proportion of the ingredients will vary with the purity of the lime, that of ordinary so-called good lime it may require 1.25 kilos to 1 k of sodium hydroxide and sometimes a little less water than stated befo The best proportion of the ingredients at hand to use may, therefo at times have to be determined experimentally.

The pieces of soda lime should be porous, light gray in color and ha enough to break and crumble when pounded. They are broken up a sifted and the granules of about 1/16 inch or a little more in diamet are used in the U-tubes for carbon determinations.

Hydrogen Determination.—By means of the bomb calorimeter it possible also to determine hydrogen, but it is a much more difficult an tedious operation, and it is very hard on the bomb, and with the kind bombs in use at present, the writer considers it too costly and henc impracticable. Trials were made and it was found that the escapin acids attack the apparatus too much; but as soon as the bomb ca be made with platinum or other non-corroding lining all through the ga outlet, a method for hydrogen can doubtless be worked out successfully

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.

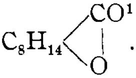
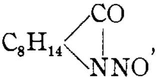
MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES I. HYDROXYLAURONIC ACID AND ISOCAMPHOLACTONE.

BY W. A. NOYES AND A. W. HOMBERGER.

Received December 21, 1908.

Terpenes, camphor and their derivatives often undergo molecular rearrangements which render conclusions drawn with regard to their structure fallacious. Very little is known with regard to the laws governing such rearrangements and it seems possible that a careful study of some of these changes may throw additional light upon the nature of the forces which exist in molecules containing carbon. The first step in such a study must consist in establishing the structure of compounds which result from such rearrangements. From the nature of the case this is often extremely difficult as we have very little to guide us in deciding whether a rearrangement has taken place in a given reaction or not. In the end, one is dependent on that sort of cumulative evidence which is so characteristic of many of the most difficult problems of organic chemistry and which is so trying to minds which desire an absolute proof for everything that is to be accepted as scientific.

The work described in this paper has, of course, made very little progress toward the study of the larger question and is quite incomplete. As it must be discontinued for some time, however, it seems desirable to record, briefly, the results obtained.

a-Camphoramidic acid, $C_8H_{14}(CO_2H)CONH_2$, gives with sodium hypobromite, aminolauronic acid, $C_8H_{14}(CO_2H)NH_2$, in which the carboxyl is tertiary and the amino group secondary. When aminolauronic acid is treated with nitrous acid it gives, chiefly, γ-lauronolic acid, $C_8H_{13}CO_2H$, laurolene, C_8H_{14}, and isocampholactone,  $C_8H_{14}\left<\begin{array}{l}CO\\ |\\ O\end{array}\right.$[1]. The nitroso derivative of the anhydride of aminolauronic acid,  $C_8H_{14}\left<\begin{array}{l}CO\\ |\\ NNO\end{array}\right.$, gives the same products in different proportions and some other compounds, which need not be considered here, when it is boiled with a solution of sodium hydroxide.[2] When the ethyl ester of aminolauronic acid, $C_8H_{14}(NH_2)CO_2C_2H_5$, is treated with nitrous acid it gives a mixture of the esters of γ-lauronolic acid and of hydroxylauronic acid,[3] $C_8H_{14}(OH)CO_2C_2H_5$.

The ethyl ester of aminolauronic acid was prepared by heating 20 grams of aminolauronic acid hydrochloride, $C_8H_{14}(NH_2HCl)CO_2H$, 6 cc. of concentrated sulphuric acid and 80 cc. of absolute alcohol on a water bath in a stout bottle connected with an upright condenser, the top of which was connected with a glass tube dipping under a column of 50 cm. of mercury. After heating for 48 hours the alcohol was distilled under diminished pressure, water and a slight excess of sodium hydroxide were added and the ester taken up with ether. The yield was 35 per cent. Yields of 50 to 65 per cent. were obtained with pressure bottles but the bottles often exploded owing to the pressures developed from the ethyl chloride formed.

The ester of aminolauronic acid was treated with a little less than the calculated amount of sulphuric acid (25 per cent.), the solution cooled and the calculated amount of sodium nitrite (1 : 5) added carefully, with cooling. After several hours the layer of esters formed was taken up with ether, washed with a dilute solution of sodium carbonate and with water, dried with anhydrous sodium sulphate, and distilled under diminished pressure. The weight of mixed esters obtained was only one-half that of the aminolauronic ester.

At a pressure of 25 mm. the *γ-lauronolic ester*, $C_8H_{13}CO_2C_2H_5$, comes over at 110–115°. The specific gravity, $d_4^{20} = 0.9514$. The specific rotation, $[\alpha]_D^{26°} = +56.6°$.

The *hydroxylauronic ester*, $C_8H_{14}(OH)CO_2C_2H_5$, boils at 150° at 30 mm. The specific gravity, $d_4^{20} = 1.100$. The specific rotation $[\alpha]_D^{33.5°} = +6.73$.

Analysis:

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[1] Noyes, *Am. Chem. J.*, **17**, 432.

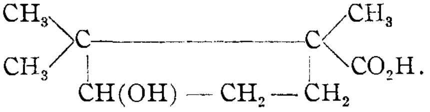
[2] Noyes and Taveau, *Ibid.*, **32**, 285; **35**, 379. Bredt, who first studied this reaction, mentions only isocampholactone as resulting from this decomposition. *Ber.*, **35**, 1291.

[3] Noyes, *Am. Chem. J.*, **18**, 687.

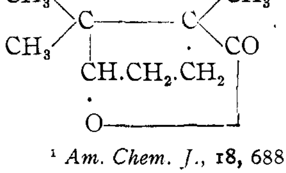
Calculated for $C_8H_{14}(OH)CO_2C_2H_5$: C, 65.94; H, 10.06.
Found: C, 66.08, 65.86; H, 9.96, 9.78.

The copper salt of the acid gave 15.01 and 14.88 per cent. Cu. Calculated for $(C_8H_{14}(OH)CO_2)_2Cu + H_2O$, 15.01 per cent. The salt is nearly insoluble in water.[1]

It has not been found possible to obtain the free hydroxy acid in any other form than as a viscous liquid. In a paper published by one of us some years ago[2] it was stated that the acid loses carbon dioxide and gives a ketone when treated with Beckmann's mixture. The experiment was repeated under conditions which permitted of determining the amount of carbon dioxide evolved. It was found that this corresponded to about 14 per cent. of the acid used. It was not found possible, however, to obtain the ketone in sufficient amount for its identification.

The formation of a ketone and loss of carbon dioxide from hydroxylauronic acid on treatment with Beckmann's mixture led one of us formerly to the opinion that the carboxyl groups of camphoric acid are joined to adjacent carbon atoms. Since then it has been demonstrated conclusively that this is not the case, and if aminolauronic and hydroxylauronic acids are formed from camphoric acid without molecular rearrangement the hydroxylauronic acid must have the formula  The fact that hydroxylauronic acid does not readily form a lactone gives some ground for accepting this formula, since its conduct in this regard corresponds with that of dihydrohydroxycampholytic acid, which almost surely has the formula  Further evidence in support of the formula has been secured by oxidizing hydroxylauronic acid to active camphoronic acid by means of nitric acid. The active camphoronic acid was identified by means of its difficultly soluble barium salt and by the melting point of the free acid, 156°, and of the anhydride, 135°–136°.

Oxidation of Isocampholactone.—From its method of formation isocampholactone should have the formula



If this is correct, the corresponding hydroxy

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[1] *Am. Chem. J.*, **18**, 688.

[2] *Loc. cit.*

acid, $C_8H_{14}(OH)CO_2H$, must be a stereoisomer of hydroxylauronic acid. In order to obtain further light on this question isocampholactone has been subjected to oxidation. Three grams of the lactone were heated for 72 hours with nitric acid (sp. gr. 1.27) in a 50 cc. flask sealed to an upright condenser. The heating was continued till the oily layer of lactone disappeared, a little concentrated acid being added from time to time. The study of the products of the oxidation is still quite incomplete. The products thus far obtained are a lactone, $C_8H_{12}O_4$, an acid melting at 228°, probably camphononic acid, and a compound, probably a lactone, which melts at 111°.

The *lactone*, $C_8H_{12}O_4$, is the chief product of the oxidation. It partly sublimes into the condenser during the oxidation and the remainder separates in crystalline form on cooling the solution. It is quite volatile and crystallizes from ligroin in needles. It is moderately soluble in ligroin, more easily soluble in ether and benzene. It melts at 122° and boils at 272°. A part of the analyses were not very satisfactory, possibly because of a partial hydrolysis of the lactone group.

Calculated for $C_8H_{12}O_4$:	C, 55.79;	H, 7.03.
Found:	C, 56.09, 56.38, 55.89, 54.85;	H, 7.19, 7.01, 7.25.
	54.81, 54.9, 54.9	7.12, 7.24, 7.12, 6.95.

The analyses were made with four different preparations.

Victor Meyer determinations gave a molecular weight of 164, 176.6, 180, 175, 166.2; average, 172; calculated, 172.1.

The molecular weight found by the lowering of the freezing point of glacial acetic acid was 175.3.

When the lactone is warmed with a solution of barium hydroxide or of sodium hydroxide it dissolves and somewhat more than one equivalent of the alkali is neutralized but the results were not concordant or satisfactory. As the presence of two lactone groups is impossible in a compound of this formula, it seems probable that the compound is decomposed by the alkali.

The formation of camphononic acid in the oxidation, if confirmed, will, of course, point to the formula given above for isocampholactone. We do not, however, feel justified in drawing any conclusions with regard to its structure from the work done thus far.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, OF THE OHIO STATE UNIVERSITY.]

THE ACTION OF UNSYMMETRICAL BENZOYLPHENYLHYDRAZINE ON ORTHOBENZOQUINONE.

BY WILLIAM MCPHERSON AND H. J. LUCAS.

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The action of the unsymmetrical acyl phenylhydrazines on parabenzoquinone has been shown[1] to be as follows:

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[1] *Ber.*, 28, 2414. *Am. Chem. J.*, 22, 364. THIS JOURNAL, 22, 141; 30, 816.