special interest since in the previous cases, doubtless due to the selective action, only one compound has been isolated from such reactions.

## Summary

A study has been made of allyl and acyl substituted thiazolidones and of the use of mono- and diphenyl halogen acetyl chlorides and esters in the synthesis of thiazolidones and in one case of an imidazolone.

The diphenylchloroacetyl chloride gave with methylphenyl thiourea the two possible thiazolidones. It was noted also that the two phenyl groups at position 5 stabilize the thiazolidone ring toward hydrolysis as does the benzal group at the same position.

LAWRENCE, KAN. RECEIVED SEPTEMBER 30, 1936

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[CONTRIBUTION FROM THE WALKER CHEMICAL LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

# Ethyl Imidocyclopropanecarboxylate Hydrochlorides[1]

BY JOHN B. CLOKE, EDWIN C. KNOWLES AND RAYMOND J. ANDERSON

**Preparation.**—The imido ester salts were prepared by the general method of Pinner.[2] Thus, the ethyl imidocyclopropanecarboxylate hydrochloride (I) was obtained by the action of dry hydrogen chloride on an ether solution of ethanol and cyclopropyl cyanide as follows

$$\underline{CH_2CH_2CH}CN + HOC_2H_5 + HCl \longrightarrow$$

$$\underline{CH_2CH_2CH}—C(=NH_2Cl)OC_2H_5 \quad (I)$$

Similarly, the ethyl imido-1-phenylcyclopropanecarboxylate hydrochloride

$$\underline{CH_2CH_2C}(C_6H_5)—C(=NH_2Cl)OC_2H_5 \quad (II)$$

was obtained from 1-phenyl-1-cyanocyclopropane.[3]

**Decomposition by Heat.**—Pinner[4] many years ago found that the ordinary alkyl imido ester hydrochlorides are decomposed by the action of heat to give an amide and an alkyl chloride. His equation for the pyrolysis was

$$R—C(=NH_2Cl)OR' + \text{heat} \longrightarrow R—CO—NH_2 + R'Cl$$

Several years later, however, Stieglitz[5] in a much more critical study of this reaction pointed out that certain facts are more in harmony with the carbonium, $(R)(NH_2)(OR')CCl$, than with the enammonium structure for the pyrolyzing imidoester salt. His present view, which differs from this one, will be considered in a subsequent communication on this problem.

Following the observation[6] that a cyclopropyl ketimmonium chloride $\underline{CH_2CH_2CH}—C(=NH_2Cl)—R$, rearranges when heated to give the isomeric pyrrolinium chloride, $\underline{CH_2CH_2CH=C(R)N}H_2Cl$, it appeared to be quite possible that the analogous imido ester derivatives such as (I) and (II) might likewise undergo a ring rupture in addition to the Pinner–Stieglitz reaction. However, the work reported in this paper, which was undertaken largely to provide an answer to this question, has demonstrated that (I) and (II) decompose normally according to the Pinner–Stieglitz reaction to give cyclopropanecarbonamide, $\underline{CH_2CH_2CH}—CONH_2$, and 1-phenylcyclopropanecarbonamide

$$\underline{CH_2CH_2C}(C_6H_5)—CONH_2,$$

respectively. No ethoxypyrrolinium salts were detected in the cases thus far investigated. In future work an effort will be made to obtain a definite explanation of this notable ring stability.

**Decomposition by Water.**—In aqueous solution the imido esters undergo two concurrent reactions. In the first place, they decompose into a nitrile and an alcohol or phenol; and, in the second, they react with water to give the ordinary ester and ammonia, $R—C(=NH)-OR' + H_2O = RCOOR' + NH_3$. The first of these reactions is accelerated by bases, whereas the second is favored by acids. The imido ester hydrochlorides, therefore, are normally decomposed by water to give the ordinary ester and ammonium chloride in accordance with the monomolecular law, although some of them undergo a significant decomposition into nitrile, hydrochloric acid and an alcohol or phenol. Many years ago Stieglitz

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[1] The data reported herein have been taken from theses presented to the Rensselaer Polytechnic Institute by Edwin Chandler Knowles and Raymond J. Anderson. The work on the unsubstituted cyclopropane derivatives was done by R. J. A. and that on the phenylated compounds by E. C. K.

[2] Pinner, "Die Imidoäther und ihre Derivate," Berlin, 1892.

[3] Knowles and Cloke, THIS JOURNAL, **54**, 2028 (1932).

[4] Pinner, *Ber.*, **16**, 355, 1654 (1883).

[5] Stieglitz, *Am. Chem. J.*, **21**, 101 (1899); Lengfeld and Stieglitz, *ibid.*, **16**, 76 (1894).

[6] Cloke, THIS JOURNAL, **51**, 1174 (1929).

and his collaborators[7] made an extensive study of the decomposition of a variety of imido ester salts. The measurements reported in this paper were made in order to compare the characteristics of the cyclopropyl radicals with the alkyl and aryl radicals previously investigated. Upon the basis of these results, the cyclopropyl radicals would be classified with the so-called electronegative aryl radicals.

## Experimental Part

**Ethyl Imidocyclopropanecarboxylate Hydrochloride.**—A solution of 0.2 mole of cyclopropyl cyanide[8] and 0.205 mole of absolute alcohol in four volumes of absolute ethyl ether in a moisture-proof vessel was then cooled in an ice-bath, when a current of carefully dried hydrogen chloride was passed in until no more gas was absorbed, which required about three hours. The solution was then allowed to stand overnight, which led to the separation of a crop of white crystals. These were collected on a filter, which was supported in a moisture-proof housing, when they were washed with anhydrous ether, dissolved in anhydrous acetic acid and reprecipitated therefrom by the addition of anhydrous ether. These crystals, which again were collected on a filter and dried under diminished pressure, melted at 120°, which, however, is actually the melting point of the pyrolysis product, *viz.*, the cyclopropanecarbonamide.[9]

*Anal.* Calcd. for $C_6H_{12}ONCl$: N, 9.36. Found: N, 9.43, 9.47.

**Pyrolysis of Ethyl Imidocyclopropanecarboxylate Hydrochloride.**—The imido ester hydrochloride was heated in a test-tube, whereby a white solid condensed on the walls of the tube. The solid melted at 120°, which corresponds to the melting point of the cyclopropanecarbonamide.

*Anal.* Calcd. for $C_4H_7ON$: N, 16.45. Found: N, 16.31.

**Ethyl Imido-1-phenylcyclopropanecarboxylate Hydrochloride.**—A solution of 13.72 g. of 1-phenyl-1-cyanocyclopropane[8] and 4.45 g. of absolute alcohol in 80 cc. of anhydrous ether was treated on several successive days with carefully dried hydrogen chloride. Since only a small amount of white solid had separated at the end of ten days, about 300 cc. of anhydrous ether was added to the mixture, whereby a voluminous white precipitate separated. The crystalline mass was collected on a filter under anhydrous conditions, washed with anhydrous ether and dried in a vacuum desiccator over phosphorus pentoxide for several hours. In view of the fact that the substance, which weighed 11 g., contained 17.6% chlorine as compared with a theoretical value of 15.8%, it was dissolved in warm glacial acetic acid and reprecipitated by the addition of anhydrous ether and petroleum ether. The purified compound was collected and dried as before.

*Anal.* Calcd. for $C_{12}H_{16}ONCl$: N, 6.21; Cl, 15.72. Found: N, 6.51, 6.37; Cl, 16.1, 15.88.

**Action of Heat on above Hydrochloride.**—The ethyl imido-1-phenylcyclopropanecarboxylate melted in the vicinity of 110° with some effervescence. When the residue was recrystallized from boiling water and then thoroughly dried, it melted from 98.5–99.5°, which is the melting point of the 1-phenylcyclopropanecarbonamide.

**Ethyl Imido-2-methyl-1-phenylcyclopropanecarboxylate Hydrochloride.**—A mixture of 7.83 g. of 2-methyl-1-phenyl-1-cyanocyclopropane and 2.3 g. of absolute alcohol was saturated at 0° with dry hydrogen chloride and allowed to stand in a stoppered flask for eight days. The addition of 200 cc. of anhydrous ether to the solution gave 1.5 g. of white crystals, which were washed with dry ether and dried under diminished pressure.

*Anal.* Calcd. for $C_{13}H_{18}ONCl$: Cl, 14.8. Found: Cl, 15.93.

**Reaction Rates of Imido Ester Hydrochlorides with Water.**—The velocity with which the imido ester hydrochlorides reacted with water, $R—C(=NH_2Cl)OR' + H_2O = RCOOR' + NH_4Cl$, was ascertained by the method of Stieglitz and Derby[10] for analogous compounds. This method is based upon the fact that an imido ester can be liberated from its hydrochloride by the action of sodium hydroxide and that the free ester is much more soluble in carbon tetrachloride than it is in water, whereas the reverse solubility behavior holds for ammonia. The reaction velocity constant, $k$, was calculated from the equation for a monomolecular reaction

$$k = \frac{2.303}{t_2 - t_1} \log \frac{v_1}{v_2}$$

where $v_1$ and $v_2$ represent the relative concentrations of the imido ester hydrochloride at times $t_1$ and $t_2$.

In the work which is recorded in the following tables, a 0.05 molar aqueous solution of the imido ester salt was prepared and maintained at a definite temperature in a thermostat. Without delay a 10–20 cc. volume of the reacting solution was pipetted into a Squibb funnel which contained a carefully measured volume of 0.1 $N$ sodium hydroxide and a suitable quantity of carefully purified carbon tetrachloride. At once the mixture was well

TABLE I

Reaction: $\overline{CH_2CH_2CH}C(=NH_2Cl)OC_2H_5 + H_2O = \overline{CH_2CH_2CH}COOC_2H_5 + NH_4Cl$; temp., 25°; concentration of initial solution, 0.05 $M$; volume of individual samples, 10 cc.; $t$ = time in minutes from moment of dissolving; $v_b$ = volume of 0.1 $N$ NaOH in cc.; $v_a$ = volume of 0.1 HCl.

| $t$ | $v_b$ | $v_a$ | $v_b - v_a$ | $k$ |
|---|---|---|---|---|
| 2 | 7.17 | 2.19 | 4.98 | .... |
| 60 | 7.17 | 2.69 | 4.48 | 0.00182 |
| 180 | 7.17 | 3.55 | 3.62 | .00179 |
| 420 | 7.17 | 4.83 | 2.34 | .00181 |
| 780 | 7.17 | 5.86 | 1.31 | .00172 |
| | | | Average $k$ = | 0.00178 |

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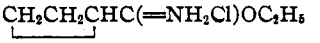
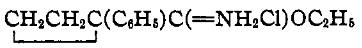
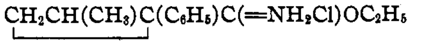
[7] Stieglitz, *Report International Congress of Arts and Science, St. Louis*, **4**, 276 (1904); *Am. Chem. J.*, **39**, 29 (1908); Stieglitz with Derby, McCracken and Schlesinger, *ibid.*, **39**, 29, 166, 402, 437, 586, 719 (1908); Stieglitz, THIS JOURNAL, **32**, 221 (1910); *ibid.*, **34**, 1687 (1912); *ibid.*, **85**, 1774 (1913); Carr, doctoral dissertation, University of Chicago, 1910.

[8] Cloke, Anderson, Lachmann and Smith, THIS JOURNAL, **53**, 2791 (1931).

[9] Dalle, *Chem. Zentr.*, **73**, I, 913 (1902); Kishner, *ibid.*, **72**, II, 579 (1901), gives 124–124.5°.

[10] Derby, *Am. Chem. J.*, **39**, 439–441 (1908).

TABLE II

| Run | Compound | °C. | Successive constants × 10⁴ | | | | | Average *k* |
|---|---|---|---|---|---|---|---|---|
| 2 |  $CH_2CH_2CHC(=NH_2Cl)OC_2H_5$ | 25 | 16.3 | 17.8 | 17.4 | 18.7 | | 0.00176 |
| 3 | | 0 | 0.939 | 1.054 | 0.968 | 1.003 | | .0000991 |
| 4 |  $CH_2CH_2C(C_6H_5)C(=NH_2Cl)OC_2H_5$ | 25 | 29.7 | 29.1 | 26.9 | 24.2 | 23.8 | .00265 |
| 5 | | 25 | 25.7 | 24.5 | 25.0 | 23.8 | | .00247 |
| 6 | | 25 | 25.7 | 24.0 | 21.8 | 19.0 | | .00226 |
| 7 |  $CH_2CH(CH_3)C(C_6H_5)C(=NH_2Cl)OC_2H_5$ | 25 | 17.2 | 14.3 | 12.6 | | | .00147 |
| 8 | | 25 | 16.8 | 12.6 | 13.3 | 11.6 | | .00136 |

shaken, the carbon tetrachloride layer was drawn off, and the extraction was repeated twice with fresh portions of this solvent. Finally the residual aqueous alkaline solution was titrated with 0.1 *N* hydrochloric acid. Table I gives the data for a typical run.

Table II presents a summary of runs similar to that recorded in Table I.

In view of the fact that compound (II) appeared to be relatively pure, the drift in the values of the constants of runs 4, 5 and 6 suggests a secondary concurrent reaction, although this has not been ascertained experimentally. Runs 7 and 8 on the methylated derivative are of qualitative value only.

## Summary

1. The hydrochlorides of ethyl imidocyclopropanecarboxylate and ethyl imido-1-phenylcyclopropanecarboxylate are pyrolyzed normally according to the Pinner–Stieglitz reaction to give the corresponding amides and ethyl chloride. No evidence was obtained of a ring rupture to give pyrrolinium salts.

2. A study of the reaction velocity constants of our imido ester salts with water and those previously determined by Stieglitz and his collaborators for other compounds shows that by this criterion the cyclopropyl radicals should be classified with the electronegative aryl radicals.

Unfinished work on the free esters and amidines will be completed and reported at a later date.

TROY, N. Y. RECEIVED OCTOBER 5, 1936

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[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY, UNIVERSITY OF NEBRASKA]

# Acetyl Derivatives of the Monobasic Sugar Acid Lactones

BY FRED W. UPSON, JOHN M. BRACKENBURY AND CARL LINN

The preparation of a number of acetyl derivatives of the monobasic sugar acid lactones is described in this paper and their properties are compared with those of the parent lactones. Since these derivatives are easily prepared, they are useful in identifying the lactones and in synthesizing other compounds.[1] Furthermore, since no other derivatives have been prepared directly from the δ-lactones the preparation of the acetyl derivatives of these lactones is of interest.

It has been shown[2] that the monobasic lactones having an amylene oxide structure, the δ-lactones, are rapidly hydrolyzed in water solution. Loder[3] found that methylation of *d*-mannonic δ-lactone yielded a derivative having the properties of the γ-lactone. A study of the acetyl compounds was undertaken in an effort to prepare derivatives directly from the δ-lactones[4] and this paper is a continuation of the earlier work of Upson and Bartz. A non-crystalline substance identified as the 2,3,4,6-tetraacetyl derivative was obtained by direct acetylation of *d*-gluconic δ-lactone. This compound though non-crystalline, showed a very rapid mutarotation in 80% acetone–water solution, and was otherwise characterized as a derivative of a δ-lactone.

The acetyl derivatives of thirteen sugar acid lactones have been prepared and their specific rotations have been determined in comparison with those of the parent lactones. The following compounds prepared for this study are already described in the literature: 2,3,5-triacetyl-*d*-xylonic[5] and *l*-arabonic,[6] γ-lactones; the 2,3,5,6-tetraacetyl derivatives of the γ-lactones of *d*-gluconic,[4] *d*-mannonic,[4] α-*d*-glucoheptonic,[4] and α-*l*-rhamnohexonic acids;[7] and 2,3,4,6-tetraacetyl-*d*-gluconic δ-lactone.[4] In addition the following

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[1] Paal and Kinscher, *Ber.*, **44**, 3543 (1911); **39**, 1361, 2823, 2827 (1906).

[2] Levene and Simms, *J. Biol. Chem.*, **65**, 31 (1925).

[3] Loder, unpublished thesis, University of Nebraska, 1927.

[4] Upson and Bartz, THIS JOURNAL, **53**, 4226 (1931).

[5] Hasenfratz, *Compt. rend.*, **196**, 350 (1933).

[6] Simon and Hasenfratz, *ibid.*, **179**, 1165 (1924).

[7] Miksic, *Vestnik Kral. Ces., Spol. Nauk.* Cl. II, 18 pp. (1926).