described above, regenerated the corresponding tris(hydroquinone dimethyl ether) in good yield.

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Condensation of Aromatic Nitro Compounds with Arylacetonitriles. VII. Some Studies Concerning the Reduction of Phenylcyanomethylenequinone Oximes[1,2]

RALPH B. DAVIS, DONALD D. CARLOS, AND GEORGE S. MATTINGLY

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana

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Raney nickel catalyzed reduction of phenylcyanomethylenequinone oxime at room temperature in the presence of ammonia or aliphatic amines produces *p*-aminobenzophenone as the major product. Similar reductions in the presence of other nucleophilic reagents produce *p*-aminophenylphenylacetonitrile. A mechanism for the formation of *p*-aminobenzophenone is offered. The catalytic and chemical reductions of six arylcyanomethylenequinone oximes in the presence of diethylamine are described and compared.

It was previously reported[3] that the catalytic reduction of phenylcyanomethylenequinone oxime, or more properly 4-oxo-α-phenyl-2,5-cyclohexadien-$\Delta^{1,\alpha}$-acetonitrile oxime, using hydrogen and Raney nickel in methanol at room temperature yielded *p*-aminophenylphenylacetonitrile. We have now found that similar reductions of the same compound in the presence of ammonia or aliphatic amines followed by treatment with water produce *p*-aminobenzophenone as the major product. Reactions in like manner in the presence of aniline, pyridine, potassium hydroxide, and other nucleophilic reagents yielded *p*-aminophenylphenylacetonitrile. It should be noted that one reduction conducted in the presence of both potassium hydroxide and diethylamine gave 2,3-bis(4′-aminophenyl)-2,3-diphenylsuccinonitrile. The results of these experiments are summarized in Table I.

TABLE I

CATALYTIC REDUCTIONS OF PHENYLCYANOMETHYLENEQUINONE OXIME USING RANEY NICKEL, HYDROGEN, AND METHANOL IN THE PRESENCE OF NUCLEOPHILIC REAGENTS AT ROOM TEMPERATURE

Nucleophilic reagent	Major product
Ammonia	4-Aminobenzophenone
n-Butylamine	4-Aminobenzophenone
n-Butylamine[a]	4-Aminobenzophenone
Diethylamine	4-Aminobenzophenone
Piperidine	4-Aminobenzophenone
Triethylamine	4-Aminobenzophenone
Aniline	4-Aminophenylphenylacetonitrile
Pyridine	4-Aminophenylphenylacetonitrile
Potassium hydroxide	4-Aminophenylphenylacetonitrile
Potassium phenolate	4-Aminophenylphenylacetonitrile
Potassium acetate	4-Aminophenylphenylacetonitrile
Potassium iodide	4-Aminophenylphenylacetonitrile
Potassum hydroxide and diethylamine	2,3-Bis-(4′-aminophenyl)-2,3-diphenylsuccinonitrile
Potassium hydroxide and pyridine	4-Aminophenylphenylacetonitrile
Potassium acetate and diethylamine	4-Aminobenzophenone

[a] No methanol was used in this reduction.

It is interesting to speculate concerning the mechanism whereby *p*-aminobenzophenone is produced. Certainly the formation of this product is dependent upon the presence of an amino function of sufficient basicity such as is provided by ammonia and aliphatic amines. Basicity alone is not the determining factor, since the use of potassium hydroxide fails to produce *p*-aminobenzophenone. The relative basicity of the amino function, however, is a determining factor, since the use of aniline and pyridine likewise fails to produce the ketone in a detectable amount.

A reduction step apparently takes place prior to an attack by water or other nucleophile. We propose a reduction as the first step in the mechanism because we have found that phenylcyanomethylenequinone oxime (**1**) fails to react with ammonia alone, with ammonia in methanol, with diethylamine alone, with diethylamine in methanol, and with diethylamine in methanol in the presence of Raney nickel, followed by treatment with water. We further propose that phenylcyanomethylenequinone oxime (**1**) is first reduced to phenylcyanomethylenequinonimine (**2**), or more accurately 4-imino-α-phenyl-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetonitrile.

It seems that the second step in the mechanism is an attack by water or other nucleophile on the intermediate imine **2**, followed by the elimination of hydrogen cyanide. Eventually there must be an attack by water. However, since the reduction mixtures contain trace amounts of water at most, it is not illogical to postulate an intermediate attack by the amine compound or by methanol, with subsequent displacement by water. The over-all result may be pictured as an amino-catalyzed attack by water, followed by elimination of hydrogen cyanide.

Finally, the amino compound plays an essential role in the production of *p*-aminobenzophenone (**4**) over and above its role as catalyst in the attack by water; otherwise the reactions in the presence of other bases such as potassium hydroxide, potassium phenolate, or potassium acetate should have produced the

(1) Previous paper: *J. Chem. Eng. Data*, **8**, 580 (1963).

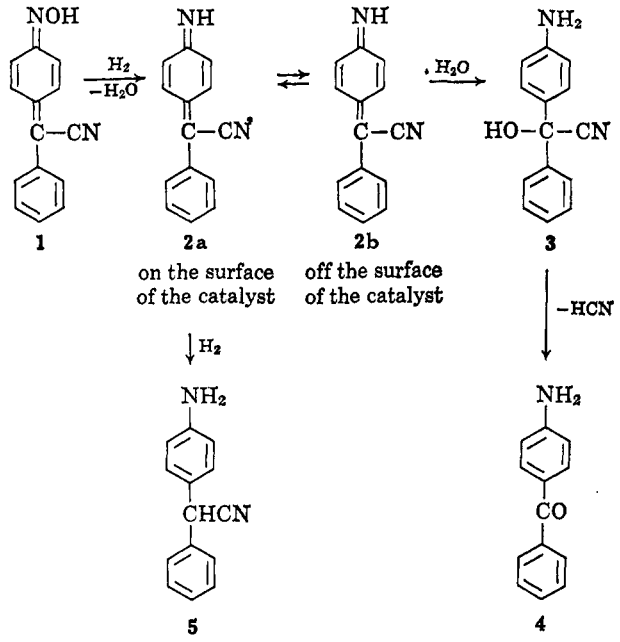
(2) This research was supported in part by National Science Foundation Grant G19165.

(3) R. B. Davis and J. D. Benigni, *J. Chem. Eng. Data*, **8**, 578 (1963).

same ketone. We postulate that the amino compound has an affinity for the surface of the Raney nickel catalyst. This affinity enables the amino compound to displace the imine intermediate **2** from the surface of the catalyst, temporarily preventing further reduction, and thus making the imine **2** vulnerable to attack by water or the other nucleophile. In the absence of an amino compound, the intermediate **2** is not desorbed from the surface of the catalyst, but is further reduced to *p*-aminophenylphenylacetonitrile (**5**).

The steps in our proposed mechanism are illustrated in Scheme I.

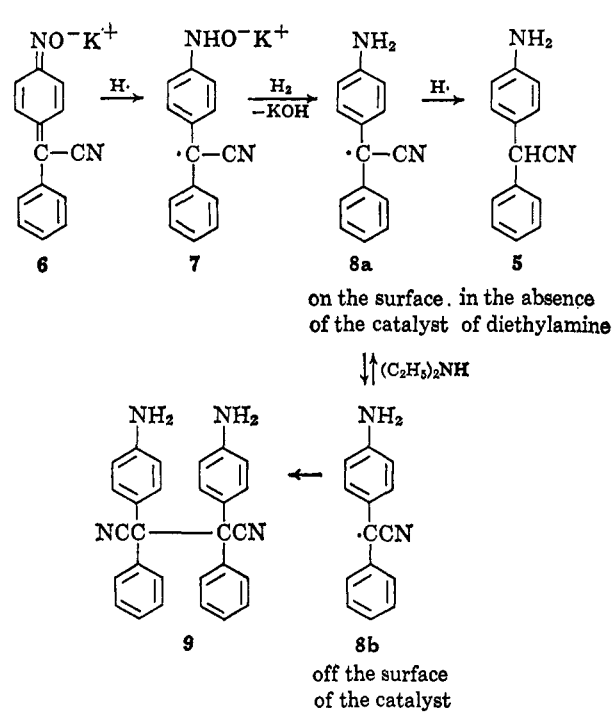
SCHEME I



Our postulate that amino compounds have an affinity for the surface of Raney nickel catalysts is not without precedent. Other investigators[4,5] have reported that ammonia is absorbed at the surface of nickel catalysts. The affinity of amino compounds for the surface of hydrogenation catalysts may play an important role in secondary amine formation[6] during the reduction of nitriles and oximes. The reaction which produced 2,3-bis(4′-aminophenyl)-2,3-diphenylsuccinonitrile (**9**) is worthy of some discussion. The species which is reduced is very likely the potassium salt of phenylcyanomethylenequinone oxime (**6**). We postulate that the anion is absorbed at the surface of the catalyst and that the diethylamine is not successful in desorbing it until it has been reduced to the *p*-aminophenylphenylacetonitrile free radical (**8**). There seems to be an addition of hydrogen atoms[7] to the quinoid system. The best evidence for the free-radical intermediate **8** is the coupling product itself (**9**) (Scheme II).

The structure of the 2,3-bis(4′-aminophenyl)-2,3-diphenylsuccinonitrile (**9**) was ascertained on the basis of elemental analysis, infrared spectrum, and its independent synthesis by the oxidative coupling of

SCHEME II



p-aminophenylphenylacetonitrile following a procedure of Kharasch,[8] who successfully coupled diphenylacetonitrile. That coupling did not take place at the amino groups was confirmed by the fact that the product failed to undergo a benzidine-type rearrangement.[9]

As was previously described, the catalytic reductions of phenylcyanomethylenequinone oxime in the presence of ammonia and aliphatic amines at room temperature produced *p*-aminobenzophenone as the major product. However, the crude material melted over a range, and infrared spectra of this material showed weak absorption peaks in the 4.47-μ region, suggesting that *p*-aminophenylphenylacetonitrile[3] might be a minor product in these reactions. We repeated a catalytic reduction of phenylcyanomethylenequinone oxime at 35° in the presence of diethylamine, and separation of the reaction mixture by means of column chromatography indicated the material recovered was approximately 84% *p*-aminobenzophenone and 16% *p*-aminophenylphenylacetonitrile. We similarly reduced five other arylcyanomethylenequinone oximes, and the results of these experiments are summarized in Table II.

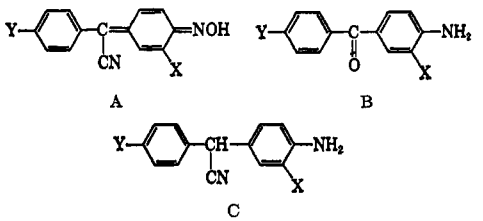
We formerly reported[3] that arylcyanomethylenequinone oximes are reduced to *p*-aminoarylarylacetonitriles using zinc and acetic acid in methanol and some water. When we repeated these experiments with the addition of diethylamine, we found that the major products were *p*-aminoaryl aryl ketones. The results of these chemical reductions in the presence of diethylamine are likewise summarized in Table II.

We postulate that there are two major factors which influence the ratio of products in the catalytic reduction of the arylcyanomethylenequinone oximes in the presence of diethylamine. The first factor is the relative affinity of the reduction intermediates for

(4) K. Azuma and A. Kobayashi, *Shokubai* (Sapporo), **10**, 1 (1954); *Chem. Abstr.*, **49**, 6707 (1955).
(5) S. Kawaguchi and H. Kihara, *J. Chem. Soc. Japan*, **75**, 15 (1954); *Chem. Abstr.*, **48**, 12341 (1954).
(6) W. H. Hartung, *J. Am. Chem. Soc.*, **50**, 3370 (1928).
(7) G. C. Bond, *Quart. Rev.* (London), **8**, 279 (1954).
(8) M. S. Kharasch and G. Sosnovsky, *Tetrahedron*, **3**, 97 (1958).
(9) C. K. Ingold and H. V. Kidd, *J. Chem. Soc.*, 984 (1933).

TABLE II

REDUCTION OF ARYLCYANOMETHYLENEQUINONE OXIMES IN THE PRESENCE OF DIETHYLAMINE



Starting material			Material isolated[a]			
	A		B		C	
No.	X	Y	M.p., °C.	Mole %	M.p., °C.	Mole %
		A. Catalytic Reductions at 35°				
1	H	H	121–123[b]	84.4	70–71[c]	15.6
2	CH_3	H	110–112[d]	63.2	107–108[e]	36.8
3	Cl	H	138–140[f]	69.0	69–70[g]	31.0
4	H	Cl	182–184[h]	82.8	70–71[i]	17.2
5	OCH_3	H	116–118[j]	27.5	46–50[k]	72.5
6[l]	H	OCH_3	120–121[m]	42.2	135[n]	57.8
		B. Chemical Reductions				
1	H	H	120–122	92.7	70–71	7.3
2	CH_3	H	110–112	67.6	107–109	32.4
3	Cl	H	137–139	68.0	69–71	32.0
4	H	Cl	183–184	89.9	71–73	10.1
5	OCH_3	H	116–118	72.7	48–50	27.3
6	H	OCH_3	134–135	74.6	134–135	25.4

[a] All melting points were determined using a copper block and are uncorrected. [b] P. J. Montagne [*Rec. trav. chim.*, **42**, 499 (1923)] reports m.p. 123°. [c] Lit.[3] m.p. 71–72°. [d] L. Chardonnens and W. Schlapback [*Helv. Chim. Acta*, **29**, 1413 (1946)] report m.p. 109–110°. [e] Lit.[3] m.p. 107–108°. [f] F. D. Chattaway [*J. Chem. Soc.*, **85**, 342 (1904)] reports m.p. 140°. [g] Lit.[3] m.p. 72–74°. [h] P. J. Montagne [*Ber.*, **49**, 2234 (1916)] reports both m.p. 104.5 and 184.5°. *Anal.* Calcd. for $C_{13}H_{10}ClNO$: C, 67.39; H, 4.35; Cl, 15.30. Found: C, 67.62; H, 4.57; Cl, 15.72. The reported melting point of 104.5° very likely involved a typographical error. [i] Lit.[3] m.p. 72–73°. [j] *Anal.* Calcd. for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.12. Found: C, 74.13; H, 5.99; N. 6.26. [k] Lit.[3] m.p. 52–54°. [l] This experiment was repeated, and there was obtained 42.0% of the ketone product and 58.0% of the nitrile product. [m] C. E. Kaslow and R. D. Stayner [*J. Am. Chem. Soc.*, **68**, 2600 (1946)] report m.p. 119–120°. [n] Lit.[3] m.p. 134–135°.

the surface of the Raney nickel catalyst. The stronger this affinity is, the greater the expected yield of *p*-aminoarylarylacetonitrile. The second factor is the relative electrophilic character of the central carbon atom of the reduction intermediates. The more electrophilic the central carbon atom is, the easier the attack by water or other nucleophile and the greater the expected yield of *p*-aminoaryl aryl ketone. In the absence of quantitative knowledge as to the strength and importance of these two effects, detailed comparisons of the relative yields of products, while interesting, are purely speculative.

For the chemical reduction of the arylcyanomethylenequinone oximes in the presence of diethylamine, it should be noted that a greater percentage of ketone was produced in all examples except one when compared to the catalytic reductions. We have offered a mechanism whereby the ketone product is obtained for the catalytic reduction. In one case at least we showed that the keto group is not introduced prior to a reduction step in the catalytic reduction. For the chemical reduction we postulate that two distinct mechanisms are responsible for the production of the ketone product in greater yield. In the chemical reduction the keto group can and very likely is introduced prior to a reduction step for at least part of the material as we have shown in a previous investigation.[10] Secondly, we postulate that part of the ketone yield is produced by the same mechanism as in the catalytic reduction.

The most striking differences between the catalytic and chemical reductions are found for the methoxy compounds, **5** and **6**. The best explanation that we can offer is that in the chemical reductions the methoxy groups associate in part at least with acetic acid molecules or with ammonium ions. The result is an increase in the electrophilic character of the central carbon atom and a decrease in affinity for the surface of the metal. Both of these effects would tend to increase the yield of ketone, as has been found.

In conclusion it should be stated that the chemical reduction of arylcyanomethylenequinone oximes using zinc and acetic acid in the presence of diethylamine is a good method for synthesizing a variety of substituted benzophenones which otherwise might be difficult to prepare.

Experimental[11,12]

Catalytic Reductions of Phenylcyanomethylenequinone Oxime at Room Temperature in the Presence of Nucleophilic Reagents. A. In the Presence of Diethylamine.—A 300-ml. hydrogenation vessel was charged with 5.0 g. (0.023 mole) of phenylcyanomethylenequinone oxime,[13] 17 g. (0.23 mole) of diethylamine, 150 ml. of absolute methanol, approximately 3 cc. of Raney nickel catalyst which had been washed three times with absolute methanol, and hydrogen at 1150 p.s.i.g. After shaking the reaction mixture for 3 hr. at room temperature, the catalyst was removed by filtration, and the filtrate was concentrated to about a quarter of its original volume under reduced pressure. About 300 ml. of water was added to the concentrated filtrate, and this mixture was allowed to stand for 6 hr. The solid which precipitated was collected by filtration, washed with water, and dried. There was obtained 4.2 g. of crude 4-aminobenzophenone, m.p. 90–115°, recrystallized from a mixture of benzene and petroleum ether (b.p. 60–71°), m.p. 121–122° (lit.[14] 123°). The infrared spectrum of the product was very similar to the infrared spectra of 4-aminobenzophenone available in the literature.[15,16] The 4-acetamidobenzophenone derivative of the product was prepared in 64% yield, m.p. 151–153° (lit.[17] 153°).

B. In the Presence of Potassium Hydroxide.—In like manner, 5.0 g. (0.023 mole) of phenylcyanomethylenoquinone oxime, 15 g. (0.23 mole) of potassium hydroxide (assay 85%) dissolved in 150 ml. of absolute methanol, approximately 3 cc. of Raney nickel catalyst, and hydrogen at 1150 p.s.i.g. gave 3.9 g. (81% yield) of 4-aminophenylphenylacetonitrile, m.p. 65–68°, recrystallized from ethanol–water, m.p. 70–72° (lit.[3] 71–72°). The infrared spectrum of this product was superimposable upon the infrared spectrum of a sample of 4-aminophenylphenylacetonitrile previously prepared.[3]

C. In the Presence of Potassium Hydroxide and Diethylamine.—In a similar manner, 10.0 g. (0.45 mole) of phenylcyanomethylenequinone oxime, 10 g. (1.15 mole) of potassium hydroxide (assay 85%) dissolved in 100 ml. of absolute methanol, 37 g. (0.49 mole) of diethylamine, about 6 cc. of Raney nickel catalyst, and hydrogen at 860 p.s.i.g. were shaken at room temperature for 3 hr. Upon opening the reaction vessel, a colorless solid was observed. The solid and catalyst were removed by

(10) R. B. Davis and J. D. Benigni, *J. Org. Chem.*, **27**, 1605 (1962).

(11) Melting points were determined using a copper block and are uncorrected.

(12) Analyses were by Midwest Microlab, Inc., Indianapolis, Ind.

(13) R. B. Davis, L. P. Pizzini, and J. D. Benizni, *J. Am. Chem. Soc.*, **82**, 2913 (1960).

(14) P. J. Montagne, *Rec. trav. chim.*, **42**, 499 (1923).

(15) D. Y. Curtin and W. R. Proops, *J. Am. Chem. Soc.*, **76**, 494 (1954).

(16) "The Sadtler Standard Spectra," Sadtler Research Laboratories, Philadelphia, Pa., Spectrum No. 18120.

(17) O. Doebner, *Ann. Chem.*, **210**, 270 (1881).

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.

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

Reductions of 2-Carboxamidotetrahydroacenaphthenone Derivatives[1]

E. CAMPAIGNE AND WENDELL L. ROELOFS[2]

The Chemistry Laboratories of Indiana University, Bloomington, Indiana 47405

Received January 12, 1965

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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(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).