filtration. Upon evaporation of the filtrate, no significant amount of water-insoluble material was obtained. The mixture of the colorless solid and catalyst was treated with 150 ml. of dimethyl sulfoxide, and the colorless solid dissolved. The catalyst was removed by filtration, and upon adding 400 ml. of water to the filtrate, the colorless solid again precipitated. It was removed by filtration, washed with water, and dried. There was thus obtained 8.0 g. (84% yield) of 2,3-bis(4′-aminophenyl)-2,3-diphenylsuccinonitrile, m.p. 178–180° dec. A sample of the product was again dissolved in dimethyl sulfoxide, this solution was filtered, and the solid was reprecipitated by the addition of water. The solid was collected by filtration, washed with water, then with hot methanol, and dried under vacuum, m.p. 181–183° dec.

Anal. Calcd. for $C_{28}H_{22}N_4$: C, 81.13; H, 5.35. Found: C, 80.85; H, 5.50.

On the basis of infrared spectra and mixture melting point, this compound was identical with that prepared by an independent method as described below. When subjected to the conditions of the benzidine rearrangement,[9] the compound underwent no change.

Independent Synthesis of 2,3-Bis(4′-aminophenyl)-2,3-diphenylsuccinonitrile.—Following a procedure similar to that of Kharasch,[8] 0.02 g. of cuprous chloride in 5 ml. of concentrated ammonium hydroxide was added to a solution of 1.0 g. (0.0048 mole) of 4-aminophenylphenylacetonitrile dissolved in 20 ml. of methanol. A precipitate formed almost immediately. After several minutes, 11.0 g. of acetic acid was added, and the mixture was allowed to stand for 10 min. The product was then collected by filtration, washed with water, then with methanol, and dried. There was obtained 0.90 g. (90% yield) of product, m.p. 182–184° dec. Purification as described for the sample above produced no change in the melting point.

Catalytic reductions of arylcyanomethylenequinone oximes in the presence of diethylamine at 35° were conducted under the same conditions using equivalent amounts of materials following the procedure described below.

Catalytic Reduction of *p*-Methoxyphenylcyanomethylenequinone Oxime.—A hydrogenation vessel was charged with 10.00 g. (0.0397 mole) of *p*-methoxyphenylcyanomethylenequinone oxime,[13] 36 g. (0.49 mole) of diethylamine, 100 ml. of methanol, about 7 cc. of Raney nickel, previously washed with methanol, and hydrogen under a pressure of 1180 p.s.i.g. The mixture was shaken and heated to 35° for 1.5 hr. The mixture was allowed to cool, the Raney nickel was removed by filtration, and about 700 ml. of water was added to the filtrate. The next day the material which precipitated was collected by filtration and dried. There was obtained 8.03 g. of material melting at 110–120°.

A 0.50-g. sample of this material dissolved in a minimum of benzene was poured onto an alumina-packed column wet with petroleum ether and was eluted systematically using in sequence petroleum ether, *benzene, ether, and methanol.* After evaporation of the solvents there was thus obtained first 0.29 g. (57.8 mole % of recovered material) of *p*-aminophenyl-*p*-methoxyphenylacetonitrile, m.p. 135–135.5° (lit.[3] 134–135°), and secondly, 0.20 g. (42.2 mole % of recovered material of 4-amino-4′-methoxybenzophenone, m.p. 118–120°, recrystallized from methanol, m.p. 120–121° (lit.[18] 119–210°).

The *p*-aminophenyl-*p*-methoxyphenylacetonitrile was identical with an authentic sample[3] on the basis of mixture melting point and infrared spectra. The infrared spectra of 4-amino-4′-methoxybenzophenone compared favorably with the infrared spectra of a sample of *p*-aminobenzophenone.

Chemical reductions of arylcyanomethylenequinone oximes in the presence of diethylamine were conducted under the same conditions using equivalent amounts of materials following the procedure described below.

Chemical Reduction of *p*-Methoxyphenylcyanomethylenequinone Oxime.—To a mixture of 6.31 g. (0.025 mole) of *p*-methoxyphenylcyanomethylenequinone oxime, 23 g. (0.30 mole) of diethylamine, and 50 ml. of methanol cooled on an ice bath was added 9.0 g. (0.15 mole) of acetic acid, 3 ml. of water, and finally 4.9 g. (0.075 mole) of zinc powder over a period of 25 min. The mixture was then cautiously heated to boiling for 0.5 hr., and filtered. To the filtrate was added 50 g. of acetic acid in 500 ml. of water. After cooling overnight, the material which precipitated was removed by filtration, washed with water, and dried. There was isolated 4.77 g. of solid, m.p. 90–115°.

Chromatographic separation of 1.00 g. of the material thus obtained using the procedure described above gave 0.25 g. (25.4 mole % of recovered material) of *p*-aminophenyl-*p*-methoxyphenylacetonitrile, m.p. 129–132°, recrystallized from benzene–petroleum ether, m.p. 134–135° (lit.[3] 134–135°), and 0.70 g. (74.6 mole % of recovered material) of 4-amino-4′-methoxybenzophenone, m.p. 112–117°, recrystallized from benzene–petroleum ether, m.p. 119–120° (lit.[18] 119–120°). The infrared spectra of these products were identical with those described above.

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[18] C. E. Kaslow and R. D. Stayner, *J. Am. Chem. Soc.*, **68**, 2600 (1946).

Reductions of 2-Carboxamidotetrahydroacenaphthenone Derivatives[1]

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Treatment of 2-carboxamido-2a-cyano-2a,3,4,5-tetrahydroacenaphthen-1-one (2) with sodium borohydride caused the reduction of the ketone along with a base-catalyzed cyclization between the cyano and carboxamido groups. Reaction of 2 with sodium borohydride and aluminum chloride gave the keto lactam 1-oxopyrrolido[3,4-*b*]-3a,4,5,6-tetrahydroacenaphthen-10-one (8), whereas lithium aluminum hydride gave a low yield of 2-carboxamido-2a,3,4,5-tetrahydroacenaphthen-1-one (9). Reduction of 2-carboxamide-3,4-trimethyleno-1-indenone (1) with sodium borohydride gave the unsaturated alcohol, the saturated alcohol, and 2-carboxamidoacenaphthen-1-ol. Effects of enolization and of base on the reduction of the carbonyl group are discussed. Only one isomer of the saturated alcohol was obtained from the above reduction, although two isomers were characterized from the hydrogenation of 1 over Raney nickel.

The ready availability of 2-carboxamido-3,4-trimethyleno-1-indenone (1)[3a] and its Michael adducts (*cf.* 2) led to a study of their reduction products. Compound 2 was prepared in quantitative yields by adding cyanide ion to 2-carboxamido-3,4-trimethyleno-1-indenone (1)[3] according to the procedure of Koelsch.[4] Treatment of 2 with sodium borohydride in methanol in the presence of base caused the reduction of the carbonyl group along with an intramolecular reaction between the cyano and carbamoyl groups to produce an iminopyrrolido derivative 3. This type of cycliza-

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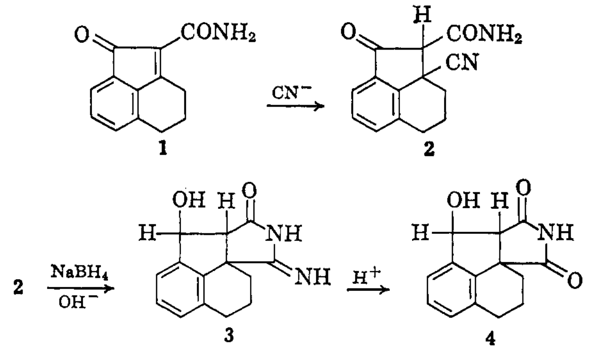
[1] Contribution No. 1290. Supported in part by a Public Health Service Fellowship No. GPM-18,661 from the Division of General Medical Sciences, in part by Public Health Service Research Grant GM-10,366-02 and in part by a grant from the Bristol Laboratories, Division of Bristol-Myers Co., Syracuse, N. Y.

[2] National Institutes of Health Predoctoral Fellow, 1962–1964.

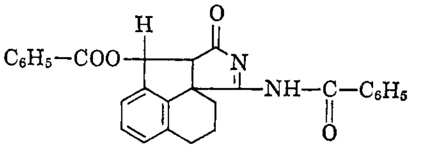
[3] (a) E. Campaigne, G. F. Bulbenko, W. E. Kreighbaum, and D. R. Maulding, *J. Org. Chem.*, **27**, 4428 (1962); (b) E. Campaigne and G. F. Bulbenko, *ibid.*, **26**, 4703 (1961).

[4] C. F. Koelsch, *ibid.*, **25**, 2088 (1960).

tion has been known for some time[5] and the mechanism has recently been discussed.[6]



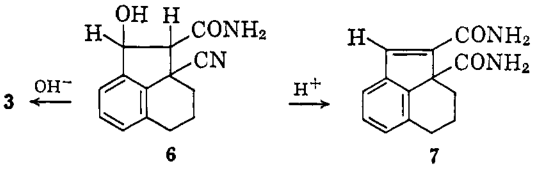
The newly formed ring could be formulated as the iminoimide 3 or as the tautomeric conjugated lactam. The difficulties in assigning structures to compounds which may be tautomers of this type have been discussed by many investigators,[7] but Johnson and Crosby[7d] favor the iminoimide structure for a derivative having an ultraviolet band at 240 $m\mu$ (ϵ 2220). Compound 3 has a shoulder at 237 $m\mu$, but the end absorption makes the estimate of the ϵ value (18,000) inaccurate. A dibenzoylated derivative of 3 prepared by a Schotten–Bauman reaction appeared to possess a fixed structure, probably 5, judging from the infrared spectrum. The infrared spectrum of 3 showed only one broad carbonyl peak at 6 μ, whereas the dibenzoylated derivative 5 produced four intense infrared absorption peaks in the carbonyl region. A peak at 5.88 μ could be assigned to the ester carbonyl, and one at 6.05 μ to the aromatic amide carbonyl absorption. A new peak at 5.65 μ was assigned to a strained γ-lactam carbonyl as seen in structure 5 and the last and most intense peak at 6.3 μ was assigned to the conjugated cyclic C=N.[8]



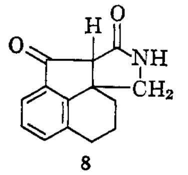
5

Attempts to acetylate 3 always resulted in the acetyl ester of 4, produced by hydrolysis of the imine to form an imide. The same ester was prepared by treatment of 3 with dilute acid followed by acetylation of the resulting imide 4.

When the reduction of the cyano adduct 2 was carried out with sodium borohydride in the absence of base, the anticipated alcohol 6 was obtained. Movement of the product as one spot on thin layer chromatography (t.l.c.) plates indicated the presence of only one isomer. Treatment of the alcohol 6 with base produced the iminopyrrolido derivative 3, whereas an attempt to form the imide directly by treatment of 6 with acid caused elimination of water from the ring, and hydration of the nitrile moiety to give the dicarboxamidoacenaphthylene derivative 7.



Reduction of the cyano adduct 2 with sodium borohydride and aluminum chloride produced the keto lactam 8. The product was characterized by a 2,4-dinitrophenylhydrazone derivative, two carbonyl absorption peaks in the infrared spectrum, an ultraviolet spectrum typical of an indanone system, and an n.m.r. spectrum which exhibited a single unsplit proton at τ 6.78 and two *gem*-protons as doublets at τ 6.07 and 6.56 in an AB pattern (J = 10 c.p.s.). The reaction may involve selective reduction of the nitrile moiety to form the corresponding amine, which then interacts with the neighboring carboxamido group, since the lactam 8 was also produced by catalytic hydrogenation of the cyano adduct 2 over Raney nickel.



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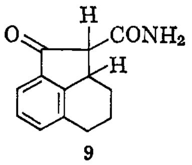

9

Attempted reduction of the cyano adduct 2 with lithium aluminum hydride produced much tar, although a small amount of the ketoamide 9 was obtained. The product could result either from replacement of cyanide ion by hydride ion, or by the Michael addition of hydride ion to 1,[9] formed by the elimination of cyanide from 1 under basic conditions.[4] Similar reductions[10] employing sodium borohydride have also been reported along with a discussion of the mechanism by Marsili.[10a] The reduction of 1 with sodium borohydride was therefore studied in order to determine whether Michael addition of hydride ion would be preferred over the reduction of the carbonyl group.

The results of the reduction of 1 with various molar ratios of sodium borohydride under several reaction conditions are summarized in Table I. The predominant product in most of the reactions was the unsaturated alcohol 10 produced by hydride attack on the carbonyl group. The second product was the saturated alcohol 11 arising from Michael addition of hydride ion to form 9, which is further reduced to 11. In the absence of base, the attack of the carbonyl group is favored, giving an increased yield of 10, whereas the presence of base must inhibit the hydride attack on carbonyl, thus increasing the Michael addition product. It is noted that an increase of base to 3% reduces the yield of 10, but does not increase the yield of 11, since less over-all reduction occurred and some starting material was recovered. This is con-

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[5] F. B. Thole and J. F. Thorpe, *J. Chem. Soc.*, **99**, 422 (1911); J. F. Thorpe and A. S. Wood, *ibid.*, 1586 (1913).

[6] J. Zabicky, *Chem. Ind.* (London), 236 (1964); A. Foucaud, *Bull. soc. chim. France*, 123 (1964).

[7] (a) H. Najer and R. Giudicelli, *ibid.*, 1231 (1961); (b) S. J. Angyal and C. L. Angyal, *J. Chem. Soc.*, 1461 (1952); (c) C. F. Howell, N. Q. Quinones, and R. A. Hardy, Jr., *J. Org. Chem.*, **27**, 1686 (1962); (d) H. E. Johnson and D. G. Crosby, *ibid.*, **27**, 1298 (1962).

[8] L. J. Bellamy "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 263.

[9] W. J. Bailey and M. E. Hermes, *J. Org. Chem.*, **29**, 1254 (1964); H. LeMoal, R. Carrie, and M. Bargain, *Compt. rend.*, **251**, 2541 (1960).

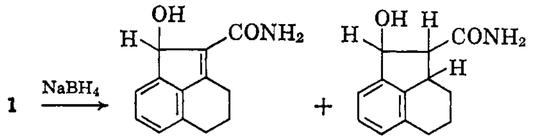
[10] (a) A. Marsili, *Ann. chim.*, **51**, 237 (1961); (b) J. A. Meschino and C. H. Bond, *J. Org. Chem.*, **28**, 3129 (1963); (c) E. Campaigne and W. L. Roelofs, *ibid.*, **30**, 396 (1965).

TABLE I
REDUCTION OF 2-CARBOXAMIDO-3,4-TRIMETHYLENO-1-INDENONE (1) WITH SODIUM BOROHYDRIDE

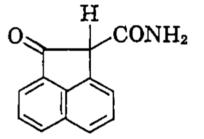
Mole ratio, **1**:NaBH$_4$	Base[a]	% yield of crude products[b] **10**	**11**	**12**
1:1	None	62 ± 2	30	...
1:1	1% NaOH	51 ± 3	43 ± 2	...
1:1	3% NaOH	37	39	*c*
1:1	7% NaOH	...	11	*d*
1:0.5	None	57 ± 1	27 ± 1	3 ± 1
1:0.5	1% NaOH	47 ± 0.5	29 ± 1	12 ± 3
1:0.25	None	43	12	*e*
1:0.25	1% NaOH	37 ± 4	15 ± 3	*e*

[a] Reactions were carried out in 50 ml. of methanol with 6 ml. of aqueous base or 6 ml. of water added. [b] Range indicates average of several trials. [c] 13% recovered starting material. [d] Mixture of **12** and **1**. [e] Mixture of **12**, **9**, and starting material as evidenced by movement on t.l.c. plates.

firmed by the low yield of only Michael adduct in the presence of 7% base.



10 **11**



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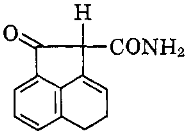
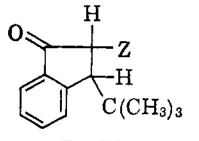
The acenaphthenone derivative **12** is most likely produced after acidification by air oxidation of species **13**, produced by isomerization of the double bond in the presence of base.[3a] This compound could also be produced in small yields by stirring **1** in dilute methanolic sodium hydroxide.

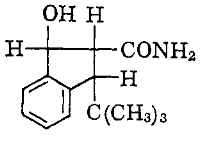


13



14a, Z = CONH$_2$
b, Z = CN

It was thought that enolization of the ketoamide **9** would prevent further reduction to the alcohol **11**, but a sample of **9** was reduced in nearly a quantitative yield to **11** in basic solution. Compounds similar to **1**, but easily enolizable,[10a,c] were reduced only to the corresponding ketones. The effect of enolization was further shown by subjecting 2-carboxamido-3-*t*-butyl-1-indanone (**14a**) and 2-cyano-3-*t*-butyl-1-indanone (**14b**)[10c] to sodium borohydride under similar conditions. The enolizable cyano ketone **14b** was not reduced by sodium borohydride in base, whereas **14a** was reduced completely to 2-carboxamido-3-*t*-butyl-1-indanol (**15**). The behavior of **9** on reduction, as well as its infrared spectrum, indicates that little enolization occurs in this molecule.



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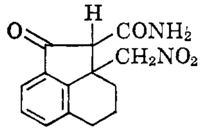

16

Only one isomer (A) of **11** was isolated from the reduction as evidenced by t.l.c. determinations of the crude product. The product would probably be the *cis* isomer in accord with the production of only the *cis* isomer from the sodium borohydride reduction of 2-methyl-1-indanone.[11] Hydrogenation of **1** over Raney nickel at 80° produced a mixture containing A and a second isomer, B. These isomers were readily separated by fractional crystallization. The slight hypsochromic shift in the infrared of the hydroxyl bands of isomer B in solution are in agreement with the nonhydrogen-bonded *trans* structure for this isomer. Hydrogenation of **1** at room temperature gave a quantitative yield of the ketoamide **9**. Isomer A was also produced when 2-carboxamido-2a-nitromethyl-2a,3,4,5-tetrahydroacenaphthen-1-one (**16**)[3a] was subjected to sodium borohydride reduction in base.

Refluxing a solution of **10** and methanol containing a small amount of base converts **10** to the ketoamide **9**. The reaction must involve abstraction of the benzylic hydrogen by base and preferred addition to the 2a-position of the resonance stabilized anion to give the enol form, which readily tautomerizes to the ketone. A comparison of the n.m.r. spectra of **10** and its acetyl derivative showed that the benzylic hydrogen was shifted downfield from τ 4.24 to 3.25 on formation of the acetate. This indicates that the hydrogen was on the same carbon as the hydroxyl group and that the structure is correct as given.

Experimental[12]

2-Carboxamido-2a-cyano-2a,3,4,5-tetrahydroacenaphthen-1-one (**2**).—According to a procedure by Koelsch,[4] 5 g. of 2-carboxamido-3,4-trimethyleno-1-indenone (**1**),[3] 20 ml. of water, 7 g. of *t*-butyl alcohol, and 2 g. of sodium cyanide were placed in a beaker and stirred for 5 min. while heating gently on the steam bath. A dark red solution resulted which was cooled to 0° after standing at room temperature for several hours. The solution was made acid to congo red with 20% sulfuric acid and diluted to 250 ml. with water. A yellow precipitate was collected by filtration, giving 5.5 g. (100%) of crude product melting at 202–205°. Several recrystallizations from 95% ethanol gave colorless crystals: m.p. 212–214°; $\lambda_{\max}^{\text{KBr}}$ 2.92 (NH$_2$), 4.5 (CN), 5.83 (CO), and 6.0 μ (CONH$_2$); $\lambda_{\max}^{95\%\ \text{EtOH}}$ 256 mμ (ϵ 10,100) and 296 mμ (ϵ 2700).

Anal. Calcd. for $C_{14}H_{12}N_2O_2$: C, 69.98; H, 5.04; N, 11.75. Found: C, 70.17; H, 5.22; N, 11.78.

The **semicarbazone** of **2** melted at 238–239°.

Anal. Calcd. for $C_{15}H_{15}N_5O_2$: C, 60.06; H, 5.08; N, 23.56. Found: C, 60.01; H, 5.65; N, 22.98.

1-Oxo-3-iminopyrrolido[3,4-*b*]-3a,4,5,6-tetrahydroacenaphthen-10-ol (**3**).—Five grams of the cyano adduct **2** was placed in 40 ml. of water and stirred during the dropwise addition of 1.5 g. of sodium borohydride in 10 ml. of 2% sodium hydroxide. The orange solution, stirred overnight, produced 4.7 g. (91%) of a fine powdery precipitate of **3**, m.p. 250–255°. It was purified by dissolving a portion in dilute phosphoric acid, treating the solution with activated carbon, filtering, and reprecipitating with dilute ammonium hydroxide. The precipitate was dissolved

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(11) T. C. Snapp, Jr., Ph.D. Dissertation, University of Mississippi, 1963.

(12) Melting points were taken on a Mel-Temp capillary melting point apparatus and are corrected. The microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Ind. Infrared spectra were determined with a Perkin-Elmer Model 137 Infracord and n.m.r. spectra were taken with a Varian A-60 instrument employing tetramethylsilane as an internal reference. The ultraviolet spectra were determined with a Cary Model 14 recording spectrgphotometer using 1-cm. sample cells with 95% ethanol as the solvent.

in a large amount of methanol and set in the refrigerator several days before collecting the fine white crystals: m.p. 274–276° dec.; $\lambda_{\max}^{\text{KBr}}$ 2.95, 3.05 (NH and OH), and 5.95–6.1 μ (amide CO); $\lambda_{\max}^{95\%\ \text{EtOH}}$ 237 mμ (ϵ 18,000) (sh).

Anal. Calcd. for $C_{14}H_{14}N_2O_2$: C, 69.40; H, 5.82; N, 11.57. Found: C, 69.62; H 6.04; N, 11.74.

The dibenzoyl derivative **5**, obtained by a standard Schotten–Bauman procedure,[13] was recrystallized from ethanol–chloroform to give white crystals: m.p. 214.5–215.5°; $\lambda_{\max}^{\text{KBr}}$ 3.0 (NH), 5.65, 5.88, 6.05 (CO–O and CO–N), and 6.3 μ (C=N).

Anal. Calcd. for $C_{28}H_{22}N_2O_4$: C, 74.67; H, 4.93; N, 6.22. Found: C, 74.75; H, 5.04; N, 6.23.

Succinimido[3,4-*b*]-3a,4,5,6-tetrahydroacenaphthen-10-ol (4).—A solution of 1 g. of **3** in 10 ml. of 20% phosphoric acid was refluxed for 2 hr. Filtration of the cooled mixture gave 0.90 (90%) of white crystals, m.p. 174–177°, soluble in 15% sodium hydroxide and reprecipitated on acidification. Recrystallization from 95% ethanol gave large colorless crystals: m.p. 183–184°; $\lambda_{\max}^{\text{KBr}}$ 2.95–3.05, 3.15 (NH and OH), 5.65 and 5.80–5.90 μ (imide carbonyl).

Anal. Calcd. for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76. Found: C, 68.82; H, 5.43; N, 5.83.

An **acetyl derivative** was formed by boiling a solution of 1 g. of **4** in 10 ml. of acetic anhydride for 5 min. followed by pouring into 50 ml. of ice water. The white solid was collected and recrystallized from water–ethanol, giving colorless crystals: m.p. 215–216°; $\lambda_{\max}^{\text{KBr}}$ 3.1 (NH), 5.65, 5.75, and 5.90 μ (CO-N-CO and CO-O).

Anal. Calcd. for $C_{16}H_{15}NO_4$: C, 67.35; H, 5.30; N, 4.91. Found: C, 67.32; H, 5.41; N, 5.02.

The same acetyl derivative was produced by heating a solution of **3** and acetic anhydride for 5 min. and recovery as above.

2-Carboxamido-2a-cyano-2a,3,4,5-tetrahydroacenaphthen-1-ol (6).—**2** (45 g.) was stirred in 150 ml. of water and 50 ml. of methanol during the dropwise addition of 5 g. of sodium borohydride in 30 ml. of water. After stirring overnight, 31 g. (69%) of a white solid, m.p. 207–210° was obtained. Recrystallization from 95% ethanol gave a pure sample: m.p. 210–211°; $\lambda_{\max}^{\text{KBr}}$ 2.9, 3.05 (NH_2), 4.5 (CN), and 6.0 μ ($CONH_2$).

Anal. Calcd. for $C_{14}H_{14}N_2O_2$: C, 69.40; H, 5.82; N, 11.57. Found: C, 69.24; H, 6.08; N, 11.36.

Acetyl Derivative.—Heating **6** in acetic anhydride followed by the addition of water yielded colorless cubic crystals: m.p. 213–215°; $\lambda_{\max}^{\text{KBr}}$ 3.0, 3.15 (NH_2), 4.5 (CN), 5.78 (CO), and 6.0 μ ($CONH_2$).

Anal. Calcd. for $C_{16}H_{15}N_2O_3$: C, 67.60; H, 5.76; N, 9.86. Found: C, 67.55; H, 5.69; N, 10.01.

Refluxing a solution of 1 g. of **6** in 10 ml. of methanol–1% sodium hydroxide (3:2) for 1 hr. yielded 0.26 g. of **3**, m.p. 273–275°, proved to be identical to the product from the reduction of **2** with sodium borohydride in base by identical infrared spectra and an undepressed mixture melting point.

2,2a-Dicarboxamido-2a,3,4,5-tetrahydroacenaphthylene (7).—A solution of 2 g. of **6** in 15 ml. of concentrated sulfuric acid was heated on the steam bath for 10 min. and then poured into 100 ml. of water and heated for 5 min. at 100° on an electric hot plate. Cooling produced 1.6 g. (80%) of the diamide **7**, m.p. 198–203°, recrystallized from 95% ethanol to white crystals: m.p. 204–205°; $\lambda_{\max}^{\text{KBr}}$ 2.9–3.2 (NH_2), 5.9, 6.05 (amide CO), 6.3 μ (conjugated phenyl); $\lambda_{\max}^{95\%\ \text{EtOH}}$ 234 mμ (ϵ 8000) and 298 mμ (ϵ 10,500).

Anal. Calcd. for $C_{14}H_{14}N_2O_2$: C, 69.42; H, 5.81; N, 11.57. Found: C, 69.18; H, 6.05; N, 11.58.

1-Oxopyrrolido[3,4-*b*]-3a,4,5,6-tetrahydroacenaphthen-10-one (8). A.—The method of Brown and Subba Rao[14] was used as follows.[15] To a mixture of 1.7 ml. of bis(2-methoxyethyl) ether (diglyme), 0.446 g. (3.33 mmoles) of aluminum chloride, and 0.80 g. (3.33 mmoles) of **2** cooled to 0° was added dropwise 10 ml. of 1 *M* sodium borohydride (10 mmoles) in diglyme over a period of 40 min. The mixture was stirred at room temperature for 18 hr., then acidified with 10 ml. of 50% aqueous acetic acid. The solvents were removed *in vacuo;* the residue was dissolved in chloroform, washed with water, dried, and evaporated to yield 460 mg. (61%) of a white powder. Recrystallization from 95% ethanol gave a pure sample with m.p. 256–257°; $\lambda_{\max}^{\text{KBr}}$ 3.1 (NH), 5.79–5.83, and 6.0 μ (ketone and lactam CO). An n.m.r. spectrum taken in deuteriochloroform showed a singlet at τ 6.78 (1 proton) and two doublets in an AB pattern at τ 6.69 and 6.40 (J = 10 c.p.s., 1 proton each) along with aromatic and aliphatic multiplets; $\lambda_{\max}^{95\%\ \text{EtOH}}$ 260 mμ (ϵ 11,300) and 304 mμ (ϵ 2500).

Anal. Calcd. for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.76; N, 6.16. Found: C, 74.12; H, 6.16; N, 6.23.

A **2,4-dinitrophenylhydrazone** derivative melted at 304–305°.

Anal. Calcd. for $C_{20}H_{17}N_5O_5$: C, 58.96; H, 4.21; N, 17.19. Found: C, 59.33; H, 4.29; N, 17.48.

B.—A mixture of 2 g. of **2** and 0.5 teaspoon of Raney nickel in 200 ml. of absolute ethanol was shaken under hydrogen at 3-atm. pressure and 80° for 15 hr. The catalyst was filtered and the solvent was evaporated *in vacuo*. The residue was washed with ether to yield 1.56 g. (76%) of the lactam **8**, which, after recrystallization from 95% ethanol, melted at 255–256°, and did not depress the melting point of the sample prepared by procedure A.

2-Carboxamido-2a,3,4,5-tetrahydroacenaphthen-1-one (9).—A mixture of 2 g. of lithium aluminum hydride and 100 ml. of tetrahydrofuran was stirred for about 10 min. followed by the dropwise addition of 4 g. (0.017 mole) of cyano adduct **2**. After stirring an additional 15 hr. a saturated aqueous solution of sodium sulfate was added dropwise to decompose excess lithium aluminum hydride. Ten milliliters of 10% sodium hydroxide was added, and the salts were filtered and washed with tetrahydrofuran. The combined tetrahydrofuran layers were evaporated, and the oily residue was extracted with hot 10% hydrochloric acid. Extraction of the aqueous acidic layer with ether and evaporation of the ether left yellow crystals. Recrystallization from ethyl acetate yielded 0.6 g. (17.6%) of colorless cubic crystals: m.p. 176–177°; $\lambda_{\max}^{\text{KBr}}$ 2.96, 3.1 (NH_2), 5.85 (CO), and 6.0 μ ($CONH_2$); $\lambda_{\max}^{\text{CHCl}_3}$ 5.91 μ (CO and amide CO); $\lambda_{\max}^{95\%\ \text{EtOH}}$ 257 mμ (ϵ 11,300) and 304 mμ (ϵ 2830). An n.m.r. spectrum taken in deuteriochloroform showed a doublet at τ 6.85 (J = 6 c.p.s., 1 proton), a quartet at τ 6.52 (J = 6 c.p.s., 1 proton), the aromatic protons in an AB_2 pattern at τ 2.5 and 2.7, and the remaining aliphatic protons in complex multiplets.

Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.53; H, 6.09; N, 6.59. Found: C, 72.50; H, 6.33; N, 6.65.

A **2,4-dinitrophenylhydrazone** derivative was readily prepared and recrystallized from 95% ethanol to give red crystals, m.p. 257–258°.

Anal. Calcd. for $C_{19}H_{17}N_5O_5$: C, 57.71; H, 4.34. Found: C, 57.75; H, 5.54.

No identifiable product was isolated on basification of the acidic mother liquors.

Reduction of 2-Carboxamido-3,4-trimethyleno-1-indenone (1) with Sodium Borohydride.—The results of the reaction of **1** with sodium borohydride in mole ratios of 1:1, 1:0.5 and 1:0.25 of **1** to sodium borohydride are summarized in Table I. The procedure used was as follows. To a mixture of 2.13 g. (0.01 mole) of **1** in 50 ml. of methanol was added a solution of 0.38 g. (0.01 mole), 0.19 g. (0.005 mole), or 0.095 g. (0.0025 mole) of sodium borohydride in either 6 ml. of aqueous sodium hydroxide or 6 ml. of water. After stirring the mixture for 2 hr., a precipitate (residue A) was collected by filtration. The methanol was evaporated with a stream of air and 20 ml. of water was added to the residue. The precipitate (residue B) was collected by filtration. The mother liquor was acidified with dilute sulfuric acid and the precipitate (residue C) was collected by filtration.

Residue A contained only 2-carboxamido-3,4-trimethyleno-2-inden-1-ol (**10**). Recrystallization from 95% ethanol gave an analytical sample of colorless crystals: m.p. 238–239°; $\lambda_{\max}^{\text{KBr}}$ 2.95, 3.05, 3.17 (OH and NH_2), 6.0 (amide CO), and 6.3 μ (conjugated phenyl); $\lambda_{\max}^{95\%\ \text{EtOH}}$ 237 mμ (ϵ 16,900), 245 (15,900), and 304 (10,500). An n.m.r. spectrum in trifluoroacetic acid showed a singlet at τ 4.24 (1 proton).

Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.55; H, 6.09; N, 6.51. Found: C, 72.26; H, 5.94; N, 6.57.

The **acetylated derivative** of **10** was prepared by heating a solution of **10**, sodium acetate, and acetic anhydride on the steam bath for 4 hr. After pouring the solution over ice–water, the precipitate was collected and recrystallized from 95% ethanol to give colorless crystals: m.p. 191–193°; $\lambda_{\max}^{\text{KBr}}$ 2.9, 3.0 (NH_2), 5.8 (CO), and 6.1 μ (amide CO); $\lambda_{\max}^{95\%\ \text{EtOH}}$ 235 mμ (ϵ 15,000), 242

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[13] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Investigation of Organic Compounds," 4th Ed., John Wiley and Sons, New York, N. Y., 1958, p. 98.

[14] H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **78**, 2582 (1956).

[15] The authors acknowledge the assistance of R. F. Weddleton in checking the yields of this reaction.

(13,200), and 300 (8100). An n.m.r. spectrum taken in trifluoroacetic acid showed the benzylic proton as a singlet at τ 3.25.

Residue B consisted of 2-carboxamido-3,4-trimethyleno-1-indanol (**11**). Movement of the crude product on t.l.c. plates eluted with chloroform–methanol (5:1) showed the presence of only one isomer. Recrystallization of **11** from 95% ethanol yielded white flakes: m.p. 190–191°; λ_{max}^{KBr} 2.95, 3.05, 3.18 μ (OH and NH_2), 5.95, and 6.08 μ (amide CO); $\lambda_{max}^{CHCl_3}$ 2.95, 3.05, 3.1 (OH and NH_2), and 5.95 μ (amide CO).

Anal. Calcd. for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.98; H, 7.09; N, 6.75.

Residue C contained 2-carboxamido-1-acenaphthenone (**12**) along with traces of the ketoamide **9** and starting material, depending on the reaction conditions. Recrystallization of **12** from 95% ethanol gave an analytical sample: m.p. 221–223°; λ_{max}^{KBr} 2.97, 3.12 (NH_2), 5.85 (CO), and 5.98 μ (amide CO); $\lambda_{max}^{95\%\ EtOH}$ 228 mμ (ϵ 12,480), 244 (7360), 252 (7360), 280–285 (2660), 303 (2880), 315 (2450), and 335 (1810). An n.m.r. spectrum taken in trifluoroacetic acid showed the single aliphatic proton at τ 5.08.

Anal. Calcd. for $C_{13}H_9NO_2$: C, 73.92; H, 4.27; N, 6.63. Found: C, 73.53; H, 4.19; N, 6.61.

A summary of the R_f values of the above products of the reduction on t.l.c. plates eluted with chloroform–methanol (5:1) is as follows: **1**, 0.69; **9**, 0.65; **10**, 0.49; **11**, 0.42; and **12**, 0.40.

Reduction of 2-Carboxamido-2a,3,4,5-tetrahydroacenaphthen-1-one (**9**).—To a solution of 2.17 g. of **9** in 50 ml. of methanol was added 0.38 g. of sodium borohydride in 6 ml. of 1% NaOH and the whole was stirred for 2 hr. The solvent was evaporated and the precipitate was collected to give 2.04 g. (94%) of **11**, m.p. 188–190°, by mixture melting point and identity of the infrared spectra. T.l.c. determinations proved the presence of only one isomer.

Reduction of 2-Carboxamido-3-*t*-butyl-1-indanone (**14a**).—To a solution of 1.43 g. (6.2 mmoles) of **14a** in 25 ml. of methanol was added 0.24 g. (6.3 mmoles) of sodium borohydride in 6 ml. of 1% sodium hydroxide. After stirring for 2 hr., the solvent was evaporated and the precipitate was collected to give 1.40 g. (97%) of the corresponding alcohol **15**, m.p. 150–160°. T.l.c. determinations showed the presence of two substances, but several recrystallizations from ethyl acetate gave one isomer with m.p. 199–200°; λ_{max}^{KBr} 2.95–3.05 (OH and NH_2) and 6.05 μ ($CONH_2$).

Anal. Calcd. for $C_{14}H_{19}NO_2$: C, 72.06; H, 8.21; N, 6.03. Found: C, 72.36; H, 8.41; N, 5.96.

Treatment of **14b** under similar conditions resulted in the recovery of 97% of starting material.

Hydrogenation of 1 over Raney Nickel. A.—A mixture of 3 g. of **1**, 0.5 teaspoon of wet Raney nickel, and 100 ml. of absolute ethanol was subjected to hydrogenation at 45 p.s.i. at 80° for 40 hr. Filtration and evaporation of the solvent yielded 2.95 g. (96%) of **11**, m.p. 153–164°. T.l.c. determinations indicated the presence of two isomers in almost equal proportions. Recrystallizations of the mixture from ethyl acetate yielded the more insoluble isomer of **11**, m.p. 190–191°. The R_f value (0.42) of this isomer proved it to be the same as that prepared from the sodium borohydride reduction of **1**. By gradually evaporating the mother liquor and periodically collecting the crystals, a crop was finally collected which consisted entirely of the second isomer, m.p. 145–149°. Recrystallization from 95% ethanol gave colorless crystals, m.p. 154–155°. This isomer had an R_f value of 0.45 on t.l.c plates eluted with chloroform–methanol (5:1): λ_{max}^{KBr} 2.98, 3.05, 3.12 (NH and OH), and 5.95 μ (amide CO); $\lambda_{max}^{CHCl_3}$ 2.84, 2.95 (OH and NH_2), and 5.98 μ (amide CO).

Anal. Calcd. for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.60; H, 6.98; N, 6.25.

A mixture melting point of the two isomers of **11** melted at 143–150°.

B.—A mixture of 3 g. of **1**, 0.5 teaspoon of wet Raney nickel, and 100 ml. of absolute ethanol was subjected to hydrogenation at 45 p.s.i. at room temperature for 16 hr. Filtration of the catalyst and evaporation of the solvent yielded 2.97 g. (98%) of **9**, m.p. 174–176°, by identical infrared spectra and R_f values.

Reduction of 2-Carboxamido-2a-nitromethyl-2a,3,4,5-tetrahydroacenaphthen-1-one (**16**).—**16**[3a] (0.5 g., 0.0017 mole) in 20 ml. of ethanol was stirred during the dropwise addition of 0.5 g. of sodium borohydride in 5 ml. of 2% sodium hydroxide. The solution was refluxed several hours and cooled overnight. The ethanol was distilled and the residue was cooled to give 0.15 g. (39%) of **11**, which, after recrystallization from ethanol, melted at 191–192°. The product was the same as that produced by the reduction of **1** with sodium borohydride as evidenced by the infrared spectrum, mixture melting point, and movement on t.l.c. plates.

Isomerization of 2-Carboxamido-3,4-trimethyleno-1-indenol (10) with Base.—A mixture of 1 g. of **10**, 500 ml. of methanol, and 6 ml. of 1% sodium hydroxide was refluxed for 4 hr. Acidification of the resulting solution and evaporation of the solvent yielded 0.8 g. of a precipitate of **9**, m.p. 155–159°, as evidenced by its infrared spectrum and movement on t.l.c. plates.

Amine-Catalyzed Isomerization of Nitrosocyclohexane to Oxime

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The subject reaction followed the kinetic expression, rate = $k[\text{amine}]^2[\text{dimer}]$, with an activation energy of 26 kcal. In nine liquid aliphatic amines the rate constant increased with increasing electron density about the amine nitrogen: $k_{max}(Et_3N)/k_{min}(n\text{-}BuNH_2) = 2$. The rate constant increased with decreasing solvent polarity: $k(\text{hydrocarbon})/k(CH_3OH\text{-}H_2O) = 3.5$. An interpretation of the observed results is offered.

In 1958 Gowenlock and Lüttke[1] called attention to the paucity of kinetic data on the dimerization and the isomerization (to oxime) of primary and secondary nitroso compounds. Knowledge of the dimerization reaction was largely limited to the qualitative observation that colorless solutions of nitroso dimers gave, on heating, blue or green solutions of the corresponding monomers which reverted to the colorless dimers on cooling. Recently, Burrell[2] determined the rate of dimerization of nitrosocyclohexane, the constant for monomer–dimer equilibrium, and, hence, the rate of dimer dissociation over a wide temperature range. It is the only work of this kind reported to date. The opinion was early expressed,[3] and then assumed to be true,[4] that primary and secondary nitroso compounds were unstable and rapidly isomerized to oximes at room temperature. Subsequent work, however, has shown that these compounds are reasonably stable[5-7]; they

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