mixture was stirred at 25° for 33 hr. The yellow solution was transferred to a 500-ml separatory funnel and added dropwise to 1 l. of water. The aqueous mixture was stirred rapidly for 5–10 min to ensure hydrolysis of methanesulfonic anhydride and was then extracted with chloroform (4 × 300 ml). The extract was washed once with dilute aqueous sodium bicarbonate (200 ml) and once with water, dried over magnesium sulfate, and concentrated. The fragrant oil remaining was distilled at 90–91° (2 Torr) to give 4.08 g (92%) of dihydrojasmone in 97% purity as judged by glpc (10 ft × 0.125 in., 15% OV-101 on 60/80 Chromosorb G, 200°). The semicarbazone was prepared, mp 176–177° (lit.[12] mp 175–176°).

Preparation of ε-Caprolactam.—The following is a typical preparation of amides from oximes using 1:10 phosphorus pentoxide–methanesulfonic acid. A 2.0-g portion of cyclohexanone oxime was added in small portions to 50 g of rapidly stirred 1:10 phosphorus pentoxide–methanesulfonic acid. Each batch of oxime was added only after the previous one had dissolved; the whole process required about 5 min. The colorless reaction mixture was then heated with stirring to 100°. One hour later the yellow solution was quenched in aqueous saturated sodium bicarbonate (200 ml) and extracted with chloroform (3 × 100 ml). The extract was dried with magnesium sulfate and evaporated. The crude product was crystallized from ether–hexane to give 1.92 g (96%) of ε-caprolactam as colorless crystals, mp 68–69° (lit.[8a] mp 65–68°).

Acknowledgment.—This work was supported generously by the National Science Foundation and the National Cancer Institute of the National Institutes of Health. G. R. C. is grateful to the National Institute of Allergy and Infectious Diseases of the NIH for a postdoctoral fellowship.

Registry No.—Phosphorus pentoxide–methanesulfonic acid, 39394-84-8.

(12) H. Staudinger and L. Ruzicka, *Helv. Chim. Acta*, **7**, 245 (1924).

An Improved Aromatization of α-Tetralone Oximes to *N*-(1-Naphthyl)acetamides[1]

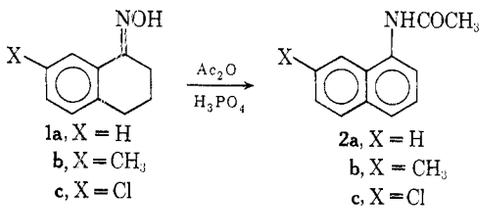
MELVIN S. NEWMAN* AND WILLIAM M. HUNG

Evans Chemistry Laboratory of The Ohio State University, Columbus, Ohio 43210

Received July 12, 1973

The conversion of oximes of substituted cyclohexenones to aromatic amines has been carried out frequently by heating in acetic acid–acetic anhydride containing dissolved hydrogen chloride or hydrogen bromide. This reaction, originally discovered by Semmler,[2] has been applied to methylated cyclohexenones,[3] tetralones,[4,5] and 1- and 4-keto-1,2,3,4-tetrahydrophenanthrenes,[5] although the yields rarely exceeded 50%. Because of the potential value of this type of intramolecular oxidation–reduction reaction for the synthesis of intermediates needed for the synthesis of polycyclic aromatic compounds, we decided to seek an improved method for carrying out such reactions.

We have found that on heating the oxime in acetic anhydride and anhydrous phosphoric acid at 80° for 30 min the yield of amine lies in the 82–93% region. By this method we have converted the oximes of α-tetralone (**1a**), 7-methyl-α-tetralone (**1b**), 7-chloro-α-tetralone (**1c**), and 4-keto-1,2,3,4-tetrahydrophenanthrene (**3**) into the corresponding acetylamino compounds (and/or amines) in 82, 91, 93, and 82% yields, respectively.



1a, X = H
b, X = CH_3
c, X = Cl

2a, X = H
b, X = CH_3
c, X = Cl

In one attempt to treat the oxime of 6-methoxy-α-tetralone under the new conditions, such a mixture of products was obtained (including nuclear acetylated material) that no further study of this compound was made.

Experimental Section

α-Tetralone (**1a**) and 6-methoxy-α-tetralone were purchased from the Aldrich Chemical Co., Milwaukee, Wis. 7-Methyl-α-tetralone (**1b**) was prepared as described.[6] 7-Chloro-α-tetralone[4a] (**1c**) was best prepared by heating a solution of 45 g of γ-(*p*-chlorophenyl)butyric acid[7] in 360 g of 115% polyphosphoric acid[8] at 90° for 30 min. The neutral fraction of the reaction products was crystallized from ether–petroleum ether (bp 35–60°) to yield 36.9 g (90%) of **1c**, mp 94.5–96.0°, pure enough for conversion to the oxime. Attempts to cyclize γ-(*p*-chlorophenyl)butyric acid with anhydrous hydrogen fluoride afforded **1c** in very low yield.

The oximes were prepared by refluxing a solution of the tetralone (0.1 mol), hydroxylamine hydrochloride (0.12 mol), pyridine (10 ml), and absolute ethanol (100 ml) for 4 hr. The oximes, after recrystallization from ether–petroleum ether, were obtained in 95–98% yield. The oxime **1c** was light sensitive.

Aromatization of Oximes.—In a typical experiment, 17.5 g (0.1 mol) of 7-methyl-α-tetralone oxime,[9] mp 100–101°, was added to a well-mixed solution of acetic anhydride (204 g, 2.0 mol) and anhydrous phosphoric acid (196 g, 2.0 mol).[10] The mixture was held at 80° for 30 min and the resulting light brown solution was poured in 1.5 l. of ice water. The solid was collected and washed with water to yield 12.8 g of *N*-(7-methyl-1-naphthyl)acetamide[6] (**2b**), mp 176–178°, after drying. The aqueous filtrate was made basic with sodium hydroxide and treated with 50 ml of acetic anhydride. The amide thus formed (5.2 g) was added to the first portion. The combined yield was 91%.

In a similar way **1a**,[11] mp 100.5–101.5°, **1c**,[4a] mp 124–125°, and **3**,[12] mp 174–175°, were converted into *N*-(1-naphthyl)acetamide (**2a**), mp 153–155°, *N*-(7-chloro-1-naphthyl)acetamide (**2c**), mp 196–197°, and *N*-(4-phenanthryl)acetamide,[12] mp 192–194°, in 82, 93, and 82% yields, respectively. In all cases, both amide and amine hydrochloride were formed. The yields reported include the amide formed from the amine as described.

Anal. Calcd for $C_{12}H_{10}ClNO$ (**2c**): C, 65.6; H, 4.6; N, 6.4; Cl, 16.2. Found: C, 65.8; H, 4.7; N, 6.4; Cl, 16.0.

In the case of **1c**, the reaction on 0.1 mol was carried out as described but with only one quarter of the amounts of acetic

(1) This research was supported by Grant No. CA-07394 from the National Institutes of Health.

(2) W. Semmler, *Ber.*, **25**, 3352 (1892). See also L. Wolff, *Justus Liebigs Ann. Chem.*, **322**, 351 (1902).

(3) F. M. Beringer and I. Ugelow, *J. Amer. Chem. Soc.*, **75**, 2635 (1953).

(4) (a) O. Schrader, *et al.*, *Ber.*, **63**, 1308 (1930); (b) A. Hardy, E. R. Ward, and L. A. Day, *J. Chem. Soc.*, 1979 (1956); (c) W. Adcock and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **89**, 386 (1967).

(5) W. Langenbeck and K. Weissenborn, *Ber.*, **72**, 724 (1939). See also F. M. Beringer, L. L. Chang, A. N. Fenster, and R. R. Rossi, *Tetrahedron*, **25**, 4339 (1969).

(6) L. Ruzicka and E. Morgeli, *Helv. Chim. Acta*, **19**, 377 (1936).

(7) S. Skraup and E. Schwamberger, *Justus Liebigs Ann. Chem.*, **462**, 135 (1928).

(8) We thank the FMC Corp., New York, N. Y., for a generous gift of 115% polyphosphoric acid.

(9) R. Huisgen and V. Vossius, *Monatsh. Chem.*, **88**, 517 (1957).

(10) Anhydrous phosphoric acid was prepared as described by R. E. Ferrel, H. S. Olcott, and H. Fraenkel-Conrat, *J. Amer. Chem. Soc.*, **70**, 2101 (1948).

(11) F. S. Kipping and A. Hill, *J. Chem. Soc.*, **75**, 150 (1899).

(12) J. W. Krueger and E. Mosettig, *J. Org. Chem.*, **3**, 340 (1938).

anhydride and phosphoric acid reagent. The same yield of **2c** was obtained.

Registry No.—1a oxime, 3349-64-2; 1b, 5462-81-7; 1c oxime, 42071-42-1; 2a, 42071-43-2; 2b, 42071-44-3; 2c, 42071-45-4; 3, 781-23-7; *N*-(4-phenanthryl)acetamide, 42071-47-6; γ-(*p*-chlorophenyl)butyric acid, 4619-18-5.

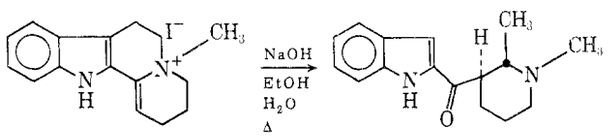
New Reactions of 3-Vinylindoles. II. Synthesis of 1,2-Dimethyl-3-(2-indolylcarbonyl)piperidine

GORDON W. GRIBBLE[1]

Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755

Received July 19, 1973

In 1968, we reported[2] that 5-methyl-2,3,4,6,7,12-hexahydroindolo[2,3-*a*]quinolizinium iodide (**1**) is converted on prolonged heating in aqueous ethanolic sodium hydroxide into 1,2-dimethyl-3-(2-indolylcarbonyl)piperidine (**2**), the product of a remarkable structural transformation.



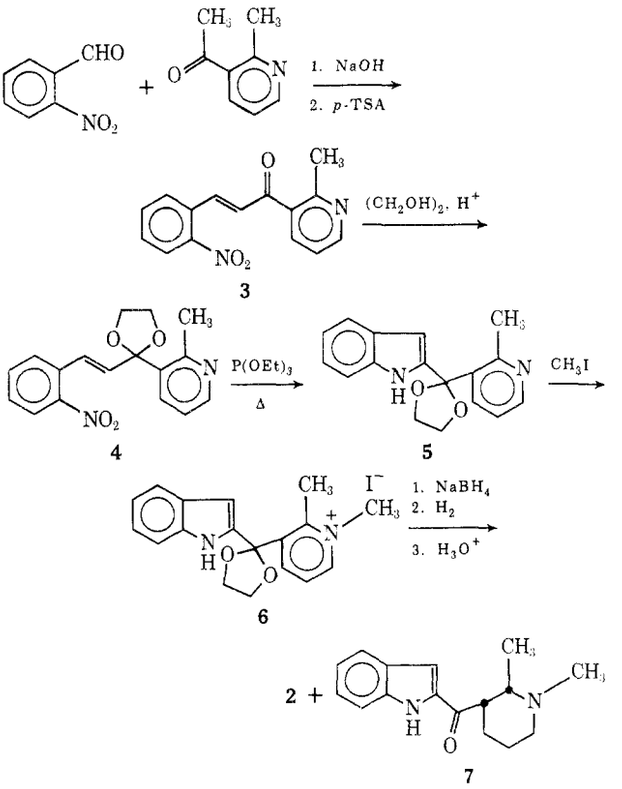
1 **2**

Our original assignment was based on degradative studies, model reactions, and mechanistic considerations.[2] The complexity of the **1** → **2** rearrangement and the potential importance of the observed nucleophilic reactions of the intermediate 3-vinylindoles demanded further investigation of this transformation.

We now wish to describe an independent synthesis of 2-acylindole **2** which confirms the originally proposed structure. Our synthesis of **2** is outlined in Scheme I. An aldol condensation[3] between 2-methyl-3-acetylpyridine[4] and 2-nitrobenzaldehyde gives the unsaturated ketone **3** (17%) after dehydration of the intermediate ketol. Ketalization with ethylene glycol affords the nitrostyrene ketal **4** (97%) which on heating with triethyl phosphite[3] gives indole ketal **5** (52%).[5] Treating **5** with methyl iodide yields pyridinium salt **6** (~100%), which on successive exposure[6] to sodium borohydride, hydrogen, and aqueous acid gives a mixture of 2-acylindoles **2** and **7** (36% from **6**).[7]

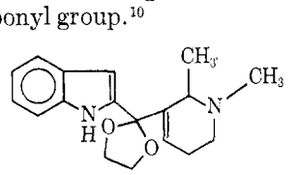
The mixture of 2-acylindoles could be separated by column chromatography into a major (92%) and a minor (8%) compound. The minor 2-acylindole is identical with the 2-acylindole obtained from **1**.

SCHEME I



3 **4** **5** **6** **7**

Furthermore, the major 2-acylindole is completely converted into the minor 2-acylindole under the basic reaction conditions. On this basis, we assign the major 2-acylindole to the presumed less stable cis configuration **7** and the minor 2-acylindole to the more stable trans configuration **2**. In our original work[2] we made no attempt to assign stereochemistry to the single 2-acylindole obtained from **1**. If the intermediate tetrahydropyridine from **6** is **8**, as seems likely,[8] then it is reasonable to suppose that catalytic hydrogenation will proceed on the side away from the allylic methyl group to give mainly the cis configuration[9] **7**, after regeneration of the carbonyl group.[10]



8

Experimental Section

Melting points were determined in open capillaries with a MelTemp Laboratory Devices apparatus and are uncorrected. Infrared spectra were measured with Perkin-Elmer 137 or 337 instruments. Nmr spectra were obtained with a Perkin-Elmer R-24 spectrometer. Woelm alumina was used for column chromatography and silica gel G (Merck) was used for thin layer chromatography (tlc). The tlc solvent system generally used was EtOAc–Et_3N (~95:5) and plates were developed with a spray of 3% $Ce(SO_4)_2$–10% H_2SO_4 followed by a brief heat treat-

(1) Recipient of a Public Health Service Research Career Development Award (1 KO4-GM 23756) from the National Institute of General Medical Sciences.

(2) L. J. Dolby and G. W. Gribble, *Tetrahedron*, **24**, 6377 (1968).

(3) R. J. Sundberg, H. F. Russell, W. V. Ligon, Jr., and L.-S. Lin, *J. Org. Chem.*, **37**, 719 (1972).

(4) A. Dornow and W. Schacht, *Chem. Ber.*, **82**, 117 (1949).

(5) Attempts to cyclize **3** with triethyl phosphite give either no reaction or, on prolonged heating, no recognizable products.

(6) Attempts to hydrogenate **6** directly to the piperidine ketal are unsatisfactory.

(7) The crude reaction product also appears to contain the alcohols[2] (14%) corresponding to **2** and **7**, probably resulting from partial deketalization during $NaBH_4$ reduction.

(8) R. E. Lyle and P. S. Anderson, *Advan. Heterocycl. Chem.*, **6**, 45 (1966).

(9) The catalytic hydrogenation of 1,2,3-trimethylpyridinium iodide gives 99% cis product: M. Tsuda and Y. Kawazoe, *Chem. Pharm. Bull.*, **18**, 2499 (1970).

(10) The small amount of **2** obtained probably does not arise by acid-catalyzed epimerization during the deketalization, because treating **7** under acidic conditions (aqueous ethanolic HCl, reflux, 2 hr) does not convert it to **2**.