Heating 22.2 g. (0.22 mole) of the above carbinol for two hours with 29 g. (0.2 mole) of *t*-butylacetyl chloride, b. p. 79° at 150 mm., n^{20}_D 1.4215, and fractionation through column X gave: 1–2, 7.7 g., b. p. 78–140° at 150 mm., n^{20}_D 1.4050–1.4190; 3–5, 22.2 g., 104° at 26 mm., 1.4198–1.4202; residue 4.8 g.

Fractions 3–5 represented a 57% yield of neopentylcarbinyl *t*-butylacetate. Saponification of 16.0 g. of this ester with alcoholic potassium hydroxide gave neopentylcarbinol, α-naphthylurethan m. p. and mixed m. p. 81–82°; and *t*-butylacetic acid, anilide m. p. and mixed m. p. 130–130.5°.

Preparation of Ethyl *t*-Butylacetate.—A mixture of 57.5 g. (0.54 mole) of *t*-butylacetic acid, n^{20}_D 1.4096, 125 cc. of absolute ethyl alcohol, and 25 cc. of concd. sulfuric acid was refluxed fifteen hours. The mixture was dissolved in ether, washed with water and dilute potassium carbonate solution, dried over magnesium sulfate, and fractionated through column X to give 60.1 g. or a 77% yield of ester of b. p. 102° at 740 mm., n^{20}_D 1.4032–1.4040.

Summary

1. Ethyl, *n*-propyl, *n*-butyl, and *n*-amyl Grignard solutions, when added to a slight excess of *t*-butylacetyl chloride, gave ketones of the type $(CH_3)_3CCH_2COR$ in about 51, 37, 34, and 29% yields, respectively. They also gave esters of the type $(CH_3)_3CCH_2CHROCOCH_2C(CH_3)_3$. The latter were obtained in about 7, 20, 23, and 21% yields, respectively, from the four Grignard solutions.

2. Ethyl *t*-butylacetate and neopentylcarbinyl *t*-butylacetate have been prepared.

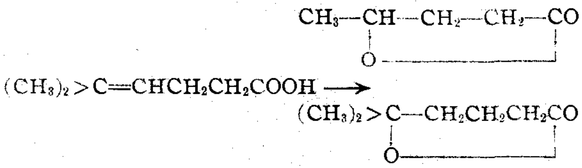
STATE COLLEGE, PENNA. RECEIVED AUGUST 24, 1938

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

Lactone Formation in the Addition Product of Maleic Anhydride and Bicyclohexenyl

BY ROGER ADAMS AND E. E. GRUBER[1]

The addition of maleic anhydride to bicyclohexenyl takes place readily with the formation of $\Delta^{4a,5a}$ - dodecahydrophenanthrene - 9,10 - dicarboxylic acid anhydride (I).[2] During the course of the study of this compound, several reactions were noted which have a general bearing upon lactone formation of γ,δ-unsaturated acids. Linstead has demonstrated[3] that the ease and direction of lactonization of aliphatic γ,δ-olefinic acids depend on the substituents on the δ-carbon. The formation of a γ-lactone is favored if hydrogens, a δ-lactone if alkyl groups, are present. Lactonization is promoted by mineral acids and in some cases merely by heating the olefinic acids.



$$CH_2{=}CH{-}CH_2CH_2COOH \longrightarrow \underbrace{CH_3{-}CH{-}CH_2{-}CH_2{-}CO}_{O}$$

$$(CH_3)_2{>}C{=}CHCH_2CH_2COOH \longrightarrow \underbrace{(CH_3)_2{>}C{-}CH_2CH_2CH_2CO}_{O}$$

When I or its anhydride (V) is esterified with absolute ethanol and hydrogen chloride, a monoethyl ester lactone (II) is obtained. Saponification of this compound gives a sodium salt of an hydroxy acid (III) which on acidification results not in the hydroxy dibasic acid but in a lactone acid (IV). By the action of heat or acetic anhydride, I forms the anhydride (V) which upon treatment with cold sodium ethylate leads to an ester acid (VI). Hot sodium ethylate, however, results in a complicated reaction, the character of which was not determined. The ester acid (VI) can be hydrolyzed by boiling with dilute alkali to the dibasic acid (I). Heating I alone gives a mixture of anhydride (V) and lactone (IV).

Of significance is the fact that the action of bromine in carbon tetrachloride differentiates between the dibasic acid derivatives and the lactone acid derivatives. Thus, compounds I, V and VI absorb bromine while compounds II and IV do not.

As lactonization of one of the carboxyls results when I or V is esterified and no diethyl ester may be isolated, it is obvious that lactonization of the second carboxyl is the more rapid of the competing reactions. Lactonization also takes place merely by heating the acid (I) in acetone solution in presence of hydrochloric acid; lactone (IV) is formed.

The structures of the lactones obviously may be either those given in II and IV or the isomeric γ-lactones. Stereochemically the γ- or δ-lac-

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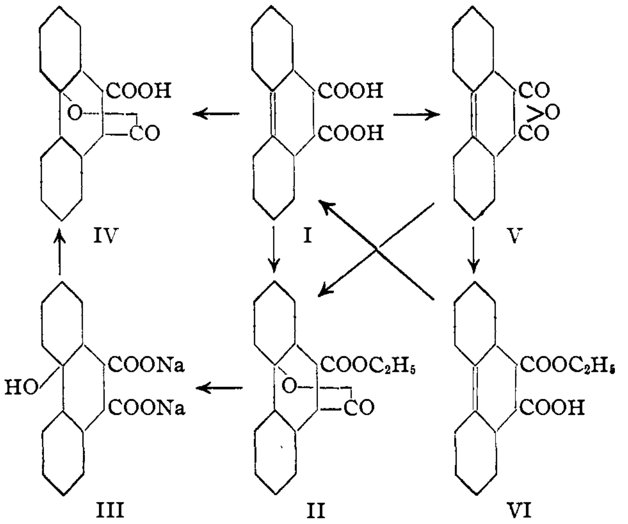
[1] Portion of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in chemistry.

[2] Gruber and Adams, THIS JOURNAL, **57**, 2555 (1935).

[3] Linstead and others, *J. Chem. Soc.*, 115 (1932); *ibid.*, 557, 561, 568, 577, 580 (1933).



tones might form with equal ease. It seems likely, in view of Linstead's work, that the factors which lead to δ-lactone formation are probably more influential than those which lead to the γ-lactone.

Unfortunately, all of the reactions described are accompanied by side-products of an oily character which exclude quantitative studies.

Experimental

$\Delta^{4a,5a}$-Dodecahydrophenanthrene-9,10-dicarboxylic Acid.—The preparation of this product and its lactone was described previously.[2] The anhydride is also conveniently formed from the acid by the action of acetic anhydride.

$\Delta^{4a,5a}$-Dodecahydrophenanthrene-9,10-dicarboxylic Acid Anhydride.—A solution of 2 g. of dibasic acid in 20 cc. of acetic anhydride was refluxed for five hours. The acetic anhydride and acetic acid were removed by distillation *in vacuo* and the residue extracted with 125 cc. of hot ligroin (b. p. 60–110°). Upon filtering and evaporating to 75 cc., a tan precipitate separated on cooling. Purification from cyclohexane gave colorless crystals of m. p. 121°. The yield was low.

Monoethyl Ester of Hydroxytetradecahydrophenanthrene-9,10-dicarboxylic Acid Lactone (II).—Dry hydrogen chloride was bubbled through a solution of 11 g. of $\Delta^{4a,5a}$-dodecahydrophenanthrene-9,10-dicarboxylic acid in 150 cc. of absolute ethanol for one and one-half hours and the mixture was then refluxed on a steam cone for one hour. About 50 cc. of ethanol was distilled off and the residue poured into 200 cc. of ice water. The oil was extracted with benzene, the solution washed with dilute aqueous sodium carbonate and 10% sulfuric acid, then evaporated and the oil distilled *in vacuo*, b. p. 225–250° at 13 mm.; yield 8.2 g. (68%). After standing in a desiccator for several days, it solidified and was recrystallized from cyclohexane; white microcrystals, m. p. 109–110°.

Anal. Calcd. for $C_{18}H_{26}O_4$: C, 70.54; H, 8.56. Found: C, 70.29; H, 8.61.

The product is insoluble in cold or warm 10% aqueous sodium hydroxide but goes into solution on prolonged boiling.

A second procedure using the anhydride follows: dry hydrogen chloride was bubbled for three-quarters of an hour through a solution of 2 g. of dodecahydrophenanthrene-9,10-dicarboxylic acid anhydride in 30 cc. of absolute ethanol. After refluxing for about twenty-four hours on a steam cone, the alcohol was evaporated by means of a stream of warm air and the residue poured into water. Extraction with benzene and purification as described above gave the same product.

Tetradecahydrophenanthrene-9,10-dicarboxylic Acid Lactone (IV). Compound III as Intermediate.—A solution of 1.5 g. of the ethyl ester of the lactone in 10 cc. of 5% sodium hydroxide was refluxed for a few hours until all the solid had dissolved. Upon cooling, a solid precipitated. This proved to be a disodium salt.

Anal. Calcd. for $C_{16}H_{22}O_5Na_2$: Na, 13.51. Found: Na, 13.81.

The sodium salt, as well as the filtrate from the sodium salt, on acidification gave a precipitate, which still contained sodium. If, however, it was warmed with hydrochloric acid, a crystalline product separated on cooling. After purification from dilute acetone, it formed long blunt prisms, m. p. 246–247°.

Anal. Calcd. for $C_{16}H_{22}O_4$: C, 69.02; H, 7.97; neut. equiv., 278. Found: C, 69.14; H, 8.09; neut. equiv., 278.

Monoethyl-$\Delta^{4a,5a}$-dodecahydrophenanthrene-9,10-dicarboxylate (VI).—To a cold solution of 0.2 g. of sodium in 20 cc. of absolute ethanol was added 3 g. of $\Delta^{4a,5a}$-dodecahydrophenanthrene-9,10-dicarboxylic acid anhydride. After standing a day at room temperature, the alcohol was evaporated by means of a stream of air. The solid residue was dissolved in 35 cc. of water and acidified with dilute hydrochloric acid. The clumpy precipitate was allowed to dry and any material that gradually separated from the acidified solution added to it. Crystallization from cyclohexane, followed by several crystallizations from dilute acetone, gave small white plates, m. p. 127–128°.

Anal. Calcd. for $C_{18}H_{26}O_4$: C, 70.54; H, 8.56; neut. equiv., 306. Found: C, 70.71; H, 8.52; neut. equiv., 323.

Effect of Heat upon $\Delta^{4a,5a}$-Dodecahydrophenanthrene-9,10-dicarboxylic Acid.—A sample of 0.9 g. of acid was heated in a test-tube at 200–210° for fifteen minutes. Upon cooling, 30 cc. of cyclohexane was added and the mixture heated to boiling. Insoluble material was filtered from the hot solution. This solid product was crystallized from dilute acetone and prisms were obtained which proved to be lactone acid (IV).

Heating the acid (I) above its melting point, and direct extraction of the reaction mass with petroleum ether gave a small amount of crystalline material, m. p. 123–123.5°, which proved to be anhydride.

Conversion of $\Delta^{4a,5a}$-Dodecahydrophenanthrene-9,10-dicarboxylic Acid to Tetradecahydrophenanthrene-9,10-dicarboxylic Acid Lactone (IV).—To a solution of 2 g. of dicarboxylic acid in 50 cc. of acetone was added 10 cc. of concentrated hydrochloric acid. After refluxing for four to five hours the solution was poured into ice water and filtered. The filtrate upon evaporation left a brown crystalline residue which was recrystallized from dilute acetone; m. p. 213°.

Since the neutral equivalent determination indicated that the material was probably impure lactone acid, it was recovered and subjected to three more recrystallizations. This treatment yielded long blunt prisms, m. p. 242–244°, which proved to be the lactone acid by mixed melting point.

Summary

$\Delta^{4a,5a}$-Dodecahydrophenanthrene-9,10-dicarboxylic acid and its anhydride are converted into a lactone ester and not into a diester upon esterification. Saponification of this lactone ester with alkali gives the alkali salt of an hydroxy dibasic acid which on acidification gives a monobasic acid monolactone. It is assumed by analogy to previous results on the study of γ,δ-olefinic acids that in these molecules a δ-lactone probably has formed.

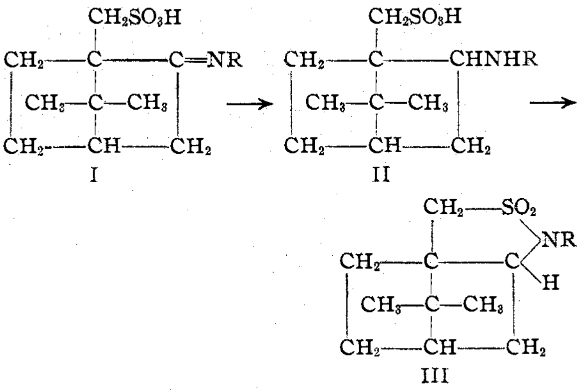
Urbana, Illinois Received September 30, 1938

[Contribution from the Chemical Laboratory of the University of Illinois]

Anomalous Mutarotation of Salts of Reychler's Acid. VI. Synthesis and Structure of the Sultam of 2-(N-Methylamino)-*d*-camphane-10-sulfonic Acid

By R. L. Shriner, James A. Shotton and Harry Sutherland

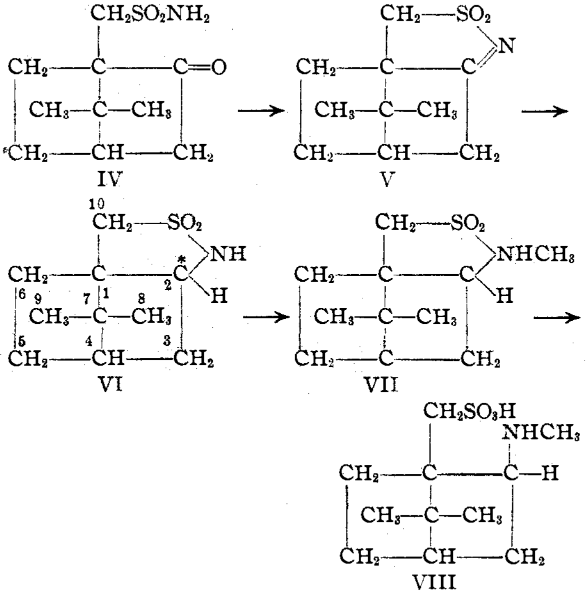
One of the reactions used to establish the ketimine structure (I) of the dehydration products of primary amine salts of Reychler's acid[1] was reduction to the substituted amino sulfonic acid (II). The two forms of the latter underwent dehydration, producing compounds whose analyses and properties indicated the sultam structure,[1c] (III).



I II III

The purpose of the present investigation was to synthesize one of these sultams by an independent method in order to establish this structure.

Accordingly, use was made of an observation by Reychler[2] that *d*-camphor-10-sulfonamide (IV) underwent dehydration to an anhydro compound to which Armstrong and Lowry[3] had assigned the structure shown in formula V. In the present work this anhydramide was reduced catalytically with hydrogen and Raney nickel to the sultam, VI. Although the latter may exist in two diastereoisomeric forms, since carbon atom 2 is now asymmetric (*), only one form actually was produced. The sodium salt of this sultam was treated with methyl iodide and the N-methyl sultam, VII, obtained. Hydrolysis by means of concentrated hydrochloric acid opened the heterocyclic ring and produced the α-form of 2-(N-methylamino)-*d*-camphane-10-sulfonic acid (VIII). Although Reychler's acid and its amide are dextrorotatory, all the derivatives V, VI, VII and VIII were levorotatory; the specific rotations being −32, −33, −59 and −98°, respectively.



IV V VI VII VIII

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[1] (a) Schreiber and Shriner, This Journal, **57**, 1306 (1935); (b) *ibid.*, **57**, 1445 (1935); (c) *ibid.*, **57**, 1869 (1935); Sutherland and Shriner, *ibid.*, **58**, 62 (1936); *ibid.*, **60**, 1314 (1938).

[2] Reychler, *Bull. soc. chim.*, **19**, 127 (1898).

[3] Armstrong and Lowry, *J. Chem. Soc.*, **81**, 1448 (1902); Lowry and Desch, *ibid.*, **95**, 1340 (1909); Richards and Lowry, *ibid.*, **127**, 1503 (1925).