Anal. Calcd. for $C_{16}H_{22}N_2O_7$: C, 54.23; H, 6.26; N, 7.91. Found: C, 54.57; H, 6.34; N, 7.95.

*2-Amino-N-*D*-ribosylacetamide* (XII). The benzyl ester X (1.7 g.) was dissolved in 200 ml. of boiling absolute methanol under reflux; the solution was cooled in ice, quickly added to a suspension of the catalyst (10% palladium on carbon) in 10 ml. of ice cold methanol in the bottle of a Parr hydrogenator, and hydrogenated in the customary manner. The suspension was filtered and the colorless filtrate was evaporated to dryness, giving a quantitative yield of colorless crystals which were stirred with cold methanol and filtered; m.p. 180° dec. (softens at 177°), $[\alpha]_D^{25}$ $-17.8°$ (*c*, 0.956 in water).

Anal. Calcd. for $C_7H_{14}N_2O_5$: C, 40.77; H, 6.84; N, 13.59. Found: C, 40.81; H, 6.84; N, 13.67.

*2-(Methylamino)-N-*D*-ribosylacetamide* (XIII). The benzyl ester XI (1.8 g.) was hydrogenolyzed as for the preparation of XII, giving 0.9 g. of colorless crystals, m.p. 182° dec. Recrystallized from absolute methanol (70 volumes), it had a m.p. of 192–193°, $[\alpha]_D^{26}$ $-31.9°$ (*c*, 0.094 in water).

Anal. Calcd. for $C_8H_{16}N_2O_5$: C, 43.63; H, 7.32; N, 12.72. Found: C, 43.78; H, 7.47; N, 12.88.

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MEDICINAL CHEMISTRY
MELLON INSTITUTE
PITTSBURGH 13, PA.

(2-Carboxyethyl)succinic Anhydride[1]

J. W. LYNN AND R. L. ROBERTS

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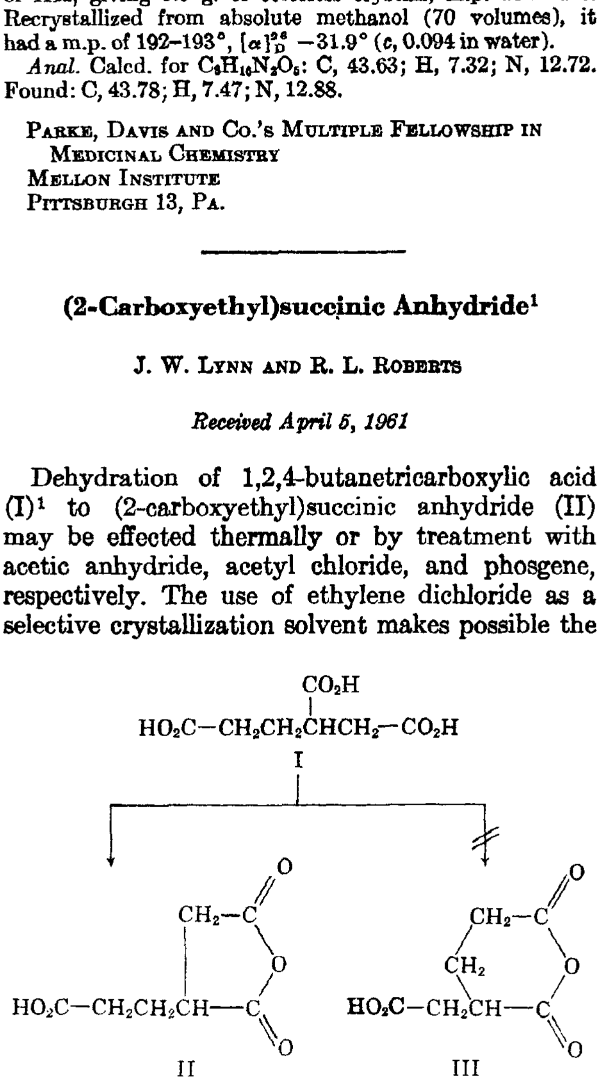
Dehydration of 1,2,4-butanetricarboxylic acid (I)[1] to (2-carboxyethyl)succinic anhydride (II) may be effected thermally or by treatment with acetic anhydride, acetyl chloride, and phosgene, respectively. The use of ethylene dichloride as a selective crystallization solvent makes possible the isolation of II in high yield and purity from hitherto intractable residues.



That the anhydro acid possesses the succinic structure, II, rather than the isomeric glutaric structure, III, is indicated by comparison of the infrared absorption maxima characteristic of the anhydride doublet as shown in the table below.

INFRARED ABSORPTION MAXIMA,[a] μ, FOR ANHYDRIDE DOUBLET

	I	Succinic Anhydride	Glutaric Anhydride
C=O	5.38	5.36	5.63
	5.60	5.60	5.70
C—O—C	8.13	8.10	8.11
	8.20	8.30	8.19

[a] Taken with a Baird Model 4–55 infrared double-beam spectrophotometer of a 1% KBr plaque, calibrated against polystyrene.

EXPERIMENTAL[2]

(2-Carboxyethyl)succinic anhydride (II). a. *By thermal dehydration of* I. A mixture of 577 g. (3 moles) of I and 1200 g. of dry nonane was heated to reflux, removing water of dehydration from the heterogeneous azeotrope over a period of 15 hr. The product mixture was cooled, nonane removed from the insoluble crude product by decantation, the anhydro acid taken up in hot ethylene dichloride, treated with decolorizing carbon, and then cooled to crystallize. Filtration gave 468 g., an 87.8% yield, of fine, white crystals (m.p. 63–64°, 96.7% purity by anhydride titration with aniline/sodium hydroxide).

Anal. Calcd. for $C_7H_8O_5$: C, 48.84; H, 4.68. Found: C, 48.83; H, 4.72.

Evaporation of the ethylene dichloride filtrates gave an additional 31 g., a 4.8% yield, of II.

b. *By dehydration with acetic anhydride.* A mixture of 380 g. (2 moles) of I, 221 g. (2.15 moles) of acetic anhydride and 700 g. of ethylbenzene was fractionally distilled at 50 ml. pressure to remove the acetic acid–ethylbenzene azeotrope (b.p. 47°/50 mm.) during 25 hr. Titration of the distillate indicated the theoretical amount of acetic acid. The reaction mixture was cooled, the supernatant ethylbenzene was decanted from the insoluble crude product, and the product was taken up in hot ethylene dichloride, treated with decolorizing carbon and cooled to crystallize. Filtration gave 313 g., a 91% yield, of fine white crystals (m.p. 62–63°, 100% purity by anhydride titration with aniline/sodium hydroxide).

Anal. Calcd. for $C_7H_8O_5$: C, 48.84; N, 4.68. Found: C, 49.14; H, 4.68.

The anilic acid prepared by reaction with aniline in chloroform melted at 144–145° (from water).

Anal. Calcd. for $C_{13}H_{15}NO_5$: C, 58.86; H, 5.70; N, 5.28. Found: C, 58.58; H, 5.90; N, 5.85.

c. *By dehydration with acetyl chloride.* A mixture of 190 g. (1 mole) of I, 235 g. (3 moles) of acetyl chloride, and 300 g. of 1,4-dioxane was charged to a flask and heated slowly with agitation to 60–70°. The weight of hydrogen chloride evolved was determined by bubbling the blow-off gases through a water bottle and recording the weight gain. After 7.5 hr., the evolution of hydrochloric acid had essentially ceased. The reaction mixture was cooled and stripped of excess acetyl chloride and solvent under reduced pressure at 25°. The solid residue was dissolved in hot ethylene dichloride, treated with decolorizing carbon, and filtered. Upon crystallization, there was obtained a total of 134 g., a 78% yield of II (m.p. 63–64°). Infrared maxima: 3.80, 5.38, 5.60, 8.13, 8.20, 10.85 μ.

Evaporation of the filtrate gave 30 g. of unchanged I.

d. *By dehydration with phosgene.*[3] A solution of 56 g. (0.295 mole) of I in 300 ml. of dry acetone was treated with a

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(1) For previous paper of this series, see *J. Org. Chem.*, 26, 3757 (1961).

(2) All temperatures are uncorrected.

(3) We are indebted to Dr. T. K. Brotherton for this experiment.

solution of 59.6 g. (0.59 mole) of triethylamine in 100 ml. of acetone at ambient temperature. With vigorous agitation, 29.2 g. (0.295 mole) of liquid phosgene was added to the mixture at 0° during 10-min. period. The resulting mixture was filtered and the filtrate was evaporated to a temperature of 60° at 2 mm., leaving a 56-g. residue. Crystallization from acetic acid furnished 46.5 g., a 91.4% yield, of crude II melting at 56–59°.

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Research Department
Union Carbide Chemicals Co.
South Charleston 3, W. Va.

Decarboxamidation[1]

E. Campaigne and G. F. Bulbenko

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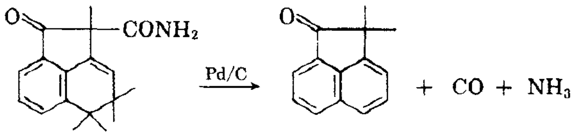
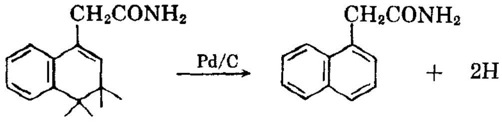
2-Carbamoyl-4,5-dihydro-1-acenaphthenone (I) is readily prepared by ring-closure of 1,2,3,4-tetrahydro-1-naphthylidenemalononitrile in concentrated sulfuric acid.[2] When I was refluxed in xylene with 30% palladium on charcoal, a quantitative evolution of ammonia, and a 65% yield of acenaphthenone (II) was obtained. II was identified by comparison of derivatives and spectra with those of an authentic specimen of acenaphthenone.



I II

The quantitative removal of carbon monoxide and ammonia from a carboxamide is apparently a new reaction, which we have called "decarboxamidation." Some preliminary experiments have been carried out to determine the scope and limitations of this reaction, using only palladium on charcoal as catalyst. The possibility that other catalysts may be more effective in bringing this reaction about has not been explored. I has three important structural characteristics. It is a β-ketoamide, it is a partially hydrogenated aromatic which is easily dehydrogenated, and it may be regarded as an β-arylpropionamide.

Two types of compounds, each lacking only one of these structural features, were tested for decarboxamidation. 3,4-Dihydronaphthaleneacetamide (III), which lacks the β-keto function, gave 1-naphthylacetamide (IV), the simple dehydrogenated product, on treatment with palladium on charcoal. Only a small amount (4%) of ammonia could be detected. Similar treatment of benzoylacetamide, lacking the partially-hydrogenated aromatic function, led to more complex results. The products in this case included carbon monoxide, ammonia (30%), and acetophenone (30%), and a high-melting yellow amide having the empirical formula $C_{19}H_{16}O_2N_2$.



III IV

From these data, one must conclude that decarboxamidation over palladium on charcoal is largely peculiar to β-ketoamides, and occurs through a complex free-radical process. This latter process is greatly simplified by the presence of hydrogen donors. Thus 2-carbamoyl-4,5-dihydroacenaphthenone (I) is ideally constituted to undergo this decomposition, having two hydrogens readily available to satisfy the carbon and nitrogen radicals produced. The first steps of this decomposition are probably as follows:

$$\mathrm{RCO\underset{|}{C}HCONH_2} \longrightarrow \mathrm{RCO\underset{|}{C}H\cdot} + \cdot\mathrm{CONH_2} \qquad (1)$$

$$\cdot\mathrm{CONH_2} \longrightarrow \cdot\mathrm{NH_2} + \mathrm{CO} \qquad (2)$$

$$\mathrm{R'H} + \cdot\mathrm{NH_2} \longrightarrow \mathrm{R'\cdot} + \mathrm{NH_3} \qquad (3)$$

EXPERIMENTAL

Decarboxamidation of I. A solution of 5 g. (0.023 mole) of I in 50 ml. of dry xylene was refluxed with 2 g. of 5% palladium on charcoal (American Platinum Wks.) for 5 hr. The spent catalyst was then removed by filtration, and 1 g. of 30% palladium on charcoal (American Platinum Wks.) was added, and refluxing continued for 7 hr. more. During the reaction, the flask was swept by a stream of dry nitrogen, which carried the effluent gas through a Dry Ice-cooled trap, a Liebig bulb containing standard sulfuric acid, and then over a series of palladium chloride test papers[3] and out through a mineral oil bubble trap. The test papers showed the copious evolution of carbon monoxide. The ammonia gas, which had been detected by its odor in a preliminary run, was trapped in the Liebig bulb. Titration of the sulfuric acid in the trap showed that 383 mg. of ammonia (98%) was evolved.

The xylene solution was filtered and evaporated, leaving 3.5 g. (90%) of crude oily ketone. This was taken up in benzene and passed through a column of activated alumina. The fore fractions were combined and evaporated. Two recrystallizations from alcohol gave 2.6 g. of colorless needles, melting at 120–121°, which gave an intense red color with alcoholic potassium hydroxide, and a yellow-green color in concentrated sulfuric acid. These are properties characteristic of 1-acenaphthenone (II).[4] Comparison with an authentic

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(1) Contribution No. 996, taken from the thesis of G. F. B.

(2) G. F. Bulbenko, Ph.D. thesis, Indiana University, September 1958.

(3) M. B. Jacobs, *The Analytical Chemistry of Industrial Poisons, Hazards and Solvents*, Interscience, New York, 1949, p. 411.

(4) C. Gräebe and J. Jaquier, *Ann.*, **290**, 195 (1896).

(5) A. L. Green and D. H. Hey, *J. Chem. Soc.*, 4306 (1954).