ART. XL.—*On the Preparation and Properties of Hydracrylic Esters*; by W. A. DRUSHEL and W. H. T. HOLDEN.

(Contributions from the Kent Chemical Laboratory of Yale Univ.—cclxxv.)

THE esters of hydracrylic acid have up to the present time received but little attention, only the methyl and ethyl esters are mentioned in the chemical literature. The direct esterification of hydracrylic acid had apparently not been attempted until one of us * prepared ethyl hydracrylate in this laboratory by the direct esterification process. As described in the literature the indirect methods of preparation are objectionable since the esters are obtained in impure condition, containing impurities not easily removable. Obviously mineral acids can not be used as catalytic agents in the esterification of hydracrylic acid since under the necessary conditions hydracrylic acid is converted into acrylic acid and the resulting esters are chiefly acrylic esters.

The object of this investigation was to study the direct esterification of hydracrylic acid with the common alcohols, and the properties of the series of esters prepared in this way. Sodium hydracrylate was prepared from glycerine by the methods fully described in our previous paper.† The importance of keeping the solution of sodium hydracrylate slightly acid during evaporation is to be emphasized, since in alkaline solution condensation products are formed and only very little sodium hydracrylate is obtained. The best procedure appears to be nearly to neutralize β -iodopropionic acid with sodium carbonate, taking care to leave the solution distinctly acid. The solution is then treated with an excess of silver oxide freshly prepared and free from alkali. In this way the resulting solution contains sodium hydracrylate with a little silver hydracrylate. After filtering off the silver iodide the solution is treated with hydrogen sulphide to decompose any silver salt present. The silver sulphide is then filtered off and the filtrate is usually sufficiently acid to permit evaporation to dryness on the steam bath without the formation of more than very small amounts of by-products. The dry sodium hydracrylate thus prepared is further purified by recrystallization from 95 per cent alcohol. The yield is almost quantitative. Weighed portions of the purified and dried sodium hydracrylate were dissolved in the least possible amount of cold water and treated with a little less than the theoretical amount of 1:1 sulphuric acid, keeping the reaction mixture cold during the process. The water in the resulting mixture was evaporated off on the steam bath attended by only a slight loss of hydracrylic acid, leaving a residue of sodium sulphate and pure hydracrylic acid.

* This Journal, xxxix, 113-121, 1915.

† Loc. cit.

The hydracrylic acid thus prepared, in about 50 gram portions, was extracted from the residue by the absolute alcohol to be used in the subsequent esterification process.

The alcoholic solution of hydracrylic acid, about 200^{cm}³ in volume, was treated with somewhat more than the theoretical amount of anhydrous copper sulphate free from sulphur trioxide. The reaction mixture was gently boiled with a reflux condenser on a sand bath until 80 per cent to 90 per cent of the hydracrylic acid had been esterified. The course of the esterification was followed by titrating from time to time 1^{cm}³ of the reaction mixture with decinormal barium hydroxide. After the completion of the reaction the copper sulphate was filtered off, the unesterified hydracrylic acid almost neutralized with anhydrous sodium carbonate, the excess of alcohol distilled off in a water or oil bath and the residue of hydracrylic ester subjected to fractional distillation under diminished pressure, usually at 12^{mm} to 20^{mm}. The esters which were prepared in this way and whose properties were then studied are the methyl, ethyl, propyl, isopropyl, isobutyl and isoamyl esters of hydracrylic acid. The densities of these esters were determined at 0° and at 25°; the values obtained are recorded in Table I.

TABLE I.

	0°	25°
Methyl hydracrylate	1.140	1.118
Ethyl "	1.085	1.064
Propyl "	1.052	1.043
Isopropyl "	1.071	1.058
Isobutyl "	1.013	1.003
Isoamyl "	0.988	0.976

These density determinations are referred to water at 4° and were made by means of a pycnometer* of a type which was especially devised for use in the qualitative organic analysis work in this laboratory. It consists of a capillary stem about 7^{cm} in length, a bulb to contain approximately 1^{cm}³ and a drawn out capillary about 1^{cm} in length. The capillary stem is graduated so that the pycnometer shall contain exactly one cubic centimeter of water at 4°. This type of instrument has the advantage that by a single weighing it gives fairly accurate specific gravity data even in the hands of those not skilled in the use of the more complicated types.

All of the hydracrylic esters investigated boil with decomposition at atmospheric pressure. Their boiling points were therefore determined directly over a range of pressures of 15^{mm} to about 100^{mm} and from the data obtained the boiling points

* A cut of this type is published in the Journal of Industrial and Engineering Chemistry, vii, 187.

for atmospheric pressure were estimated by the graphic method. The results are recorded in Table II.

TABLE II.
Boiling points of hydracrylic esters.

Methyl ester		Ethyl ester		Isopropyl ester		Propyl ester		Isobutyl ester		Isoamyl ester	
Press. in mm.		Press. in mm.		Press. in mm.		Press. in mm.		Press. in mm.		Press. in mm.	
B.P.		B.P.		B.P.		B.P.		B.P.		B.P.	
79	12	84	12	95	12	98	12	104	15	121·5	17
87	20	91·5	19	99	20	102	19	112	20	124	20
107·5	40	95·5	22	109	35	120	43	126	45	137	36
111	56	116	62	114	42	127	62	129	50	147	58
121	94	127	102	128·5	82	142	107	143	88	159	95
184**	760	190**	760	196**	760	205**	760	212**	760	225**	760

** Calculated.

All of the esters of this series below the isobutyl ester are freely soluble in water in all proportions, but the higher homologues are not. The isobutyl ester is soluble in 18 parts of water and the isoamyl ester in 60 parts of water at room temperature.

The refractive indices of the esters were determined by means of the Pulfrich refractometer for the D line of sodium light and the following results obtained :

TABLE III.

	n	$(n-1) \frac{M}{d}$	M
Methyl hydracrylate.....	1·4306	40·10	104·0
Ethyl " ".....	1·4271	47·30	118·0
Propyl " ".....	1·4341	54·85	132·0
Isopropyl " ".....	1·4303	53·68	132·0
Isobutyl " ".....	1·4342	63·70	146·0
Isoamyl " ".....	1·4374	71·65	160·0

These indices of refraction were determined at 23° C.

Conclusions:—

1. Hydracrylic acid is obtained from glycerine in a fair yield by slight modifications of the methods described in the literature.

2. Removal of the iodine from sodium β -iodopropionate rather than from the free acid by means of silver oxide has the advantage that the reaction goes at room temperature and requires only about half of the silver oxide theoretically required when the free acid is used instead of the sodium salt. Precautions must, however, be taken to prevent the solution from becoming alkaline. This is important since on evaporat-

ing an alkaline solution of sodium hydracrylate condensation products are formed and but very little sodium hydracrylate is found in the residue.

3. Hydracrylic acid in the absence of mineral acids is easily esterified directly with methyl, ethyl, propyl, isopropyl, isobutyl and isoamyl alcohols by using anhydrous copper sulphate as a dehydrating agent. The esters are obtained in 80 per cent to 90 per cent yields.

4. The hydracrylic esters are colorless liquids with faint but characteristic ethereal odor, mostly easily soluble in water; all below isoamyl are heavier than water; all are decomposed on boiling at atmospheric pressure, but are distillable without decomposition under diminished pressure.