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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Decarboxamidation[1]

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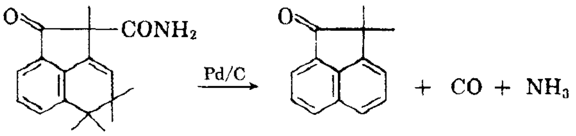
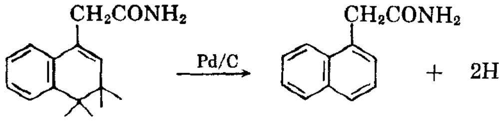
2-Carbamoyl-4,5-dihydro-1-acenaphthenone (I) is readily prepared by ring-closure of 1,2,3,4-tetrahydro-1-naphthylidenemalononitrile in concentrated sulfuric acid.[2] When I was refluxed in xylene with 30% palladium on charcoal, a quantitative evolution of ammonia, and a 65% yield of acenaphthenone (II)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



III IV

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 $C_{19}H_{16}O_2N_2$.

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:

$$\underset{|}{\text{RCOC}}\text{HCONH}_2 \longrightarrow \underset{|}{\text{RCOC}}\text{H}\cdot + \cdot\text{CONH}_2 \qquad (1)$$

$$\cdot\text{CONH}_2 \longrightarrow \cdot\text{NH}_2 + \text{CO} \qquad (2)$$

$$\text{R'H} + \cdot\text{NH}_2 \longrightarrow \text{R'}\cdot + \text{NH}_3 \qquad (3)$$

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. Graebe and J. Jaquier, *Ann.*, **290**, 195 (1896).

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

sample,[5] its oxime,[6] and picrate[4] proved the identity of this compound. A 2,4-dinitrophenylhydrazone of the authentic sample, melting at 265–270°, dec., gave an intense peak in the ultraviolet (alcohol solution) at 395 mμ (ε 39,000).

Anal. Calcd for $C_{18}H_{12}H_4O_4$: C, 62.06; H, 3.47; N, 16.19. Found: C, 61.98; H, 3.91; N, 15.95.

Dehydrogenation of III. III was prepared by treating methyl α-(3,4-dihydronaphthyl)acetate[7] with ammonia in absolute methanol. After standing for 1 month in a refrigerator, large colorless plates of III, which melted sharply at 173° after recrystallizing from water, were obtained.

Anal. Calcd. for $C_{12}H_{13}NO$: C, 76.97; H, 6.99. Found: C, 76.59; H, 7.01.

Treatment of 3.1 g. (16 mmoles) of III with palladium on charcoal in two portions, as previously described, gave 1.63 g. (53%) of colorless needles of 1-naphthylacetamide (IV) melting at 183–184°.[8] Titration of the standard acid indicated 0.627 meq. of ammonia, or 4% of the theoretical amount, was evolved. Only a trace of carbon monoxide could be detected on the test papers.

Decarboxamidation of benzoylacetamide. A solution of 13 g. (80 mmoles) of benzoylacetamide was refluxed in xylene with 2 g. of 30% palladium on charcoal for 6 hr. During this time 23.6 meq. (29.5%) of ammonia was absorbed in the Liebig bulb, and carbon monoxide was shown qualitatively by color change on the palladium chloride test paper. Concentration of the xylene solution caused crystallization of 2 g. of canary yellow prisms, melting at 300° after recrystallization from benzene. Further concentrations of the mother liquors and distillation of the residue produced 3 g. (31%) of acetophenone, identified by melting point of the 2,4-dinitrophenyl hydrazone (250–252°) and mixed melting point with an authentic sample. Other products in the residue were not isolated.

The yellow product, m.p. 300°, is as yet unidentified. The infrared spectrum showed only peaks at 3225 and 3100 cm.$^{-1}$ and at 1650, 1625, and 1575 cm.$^{-1}$ in the range above 1500 cm.$^{-1}$ This is characteristic of an amide, but no ketone carbonyl or other characteristic peaks were present. This was confirmed by the lack of a test with 2,4-dinitrophenylhydrazine solution.

Anal. Calcd. for $C_{19}H_{16}O_2N_2$: C, 74.99; H, 5.30; N, 9.21. Found: C, 75.12; H, 5.22; N, 9.41.

A sample of this amide was hydrolyzed in 15% aqueous potassium hydroxide. Ammonia was evolved, and acidification produced an acid which recrystallized from benzene as pale yellow needles melting sharply without decomposition at 234–234.5°. The infrared spectrum of this acid is characteristic of an aromatic carboxylic acid, but shows no other identifiable functional groups.

Anal. Calcd. for $C_{19}H_{15}O_3N$: C, 74.75; H, 4.95; N, 4.59. Found: C, 74.03; H, 4.58; N, 4.54.

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(6) G. T. Morgan and H. M. Stanley, *J. Soc. Chem. Ind.*, **44,** 494T (1925).

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Ring Closure of α-Tetrylidenemalononitrile[1]

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Treatment of 1,2,3,4-tetrahydro-1-naphthylidenemalononitrile (α-tetrylidenemalononitrile, I) with concentrated sulfuric acid followed by dilution with water might be expected to yield the corresponding mono- or diamides, since this is the classic method of Bouveault[2] for hydrolysis of nitriles to amides. However, when a sample of I was heated in concentrated sulfuric acid on a steam bath for 10 minutes, and then poured over ice, bright orange crystals melting at 185–190° with decomposition were obtained. The same product was formed in polyphosphoric acid heated for five hours on the steam bath and diluted. The structure of this product, obtained in yields as high as 96% from sulfuric acid, was assumed to be that of 2-carbamoyl-4,5-dihydroacenaphthenone (II).

I II

Compound II was insoluble in dilute sodium bicarbonate, but difficultly soluble in dilute sodium hydroxide, from which it reprecipitated on acidification. The infrared spectrum showed characteristic ketonic (1709 cm.$^{-1}$) and amide carbonyl (1681 cm.$^{-1}$) peaks, and no nitrile band between 2260 and 2200 cm.$^{-1}$ It formed an oxime and a 2,4-dinitrophenylhydrazone. The elemental analysis of II and its derivatives were in agreement with the structure shown.

The double bond was located in the six-membered ring, between carbon atoms 2a and 3, rather than in the five-membered ring, between carbon atoms 2 and 2a, by a comparison of ultraviolet absorption spectra. Ramirez and Kirby[3] have shown that the ultraviolet absorption spectra of 2,4-dinitrophenylhydrazones of unsaturated cyclic ketones show a bathochromic shift of the characteristic peak in the 390-mμ region when they are conjugated, but if the double bond is not conjugated, the absorption in this region will be the same as that of the 2,4-dinitrophenylhydrazone of the saturated cyclic ketone. The 2,4-dinitrophenylhydrazone of 1-acenaphthenone showed an intense peak at 395 mμ,[4] and the 2,4-dinitrophenylhydrazone of II showed an identical peak. This was taken as evidence for the location of the double bond exocyclic to the five-membered ring in II, as shown.

Ring closures of aromatic derivatives of nitriles to form six-membered rings are well known. Bradsher *et al.*[5] showed that o-biphenylylaceto-

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(1) Contribution No. 998 from this laboratory, taken from a portion of a thesis submitted by G. F. B. in partial fulfillment of the requirements of the degree of Doctor of Philosophy at Indiana University, June 1958.

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