TABLE III

NEAR ULTRAVIOLET ABSORPTION SPECTRA OF TRICYCLIC BASES IN 0.1 *N* HYDROCHLORIC ACID

Compound	Absorption maxima (mμ) and intensity (ε)[a]				Basicity,[b] pK_a
trans-Tetrahydro-2,3-trimethylenequinoline	324 (57)	267 (268)	260 (572)	244 (269)	4.47
cis-Tetrahydro-2,3-trimethylenequinoline	324 (266)	266 (267)	259 (310)	243 (850)	4.45
trans-Octahydroacridine	324 (1760)		261 (536)	242 (3000)	4.39
cis-Octahydroacridine	324 (176)		261 (360)	242 (650)	4.08
trans-Tetrahydro-2,3-pentamethylenequinoline	321 (920)		260 (380)	241 (2690)	4.63
cis-Tetrahydro-2,3-pentamethylenequinoline	321 (260)		261 (355)	242 (1080)	4.51
trans-Hexahydrocarbazole		268 (276)	261 (310)	256 (265)	4.66
cis-Hexahydrocarbazole		268 (522)	261 (576)	256 (419)	4.92

[a] The figures in parentheses refer to molecular extinction coefficient. [b] The basicity was measured at 15° in 50% aqueous alcohol.

absorption spectra with basicity. In each of four pairs cited in Table III, absorption maxima agree within the limit of 1 mμ, but those intensities were different among stereoisomers. Each of the bases possessing absorption bands of higher intensities was found to be a stronger base than the corresponding isomer. This correlation might be assumed because the strength of basicity of aromatic amines is closely associated with the resonance state of benzene, but no generalization would be safe from the few examples treated in this study. The problem will be kept under further investigation.

Acknowledgments.—The present research was conducted under the supervision of Professor Harusada Suginome, President of Hokkaido University. The author is also indebted to Professor Ken-iti Higasi for his help in revising the manuscript. Thanks are due to Mr. Seiya Suzuki for help with some of the measurements.

SAPPORO, JAPAN

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, IOWA STATE COLLEGE]

The Preparation and Dichromate Oxidation of Certain 6-Substituted Phenanthridines

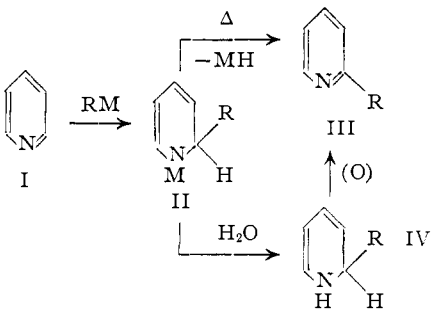
BY HENRY GILMAN AND JOHN EISCH

RECEIVED MARCH 7, 1957

The preparation of 6-substituted phenanthridines and their 5,6-dihydro derivatives by the organometallic alkylation of phenanthridine has been examined. It was found that not only do organolithium compounds (*n*-butyl- and *o*-tolyllithium) attack phenanthridine readily, but active Grignard reagents such as benzylmagnesium chloride can also add to the azomethine linkage. Finally, even ordinary Grignard reagents such as *n*-propylmagnesium bromide alkylate this heterocycle if the reaction time is protracted.

The dichromate oxidation of 6-*n*-propyl- and 6-*n*-butylphenanthridines gave, in addition to phenanthridinone, the corresponding 6-acylphenanthridines. This reaction is suggested not only to be diagnostic for 6-alkylphenanthridines but also to be a preparative method for 6-acylphenanthridines.

Although the aza-aromatic heterocycles previously studied, pyridine, quinoline and isoquinoline, are readily alkylated by organolithium compounds,[1] they react with organomagnesium compounds only with difficulty.[2] To obtain even mediocre yields, workers have resorted to such stringent reaction conditions as autoclave technique, higher-boiling solvents or dioxane media. The course of the reaction, however, seems quite analogous for organolithium and organomagnesium compounds, *i.e.*, addition of RM (M = Li, MgX) to the nitrogen heterocycle in a 1,2- or 1,4-manner. The interaction of pyridine (I) and an organometallic compound (RM) may be viewed as typical[3]



The resulting adduct II may either split out MH to give III thermally, or the dihydro compound IV obtained upon hydrolysis may be dehydrogenated.

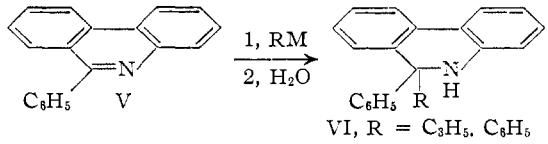
Recent investigations have demonstrated that dibenzopyridines such as phenanthridine exhibit a high order of reactivity toward allylmagnesium

(1) K. Ziegler and H. Zeiser, *Ann.*, **485**, 174 (1931).

(2) For a general review of the interaction of Grignard reagents with aza-aromatic heterocycles, see M. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice–Hall, Inc., New York, N. Y., 1954, p. 1257 *et seq.*

(3) The predominating isomer from the reaction between pyridine and organolithium compounds is the 2-isomer, whereas the action of benzylmagnesium chloride leads in small yield to a 4:1 mixture of 4-benzyl- and 2-benzylpyridines (R. A. Benkeser and D. Holton, THIS JOURNAL, **73**, 5861 (1951)). With allylmagnesium bromide the main product has been shown to be 4-allylpyridine; smaller amounts of 2-allypyridine which may have been formed could not be isolated (ref. 4).

bromide in ether, in comparison to that of benzopyridines or pyridine itself.[4] Moreover, phenanthridine gives high yields of 6-arylphenanthridines with organolithium compounds,[5] and even 6-phenylphenanthridine (V) can add phenyllithium[5] or allylmagnesium bromide to give VI.[6]



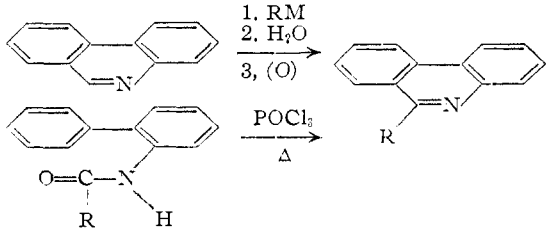
VI, R = C_3H_5, C_6H_5

In the present study it was of interest to learn whether this enhanced reactivity of phenanthridine would be reflected in its behavior toward ordinary Grignard reagents and whether organometallic alkylation was feasible for the synthesis of 6-substituted phenanthridines of various types.

Although Ziegler and Zeiser[1] have reported that *n*-butyllithium adds readily to various nitrogen bases, this reaction has not been reported for phenanthridine. Indeed, it was found that phenanthridine was immediately alkylated at −50° to give 6-*n*-butylphenanthridine in essentially quantitative yield. It may be noted that 6-*n*-butylphenanthridine could not be freed entirely of its dihydro form, as is indicated by the NH band in its infrared spectrum and the orange-yellow cast of its picrate.

A second illustration of phenanthridine's superior reactivity is its behavior with *n*-propylmagnesium bromide in ether. By prolonging the reaction time, but without use of customary "forcing" conditions, an 84% yield of 6-*n*-propylphenanthridine was secured. The excellent yield with this ordinary Grignard reagent suggests that in certain cases the organomagnesium compound may replace the organolithium compound when the latter is difficultly accessible.

In order to verify the position of the alkyl groups in 6-*n*-propyl- and 6-*n*-butylphenanthridines obtained in the foregoing experiments, the same compounds (IX and X) were synthesized unambiguously by the Morgan–Walls cyclization[7] of the suitable 2-acylaminobiphenyls (VII and VIII).



VII, R = *n*-propyl
VIII, R = *n*-butyl

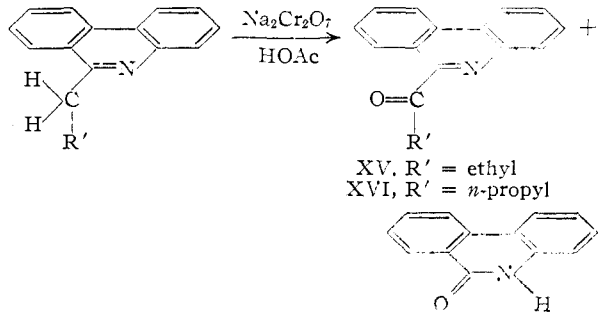
IX, R = *n*-propyl
X, R = *n*-butyl

Third, a more reactive, allylic Grignard reagent such as benzylmagnesium chloride, analogous to allylmagnesium bromide,[4] attacked phenanthridine readily to give the 6-benzyl-5,6-dihydro derivative XI in 78% yield. Since the product was not amenable to purification by crystallization, it was identified by dichromate oxidation to the known 6-benzoylphenanthridine (XII) in high yield.

Finally, a somewhat hindered aryllithium system, such as *o*-tolyllithium, added readily to the azomethine linkage in phenanthridine. Also quite significant is the fact that here the dihydro derivative XIII could be isolated as a moderately stable solid. It could be dehydrogenated smoothly by palladium in boiling mesitylene to the 6-*o*-tolyl derivative XIV which was isolated as a low melting picrate.

The above illustrated Morgan–Walls cyclization[7] of 2-acylaminobiphenyls has represented, since its introduction in 1931, the most general method for preparing 6-substituted phenanthridines. However, the use of organolithium compounds or organomagnesium reagents (when the latter are more accessible) on phenanthridine offers an attractive alternative, especially since newer methods have made phenanthridine more available in organic synthesis.[8] In addition, organometallic alkylation may be the preferred method when 6-substituted-5,6-dihydrophenanthridines themselves are desired. The latter are of interest for their potential physiological activity.[9]

The dichromate oxidation of 6-methylphenanthridines first carried out by Walls[10] led to excellent yields of phenanthridinones. The present authors examined the behavior of 6-*n*-propyl- and 6-*n*-butylphenanthridines toward sodium dichromate in glacial acetic acid to learn if the formation of phenanthridinones was general for 6-alkylphenanthridines. As phenanthridine itself was essentially unaffected by the dichromate oxidation procedure, it could then be concluded that the isolation of phenanthridinone is a diagnostic test for a 6-alkylphenanthridine. Indeed, it was found that 6-*n*-propyl- and 6-*n*-butylphenanthridines did give fair yields of phenanthridinone, but as by-products the corresponding 6-acylphenanthridines (XV and XVI) were also found.



XV, R′ = ethyl
XVI, R′ = *n*-propyl

As these ketones probably represent intermediates in oxidizing 6-alkylphenanthridines to phenanthridinones, it is feasible to prepare 6-acylphenanthridines in this way by employing milder conditions. As has been mentioned previously, the impure 6-benzyl-5,6-dihydrophenanthridine was

(4) H. Gilman, J. Eisch and T. Soddy, THIS JOURNAL, **79**, 1245 (1957).
(5) H. Gilman and R. D. Nelson, *ibid.*, **70**, 3316 (1948).
(6) H. Gilman and J. Eisch, *ibid.*, **79**, 2150 (1957).
(7) G. T. Morgan and L. P. Walls, *J. Chem. Soc.*, 2447 (1931).
(8) (a) D. W. Ockenden and K. Schofield, *J. Chem. Soc.*, 717 (1953); (b) E. C. Taylor, Jr., and N. W. Kalenda, THIS JOURNAL, **76**, 1699 (1954); (c) E. C. Taylor, Jr., and A. E. Martin, *ibid.*, **74**, 6295 (1952).
(9) (a) A. G. Caldwell, F. C. Copp and L. P. Walls, *J. Chem. Soc.*, 2698 (1950); (b) J. Finkelstein and S. Linder, THIS JOURNAL, **72**, 3282 (1950); (c) C. P. Huttrer, *ibid.*, **71**, 4147 (1949).
(10) L. P. Walls, *J. Chem. Soc.*, 1405 (1935).

transformed by this method to 6-benzoylphenanthridine in 72% yield.

Experimental

The melting points were determined on an electrically heated copper block and are corrected. All operations involved in the preparation and reaction of organometallic compounds were conducted under an atmosphere of dry, oxygen-free nitrogen.

6-*n*-Butylphenanthridine (X). Method A. From 2-Valeraminobiphenyl (VIII) and Phosphorus Oxychloride.[7]—A 500-ml., round-bottomed flask was equipped with an air condenser bearing a calcium chloride tube and the latter tube connected to a hydrogen chloride gas trap. The reaction flask was charged with 25.5 g. (0.10 mole) of 2-valeraminobiphenyl and 42 g. (0.27 mole) of phosphorus oxychloride, and this solution was heated cautiously until coloration appeared and gas evolution began. The heating was then discontinued and the reaction allowed to proceed spontaneously. When the vigorous reaction subsided, the solution was heated at the reflux temperature for 2 hr. The excess phosphorus oxychloride was removed at reduced pressure, and the residue extracted portionwise with 200 ml. of hot 6 *N* hydrochloric acid. After filtration through glass wool, the extracts were treated with excess sodium hydroxide. The liberated base was taken up in an ether–benzene mixture and dried with anhydrous sodium sulfate. After removal of the solvent the 6-*n*-butylphenanthridine distilled at 182–184° (4.0 mm.), 14.0 g. (60%). It was a pale yellow, viscous liquid, $n^{20}D$ 1.6369.

Anal. Calcd. for $C_{17}H_{17}N$: N, 5.96. Found: N, 6.06.

The picrate recrystallized from a dioxane–ethanol pair as fine, yellow needles, m.p. 195.5–197°.

Anal. Calcd. for $C_{23}H_{20}N_4O_7$: N, 12.06. Found: N, 12.11.

Method B. From Phenanthridine and *n*-Butyllithium.—In a 500-ml., three-necked flask fitted with a sealed stirrer, addition funnel and low-temperature thermometer and flushed with nitrogen, 20.0 g. (0.112 mole) of phenanthridine was suspended in 200 ml. of dry ether. After the contents of the flask were cooled to −45° by means of an acetone–Dry Ice-bath, 0.11 mole of freshly prepared *n*-butyllithium[11] in 120 ml. of ether was added to the stirred suspension during 20 minutes. The temperature was then lowered to −50° and held there for 15 minutes, during which time the reaction mixture formed a fluorescent green solution. Thereupon the solution was poured rapidly onto a slurry of Dry Ice in dry ether. After the mixture had warmed up to room temperature, it was extracted with 200 ml. of 5% potassium hydroxide solution. Separation and careful acidification of the aqueous layer gave no precipitated acid.

The ethereal layer of the carbonated mixture was dried over anhydrous sodium sulfate, filtered and the solvent removed. The residual orange liquid was heated with 30 ml. of nitrobenzene for 20 minutes to oxidize the dihydro derivative. After the nitrobenzene was distilled under water-pump vacuum, the residue was distilled at the oil-pump. The main fraction of pale orange liquid (23.7 g., 90%) boiled at 177–178° (3.4 mm.). That some dihydro form was still present was indicated by an N–H band at 3.0 μ in the infrared spectra and by the formation of an orange picrate. The product was redistilled through a short column, and a pale yellow liquid was obtained at 184° (4.0 mm.). The melting point of the picrate prepared from this fraction agreed well with that of the picrate prepared in method A, but still had an orange-yellow cast. A mixture melting point of the picrates was not depressed. The infrared spectra of the two preparations also were almost superimposable, except for the presence of an N–H band in the preparation from method B.

6-*n*-Propylphenanthridine (IX). Method A. From 2-Butyraminobiphenyl (VII) and Phosphorus Oxychloride.[7]—Analogous to the procedure detailed in method A above for the preparation of 6-*n*-butylphenanthridine, 23.9 g. (0.10 mole) of 2-butyraminobiphenyl and 38 g. (0.25 mole) of phosphorus oxychloride reacted to give, upon work-up, 16.0 g. (73%) of pale yellow 6-*n*-propylphenanthridine, b.p. 164–166° (2.0 mm.), $n^{20}D$ 1.6552.

Anal. Calcd. for $C_{16}H_{15}N$: N, 6.33. Found: N, 6.69.

The picrate formed fine, bright yellow needles from a dioxane–ethanol pair, m.p. 196–197.5°.

Anal. Calcd. for $C_{22}H_{18}N_4O_7$: N, 12.44. Found: N, 12.23.

Method B. From Phenanthridine and *n*-Propylmagnesium Bromide.—In a 500-ml., three-necked flask equipped with a sealed stirrer, addition funnel and reflux condenser were placed 21.1 g. (0.117 mole) of phenanthridine and 150 ml. of dry ether. Then 0.247 mole of *n*-propylmagnesium bromide in 120 ml. of ether was introduced, and the resulting yellow suspension stirred at the reflux temperature for 100 hr., during which time most of the solid dissolved to form a dark solution. The reaction mixture was hydrolyzed with ammonium chloride solution and the separated organic layer dried with anhydrous sodium sulfate. After filtration and distillation of the ether, the residual oil was heated with 30 ml. of nitrobenzene for 0.5 hr. The nitrobenzene was distilled at the water-pump and the remaining orange oil fractionated under reduced pressure. The main fraction consisted of 18.4 g. of yellow liquid, b.p. 163–164° (1.9 mm.), $n^{20}D$ 1.6525. Redistillation of the forerun gave an additional 3.4 g. of product for a total crude yield of 84%. The picrate prepared from this crude product melted at 194–195°. Admixed with the 6-*n*-propylphenanthridine picrate prepared in method A, the mixture melted at 194–197°. Moreover, the infrared spectra of this product and its picrate were almost superimposable with those of 6-*n*-propylphenanthridine and its picrate (method A), respectively.

2-Butyraminobiphenyl (VII).—A 500-ml., round-bottomed flask was equipped with a short air condenser which in turn bore a bent tube leading to a receiver. The reaction flask was charged with 33.9 g. (0.20 mole) of 2-aminobiphenyl, 35.4 g. (0.40 mole) of butyric acid and 0.1 g. of zinc dust. The contents were so heated during a 6 hr. period that a mixture of water and butyric acid slowly distilled into the receiver. Thereupon the warm mixture was poured into ice and the solidified product filtered off. After recrystallization from dilute ethanol, 38.2 g. (80%) of white product was obtained, m.p. 83–85°. The analytical sample was obtained from petroleum ether (b.p. 60–70°) as long, white needles, m.p. 86–86.5°.

Anal. Calcd. for $C_{16}H_{17}NO$: N, 5.87. Found: N, 5.80.

2-Valeraminobiphenyl (VIII).—By extension of the above procedure for 2-butyraminobiphenyl, 2-valeraminobiphenyl was prepared from 33.9 g. (0.20 mole) of 2-aminobiphenyl, 40.9 g. (0.40 mole) of valeric acid and 0.1 g. of zinc dust by an 8 hr. heating period. Recrystallization of the crude solid from dilute ethanol gave 41.8 g. (82%) of white product, m.p. 68–70°. The analytical sample consisted of long, white needles obtained from petroleum ether, m.p. 73–74.5°.

Anal. Calcd. for $C_{17}H_{19}NO$: N, 5.53. Found: N, 5.41.

6-Benzyl-5,6-dihydrophenanthridine (XI).—To 32.3 g. (0.180 mole) of phenanthridine suspended in 100 ml. of dry ether was added 0.26 mole of benzylmagnesium chloride in 190 ml. of ether over the course of 30 minutes. The initially formed bright yellow slurry slowly changed to a dark green solution when the reaction mixture was stirred under reflux for 24 hr. The solution was hydrolyzed with ammonium chloride solution and the resulting suspended solid filtered off. The crude white solid weighed 38.2 g. (78%) and melted between 130–133°. Although well-formed glistening white prisms could be obtained from an ethanol–benzene pair, no sample could be procured which had a consistently reproducible melting point. The melting points ranged between 125 and 134°.

Anal. Calcd. for $C_{20}H_{17}N$: N, 5.17. Found: N, 5.41.

The infrared spectrum had a pronounced N–H band at 3.05 μ. That the product was actually 6-benzyl-5,6-dihydrophenanthridine in intimate mixture with perhaps 6-benzylphenanthridine and some starting material was demonstrated by oxidation to the known 6-benzoylphenanthridine in high yield.

6-Benzoylphenanthridine (XII).—In 100 ml. of warm glacial acetic acid were dissolved 6.8 g. (0.025 mole) of impure 6-benzyl-5,6-dihydrophenanthridine melting over the range 129–133°. In the course of 20 minutes, 14.3 g. (0.047 mole) of solid sodium dichromate was introduced. The resulting green solution was refluxed for 90 minutes and then poured

(11) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, THIS JOURNAL, **71**, 1499 (1949).

into water. Cooling and filtration gave 7.0 g. (99%) of pale yellow solid, melting over the range 140–147°. From ethanol 5.1 g. (72%) of white solid melting at 150–152° was obtained. Another crystallization yielded white plates, m.p. 152–154°. The product gave a positive test for the carbonyl group with 2,4-dinitrophenylhydrazine and exhibited an intense infrared band at 6.0 μ. Ritchie reports that 6-benzoylphenanthridine melts at 152°.[12]

6-*o*-Tolyl-5,6-dihydrophenanthridine (XIII).—To 30.0 g. (0.168 mole) of phenanthridine suspended in 200 ml. of dry ether was added 0.196 mole of *o*-tolyllithium in 180 ml. of ether during 50 minutes. (The *o*-tolyllithium was previously prepared from 3.3 g., 0.50 g. atom, of lithium wire and 39.3 g., 0.230 mole, of *o*-bromotoluene in 88% yield.) The reaction mixture was stirred at room temperature for 7 hr. and the resulting green solution subsequently hydrolyzed. The suspended solid upon filtration and drying melted over the range 134–138° and weighed 9.3 g. The ethereal layer upon evaporation yielded an additional 26.7 g. of product of the same melting range. One recrystallization from an ethanol–benzene pair gave 31.5 g. (64%) of slightly tan crystals, m.p. 140–141°. The presence of a dihydro grouping was indicated by the blue fluorescence of an alcoholic solution.[9a] The analytical sample consisted of cream-colored crystals, m.p. 140.5–141.5°, which became light brown when left in the air.

Anal. Calcd. for $C_{20}H_{17}N$: N, 5.17. Found: N, 5.14.

6-*o*-Tolylphenanthridine Picrate (XIV).—The product obtained in the preceding experiment was dehydrogenated catalytically. One gram (0.0073 mole) of 6-*o*-tolyl-5,6-dihydrophenanthridine, 100 mg. of palladium-on-Darco (5% palladium) and 5 ml. of mesitylene were refluxed for 1 hr. while a rapid stream of nitrogen was swept through the reaction vessel. At the end of this time, the initial blue fluorescence of the solution had disappeared. The reaction mixture was filtered and the catalyst washed with 10 ml. of ether. The mesitylene was distilled from the filtrate, leaving an oily yellow residue. Since only an oil was obtained from 95% ethanol, the base was converted to the picrate, a crystalline yellow solid melting at 165–167°, 1.6 g. (87%). 6-*o*-Tolylphenanthridine picrate formed bright yellow prisms from 95% ethanol, m.p. 167.5–168.0°.

Anal. Calcd. for $C_{26}H_{18}N_4O_7$: N, 11.24. Found: N, 11.41.

Oxidation of 6-*n*-Butylphenanthridine.[10]—In a 250-ml., three-necked flask fitted with a condenser, stirrer and solids funnel were placed 7.8 g. (0.033 mole) of 6-*n*-butylphenanthridine and 100 ml. of glacial acetic acid. While the solution was held at incipient reflux, 14.3 g. (0.047 mole) of sodium dichromate was introduced portionwise during 75 minutes. The orange solution turned dark green during the following 2-hr. reflux period. The solution was poured into water and the precipitated tan solid was collected. When dry, the solid was extracted with two 100-ml. portions of ether. The residual tan solid weighed 2.3 g. (36%) and melted over the range 289–292°. A mixed melting point determination with an authentic specimen showed this product to be phenanthridinone.

Removal of solvent from the ether extracts left 4.0 g. (49%) of a dark yellow solid melting over the range 85–95°. Recrystallizations from 95% ethanol (Norit A) gave silky, white needles, m.p. 108–109°. This solid proved to be 6-butyrylphenanthridine (XVI) as its infrared spectrum showed an intense carbonyl band at 5.95 μ. Moreover, it formed derivatives with 2,4-dinitrophenylhydrazine and with picric acid.

Anal. Calcd. for $C_{17}H_{15}NO$: N, 5.62. Found: N, 5.52.

The 2,4-dinitrophenylhydrazone was prepared in the conventional manner. Successive recrystallizations from an ethanol–ethyl acetate pair and then a chloroform–ethanol pair gave light orange, matted needles, m.p. 158.5–161°.

Anal. Calcd. for $C_{23}H_{19}N_5O_4$: C, 64.32; H, 4.46. Found: C, 64.30; H, 4.61.

The picrate crystallized from a dioxane–95% ethanol pair as stout, yellow needles, m.p. 198–199°.

Anal. Calcd. for $C_{23}H_{18}N_4O_8$: N, 11.71. Found: N, 11.62.

Oxidation of 6-*n*-Propylphenanthridine.[10]—In a manner similar to the preceding experiment 7.3 g. (0.033 mole) of 6-*n*-propylphenanthridine in 100 ml. of glacial acetic acid was heated for 3 hr. with 14.3 g. (0.047 mole) of sodium dichromate. Dilution of the reaction mixture with water and extraction of the collected solid with ether gave a 3.4-g. (53%) residue of phenanthridinone, m.p. 292–293°.

Evaporation of the ether extracts gave 2.3 g. (30%) of impure 6-propionylphenanthridine (XV) melting from 53–57°. Recrystallizations from 95% ethanol gave white needles melting from 73–76°. This sample showed a pronounced carbonyl band at 5.9 μ in its infrared spectrum. Further purification was carried out by preparing the 2,4-dinitrophenylhydrazone. By recrystallization from a chloroform–ethanol pair this derivative formed compact orange prisms, m.p. 225.5–227.5°.

Anal. Calcd. for $C_{22}H_{17}N_5O_4$: C, 63.85; H, 4.12. Found: C, 63.61; H, 4.26.

The picrate was obtained as chartreuse-colored needles from a dioxane–ethanol pair, m.p. 195.5–197°.

Anal. Calcd. for $C_{22}H_{16}N_4O_8$: N, 12.08. Found: N, 12.34.

Attempted Oxidation of Phenanthridine.—Phenanthridine (6.6 g., 0.033 mole) was heated with 14.3 g. (0.047 mole) of sodium dichromate in 100 ml. of glacial acetic acid for 24 hr. The red solution darkened somewhat during this time. The cooled solution was poured into water and the precipitated orange solid was collected and dried. Probably this was the dichromate salt of phenanthridine, for treatment with sodium hydroxide solution regenerated phenanthridine, 6.8 g., melting from 106–111°. When heated with 50 ml. of dilute hydrochloric acid, the phenanthridine dissolved almost completely, leaving only 0.1 g. of residue.

Acknowledgments.—The authors are grateful to Dr. V. A. Fassel and Mr. R. McCord of the Institute for Atomic Research for the infrared determinations. Also, it is a pleasure to acknowledge that this work was supported in part by the United States Atomic Energy Commission under Contract No. AT(11-1)-59.

AMES, IOWA

(12) E. Ritchie, *J. Proc. Roy. Soc. N. S. Wales*, **78**, 134 (1945) [*C. A.*, **40**, 876 (1946)].