

chloride. The yield of crude octylene was 67 grams. This was fractionally distilled and finally yielded 25 grams of octylene boiling at 110.4–110.8° at 760 mm. pressure.

Calculated for  $C_8H_{18}$ : C, 85.71; H, 14.29.  
 Found: C, 85.49; 85.00; 84.72; H, 13.27; 13.50; 14.40.

Properties: Colorless, mobile liquid with a faint musty odor. Boiling point, 110.4–110.8° at 760 mm. pressure. It is not miscible with water, but mixes fairly readily with the common organic solvents.

*2,2,3-Trimethylpentane*,  $(CH_3)_3CH(CH_2)CH_2CH_3$ . — The octylene was reduced to the octane by Bedford's modification of Sabatier and Senderens' method,<sup>1</sup> by the action of hydrogen and pure nickel at 160–180°. From 12 grams of octylene, 8 grams of octane were obtained, boiling at 110.5–110.8° at 760 mm. pressure.

Calculated for  $C_8H_{18}$ : C, 84.21; H, 15.79.  
 Found: C, 84.56; 84.63; 83.64; H, 15.69; 15.60; 15.88.

Properties: Colorless, very mobile liquid, with a very faint odor. Boiling point, 110.5–110.8° at 760 mm. pressure. The specific gravity at 15° compared to water at 15° is 0.7219. The index of refraction was determined with a fine Pulfrich refractometer.  $N_D(25^\circ) = 1.4164$ .

CAMBRIDGE, MASS.

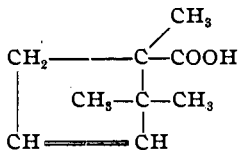
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]  
**MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES. IX.**  
**LAURONOLIC ACID AND CAMPHOLACTONE.<sup>2</sup>**

BY WILLIAM A. NOYES AND CHARLES E. BURKE.

Received June 26, 1911.

Two unsaturated acids derived from camphor, having the formula  $C_9H_{18}COOH$ , and having the carboxyl group in the tertiary position are known.

One of these has been isolated by Bredt<sup>3</sup> and since on oxidation it gives camphoronic acid he has given to it the structure



The other acid was first studied by Fittig and Woringner.<sup>4</sup> It has been obtained in two ways: first, by the decomposition of bromo-camphoric acid anhydride by boiling with water or with dilute alkali; second, by the

<sup>1</sup> The exact process is described by Clarke and Beggs in THIS JOURNAL, 34, 59.

<sup>2</sup> Abstract of a thesis presented by Charles E. Burke in partial fulfilment of the requirement for the degree of Doctor of Philosophy at the University of Illinois.

<sup>3</sup> Ber., 35, 1286.

<sup>4</sup> Ann., 227, 6.

distillation of camphanic acid, either alone or in a slow current of carbon dioxide.

Fittig and Woringer, and Aschan<sup>1</sup> assumed the acids obtained in these two ways to be identical, since they gave the same lactone, hydrobromide, amide and bromolactone. Tiemann<sup>2</sup> noticed that the two acids differed widely in their effect upon the rotation of polarized light and suggested that that obtained by the distillation of camphanic acid was probably a mixture of optical isomers, since its rotation varied from  $+110^\circ$  to  $+188^\circ$  while that obtained by the decomposition of the anhydride gave a constant rotation of  $+199^\circ$  at  $19^\circ$ .

That the acid obtained by the distillation of camphanic acid is a mixture of optical isomers we have definitely shown by a comparison of the properties of three acids prepared in the following ways:

(A) By the decomposition of active bromocamphoric acid anhydride with sodium carbonate.

(B) By the distillation of camphanic acid.

(C) From inactive (artificial) camphor in the same way as (A) above.

For these acids the following properties have been observed:

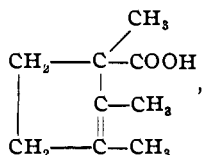
		ROTATION.			
(A) From the active anhydride.		(B) From camphanic acid.		(C) From inactive camphor.	
$[\alpha]_D^{25} = +187.7^\circ$		$[\alpha]_D = +63^\circ$ to $+180^\circ$		$[\alpha]_D = 0^\circ$	
$D_4^{25} = 1.0133$		$D_4^{25} = 1.0227$		$D_4^{25} = 1.0318$	
		DENSITY.			
Temp.	v. p.	Temp.	v. p.	Temp.	v. p.
$184^\circ$	100 mm.	$188^\circ$	100 mm.	$193^\circ$	100 mm.
		VAPOR PRESSURE.			
		INDEX OF REFRACTION.			
D	1.47586		1.47645		1.47655
C	1.47269		1.47349		1.47350
F	1.48323		1.48372		1.48372
G	1.48904		invisible		1.50861
		DISPERSION.			
D-C	0.00317		0.00296		0.00305
C-F	0.01054		0.01023		0.01022
		WATER OF CRYSTALLIZATION OF CALCIUM SALT.			
3 molecules		1.3 molecules		1 molecule.	
		MELTING POINT.			
$6.5^\circ-8^\circ$				$5^\circ-8^\circ$	

<sup>1</sup> *Ber.*, 27, 3504.

<sup>2</sup> *Ibid.*, 33, 3944.

<sup>3</sup> Professor Eijkmann kindly called our attention to the fact that the pure lauronic acid can be obtained in a crystalline form. In a private communication he states that he has obtained an acid melting at  $+13^\circ$ . Dr. Burke has very carefully repeated the preparation at the University of California but has not succeeded in obtaining an acid with a higher melting point than that given here. Professor Eijkmann's values for the index of refraction also differ slightly from ours.

Although both bromocamphoric anhydride and camphanic acid retain the gem dimethyl group, Lapworth and Lenton<sup>1</sup> have suggested for lauronolic acid the structure



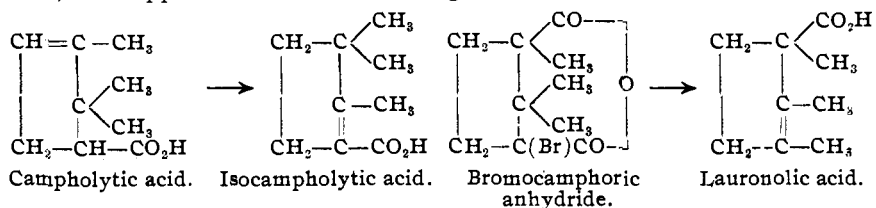
in which one methyl group has wandered, giving a 1,2,3-trimethyl compound, as being more in accord with the oxidation products obtained by Tiemann.<sup>2</sup> This structure has also been suggested by Eijkmann<sup>3</sup> from a study of the optical properties of the acid, and is substantiated by the experimental part of this paper.

By distilling a mixture of the calcium salt of lauronolic acid and soda lime an almost quantitative yield of laurylene is obtained and this has been proven by synthesis<sup>4</sup> to contain a 1,2,3-trimethyl group.

If the methyl group had not wandered, and the double bond were in the  $\Delta^3$  position, we would probably have an acid identical with the acid of Brett<sup>5</sup> and which on oxidation ought to give camphoronic acid. Oxidation of lauronolic acid, however, gives no trace of camphoronic acid.

The dissociation constant of lauronolic acid is  $1.36 \times 10^{-5}$ . That of  $\alpha$ -campholytic acid is  $1.0 \times 10^{-5}$ . Although the difference is not very great, the lauronolic acid gives a distinctly higher value for  $K$ , which is difficult to explain, if the unsaturation is  $\Delta^3$  in each case. It has been shown<sup>6</sup> that in both open chain and ring unsaturated acids a  $\Delta^2$  unsaturation invariably gives a greater dissociation constant than  $\Delta^1$  or  $\Delta^3$ . This would indicate that the double bond is  $\Delta^2$ .

The rearrangement which gives lauronolic acid is exactly parallel with the rearrangement of campholytic acid to isocampholytic ("isolauronic") acid, as is apparent from the following formulas:



<sup>1</sup> *Brit. Assoc. Report*, 1900, 327. *J. Chem. Soc.*, 77, 1057; 79, 1289.

<sup>2</sup> *Ber.*, 33, 2944.

<sup>3</sup> Private communication.

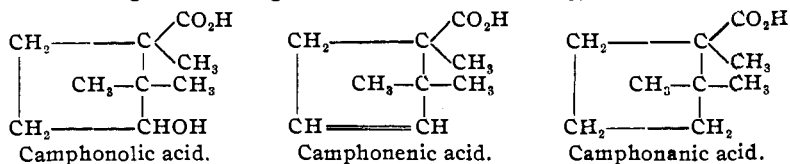
<sup>4</sup> *THIS JOURNAL*, 32, 1064.

<sup>5</sup> *Ber.*, 35, 1286.

<sup>6</sup> Derick, *THIS JOURNAL*, 32, 1339.

In both cases a methyl group in the  $\beta$ -position with regard to carboxyl shifts to the  $\gamma$ -position.

We may now distinguish, clearly, three groups of unsaturated acids having the formula  $C_9H_{13}COOH$ . (1) Campholytic and isocampholytic acids, (2) the acid obtained by Bredt by the action of quinoline upon the bromine derivative of diphenyl camphorate. He has called this isolauronic acid but as that name was formerly given to isocampholytic acid it seems best to drop it entirely from use, and in order to avoid confusion he now suggests<sup>1</sup> that this acid be called camphonenic acid, the three following acids being named as indicated. (3) The lauronic acids



which have the methyl groups in the positions, 1,2,3. These are the only acids of this formula in the camphor series, for which the structure can at present be considered as fully established.

#### Experimental Part.

*Bromocamphoric anhydride and Lauronic Acid.*—The bromocamphoric anhydride was prepared, and the decomposition into lauronic acid and camphanic acid carried out according to the method of Aschan.<sup>2</sup> In every case after extraction with ether the last traces of ether were removed from the lauronic acid by passing a current of hydrogen for from thirty to forty minutes, keeping the acid at a temperature of from 60–65° and under as low a pressure as could be obtained with a water pump, usually 30–35 mm.

If dried in a current of air or of carbon dioxide, the product soon decomposes and becomes black and tarry. With a current of hydrogen, however, we have found that the drying process may be continued indefinitely without any perceptible decomposition taking place.

One hundred grams of the anhydride yields nine to ten grams of yellowish colored acid. The crude acid gave a rotation  $[\alpha]_D^{25} = +180^\circ$  to  $+183^\circ$ .

*Purification of Lauronic Acid.*—Much difficulty has been experienced in obtaining a pure lauronic acid, owing first to the ease with which the acid decomposed, second to the tendency on long standing at ordinary temperatures, or very quickly at even moderately high temperatures, to rearrange into the racemic form. The acid used in all of this work has been obtained by recovery from the purified calcium salt; the salt was decomposed with dilute hydrochloric acid and the pure lauronic acid extracted with low-boiling ligroin and dried under diminished pressure

<sup>1</sup> Private communication.

<sup>2</sup> *Ber.*, 27, 3504.

with a current of hydrogen as described above. The acid thus obtained gave a constant rotation  $[\alpha]_D^{25} = +187.7^\circ$ .

An equally pure acid is obtained by distillation under diminished pressure with a Geryk pump, if a sufficiently low pressure can be obtained. At a pressure of  $1/2$  to 1 mm. it distils constantly at  $104^\circ$ . A thermometer in the Wood's metal bath registered  $113^\circ$ – $115^\circ$ . This acid gave approximately the same rotation as that obtained from the calcium salt.

*Calcium Salt of Lauronic Acid.*—This salt, which was obtained by neutralizing the acid with milk of lime, is very difficultly soluble in water, and more soluble in cold than in hot, so that it can be recrystallized only by evaporating the solution. On evaporation a very pure salt separated on the surface of the solution in beautiful crystals. On analysis these were found to contain three molecules of water similar to the calcium salt of Fittig and Woringer.

0.2403 gram air-dried salt lost 0.0330 gram of  $H_2O$  at  $110$ – $115^\circ$  and gave 0.0361 gram  $CaO$ .

0.2437 gram air-dried salt lost 0.0333 gram water at  $115$ – $118^\circ$  and gave 0.0336 gram  $CaO$ .

0.2501 gram air-dried salt lost 0.0336 gram water at  $110$ – $115^\circ$  and gave 0.0337 gram  $CaO$ .

Calculated for 3 mols.  $H_2O$ , 13.50.

Found: 13.73, 13.66, 13.43.

For the anhydrous salt, Ca, 11.56.

12.44, 11.40, 11.08, 11.60.

Bredt<sup>1</sup> states that he has obtained only two molecules of water of crystallization, but our results show that the acid undoubtedly contains three molecules. It loses a part of its water very readily at ordinary temperatures and, unless analyzed as soon as dry, gives results varying from one to three molecules. A sample of the salt which had been exposed to the air for two hours on a warm day gave only 6.70%  $H_2O$ .

*Crystalline Lauronic Acid.*—Fittig and Woringer attempted to crystallize lauronic acid but state that while it became very viscous in a freezing mixture it would not crystallize. In a private communication Professor Eijkmann stated that he had obtained the crystalline product and this led us to further attempts, which were successful.

The difficulty in getting the acid in crystalline form is, evidently, not on account of the low melting point of the substance, but rather on account of the tendency to supercool. When left for some time in a freezing mixture of hydrochloric acid and ice, at a temperature of  $-23^\circ$  to  $-20^\circ$ , it became very viscous but did not crystallize. With solid carbon dioxide and ether it forms a solid transparent mass, evidently simply the supercooled liquid, for on immersing in a freezing mixture at  $-20^\circ$  it partly melts, then crystallizes into a solid, white mass.

By seeding the cooled acid the crystals were obtained in beautiful

<sup>1</sup> *J. prakt. Chem.*, 83, 395 (1911).

rosettes of long, concentric needles; the center of the rosette was slightly tinged with a green coloring matter, which seems to be characteristic of these compounds. The crystals melt at  $+6.5^{\circ}$  to  $+8^{\circ}$ . (See above for Professor Eijkmann's results.)

Under atmospheric pressure the acid distils at  $230-235^{\circ}$ , but the vapor pressure at this temperature cannot be accurately determined, owing to the formation of various oxidation and decomposition products. At lower temperatures, however, the vapor pressure has been accurately determined by the method of Smith and Menzies,<sup>1</sup> using a bath of pure paraffin. At  $184^{\circ}$ , v. p. = 99-100 mm.

The specific gravity has been determined by means of a small specific gravity bulb at various temperatures.

$$D_4^{27.5} = 1.0109; D_4^{25} = 1.0133; D_4^{10} = 1.0249.$$

The rotation of the pure acid varies greatly with the temperature; the following specific rotations have been observed with the same sample of a pure acid in a ten cm. tube.

Temp.	$[\alpha]_D$ .	Temp.	$[\alpha]_D$ .	Temp.	$[\alpha]_D$ .
$28^{\circ}$	187.1	$21^{\circ}$	188.9	$10^{\circ}$	194.1
$25^{\circ}$	187.7	$15^{\circ}$	191.1	$6^{\circ}$	199.0
$23^{\circ}$	188.2	$11^{\circ}$	193.0		

Tiemann states that he has obtained a rotation of  $+199^{\circ}$  at  $19^{\circ}$ ; we have not, however, been able to obtain as high a rotation at that temperature. The acid recovered from the purified calcium salt gives a constant rotation  $[\alpha]_D^{25} = +187.7^{\circ}$ .

The index of refraction determined for the sodium line D, and the three hydrogen lines C, F and G, gave the following results: D, 1.47586; C, 1.47269; F, 1.48323; G, 1.48904.

The electrical conductivity, determined with a saturated and a dilute solution, gave the dissociation constant  $K = 1.36 \times 10^{-6}$ .

*Decomposition of Lauronic Acid into Laurolene and Carbon Dioxide.*—Blanc<sup>2</sup> obtained isolaurolene from  $\alpha$ -campholytic acid by heating in a sealed tube at a temperature of  $340^{\circ}$ . Since at such high temperatures molecular rearrangements readily occur, this method would have no value from the standpoint of structure. We have endeavored to effect the same decomposition by keeping the acid at the boiling point. After  $1-1\frac{1}{2}$  hours the acid became very dark and somewhat viscous, owing probably to the formation of oxidation products, but no hydrocarbon was formed. On distilling, all but a little resinous material came over at  $200^{\circ}-230^{\circ}$ . A considerable portion of the distilled product was insoluble in sodium carbonate. On extracting with ether and distilling off the ether this product was obtained in crystalline form, melting at

<sup>1</sup> THIS JOURNAL, 33, 897.

<sup>2</sup> Bull. soc. chim., 19, 703.

49°–50°, showing that a part of the acid had rearranged into the isomeric lactone.

To another portion of the pure acid a little zinc chloride was added before distilling. The larger part of the product distilled now at 120°–125° and on redistilling came over constantly at 120°–121°. This was evidently the hydrocarbon laurone. It gave the following rotation,  $[\alpha]_D^{30} = -5.36$ .

The hydrocarbon was also obtained by mixing the calcium salt with soda lime and distilling. The distillate was again distilled with water vapor and the hydrocarbon separated from the first few cubic centimeters of the aqueous distillate. The boiling point at atmospheric pressure was 120°–122°.

*Amide of Lauronic Acid.*—To a small portion of the acid, cooled in ice water, one molecule of phosphorus pentachloride was added. The reaction was immediate and somewhat vigorous. After completion the product was poured into ice water to decompose the oxychlorides, and the chloride of the acid extracted with a little low-boiling ligroin. Concentrated ammonium hydroxide was added to this ligroin solution and the product allowed to stand until it no longer smelled of ammonia. It was then extracted with ether, the ethereal solution dried over sodium sulfate, and the ether distilled off. A dark, oily mass remained, which crystallized after standing for some time. On recrystallizing from water a very pure white, crystalline product was obtained, which melted at 72°. Three and a half grams of the acid yielded a little over one gram of the amide. This was evidently identical with the amide of Aschan.<sup>1</sup> In a ligroin solution (0.01 g. in 1 cc.) the amide gave the rotation,  $[\alpha]_D^{25} = +94.61$ .

A nitrogen determination gave 8.96% N; calculated for  $C_8H_{13}CONH_2$ , 9.15%.

An attempt was made to saponify the amide; 0.5 gram was heated on a steam bath with 1.5 molecules of sodium hydroxide, 10% solution, for four hours. On acidifying and extracting with ether the unchanged amide was recovered.

*Dihydrolauronic Acid.*—Fittig and Woringe have prepared the hydrobromide of lauronic acid and describe it as a very unstable product which readily decomposes, giving the unsaturated acid and campholactone.

We have prepared the hydriodide by passing hydriodic acid gas through a ligroin solution of lauronic acid. Twelve grams of lauronic acid in solution in low-boiling ligroin were placed in a U tube, and a slow stream of hydriodic acid passed in as long as it continued to be absorbed, usually 1½ to 2 hours. The solution was then placed in a distilling bulb, and a current of air passed through at ordinary temperatures until

<sup>1</sup> Beilstein, *Handbuch der organischen Chemie*, [1] 708.

the ligroin was completely evaporated. The iodide thus obtained in the form of yellow plates was evidently very unstable, since on standing it continued to evolve hydriodic acid.

Various methods of reducing the iodide thus formed have been employed with varying results. The zinc-copper couple, magnesium and alcohol, zinc dust and water and zinc and hydriodic acid gave very poor results. The method which gave the best results, and the one finally adopted was zinc and absolute alcohol. To the crystals of the iodide as obtained above some zinc dust and absolute alcohol were added. There was very little evolution of gas and the product immediately passed into solution. After standing for a short time a few cubic centimeters of a solution of hydriodic acid were added and more hydriodic acid was passed through in order that any lauronolic acid which had been regenerated during the process might be again changed to the hydroiodide. Finally some hydrochloric acid was added and a somewhat vigorous evolution of hydrogen maintained for some time. After diluting with water the dihydro acid was extracted with ether and the recovered acid treated with sodium carbonate to remove a small amount of lactone which formed. Any remaining unsaturated acid was oxidized in the alkaline solution with potassium permanganate and the dihydro acid separated from the oxidation products by steam distillation.

Twelve grams of the unsaturated acid gave about three grams of the dihydro compound. Analysis:

Calculated for  $C_8H_{13}CO_2H$ : C, 69.23; H, 10.25.

Found: C, 69.03; H, 10.24.

Titration: 0.0588 gram acid required 3.85 cc. of 0.1 N NaOH for neutralization; calculated, 3.83 cc.

The following physical properties have been observed:  $D_4^{23.5} = 0.9008$ ;  $[\alpha]_D^{25.5} = +1.74^\circ$ ; v. p. at  $178^\circ = 100$  mm.; v. p. at  $215^\circ = 749$  mm. Index of refraction:  $D = 1.45786$ ;  $C = 1.45459$ ;  $F = 1.46588$ ;  $G = 1.47451$ . Dispersion:  $D-C = 0.00327$ ;  $G-C = 0.01993$ .

*The Amide of Dihydrolauronolic Acid* was prepared in the same way as the amide of lauronolic acid. It is exceedingly soluble in ether and has not been obtained in sufficient quantity to recrystallize. The crude product, washed with ether and dried on a porcelain plate, melted at  $50^\circ-51^\circ$ .

*Inactive Lauronolic Acid.*—The starting point of this preparation was artificial camphor obtained from the Ampere Electrochemical Co. of New York. The camphoric acid and bromocamphoric anhydride were prepared in the same way as the active compounds described above. The bromocamphoric acid anhydride melted at  $214^\circ$ . Mixed with the active anhydride it melted indefinitely but at about the same temperature.

On decomposing with sodium carbonate, inactive lauronolic acid and inactive camphanic acid were obtained. The inactive camphanic acid melted at  $199^\circ-200^\circ$ . The lauronolic acid thus obtained, like the active



variety, decomposed when distilled under ordinary conditions; it was purified by means of the calcium salt and also by distilling under diminished pressure. The calcium salt of the inactive acid crystallizes with one molecule of water of crystallization.

0.1385 gram air-dried salt lost 0.0070 gram  $H_2O$  and gave 0.0211 gram  $CaO$ .

0.1134 gram air-dried salt lost 0.0058 gram  $H_2O$  and gave 0.0174 gram  $CaO$ .

Calculated: For one mol.  $H_2O$ , 4.95; Ca (for anhydrous salt), 11.56. Found: I, 5.05, 11.40; II, 5.20, 11.52.

On cooling, the acid acts in the same way as the active variety; on standing in a freezing mixture at  $-20^\circ$  for some time the acid becomes very viscous but does not solidify. With solid carbon dioxide and ether it forms a transparent solid, which in a mixture of ice and hydrochloric acid partly melts and then crystallizes. The crystals melt at  $+5-8.5^\circ$ . Vapor pressure at  $192^\circ = 100$  mm. Specific gravity  $D_4^{25} = 1.0318$ . Index of refraction:  $D = 1.47655$ ;  $C = 1.47350$ ;  $F = 1.48372$ ;  $G = 1.50861$ .

*Campholactone*.—As stated above, lauronolic acid readily rearranges under certain conditions into the isomeric lactone. Much difficulty has been experienced, however, in getting the lactone in crystalline form in sufficient quantities for study.

If lauronolic acid is heated with dilute mineral acid it chars and very little is obtained from the product. Fairly good yields have been obtained, however, by allowing the acid to stand for 12–24 hours with dilute hydrochloric acid (sp. gr. 1.1) at a temperature of  $40^\circ-50^\circ$ . The unchanged acid and lactone were distilled with water vapor, the distillate made alkaline with sodium carbonate, and the lactone extracted with ether. It is quite soluble in ligroin but by cooling in a freezing mixture may be readily recrystallized from it. The pure product melts at  $50^\circ$ . Rotation,  $[\alpha]_D^{22} = -21.7^\circ$  (0.01 g. in 1 cc. of alcohol).

The lactone has been obtained in various ways from acids having widely differing rotations, but neither the method of preparation nor the rotation of the acid from which it is prepared has any influence upon the rotation of the lactone. The lactone from inactive lauronolic acid has not been prepared. That would, of course, be inactive.

*Hydroxy Acid of Campholactone*.—The lactone described above readily dissolves on warming with barium hydroxide, and the corresponding hydroxy acid is precipitated on acidifying. Fittig and Woringer state that they obtained the acid as an oil which crystallized on standing, but by first cooling in ice water both the solution of the salt and the hydrochloric acid, we obtained immediately, on acidifying, a beautiful crystalline precipitate of the hydroxy acid, m. p.  $143^\circ$ . (Tiemann gives  $144^\circ-145^\circ$  after recrystallizing from water.)

In alcoholic solution (0.01 g. in 1 cc.) the acid gave the rotation  $[\alpha]_D^{27} = +16.0^\circ$ .

*Synthesis of Acetolauroleone.*—Sometime ago Blanc prepared acetolauroleone by Friedel and Crafts' reaction and from this effected a synthesis of isocampholytic acid. It seemed possible that we might synthesize lauronolic acid by a similar process from lauroleone. We have succeeded in obtaining acetolauroleone and its semicarbazone, but have not, as yet, succeeded in obtaining from this the lauronolic acid. The work will be continued and reported in detail later.

URBANA, ILL.

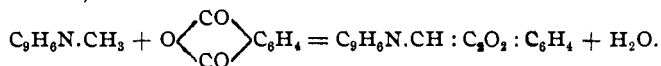
[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY,  
NO. 201.]

RESEARCHES ON QUINAZOLINES (TWENTY-EIGHTH PAPER).  
ON 4-QUINAZOLONE-2-PHTHALONES AND CERTAIN  
OF THEIR DERIVATIVES.<sup>1</sup>

BY MARSTON TAYLOR BOBERT AND MICHAEL HEIDELBERGER.

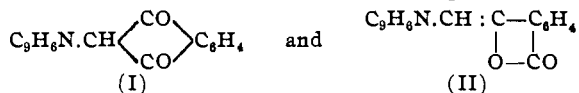
Received December 25, 1911.

The well-known quinophthalones, or quinoline yellow dyes, are produced by condensing quinaldines with phthalic anhydride,<sup>2</sup> either by the action of heat alone or in the presence of such condensing agents as zinc chloride,



The product of this reaction is the alcohol-soluble quinoline yellow, or quinophthalone, which on sulfonation yields the water-soluble quinoline yellow S.

Two formulas naturally present themselves for quinophthalone,



In fact, two isomeric quinophthalones are known.

Through the skilful investigations of Eibner and his co-workers,<sup>3</sup> it has been proven that the one ordinarily obtained (m. 235°) possesses formula I. To the isomer (m. 186°) is therefore assigned formula II. The two compounds appear to be formed in the reaction by two distinct series of changes,<sup>4</sup> and neither substance is to be regarded as an inter-

<sup>1</sup> Read at the Washington Meeting of the Society, December 28, 1911.

<sup>2</sup> Jacobsen and Reimer, D. R. P. No. 23188 (1882) and *Ber.*, 16, 513, 1082, 1892, 2602 (1883). Traub, *Ber.*, 16, 297, 878 (1883). Geigy and Königs, *Ibid.*, 18, 2407 (1885). Königs and Nef, *Ibid.*, 19, 2428 (1886). Panajotow, *Ibid.*, 28, 1511 (1895); D. R. P. Nos. 23188 and 25144. Friedländer, 1, 161, 162, *et al.*

<sup>3</sup> *Ann.*, 315, 303 (1901). *Ber.*, 34, 2303 (1901); 35, 1656, 2297 (1902); 36, 1860 (1903); 37, 3006, 3011, 3018, 3023, 3605 (1904); 38, 3353 (1905); 39, 2202, 2215, 2245 (1906). *Chem. Ztg.*, 28, 1206 (1904). *Chem. Zentralbl.*, 1905, I, 910.

<sup>4</sup> Eibner, *Ber.*, 37, 3605 (1904); *Chem. Ztg.*, 28, 1206 (1904).