ART. VI.—*On the Preparation and Hydrolysis of Ethyl Hydracrylate;* by W. A. DRUSHEL.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—cclxiii.]

HYDRACRYLIC acid is a well-known substance and has been prepared by several methods; its esters, however, have received but little attention. In Beilstein's Handbuch the ethyl ester alone is mentioned in connection with Klimenko's attempt to prepare paracrylic acid. Only three references are given to the ethyl ester in Richter's Lexikon and of these but one deals with the direct preparation of the ester. Apparently in no former investigation has hydracrylic ester been prepared by the esterification of hydracrylic acid, nor was the ester obtained in pure condition by any of the methods described in the literature. It seemed desirable therefore to prepare, if possible, hydracrylic ester by the direct esterification of hydracrylic acid in order to obtain the ester in pure condition for the purpose of determining its properties and supplying additional hydrolysis data for the series of esters studied in this laboratory.

Preparation of the Ester: (*a*) Method of Klimenko.* Klimenko obtained what he called paracrylic acid by repeatedly evaporating hydracrylic acid with concentrated hydrochloric acid. He then heated 3 grams of this acid with an excess of absolute alcohol at 150° and obtained an ester which boiled at 185° to 190° and which he believed to be ethyl hydracrylate. Ethyl hydracrylate, however, decomposes below 185° when heated at ordinary pressure. In attempting to repeat Klimenko's work the author was unable to prepare the so-called paracrylic acid by the method described. Baeyer† did not believe that Klimenko had succeeded in preparing paracrylic acid, $(C_3H_4O_2)_2$, but rather that Klimenko's acid was an unsaturated dibasic acid of the formula $C_6H_8O_4$. If Baeyer's observation was correct Klimenko's ester could not have been hydracrylic ester.

(*b*) Method of Curtius and Müller.‡ These investigators obtained impure ethyl hydracrylate by converting beta-chlorpropionic ester into beta-aminopropionic ester hydrochloride and treating this with nitrous acid. The ester contained a little chlorpropionic ester as an impurity, from which it could not be freed by fractionation. The crude ester which they obtained boiled at 80° to 84° at 12^{mm} pressure, or at 170° to 175° under ordinary pressure. The method is obviously not

* Klimenko, Rafalowicz, Jour. Russ. Chem. Soc., xxvi, 412.

† Baeyer, Ber. Dtsch. Chem. Gesellsch., xviii, 680.

‡ Curtius and Müller, Ber. Dtsch. Chem. Gesellsch., xlx, 850; xxxvii, 1276.

suitable for the preparation of the ester in sufficiently pure condition to study its properties and rate of hydrolysis.

(*c*) Method of Blaise and Maire.* Blaise and Maire passed into glacial acetic acid at 0° the formaldehyde vapor obtained by the depolymerization of trioxymethylene. The saturated acetic acid solution was then allowed to warm up slowly, resulting in a polymer of formaldehyde less complex than trioxymethylene. This polymer was condensed with bromacetic ester in the presence of zinc in a mixture of equal parts of absolute alcohol and ethyl acetate. They obtained a 40 per cent yield of ethyl hydracrylate whose boiling point was given as 81° at 13^{mm} pressure. It is to be observed that this boiling point is about the same as that given for Curtius and Müller's admittedly impure ethyl hydracrylate.

(*d*) Direct Esterification Method. In view of the instability of beta-oxyacids on heating in the presence of mineral acids, and of the work of Bogojawlensky and Narbut† on the use of anhydrous copper sulphate to facilitate esterification in the presence of acid catalyzers, and the more recent work of Clemmensen and Heitman‡ on the use of anhydrous copper sulphate in the esterification of certain oxyacids in the absence of any catalyzing acid, it seemed reasonable to expect this procedure to be applicable for the preparation of pure ethyl hydracrylate. The work of preparing ethyl hydracrylate resolved itself into two parts, 1st, the preparation of a sufficiently large amount of pure hydracrylic acid, and 2d, the esterification of the acid.

1. *The preparation of hydracrylic acid.*—Of the several methods described for the preparation of hydracrylic acid the method using glycerine as a starting-out material, with certain modifications, was found to be the most expedient for preparing the pure acid in considerable quantity. The modifications of former methods which will be pointed out resulted in increasing the yield and purity of the hydracrylic acid.

A kilo of glycerine was mixed with a liter of water and oxidized in 200$^{cm^3}$ portions by fuming nitric acid in tubes about 20^{mm} in internal diameter kept cold by running water, according to the procedure outlined by Mulder.§ After the oxidation was complete the liquid was concentrated in 400$^{cm^3}$ portions on the steam bath to remove any dissolved nitrous acid. On cooling some oxalic acid crystallized out. The filtrates from the several 400$^{cm^3}$ portions were combined and treated with a little more than enough calcium carbonate to precipitate out the dissolved oxalic acid as calcium oxalate, which was removed by filtration. The filtrate was diluted with water to 3 liters

* Blaise and Maire, C. r. d. l'Acad. des Sciences, cxlii, 215–17.
† Bogojawlensky and Narbut, Ber. Dtsch. Chem. Gesellsch., xxxviii, 3344.
‡ Clemmensen and Heitman, Am. Chem. Jour., xl, 319.
§ Mulder, Ber. Dtsch. Chem. Gesellsch., ix, 1902.

and heated to about 80°. The hot solution was neutralized with calcium carbonate, making use of mechanical stirring to facilitate the solution of the carbonate. The solution was allowed to stand over night for the main portion of the calcium glycerate to crystallize out. This first crop of calcium glycerate after washing with a little cold water was sufficiently pure for further use. The mother liquor, after making faintly acid to prevent darkening on heating, was concentrated on the steam bath and set aside to crystallize. After recrystallizing this second crop of calcium glycerate it was sufficiently pure, and was added to the first crop. The calcium glycerate so prepared was dissolved in hot water and treated with the theoretical amount of dissolved oxalic acid, the calcium oxalate was filtered off and the filtrate concentrated on the steam bath to a specific gravity of 1·26, containing about 61 per cent of glyceric acid. This is the most favorable concentration for converting glyceric acid into beta-iodopropionic acid by the action of phosphorus iodide.

For the preparation of beta-iodopropionic acid a modification was introduced into the method of Wislicenus* and Erlenmeyer,† making use of solid yellow phosphorus instead of the carbon disulphide solution, whereby at last 90 per cent of the glyceric acid was converted into the iodopropionic acid. One hundred grams of iodine were placed into a 750^{cm^3} round-bottom flask and covered with 100 grms. of 61 per cent aqueous glyceric acid. Then 15 grms. of yellow phosphorus were added during the course of five minutes in pieces of about 1 grm. each, shaking the flask after the addition of each piece and cooling the flask by immersing it in a cold water bath from time to time. The flask was next connected with a condenser tube to serve as a reflux condenser, and the mixture cautiously warmed on a water bath to start the reaction of the phosphorus iodide with the glyceric acid. The reaction soon tends to become violent with the loss of large quantities of hydriodic acid. In order to prevent the loss of hydriodic acid as far as possible, the reaction was moderated by immersing the flask in cold water for a few minutes from time to time. After the first vigorous reaction was over the mixture was heated on the boiling water bath for half an hour, poured into a beaker, covered with a watch glass and set aside over night to crystallize. The crystals of pure beta-iodopropionic acid were then filtered off with suction, washed with a little cold water, the filtrate boiled for an hour with a reflux condenser and again set aside to allow more beta-iodopropionic acid to crystallize out. The two crops of crystals were combined and

* Wislicenus, Ber. Dtsch. Chem. Gesellsch., viii, 1207.
† Erlenmeyer, Ann. Chem. Pharm., cxci, 284.

recrystallized from a little hot water, yielding white pearly plates of pure beta-iodopropionic acid.

To prepare the sodium salt of hydracrylic acid a modification was introduced into the method of Wislicenus* for the conversion of beta-iodopropionic acid into hydracrylic acid by the action of freshly prepared silver oxide. Sokolow† observed that when a water solution of beta-iodopropionic acid is boiled with freshly prepared silver oxide the iodine is quickly fixed as silver iodide and that in solution are dihydracrylic acid, $C_6H_{10}O_6$, and an isomer of this acid besides the hydracrylic acid sought. Moldenhauer‡ also made the observation that considerable lactic acid is formed in this procedure. In order to avoid the formation of lactic acid and the acids identified by Sokolow, Wislicenus heated his solution below 100° while fixing the iodine by means of silver oxide. The silver which combined with the hydracrylic acid formed in the reaction he removed by means of hydrogen sulphide, neutralized the acids in solution with sodium carbonate and evaporated to complete dryness. From the dry mixture of sodium salts Wislicenus extracted sodium hydracrylate with boiling 95 per cent alcohol, leaving in the residue the sodium salts of Sokolow's acids.

It was found preferable to modify this procedure by neutralizing the beta-iodopropionic acid with sodium carbonate, and then removing the iodine by acting upon a concentrated solution of sodium beta-iodopropionate with a slight excess of freshly prepared silver oxide at room temperature, making use of mechanical stirring during the process of replacing the iodine by the OH group. To remove completely the iodine from the sodium salt of 400 grms. of beta-iodopropionic acid by this procedure required about two hours, but the resulting sodium hydracrylate was apparently free from the salts of the acids formed by the older methods and identified by Sokolow and others. After the complete fixation of the iodine as indicated by no further change in the color of silver oxide when added to the solution, the precipitated silver iodide was filtered off and the filtrate evaporated to complete dryness over the steam bath. It is important that the sodium hydracrylate should be evaporated to complete dryness in order to be able to purify the salt by crystallization from 95 per cent alcohol. The dried residue of sodium hydracrylate was dissolved in boiling 95 per cent alcohol, and allowed to crystallize out on cooling. The residue of sodium salt was completely dissolved by the hot alcohol, indicating the absence of the sodium salts of Sokolow's acids. The crystallized sodium hydracrylate was treated with a little less than the theoretical amount of dilute

* Wislicenus, Ann. Chem. Pharm., clxvi, 10.
† Sokolow, ibid., cl, 167.
‡ Moldenhauer, ibid., clxvi, 10.

(1 : 3) sulphuric acid in the cold. The excess of water was then evaporated off on the steam bath, the hydracrylic acid was extracted from the residue of sodium sulphate with absolute alcohol and the alcoholic solution of hydracrylic acid, free from sulphuric acid, was used in the esterification experiments to be described.

2. *The esterification of hydracrylic acid.*—In the preparation of one sample of hydracrylic acid a very slight excess of sulphuric acid was used in liberating the hydracrylic acid. The hydracrylic acid without purification from the trace of sulphuric acid was esterified by boiling with a large excess of absolute alcohol for twelve hours without the addition of any catalyzing acid. About two-thirds of the acid was esterified, but a relatively large proportion of the resulting ester proved to be acrylic ester. A second sample of hydracrylic acid free from sulphuric acid was esterified by boiling with a large excess of absolute alcohol in the presence of anhydrous copper sulphate prepared by the gentle ignition of crystallized copper sulphate, but not freed from the traces of sulphuric acid formed in the process of dehydration. Here again the esterification proceeded rapidly until about 70 per cent of the acid was esterified, but as before, the result was a mixture of acrylic and hydracrylic esters. It seemed, therefore, necessary to avoid even very small amounts of mineral acids in the esterification of hydracrylic acid in order to prevent the formation of acrylic ester.

Wislicenus* suggested the use of the vapor from boiling absolute alcohol as an efficient dehydrating agent in esterification. The inefficiency of absolute alcohol alone as well as that of absolute alcohol vapor passed through the reaction mixture and the superiority of anhydrous copper sulphate as a dehydrating agent are shown in the following experiment: Thirty-two grams of hydracrylic acid free from sulphuric acid were first boiled, with a reflux condenser, with 200^{cms} of absolute alcohol for three hours, giving 9·4 per cent of the theoretical yield of ester; at the end of six hours 17 per cent of the acid was esterified. Then the reaction flask was heated at 110° and absolute alcohol vapor passed through the reaction mass, giving at the end of two hours 40 per cent of ester, and after two hours more only 42 per cent of ester. The current of absolute alcohol vapor was then discontinued and about 30 grms. of anhydrous copper sulphate, free from sulphuric acid, were added and the reaction mixture gently boiled, giving after three hours 74 per cent of ester, and after three hours more 83 per cent of the acid was esterified. The ester formed was found to be hydracrylic ester free from acrylic ester.

* Wislicenus, Ann. Chem. Pharm., clxiv, 181.

In another experiment 26·4 grms. of hydracrylic acid were gently boiled with 200$^{cm^3}$ of absolute alcohol in the presence of about 50 grms. of anhydrous copper sulphate freed from sulphuric acid, by means of absolute alcohol. At the end of three hours 66 per cent of the acid was esterified, at the end of six hours 71·4 per cent; at the end of nine hours 83 per cent of the theoretical amount of ester was formed and the boiling was discontinued. To remove the unesterified hydracrylic acid in this and in the previous experiment a little less than the theoretical amount of anhydrous sodium carbonate was added to the esterification mixture and the excess of alcohol was distilled off on the water bath. The hydracrylic ester was extracted from the residue with dry ether and the ether distilled off on a warm water bath, finally heating the water bath to boiling. From the two experiments 53 grms. of crude hydracrylic ester were obtained which on fractionation under diminished pressure yielded 45 grms. of ethyl hydracrylate boiling at 95·5° to 96° at a pressure of 20^{mm} to 22^{mm}. The saponification equivalent of the ester so prepared was found to be 119, and the saponification equivalent calculated from the formula $CH_2OH.CH_2.COOC_2H_5$ is 118. When the ester was dissolved in an equal volume of water and was treated with phosphorus and iodine both beta-iodopropionic acid and beta-iodopropionic ester were obtained. The ester at 20° has a density of 1·059, and like lactic ester is soluble in water in all proportions. These properties were considered sufficient to identify the ester as pure ethyl hydracrylate. The ester has a faint ethereal odor, much less pronounced than that of lactic ester. It is unusually stable in water solution, hydrolyzing very slowly in the absence of a catalyzing acid or alkali.

Hydrolysis of the Ester.—Two and a half cubic centimeters of ethyl hydracrylate were dissolved in 250$^{cm^3}$ of decinormal hydrochloric acid and hydrolyzed at 25°, 35° and 45°. The course of the reaction was followed by titrating 25$^{cm^3}$ portions of the mixture at intervals as fully described in previous papers.* The results of the velocity measurements are recorded in Table I. In Table II are recorded summary results obtained partly simultaneously with the reaction velocity measurements of ethyl hydracrylate and taken partly from the results obtained by Dean.† A striking contrast appears between the effects of alpha hydroxyl and beta hydroxyl on the velocity of hydrolysis of the esters in acid solution. This retarding effect of the beta hydroxyl on the hydrolysis velocity of the ester was predicted by Dean‡ for ethyl hydracrylate from his study of

* This Journal, xxxv, 486, 1913.
† Dean, this Journal, xxxv, 486, 1913.
‡ Dean, loc. cit.

the hydrolysis of lactic ester, glyceric ester and the esters of the oxybutyric acids. From an examination of the velocity constants of ethyl propionate, ethyl lactate, ethyl hydracrylate and ethyl glycerate in Table II it is obvious that the effects of alpha and beta hydroxyl groups on the hydrolysis velocity are independent of each other. By comparing the constants for ethyl propionate and ethyl lactate it is seen that alpha hydroxyl here produces a slight accelerating effect at 25° which, however, falls off at the higher temperatures. The beta hydroxyl produces a very marked retardation in the hydrolysis velocity as will be seen by comparing the constants for ethyl propionate and ethyl hydracrylate. This effect does not fall off materially at the higher temperatures, as is shown by the fact that the ratio of the constants of these two esters is very nearly the same at each temperature at which velocity measurements were made. The combined effect of alpha and beta hydroxyl groups on the hydrolysis velocity is shown in the constants for ethyl glycerate. If the slight accelerating effect of alpha hydroxyl and the very marked retarding effect of beta hydroxyl are both taken into account we would expect the constants for ethyl glycerate to be but slightly larger than those of ethyl hydracrylate at 25°, the percentage of difference falling off slightly at the higher temperature. This expectation is fully borne out by the experimental results. At 25° the constants for ethyl glycerate is 13·5 per cent larger than that of ethyl hydracrylate, at 35° it is 7·9 per cent larger and at 45° the difference is but 2·5 per cent. The velocity constants in Tables I and II were all calculated from the usual titration formula for first order reactions. The temperature coefficient for ethyl hydracrylate is 2·46 for 25° to 35°, and 2·44 for 35° to 45°.

Ethyl hydracrylate was also hydrolyzed in N/80 sodium hydroxide solution at 0° and at 25°, and the course of the reaction followed by the titration method fully described in Dean's paper* on the saponification of the esters of other oxyacids. These results are recorded in Table III, and are in accord with the results obtained for the esters of other oxyacids.

Summary: 1. Hydracrylic acid may be conveniently prepared from glycerine by introducing the following modifications into the older methods: oxidation of glycerine by fuming nitric acid and formation of the calcium salt instead of the lead salt; liberation of the glyceric acid by means of oxalic acid and conversion into beta-iodopropionic acid with iodine and solid yellow phosphorus instead of a carbon disulphide solution of phosphorus; neutralization of the beta-iodopropionic acid with sodium carbonate before removal of the iodine by

* Dean, this Journal, xxxv, 605, 1913.

TABLE I—ETHYL HYDRACRYLATE.

Hydrolysis in Decinormal Hydrochloric Acid.

	25°	35°	45°
Time of reaction in minutes	7240	2840	1390
Velocity constants.....	10^5K	10^5K	10^5K
	16·6	39·9	98·0
	16·6	39·8	98·6
	16·4	41·4	100·3
	16·0	40·4	97·9
	16·1	40·5	98·6
	16·6	39·3	98·9
	15·8	41·0	97·3
Averages.....	16·3	40·4	98·5
Averages of duplicate series	16·2	40·9	99·0

TABLE II—OXYPROPIONIC ESTERS: SUMMARY.

Hydrolysis in Decinormal Hydrochloric Acid.

Temperature	Ethyl propionate	Ethyl lactate	Ethyl hydracrylate	Ethyl glycerate
	10^5K	10^5K	10^5K	10^5K
25°	71·2	76·1	16·3	18·5*
	71·6*	74·4*	16·2	
35°	177·1	177·5	40·4	43·6*
	179·0*	179·0*	40·9	
45°	405·3	396·6	98·5	101·0*
	406·0*	396·0*	99·0	

* Determined by Dean, this Journal, xxxv, 486, 1913.

TABLE III—ALKALINE HYDROLYSIS IN N/80 SODIUM HYDROXIDE.

Ethyl Hydracrylate			Summary				
Temperature	0°	25°		Ethyl propionate	Ethyl lactate	Ethyl hydracrylate	Ethyl glycerate
Time	30 min.	12 min.					
Constant	K	K		K	K	K	K
	1·86	10·6	0°	1·16*	14·6*	1·83	9·02*
	1·63	11·0	25°	5·94*	63·7*	10·2	67·3*
	1·93	10·6					
	1·81	9·7					
	1·85	10·8					
	1·87	9·5					
	1·85	9·0					
Averages	1·83	10·2					

* Taken from Dean's tables, this Journal, xxxv, 608.

the action of silver oxide; substitution of hydroxyl for iodine in beta-iodopropionic acid by acting on a concentrated solution of the sodium salt in the cold with silver oxide, using mechanical stirring, instead of treating the hot dilute solution of the free acid with silver oxide.

2. Hydracrylic acid free from a mineral acid may most conveniently be esterified by boiling with an excess of absolute alcohol in the presence of anhydrous copper sulphate free from sulphuric acid.

3. Hydracrylic ester boils at 95° to 96° under a pressure of 20^{mm} without decomposition, but with decomposition at ordinary pressure. The ester has a density of 1·059 at 20° and is soluble in water in all proportions, but is hydrolyzed only very slowly by water in the absence of a catalyst.

4. On hydrolysis in the presence of an acid catalyst the beta hydroxyl shows a very marked retarding effect on the velocity of the reaction, while in alkaline hydrolysis the beta hydroxyl produces a distinct accelerating effect.