EXPERIMENTAL[1]

n-Octyllithium.[2] A suspension of 13.7 g. (1.97 g.-atoms) of lithium wire, cut into 2–3 mm. lengths, in 320 ml. of ethyl ether was stirred at −15 to −30° while a solution of 155 g. (0.8 mole) of *n*-octyl bromide in 100 ml. of ethyl ether was added during 45 min. The temperature was maintained at −15 to −30° for 2 hr. and then at −5 to 0° for 1 hr. After filtration the yield was 87%, as determined by the double titration procedure.[3]

This method was also used for the preparation of 2-ethylhexyllithium and 2-cyclohexylethyllithium from 2-ethylhexylbromide and 2-cyclohexylethyl bromide, respectively.

2-Octyllithium.[4] A solution of 74.3 g. (0.5 mole) of 2-octyl chloride in 200 ml. of pure pentane was added during 3 hr. to a stirred refluxing suspension of 13.9 g. (2.0 g.-atoms) of lithium foil in 200 ml. of pentane. The refluxing was continued for a further 2 hr. After filtration the yield was 76% according to the double titration procedure.

General synthetic method. A. Preparation of triphenyl-n-octylsilane. A suspension of 56 g. (0.19 mole) of triphenylchlorosilane in 235 ml. of ethyl ether was maintained at −20 to −10° while an ether solution of 0.21 mole of *n*-octyllithium was added during 15 min. The mixture was allowed to come to room temperature and stirred for 10 hr., by which time Color Test I[5] was negative. After hydrolyzing the reaction mixture with cold dilute sulfuric acid, the ether layer was separated, dried over sodium sulfate, and distilled, giving a main fraction distilling at 182° (0.02 mm.) and melting at 72–74°. One recrystallization from absolute ethanol gave 54 g. (76%) melting at 73–75°.

Anal. Calcd. for $C_{26}H_{32}Si$: Si, 7.54. Found: Si, 7.51, 7.46.

This same procedure was used with all of the compounds, Table I, with the exception of those prepared from silicon tetrachloride.

B. Preparation of tetra-n-octylsilane. A solution of 14.1 g. (0.083 mole) of silicon tetrachloride in 170 ml. of ethyl ether was maintained at −20° while an ether solution of 0.39 mole of *n*-octyllithium was added rapidly. The mixture was kept at room temperature for 10 hr. and then was refluxed for 8 hr., by which time Color Test I was negative. Working up as in procedure A gave a main fraction of 25.3 g. (63%) distilling at 191–192° at 0.15 mm., n_D^{20} 1.4589, d_4^{20} 0.822.

Anal. Calcd. for $C_{32}H_{68}Si$: Si, 5.84. Found: Si, 5.86, 5.85.

Silicon analyses. The procedure usually used in this laboratory,[6] in which about a 0.2-g. sample is wetted with a few drops of nitric acid, digested with 1 ml. of concentrated sulfuric acid, and finally ignited gave erratically low results with some of these compounds. Successful analyses were obtained by digestion of the samples in covered Vycor crucibles with 3 ml. of a 2:1 mixture of sulfuric and nitric acids. Additional nitric acid was added as necessary to complete the oxidation.

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(1) All melting and boiling points are uncorrected. All operations involving organolithium compounds were carried out under an atmosphere of dry oxygen-free nitrogen in sodium-dried solvents.

(2) For a general reference to the preparation of aliphatic lithium compounds see, H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949).

(3) H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

(4) D. S. Tarbell and M. Weiss, *J. Am. Chem. Soc.*, **61**, 1203 (1939), obtained a 56% yield from the chloride by a similar procedure in ethyl ether solution.

(5) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

(6) H. Gilman, B. Hofferth, H. W. Melvin, and G. E. Dunn, *J. Am. Chem. Soc.*, **72**, 5767 (1950).

A Synthesis of 5-Ketolilolidine[1]

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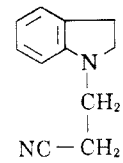
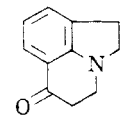
Our interest in the synthesis of 5-ketolilolidine (II) arose from the consideration that this compound would be a useful intermediate in syntheses directed toward apo-β-erythroidine and related compounds.[2] Braunholtz and Mann have reported the cyclization of aromatic cyanoethyl amines to give ketojulolidine derivatives,[3a,b] and it seemed likely that *N*-(β-cyanoethyl)indoline (I) would undergo cyclization in a similar manner to give 5-ketolilolidine (II).



I



II

Preparation of the starting material, *N*-(β-cyanoethyl)indoline, was readily accomplished by the addition of acrylonitrile to indoline. However, when *N*-(β-cyanoethyl)indoline was treated with aluminum chloride and hydrochloric acid in chlorobenzene, as described for the preparation of 1,6-diketojulolidine,[3] the only apparent reaction was one of dissociation to indoline and acylonitrile. The conditions for effecting cyclizations of this type seem to be quite critical and eventually it was found that, by the use of anhydrous aluminum chloride in *o*-dichlorobenzene, 5-ketolilolidine could be obtained consistently in yields varying from 8 to 13%. In the isolation procedure developed, 5-ketolilolidine was separated from the other reaction products by use of Girard's reagent and a product of high purity resulted. For purposes of characterization, the oxime and 2,4-dinitrophenylhydrazone derivatives were prepared. Also, to establish its identity, 5-ketolilolidine was reduced by the Wolff-Kishner procedure and the properties of the product were shown to be in agreement with those reported for lilolidine.[4]

Because of the low yields encountered in the cyclization step, alternate methods were investigated but without success. Hydrolysis of *N*-(β-cyanoethyl)indoline occurred smoothly to give the corresponding acid, *N*-(β-carboxyethyl)indoline. But,

(1) Aided by a grant from the United Cerebral Palsy Association, Inc.

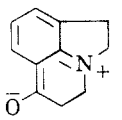
(2) M. F. Grundon, G. L. Sauvage, and V. Boekelheide, *J. Am. Chem. Soc.*, **75**, 2550 (1953).

(3) (a) J. T. Braunholtz and F. G. Mann, *J. Chem. Soc.*, 1817 (1953); (b) J. A. C. Allison, J. T. Braunholtz, and F. G. Mann, *J. Chem. Soc.*, 403 (1954).

(4) G. Barger and E. Dyer, *J. Am. Chem. Soc.*, **60**, 2414 (1938).

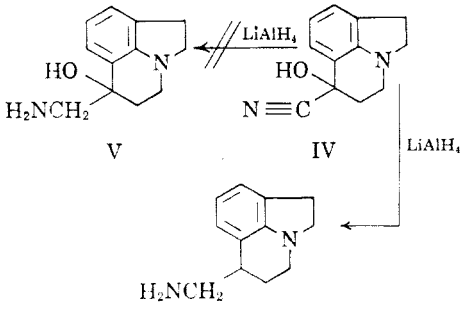
again, attempted cyclization with the usual Friedel-Crafts reagents was unsuccessful.

The infrared spectrum of 5-ketolilolidine shows strong absorption at 6.04 μ. Since the usual region for absorption by aromatic ketones is about 5.95–5.98 μ,[5] it would appear that there is appreciable interaction between the amine and carbonyl functions, probably due to contributions of the type shown by III. Support for this hypothesis comes from the fact that the molecule is only feebly basic and is readily extracted from aqueous acid. Under the usual conditions, 5-ketolilolidine did not form either a picrate or hydrochloride.



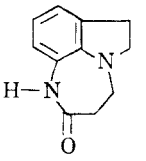
III

Attempts to effect a ring expansion of 5-ketolilolidine by reaction with diazomethane led to recovery of the unchanged ketone. Similarly, 5- ketolilolidine was unaffected by treatment with nitromethane under the usual conditions for condensation. Again, the lack of reactivity may be a reflection of the interaction of the carbonyl and amine functions. By the use of forcing conditions it was possible to obtain the corresponding cyanohydrin (IV). However, reduction of the cyanohydrin with lithium aluminum hydride did not lead to the expected amino carbinol (V) but, instead, gave an oxygen-free product for which we tentatively assign structure VI.

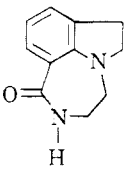


V IV VI

In view of our lack of success with the conventional methods for ring expansion of ketones, we tried ring expansion procedures involving introduction of nitrogen for purposes of comparison. Although various attempts to effect a Beckmann rearrangement of the oxime of 5-ketolilolidine were unsuccessful, the direct reaction of hydrazoic acid with the ketone by the Schmidt procedure did give a product having the composition expected of the desired amide. By analogy, it would be expected that this product should be VII. However, the spectra and properties of the product could be accommodated equally well by structure VIII; conclusive evidence is not available to decide between the two possibilities.



VII



VIII

EXPERIMENTAL[6]

N-(β-Cyanoethyl)indole, I. A mixture of 25.0 g. of indoline and 23.0 g. of freshly distilled acrylonitrile in 25 ml. of acetic acid was heated in a sealed tube at 145° for 12 hr. At the end of this time, the contents of the tube were removed and fractionally distilled. The portion boiling at 150–160° at 2 mm. was collected and then redistilled to give 31.5 g. (87%) of a pale yellow, viscous oil; b.p. 129–133° at 1 mm., n_D^{25} 1.5748. On standing, the oil crystallized and could be obtained from a hexane-benzene mixture as transparent plates, m.p. 104–105°.

Anal. Calcd. for $C_{11}H_{12}N_2$: C, 76.71; H, 7.02; N, 16.27. Found: C, 76.60; H, 7.16; N, 15.82.

The corresponding *methiodide* was prepared for characterization and was obtained after crystallization from a hexane-ethanol mixture as hexagonal plates, m.p. 142–144°.

Anal. Calcd. for $C_{12}H_{15}N_2I$: C, 45.91; H, 4.82. Found: C, 45.78; H, 4.92.

N-(β-Carboxyethyl)indoline. A mixture of 1.5 g. of *N*-(β-cyanoethyl)indoline and 15 ml. of a 10% aqueous sodium hydroxide solution was boiled under reflux until a clear solution resulted (2.5 hr.). When the cold solution was brought to *p*H 5.0 by addition of acid, an oil separated which slowly solidified. Crystallization of the resulting solid from ethanol gave 900 mg. (54%) of white crystals, m.p. 77–78.5°.

Anal. Calcd. for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85. Found: C, 69.37; H, 6.94.

Attempts to convert this acid to 5-ketolilolidine under the usual conditions for Friedel-Crafts type cyclizations were unsuccessful.

5-Ketolilolidine, II. To a mixture of 50 g. of anhydrous aluminum chloride in 30 ml. of *o*-dichlorobenzene there was added 10.0 g. of freshly distilled *N*-(β-cyanoethyl) indoline. The mixture became warm and turned a deep red; it was then heated at 185° for 8 hr. with rapid stirring. At the end of this time the warm mixture was poured onto crushed ice and the *o*-dichlorobenzene was removed by steam distillation. The aqueous solution was then exhaustively extracted with chloroform (700 ml.). In this way the cyclization product was separated from indoline and other basic substances which remained in the aqueous layer. The combined, fluorescent, chloroform extracts were dried, concentrated, and the residual oil was distilled. From spectral analysis and from tests with 2,4-dinitrophenylhydrazine reagent, the main ketone-containing fraction was determined to be that boiling in the range of 120–140° at 0.7 mm. and this amounted to 4.1 g. To obtain the 5-ketolilolidine in a pure state it was dissolved in a solution containing 50 ml. of ethanol, 5 ml. of glacial acetic acid and 5 g. of Girard's P Reagent. After the solution had been boiled under reflux for 2 hr., it was poured into a solution of 4.0 g. of potassium hydroxide in 250 ml. of water. Unreacted mate-

(5) V. Boekelheide and J. Godfrey, *J. Am. Chem. Soc.*, **75**, 3679 (1953).

(6) All melting points are corrected. Analyses by Miss A. Smith.

rial was removed by extraction with ether, and the solution was made acidic by addition of 25 ml. of concentrated hydrochloric acid. After the solution had stood for 2 hr., it was again extracted with ether. Concentration of the ether solution gave 1.3 g. (13%) of a yellow solid which, after sublimation at 70–80° at 0.5 mm., melted at 54–57°. Recrystallization from hexane gave 1.13 g. of yellow needles, m.p. 58–59°, which showed a greenish fluorescence. The infrared spectrum of this ketone had a single strong band at 6.04 μ in the carbonyl region.

Anal. Calcd. for $C_{11}H_{11}NO$: C, 76.27; H, 6.40; N, 8.09. Found: C, 76.05, 76.25; H, 6.81, 6.65; N, 8.00.

The *2,4-dinitrophenylhydrazone* of 5-ketolilolidine was obtained after crystallization from a hexane-dioxane mixture as scarlet-black crystals, m.p. above 270° w. decomp.

Anal. Calcd. for $C_{17}H_{15}N_5O_4$: C, 57.78; H, 4.28. Found: C, 57.76; H, 4.39.

The *oxime* of 5-ketolilolidine was obtained after crystallization from hexane as yellow needles, m.p. 152–154°.

Anal. Calcd. for $C_{11}H_{12}N_2O$: C, 70.18; H, 6.43. Found: C, 69.79; H, 6.37.

Reduction of 5-ketolilolidine to lilolidine. To a solution of 510 mg. of 5-ketolilolidine in 20 ml. of trimethylene glycol there was added 4 ml. of hydrazine hydrate and 1.0 g. of potassium hydroxide, and the mixture was heated at 180° for 1.5 hr. The temperature was then raised to 215° and heating was continued for an additional 2 hr. After the solution had cooled, it was poured into water and extracted with chloroform. The chloroform extracts were dried, concentrated, and the residue was dissolved in ether. The ether solution was extracted with 6*N* hydrochloric acid. The aqueous layer was made basic and again extracted with ether. Concentration of the ether extract followed by distillation gave 90 mg. of a yellow oil, b.p. 90–100° at 0.5 mm. The *picrate* of this oil formed readily and was obtained, after crystallization from ethanol, as yellow plates, m.p. 167.5–168.5° (Barger and Dyer[4] report the m.p. of lilolidine picrate as 168–170°).

Anal. Calcd. for $C_{17}H_{16}N_4O_7$: C, 52.58; H, 4.15. Found: C, 52.75; H, 4.36.

5-Ketolilolidine cyanohydrin, IV. A solution of 600 mg. of 5-ketolilolidine and 10 mg. of potassium cyanide in 5 ml. of anhydrous hydrogen cyanide was allowed to stand at 5° for 3 hr. At the end of this time, the excess hydrogen cyanide was allowed to evaporate and the residue was extracted with boiling hexane. Concentration of the hexane solution followed by cooling gave 200 mg. (28%) of yellow needles, m.p. 110–112°. From the hexane-insoluble residue 360 mg. of 5-ketolilolidine was recovered.

Anal. Calcd. for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04. Found: C, 72.26; H, 6.30.

Lithium aluminum hydride reduction of the cyanohydrin of 5-ketolilolidine. A solution of 170 mg. of 5-ketolilolidine cyanohydrin in ether was added to a solution 1.0 g. of lithium aluminum hydride in ether. The mixture was boiled under reflux for 24 hr. and then decomposed by addition of 20 ml. of 10% aqueous sodium hydroxide solution. The ether layer was separated, dried, and concentrated. Distillation of the residue gave 50 mg. of a yellow oil, b.p. 130° at 0.005 mm., to which structure VI is assigned.

Anal. Calcd. for $C_{12}H_{16}N_2$: C, 76.56; H, 8.57. Found: C, 76.98; H, 8.73.

Schmidt Reaction with 5-ketolilolidine. To a solution of 1.0 g. of 5-ketolilolidine in 20 ml. of chloroform, there was added a prepared solution obtained by treating 2.0 g. of sodium azide in 70 ml. of chloroform with 1.2 g. of concentrated sulfuric acid. The rapidly stirred mixture maintained at 30° was then treated dropwise with an additional 2.0 g. of sulfuric acid. After stirring an additional hour, the mixture was poured into 30 ml. of water. Separation of the chloroform layer followed by concentration gave 420 mg. of an amorphous powder. Repeated crystallization of this from hexane gave 195 mg. (18%) of yellow plates, m.p. 140–141°, softening at 138°. The infrared spectrum of the crystals (VII or VIII) showed NH absorption at 2.52 μ and carbonyl absorption at 6.11 μ. The ultraviolet absorption spectrum of the crystals showed maxima at 227 mμ (log ϵ, 4.19), 263 (3.71), 310 (3.49) and 353 (3.40).

Anal. Calcd. for $C_{11}H_{12}N_2O$: C, 70.19; H, 6.43; N, 14.9. Found: C, 69.7; H, 6.7; N, 14.8.

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Preparation of 7-Nitro-1-naphthylamine and 7,7′-Dinitro-1,1′-azonaphthalene

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Recent publications[1,2] on the chemistry of 7-nitro-1-naphthylamine prompt us to report some observations on the preparation of this amine, which was needed for diazo-coupling to 7,7′-dinitro-1,1′-azonaphthalene.

We have followed the method of Schroeter[3] in preparing the amine by a Semmler aromatization.[1] However, the directions given in the literature are rather scant,[1,3] and it was because of this that, in improvising on the directions, the following observations were made. These observations may be of interest and of help to others.

The oxime of 7-nitro-α-tetralone is best prepared by heating an aqueous ethanol solution of the ketone, hydroxylamine hydrochloride, and sodium acetate. Several attempts with the use of sodium hydroxide to neutralize hydroxylamine hydrochloride in preparing the oxime gave only starting material. The oxime acetate may be conveniently prepared by acetylating the oxime in pyridine with acetic anhydride.

The oxime acetate is very sensitive to light. Sunlight, both direct and indirect, and even electric light, cause the solid oxime acetate to turn pink. The discoloration occurs on the surface exposed to the light; under-surfaces remain white. The solid turns pink even when in suspension in the aqueous pyridine–acetic acid solution from which it is first precipitated. After observing this we carried out all subsequent preparations in subdued light and stored the oxime acetate in protected bottles. We do not know whether the use of pink material will affect subsequent reactions in which the oxime acetate is used. The color change is reversible if, after a few minutes of exposure, the solid is placed in the dark. However, exposures of longer than five minutes appear to be irreversible, and exposures of an hour or more turn the solid a tan color. From the directions

(1) A. Hardy, E. R. Ward, and L. A. Day, *J. Chem. Soc.*, 1979 (1956).

(2) A. Hardy and E. R. Ward, *J. Chem. Soc.*, 2634 (1957).

(3) G. Schroeter, *Ber.*, **63**, 1308 (1930).