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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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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nitrile and its derivatives could be converted to phenanthrylamines by an intramolecular Hoesch reaction. Earlier Chu and Shen[6] reported the formation of 9,9-dibutyl-10-phenanthrone when *o*-biphenylyldibutylacetonitrile was treated with concentrated sulfuric acid. Dufraisse *et al.*[7] claim to have converted 1,3-diphenylisopropylidenemalononitrile to 1-amino-2-cyano-3-benzylnaphthalene by sulfuric acid treatment. All these examples involve formation of six-membered rings. The present report is, to our knowledge, the first example of a five-membered ring formed by cyclization of an ylidenemalononitrile derivative.

II is interesting, as it is readily prepared in quantity by a simple beaker reaction from available materials, and possesses four reactive functional groups, ketone, active hydrogen, carboxamide, and double bond. Its structure was confirmed by the results of the following chemical studies.

When II was refluxed in 15% sodium hydroxide solution for twelve hours, it underwent characteristic acid cleavage of β-keto acid derivatives, to form 8-carboxy-3,4-dihydro-1-naphthaleneacetic acid (III). The structure of III was confirmed by the infrared spectrum, which showed a characteristic doublet (1720, 1690 cm.$^{-1}$) for aromatic and aliphatic carboxyl groups, and by the ultraviolet spectrum which had two peaks, λ_{max} 263 mμ/ϵ 8300 and 300 mμ/ϵ 3700 in ethanol. The lack of an intense peak in the 275 mμ region (ϵ 20,000), characteristic of the cinnamic acid structure,[8] and the presence of a similar peak (261 mμ, ϵ 6000) in the spectrum of 3,4-dihydronaphthaleneacetic acid, locate the double bond in the position assigned. III was converted to 8-carboxy-1-naphthylacetic acid (IV)[9] by dehydrogenation over palladium on carbon.

II underwent an unusual reaction, "decarboxamidation,"[4] which served to confirm the structure. Refluxing II with palladium-on-charcoal in xylene caused the evolution of carbon monoxide and ammonia, and produced 1-acenaphthenone.

EXPERIMENTAL

Spectra. The ultraviolet spectra were determined in ethanol on a Beckman DK-1 double beam recording spectrograph, using 1.00-cm. silica cells. The infrared spectra were obtained in potassium bromide mulls using a Perkin-Elmer Infracord spectrometer.

Reaction of I *with sulfuric acid.* A solution of 20 g. (0.1 mole) of I, prepared in 81% yield by the method of Mowry,[10] in 100 ml. of concd. sulfuric acid was warmed on a steam bath until the color became a deep burgundy red (about 5 min. was usually required). The solution was then cooled to room temperature and stirred into about 500 g. of ice. The black tarry-appearing aqueous solution, after standing overnight, deposited orange crystals of II. The crude product (17 g., 96%) melted at 185–190° dec. Recrystallization from methanol gave fine long needles of intense orange-gold color which decomposed in the range of 203–205°.

Anal. Calcd. for $C_{13}H_{11}NO_2$: C, 73.20; H, 5.16; N, 6.57. Found: C, 73.17; H, 5.20; N, 6.45.

The compound exhibited infrared peaks at 3058 cm.$^{-1}$ (NH_2), 1701 cm.$^{-1}$ (ketone), 1681 cm.$^{-1}$ (amidecarbonyl) and 1600 cm.$^{-1}$ (C=C).

The 2,4-dinitrophenylhydrazone of II was readily obtained and melted at 244° dec. It showed a characteristic ultraviolet absorption peak in alcohol at 395 mμ, ϵ 42,700.

Anal. Calcd. for $C_{19}H_{15}N_5O_5$: N, 17.8. Found: N, 18.0.

The oxime of II was formed as yellow needles after two recrystallizations from ethanol, and melted at 238° dec.

Anal. Calcd. for $C_{13}H_{12}N_2O_2$: N, 12.2. Found: N, 11.9.

II could be recrystallized from hot water, but was insoluble in cold 5% sodium carbonate. It was slowly soluble in 10% sodium hydroxide, from which it was reprecipitated on acidification.

Reaction of I *with polyphosphoric acid.* Two grams of I was stirred in 80 ml. of polyphosphoric acid, and heated on a steam bath for 5 hr. The clear reddish solution was poured over cracked ice and allowed to stand overnight. The crude yellow-orange precipitate weighed 1.9 g. (86%) and melted from 170–180°. One recrystallization from methanol yielded golden-orange needles identical to II.

Basic hydrolysis of II. Two grams of II slowly dissolved when refluxed for 12 hr. in 25 ml. of 15% sodium hydroxide solution. The alkaline aqueous solution was extracted with ether, and then acidified with hydrochloric acid.The cloudy acidic solution was extracted with three portions of ether, and these extracts combined, dried, and evaporated. The residue was recrystallized twice from benzene, giving 1.24 g. (87%) of buff colored crystals of III, melting at 177–178°.

Anal. Calcd. for $C_{13}H_{12}O_4$: C, 67.23; H, 5.20; Neut. equiv., 116.0. Found: C, 67.55; H, 5.39; Neut. equiv., 115.6.

The infrared spectrum of III showed peaks at 3150 cm.$^{-1}$ (—OH) 1720, 1690 cm.$^{-1}$ (aliphatic and aromatic COOH carbonyl) and 1565 cm.$^{-1}$ (C=C). The ultraviolet spectrum (in ethanol) showed peaks at 263 mμ (ϵ 8300) and 300 mμ (ϵ 3700).

A sample of 3,4-dihydronaphthalene-1-acetic acid, prepared by the method of Schroeter,[11] *via* a Reformatsky reaction with α-tetralone and hydrolysis of the ester, recrystallized as colorless needles from petroleum ether (b.p. 30–60°) and melted at 103–104°, in agreement with Schroeter.[11] The ultraviolet spectrum of this acid showed λ_{max} 261 mμ, ϵ 6000.

Dehydrogenation of III. A solution of 0.6 g. of III in 50 ml. of dry xylene was refluxed with 1 g. of 30% palladium on charcoal (American Platinum Wks.) for 7 hr. The solution was filtered and concentrated at reduced pressure. The oily residue was crystallized from ethyl acetate as short colorless needles melting at 215–216° dec. Rule and Turner[8] report the melting point of 8-carboxy-1-naphthaleneacetic acid (IV) to be 213–214° dec.

Anal. Calcd. for $C_{13}H_{10}O_4$: C, 67.82; H, 4.37; neut. equiv., 115.2. Found: C, 67.97; H, 4.69; neut. equiv., 114.6.

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