yl esters were prepared by direct esterification of 10-hendecenoic acid with the appropriate alcohol, naphthalene-2-sulfonic acid being employed as the catalyst and benzene as an entraining agent to remove the water formed during the reaction.[2,3,7] The methallyl and furfuryl esters were prepared by the alcoholysis of methyl 10-hendecenoate with the appropriate alcohol, the corresponding sodium alcoholate being employed as catalyst.[2,3,7,8] The yields and characteristics of the esters are summarized in Table I. In general, yields were high. The products were colorless, odorless, water-insoluble, high-boiling liquids, with the exception of furfuryl 10-hendecenoate, which was pale yellow.

To obtain information regarding their polymerizability the vinyl, 2-chloroallyl, allyl and methallyl esters were heated with small quantities of benzoyl peroxide. Vinyl 10-hendecenoate was heated at 100° in the presence of 1% of benzoyl peroxide as initiator. In less than one hour, considerable insoluble material had formed, and within two hours the product appeared to be completely converted to a soft, crumbly, transparent gel. At 80°, approximately sixteen hours was required to obtain complete gelation. Gelation was considered complete when no liquid could be seen in the test tube in which the polymerization was being carried

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[2] Swern, Billen and Knight, THIS JOURNAL, **69**, 2439 (1947).

[3] Swern and Jordan, *ibid.*, **70**, 2334 (1948).

[4] Imperial Chemical Industries, Ltd., British Patent 581,501 (1946).

[5] Renault, French Patent 846,063 (1939).

[6] Toussaint and MacDowell, U. S. Patent 2,299,862 (1942).

[7] Swern and Jordan, THIS JOURNAL, **67**, 902 (1945).

[8] Swern, Jordan and Knight, *ibid.*, **68**, 1673 (1946).

TABLE I

CHARACTERISTICS OF UNSATURATED ALCOHOL ESTERS OF 10-HENDECENOIC ACID, $CH_2=CH-(CH_2)_8-CO-O-R$

R	Yield,[a] %	Boiling point °C.	Mm.	Iodine no.[b] (Wijs, 1 hr.) Calcd.	Found	Sapon. equiv.[b] Calcd.	Found	Carbon, %[c] Calcd.	Found	Hydrogen, %[c] Calcd.	Found	$n^{30}D$ (Abbe)[d]	d^{30}_4	Mol. refr. Calcd.	Found
Vinyl	70	124–124.5	10	241	238	...	...	74.2	74.6	10.5	10.6	1.4442	0.8799	63.0	63.5
Allyl	90	179.5–180	50	226	227	224	225	75.0	74.8	10.8	11.0	1.4448	.8802	67.6	67.9
2-Chloroallyl	90	144.5–145.5	4.5	...	...	...	...	65.0	64.7	8.96	9.24	1.4569	.9711	72.4	72.5
Methallyl (2-methylallyl)	70	151–152	10	213	214	238	239	75.6	75.8	11.0	10.8	1.4467	.8778	72.2	72.4
Crotyl	90	157–158	10.5	213	212	238	241	75.6	75.5	11.0	11.2	1.4486	.8796	72.2	72.7
3-Buten-2-yl (1-methylallyl)	85	145–146	11	213	212	238	241	75.6	75.8	11.0	11.1	1.4417	.8700	72.2	72.6
Furfuryl	40	164–165	4.3	...	...	264	261	72.7	72.5	9.15	8.94	1.4671	.9675	75.8	75.8

[a] Purified products after two vacuum distillations. [b] Analyses by R. E. Koos, of the Oil and Fat Division of this Laboratory. In the analysis of the vinyl ester, a 200% excess of iodine chloride reagent was employed.[3] [c] Analyses by Mary Jane Welsh, of the Analytical and Physical Chemistry Division of this Laboratory. [d] Δn per degree = -0.0004.

out, and a small quantity of gel squeezed between sheets of absorbent paper produced no oily stain. 2-Chloroallyl 10-hendecenoate was converted to a soft, transparent, pale-yellow, crumbly gel when heated for sixty-five hours at 50°, forty-eight hours at 65–70°, and then for twenty-four hours at 85°, in the presence of 0.5% of benzoyl peroxide as initiator. When allyl and methallyl 10-hendecenoates were similarly treated, they displayed little tendency to polymerize, as evidenced by reduction in their iodine numbers of only about 10%.

These four esters were also copolymerized with vinyl acetate in the presence of 0.5% of benzoyl peroxide as initiator, according to a previously described procedure.[2,9] The copolymers ranged from hard, glasslike, tough, insoluble resins from 1 to about 20% of hendecenoate; they remained tough but became elastic in the range of from 20 to 40% of hendecenoate, and at higher contents they became soft and crumbly. They were all colorless except the chloroallyl hendecenoate–vinyl acetate copolymer which was pale yellow at 40 to 60% of hendecenoate. The insoluble copolymers charred before melting when heated on a spatula over an open flame. Of special interest were the copolymers containing 20–40% of vinyl or 2-chloroallyl 10-hendecenoate and 20% of allyl or methallyl 10-hendecenoate, since these products were both tough and elastic.

Vinyl and 2-chloroallyl 10-hendecenoates show a greater tendency to cross link than the corresponding oleates,[2] which do not form gels even when heated for about sixty hours at 100° in the presence of 1% of benzoyl peroxide.

In view of the known lack of reactivity of crotyl, 3-buten-2-yl and furfuryl esters in peroxide-initiated polymerizations, no work was done on them.

Experimental Details

All operations were conducted in an atmosphere of nitrogen.

Starting Materials.—Two kilograms of commercial 10-hendecenoic acid was distilled through a fractionating column 4 feet long and 1 inch in diameter packed with $^{3}/_{32}$-inch glass helices. The main fraction was a colorless liquid, b. p. 179–80° at 26.5 mm., $n^{30}D$ 1.4457 and m. p. 23.4–23.8° (lit.[10] 24.6°), which amounted to about 1350 g. and consisted of 10-hendecenoic acid of about 98–99% purity (iodine number: calcd., 138; found, 137. Neutralization equivalent: calcd., 184; found, 186). This was recrystallized from petroleum naphtha, hexane fraction, boiling range, 63–70°, at −20° (4 ml. of solvent per g. of solute), yielding 1050 g. of pure 10-hendecenoic acid in the form of large, pearly flakes, m. p. 24.3–24.5° (iodine number: found, 137. Neutralization equivalent: found, 185). Methyl 10-hendecenoate was prepared from the pure acid by refluxing it for four hours with a 500% molar excess of anhydrous methyl alcohol containing concentrated sulfuric acid (2% of the weight of 10-hendecenoic acid) as catalyst. The reaction mixture was poured into a large quantity of warm water, and the upper layer was washed with water until free of sulfuric acid. The crude ester was dried by heating to 100° under moderate vacuum in a stream of nitrogen, and it was then vacuum distilled. Pure methyl 10-hendecenoate, b. p. 142° at 26 mm. and $n^{30}D$ 1.4349, was obtained in more than 90% yield. (Iodine number: calcd., 128; found, 127. Saponification equivalent: calcd., 198; found, 199.)

Vinyl acetate (stabilized) and allyl, 2-chloroallyl, methallyl, crotyl, 3-buten-2-yl and furfuryl alcohols, the purest commercial grades obtainable, were distilled immediately before use through a fractionating column 40 inches long and 1 inch in diameter packed with $^{2}/_{32}$-inch glass helices.

Esterification Procedures.—The methods described in two previous papers[2,3] were employed.

Polymerization of Vinyl, 2-Chloroallyl, Allyl and Methallyl 10-Hendecenoates.—Benzoyl peroxide (0.5 to 1% by weight of monomer) was added to freshly distilled samples of each of the esters, contained in test-tubes, and the polymerizations were conducted as described earlier in the paper. A thermostatically controlled oven or oil-bath was employed.

Copolymerization of 10-Hendecenoates with Vinyl Acetate.—The copolymerizations were conducted as previously described.[2,9]

Summary

Seven esters of 10-hendecenoic (undecylenic) acid, namely, vinyl, allyl, 2-chloroallyl, methallyl (2-methylallyl), crotyl, 3-buten-2-yl and furfuryl 10-hendecenoate, have been prepared in good yield from 10-hendecenoic acid or its methyl ester and the appropriate alcohol. Some of their characteristics have been determined.

The vinyl, 2-chloroallyl, allyl and methallyl

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[9] Guile and Huston, "A Revised Laboratory Manual of Synthetic Plastics and Resinous Materials," Michigan State College, Lansing, Mich., 1944, p. 99.

[10] Ashton and Smith, *J. Chem. Soc.* 435 (1934).

esters were polymerized with benzoyl peroxide as initiator. The first two esters were readily converted to gels, whereas the last two showed relatively little tendency to polymerize. Copolymerization of the esters with vinyl acetate over the range of from one to forty per cent. hendecenoate yielded insoluble copolymers which ranged in physical appearance from hard, glass-like resins to soft, crumbly gels.

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[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

Cation Complexes of Compounds Containing Carbon–Carbon Double Bonds. II. The Solubility of Cuprous Chloride in Aqueous Maleic Acid Solutions[1]

BY L. J. ANDREWS AND R. M. KEEFER

Data have been reported previously[2] which illustrate that the solubility of cuprous chloride in aqueous maleic acid solutions varies markedly with the hydrogen ion concentration of the medium. These data were interpreted on the assumption that $H_2M \cdot CuCl$ and $HM \cdot CuCl^-$ were the only water soluble complexes formed in appreciable quantities under the experimental conditions used.[3] More recently[1,4] it has been observed that the extent of formation of water soluble cuprous complexes of compounds containing carbon–carbon double bonds generally depends on the chloride ion concentration of the medium. Accordingly additional experiments with maleic acid have been made, the results of which are reported here. These new data indicate that, in addition to the aforementioned complexes, $H_2M \cdot Cu^+$ and $HM \cdot Cu$ may be formed in significant amounts.

Experimental

The Solubility Measurements.—The methods for preparation of the maleic acid–cuprous chloride solutions and the method of analysis for cuprous content have been described in detail previously.[1,2] As reported earlier the solutions of the maleic acid complexes are intensely yellow colored.[2]

Results

The measured solubilities of cuprous chloride in moles per liter (Cu^+_T) in aqueous solutions as influenced by changes in the initial concentrations of maleic acid (H_2M_i), hydrogen ion and chloride ion are given in Table I. The ionic strengths of the solutions were in the neighborhood of 1.0 (runs 1–9) or 0.1 (runs 10–27). No attempt was made to apply activity coefficient corrections to the concentrations of the complexes in the calculation of equilibrium constants as described later.[5]

TABLE I

THE SOLUBILITY OF CUPROUS CHLORIDE IN AQUEOUS SOLUTIONS OF MALEIC ACID AT 25°[a]

	Concns., mole/liter						
Run	(H_2M_i)	(HCl_i)	(H^+)	(H_2M)	(Cl^-), $\times 10^3$	(Cu^+_T) $\times 10^3$ meas.	calcd.
1	0.202	0	1.03	0.187	7.1	11.8	12.0
2	.101	0	1.02	.094	5.1	7.7	7.7
3	.0503	0	1.02	.045	3.5	4.8	5.0
4	.202	0.100	1.03	.193	94.5	11.0	10.7
5	.101	.100	1.02	.097	94.2	8.0	8.4
6	.0503	.100	1.02	.048	94.0	6.8	7.3
7	.184	.0091	1.03	.174	12.3	9.2	8.6
8	.101	.0100	1.02	.097	11.6	5.3	5.2
9	.0503	.0100	1.02	.048	10.5	3.0	3.0
10	.202	0	0.138	.159	11.0	19.2	18.8
11	.152	0	.129	.117	9.7	16.0	15.8
12	.101	0	.122	.075	7.9	12.8	12.2
13	.0505	0	.113	.036	5.6	8.3	8.1
14	.202	0.100	.133	.166	94.0	14.2	14.4
15	.152	.100	.126	.124	95.0	12.4	12.5
16	.101	.100	.118	.081	94.0	10.9	10.6
17	.202	.0100	.136	.161	16.8	15.8	15.5
18	.101	.0100	.120	.079	14.2	9.6	9.4
		(KCl)					
19	.202	0	.067	.134	13.6	24.0	24.3
20	.101	0	.043	.056	10.4	17.0	17.1
21	.0504	0	.028	.021	7.9	11.8	11.8
22	.202	0.100	.060	.139	96.1	17.6	17.8
23	.152	.100	.051	.098	96.0	15.4	15.9
24	.101	.100	.040	.060	95.3	12.8	13.3
25	.202	.010	.062	.136	19.1	20.2	21.0
26	.152	.010	.053	.096	18.4	17.3	17.7
27	.101	.010	.043	.057	16.5	14.1	13.8

[a] In runs 1–9 μ was adjusted to 1.0 by the addition of perchloric acid before the addition of maleic acid and cuprous chloride. Similarly in runs 10–18 μ was adjusted to 0.10. In runs 19–27 μ was adjusted to 0.100 by the addition of sodium perchlorate.

It is apparent that an increase in the hydrogen ion concentration of the solutions results in a decrease in the solubility of cuprous chloride (*cf.* runs 1, 10 and 19 at constant initial maleic acid concentration). Similarly an increase in chloride ion concentration inhibits the formation of the maleic acid complexes. This effect is not immediately obvious in terms of Cu^+_T values since they include the concentrations of $CuCl_2^-$.

On the basis of these qualitative observations it has been postulated that equations (1)–(7) are sufficient to account for the equilibrium conditions in these solutions, and the solubility data have been used to calculate the val-

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[1] For paper I of this series see Keefer and Andrews, THIS JOURNAL, **71**, 1723 (1949).

[2] Andrews and Keefer, *ibid.*, **70**, 3261 (1948).

[3] The terms H_2M and HM^- are used, respectively, to represent maleic acid and acid maleate ion.

[4] Keefer, Andrews and Kepner, *ibid.*, **71**, 2381 (1949).

[5] This seems justifiable since the concentrations are sufficiently high in these solutions so that the electrostatic effects no longer change rapidly with concentration and are small enough so that non-electrostatic forces are still small. For hydrochloric acid, the two effects compensate almost exactly at these two concentrations. *Cf.* Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, p. 475.