Chemistry of Alkali Metal-unsaturated Hydrocarbon Adducts. II. Radical-Anion Intermediates in the Metal Reductions of Aza-Aromatic Heterocycles[1]

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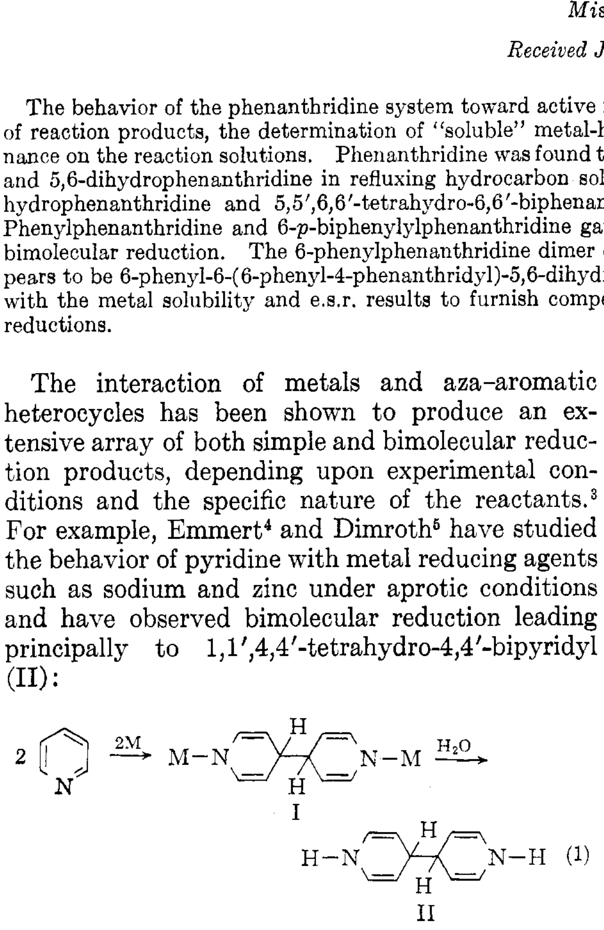
The behavior of the phenanthridine system toward active metals (Li, Na, Mg—MgI_2) was characterized by the isolation of reaction products, the determination of "soluble" metal-heterocycle ratios, and the measurement of electron spin resonance on the reaction solutions. Phenanthridine was found to yield 6,6'-biphenanthridyl, 5,6-dihydro-6,6'-biphenanthridyl, and 5,6-dihydrophenanthridine in refluxing hydrocarbon solvents with sodium or magnesium-magnesium iodide; 5,6-dihydrophenanthridine and 5,5',6,6'-tetrahydro-6,6'-biphenanthridyl were obtained from lithium in tetrahydrofuran. 6-Phenylphenanthridine and 6-*p*-biphenylylphenanthridine gave only the corresponding dihydro products with no trace of bimolecular reduction. The 6-phenylphenanthridine dimer obtained from 6-phenylphenanthridine and mesityllithium appears to be 6-phenyl-6-(6-phenyl-4-phenanthridyl)-5,6-dihydrophenanthridine. The foregoing chemical data are combined with the metal solubility and e.s.r. results to furnish compelling evidence for a radical-anion mechanism for such metal reductions.

The interaction of metals and aza-aromatic heterocycles has been shown to produce an extensive array of both simple and bimolecular reduction products, depending upon experimental conditions and the specific nature of the reactants.[3] For example, Emmert[4] and Dimroth[5] have studied the behavior of pyridine with metal reducing agents such as sodium and zinc under aprotic conditions and have observed bimolecular reduction leading principally to 1,1',4,4'-tetrahydro-4,4'-bipyridyl (II):



The intermediate II may be isolated as the N,N'-diacetyl derivative in the case of the Dimroth reaction (zinc and acetic anhydride),[5] or it may undergo air-oxidation upon work-up to yield 4,4'-bipyridyl.[4] Analogous reductive couplings have been reported for the quinoline,[6] isoquinoline,[7,8] and acridine[9] systems. Although the union of the two aza-aromatic moities is mainly through the available α and γ positions of the pyridinoid ring, this is not always the case. Thus at higher temperatures the reaction of pyridine with sodium takes a more complex course, giving 2,2'-, 3,3'-, 2,4'-, and 4,4'-bipyridyls.[10] Moreover, the principal product resulting from the action of sodium on quinoline is 2,3'-biquinolyl,[11] rather than the expected 2,2'- or 4,4'-isomer.[6] It has further been observed that 4,4'-bipyridyl can be formed from pyridine and potassium metal directly in the absence of moisture and oxygen.[12] This stresses the fact that intermediates such as II need not be precursors in every case of bimolecular reduction.

Although the mechanism of these metal reductions apparently involves electron transfer from the metal to the heterocycle, it was unclear whether the reaction was completed on the metal surface, what the number of transferred electrons per molecule was, and what factors determined the positions of coupling and the state of reduction of the bimolecular products. To shed light upon the mechanism of such metal-heterocycle interactions, it would be pertinent to obtain direct evidence for the types of intermediates present in metal-heterocycle solutions and to make a careful product analysis of such metal reduction processes. To this end, the behavior of phenanthridine (IIIa) and certain of its derivatives toward active metals in hydrocarbon and in ether solution was investigated. This previously neglected heterocyclic system offers several advantages for a study of this kind. First, since the pyridinoid ring has only one available position, α to the nitrogen, only one bimolecular reduction product would be expected and hence the reversibility of dimer formation could be tested; second, the proximity of the α-position and the nitrogen would permit the importance of steric factors in coupling to be evaluated; third, dihydro reduction products of phenanthridine are relatively more stable than those of pyridine and quinoline[13];

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(3) For recent surveys of the metal reductions of nitrogen heterocycles, *cf.* (a) F. W. Bergstrom, *Chem. Rev.*, **35**, 108 (1944). (b) J. Eisch and H. Gilman, *ibid.*, **57**, 525 (1957).

(4) B. Emmert, *Ber.*, **47**, 2598 (1914); **49**, 1060 (1916); **50**, 31 (1917).

(5) D. Dimroth and R. Heene, *ibid.*, **54**, 2934 (1921).

(6) H. Weidel, *Monatsh.*, **2**, 491 (1881).

(7) A. Fernan, *ibid.*, **14**, 60 (1893).

(8) I. W. Elliott, Jr. and R. B. McGriff, *J. Org. Chem.*, **22**, 515 (1957).

(9) W. Schlenk and E. Bergmann, *Ann.*, **463**, 281 (1928).

(10) C. R. Smith, *J. Am. Chem. Soc.*, **46**, 414 (1924).

(11) A. Einhorn and P. H. Herman, *Ann.*, **287**, 42 (1893).

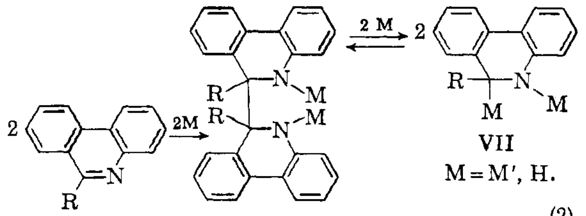
(12) R. L. Ward, *J. Am. Chem. Soc.*, **83**, 3623 (1961).

(13) (a) H. Gilman, J. Eisch, and T. Soddy, *ibid.*, **79**, 1245 (1957); (b) H. Gilman and J. Eisch, *ibid.*, **79**, 2150 (1957); (c) *ibid.*, **79**, 4423 (1957).

and fourth, since recent studies have demonstrated the ease with which biphenyl derivatives add electrons,[14] the phenanthridine system (a bridged biphenyl type) should also form metal adducts readily.

The behavior of phenanthridine, 6-phenylphenanthridine and 6-*p*-biphenylylphenanthridine toward active metals was investigated by means of three approaches. First, the products resulting from the action of metals on these heterocycles and subsequent hydrolysis were isolated and identified. Second, the solubilities of sodium and lithium in solutions of the individual heterocycles were determined to ascertain the average solution species resulting from such interactions. Third, the metal-heterocycle solutions were examined by electron spin resonance spectroscopy to verify the presence of organic free radicals in solution.

Although various reduction products were isolated from phenanthridine–metal systems, the behavior of this system toward lithium in tetrahydrofuran proved the most instructive. Initially a deep red color developed, succeeded by the formation of a copious yellow precipitate and then gradually by the final appearance of an olive-green solution. Hydrolysis at the yellow precipitate state (IVa) yielded exclusively the easily oxidizable 5,5′,6,6′-tetrahydro-6,6′-biphenanthridyl (V), which was characterized as its N,N′-diacetyl derivative. It is noteworthy that this product gave phenanthridine upon oxidation rather than 6,6′-biphenanthridyl (VI) (*cf. infra*). On the other hand, hydrolysis at the olive-green stage (VIIa) gave principally 5,6-dihydrophenanthridine (IX). Therefore, these observations can be formulated in the following manner:



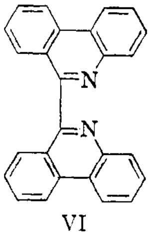
IIIa. R = H
b. R = C_6H_5
c. R = p-C_6H_5–C_6H_4

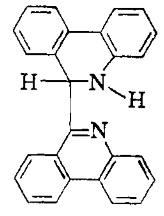
IV. M = M′
V. M = H.

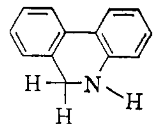
VII
M = M′, H.

(2)

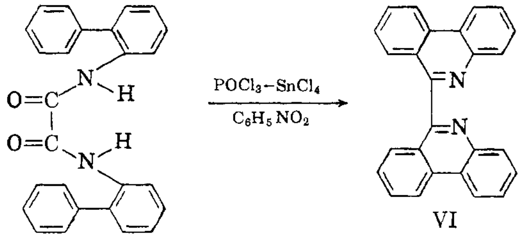
Interaction of phenanthridine with sodium in toluene and subsequent hydrolysis also resulted in the formation of V, but at a much slower rate. At higher temperatures, however, 6,6′-biphenanthridyl (VI), 5,6-dihydro-6,6′-biphenanthridyl (VIII) and 5,6-dihydrophenanthridine (IX) were obtained directly when sodium–phenanthridine ratios of 1:1 were employed. Treatment of the oxidizable crude products with acetic anhydride transformed V, VIII, and IX into the corresponding stable acetyl derivatives which were more readily characterized. In an analogous fashion, phenanthridine and the magnesium–magnesium (II) iodide system[15] in refluxing ether–benzene provided chiefly the aromatized coupling product, 6,6′-biphenanthridyl (VI), directly.


VI


VIII

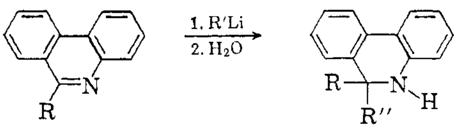

IX

The structure proofs of these metal reduction products were accomplished by a combination of synthetic, degradative, and analytical procedures. The unknown dimer, 6,6′-biphenanthridyl (VI), was synthesized unambiguously by a dual ring closure on N,N′-di(*o*-biphenylyl)oxamide[16]:



VI (3)

The known monomeric product, IXa, was prepared by the reduction of phenanthridine itself with lithium aluminum hydride[17] or with tin and hydrochloric acid:[18]



III   IXa. R, R″ = H.   (4)

R = H or C_6H_5
R′ = AlH_4, C_6H_5, p-C_6H_5—C_6H_4
R″ = H, C_6H_5, p-C_6H_5—C_6H_4

The partially reduced dimers, 5,5′,6,6′-tetrahydro-6,6′-biphenanthridyl (V) and 5,6-dihydro-6,6′-biphenanthridyl (VIII), were characterized by the elemental analysis, molecular weight estimation and infrared examination of the stable diacetyl and monoacetyl derivatives, respectively. Both V and VIII were readily oxidized in air, the former yielding solely phenanthridine, the latter giving 6,6′-

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[14] J. Eisch and W. Kaska, *Chem. Ind.* (London), 470 (1961), and Paper I of this series, J. J. Eisch and W. C. Kaska, *J. Org. Chem.*, **27**, 3745 (1962).

[15] It was postulated by M. Gomberg and W. E. Bachmann, *J. Am. Chem. Soc.*, **49**, 236 (1927), that in certain solvents magnesium and magnesium(II) iodide are in equilibrium with magnesium(I) iodide, an effective reducing agent.

[16] *Cf.* G. T. Morgan and L. P. Walls, *J. Chem. Soc.*, 2447 (1931), for the scope of this phenanthridine synthesis.

[17] W. C. Wooten and R. C. McKee, *J. Am. Chem. Soc.*, **71**, 2946 (1946).

[18] A. Pictet and H. J. Ankersmit, *Ann.*, **266**, 138 (1891).

biphenanthridyl. In addition, when 5,5′,6,6′-tetrahydro-6,6′-biphenanthridyl (V) was heated at 200° under a nitrogen atmosphere for several hours, it decomposed to yield phenanthridine and 5,6-dihydrophenanthridine. These foregoing and related transformations are summarized in Chart I.

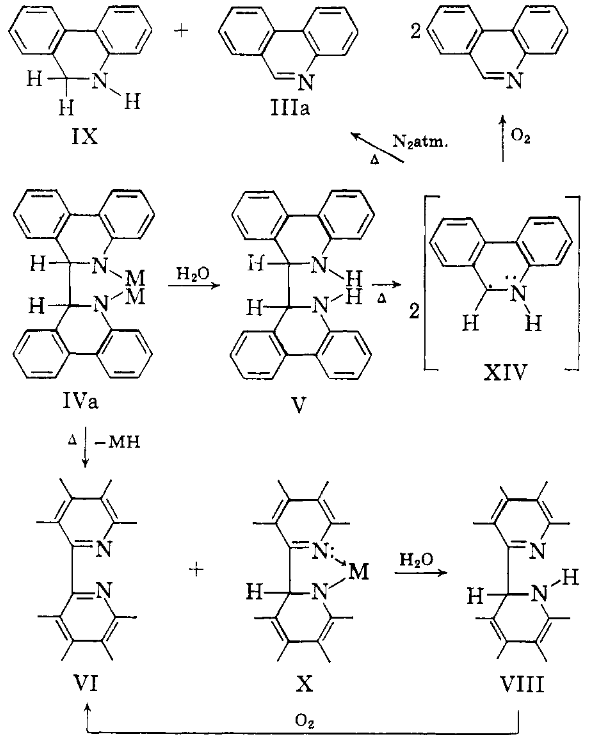
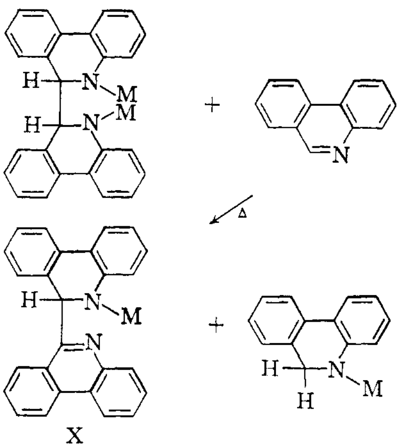


Chart I

The genesis and interrelationship of the bimolecular reduction products of phenanthridine (V, VI, and VIII) merit special comment. Since 5,5′,-6,6′-tetrahydro-6,6′-biphenanthridyl (V) undergoes air oxidation to produce only phenanthridine, the 6,6′-biphenanthridyl (VI) and 5,6-dihydro-6,6′-biphenanthridyl (VIII) cannot arise from the air oxidation of V during work-up. Rather it is felt that the intermediate IVa suffers elimination of metal hydride (NaH, MgH_2)[13a,c] at the higher temperatures employed during the metal–heterocycle reaction proper. The resulting metal hydride does not remain free in the reaction mixture, since no gas evolution was observed when 1.0 equivalent of phenanthridine reacted with 0.70 equivalent of sodium metal to completion in refluxing toluene and the resulting system hydrolyzed. Significantly, a considerable amount of 5,6-dihydrophenanthridine (IX) was a by-product in such runs, even through the amount of available sodium would strongly discourage the formation of IX by the direct reduction of phenanthridine by two equivalents of sodium (VIIa in equation 2). Consequently, these observations are consistent with the thermal elimination of metal hydride from IVa and its addition to unreacted phenanthridine [either in a stepwise or concerted manner (equation 5)]. The facile reduction of phenanthridine by lithium aluminum hydride[17] attests to the feasibility of such a process:



(5)

By the reaction of the same metal reducing agents, in turn, with 6-phenylphenanthridine (IIIb) and 6-p-biphenylylphenanthridine (IIIc) and hydrolytic work-up, only the monomeric 5,6-dihydrophenanthridines (VII. R = C_6H_5 or p-C_6H_5-C_6H_4; M = H) could be detected. The structures of these monomeric reduction products were verified by their independent synthesis according to equation 4, where R = C_6H_5, R′ = AlH_4, and R″ = H in the 6-phenylphenanthridine case (IIIb), and R = H and R′,R″ = p-C_6H_5—C_6H_4 in the 6-p-biphenylylphenanthridine case (IIIc). No trace of bimolecular reduction products could be found.[19] Hence, this supports the exclusive formation of VIIb and VIIc in equation 2.

In this connection it is relevant to recall that Gilman and Nelson[20] have encountered a dimer of 6-phenylphenanthridine of unknown structure as a product of the reaction of mesityllithium with 6-phenylphenanthridine. As this dimerization might seem at first glance analogous to the formation of benzopinacol from the interaction of benzophenone and certain Grignard reagents,[21] the structure of this unknown dimer might be postulated to be that given in IV (R = C_6H_5, M = H). However, the failure of several modifications for the attempted bimolecular reduction of 6-phenylphenanthridine strongly indicates that a structure such as IV would be too unstable to allow the isola-

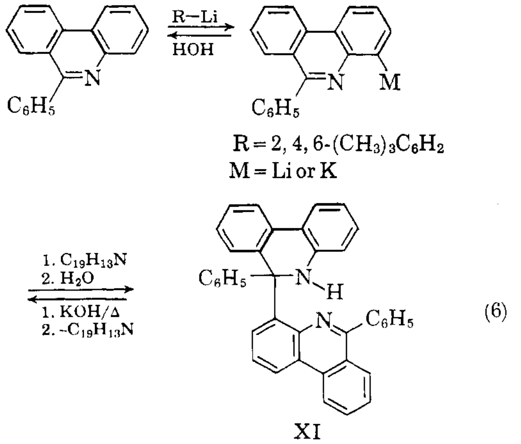
(19) The "open" model of 6-phenylphenanthridine (IIIb), benzophenone anil, has been reported by W. E. Bachmann, *J. Am. Chem. Soc.*, **53**, 2672 (1931), to be reduced by magnesium–magnesium(II) iodide in ether–benzene to yield solely benzhydrylaniline. Upon repeating this experiment, one of us (J.J.E.) has isolated a 2% yield of *sym*-tetraphenylethane. This suggests the occurrence of some bimolecular coupling with accompanying C—N cleavage.

(20) H. Gilman and R. D. Nelson, *ibid.*, **70**, 3316 (1948).

(21) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, p. 165, conclude that the reported cases of bimolecular coupling with alkyl- or arylmagnesium halides and aromatic ketones must be traced to residual magnesium metal in the solution. Triphenylmethylmagnesium halides seem to be one of the few authenticated systems capable of causing bimolecular reduction in the absence of magnesium metal or transition metal catalysts.

tion of the dimer. Such a highly arylated ethane system possesses structural features similar to those of hexaphenylethane and hence might have a great tendency to dissociate.[22]

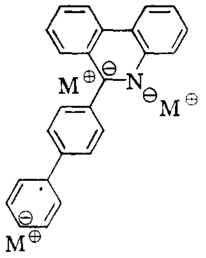
To gain assurance that Gilman and Nelson's dimer is not the bimolecular reduction product IV (R = C_6H_5, M = H) sought for in this present work, this dimer was examined by chemical and spectroscopic means. It was found to form a bright yellow picrate,[23] thus indicating the presence of the $>C{=}N-$ linkage. Furthermore, fusion of the dimer with molten potassium hydroxide regenerated 6-phenylphenanthridine exclusively. Finally, the infrared spectrum of the dimer displayed characteristic absorptions for the N—H group (3250 cm.$^{-1}$), the C=C and C=N functions (1610, 1595, and 1590 cm.$^{-1}$) and C—H deformations characteristic of two vicinal tri-substituted benzenoid or pyridinoid rings.[35] All these data taken together are inconsistent with structure IV (R = C_6H_5, M = H) for the dimer. On the other hand, the properties of this dimer and its mode of formation strongly suggest its identity to be 6-phenyl-6-(6-phenyl-4-phenanthridyl)-5,6-dihydrophenanthridine (XI). A reasonable pathway for the dimerization of 6-phenylphenanthridine would be the metalation of 6-phenylphenanthridine by mesityllithium at the 4-position (*ortho* to the nitrogen),[24] since the steric bulk of mesityllithium might well obstruct its addition to the azomethine linkage. The resulting 4-(6-phenylphenanthridyl)-lithium would be significantly less hindered than mesityllithium and could thus add across the azomethine linkage of another 6-phenylphenanthridine molecule. The observed degradation of the dimer by molten potassium hydroxide would be the reverse of the foregoing process:



(6)

XI

As a correlative of the product analysis discussed above the determination of the average number of metal atoms associated with the phenanthridine heterocycles in solution became of interest in this study. Therefore, the solubilities of sodium in toluene solutions of phenanthridine derivatives and of lithium in tetrahydrofuran solutions were estimated, in order to obtain "soluble" alkali metal–heterocycle ratios for the various solutions. The maximum ratios and the attendant colors observed with 0.02 molar solutions of the heterocycles at 25° are summarized in Table I. With reference to equation 2, these values indicate that with phenanthridine itself there exists an equilibrium between 1:1 metal–phenanthridine adducts (such as the dimer IVa) and 2:1 adducts (typified by VIIa).[25] The reduction products isolated from the hydrolyzed reaction mixture at different stages support the occurrence of both bimolecular and monomolecular reduced phenanthridines. In the case of 6-phenylphenanthridine it is seen that there is essentially a maximum of two metal atoms associated with each heterocyclic molecule. Although the experimental values are somewhat over 2.0, this deviation may be due to adventitious sources of alkali and may not be significant. Again, the isolation of only monomeric reduction products of type VIIb is in accord with the observed metal–heterocycle ratio. Finally, with the 6-*p*-biphenylylphenanthridine system the values definitely point to the association of almost three metal atoms with each heterocycle molecule (XII). It seems that in this case the presence of an additional biphenyl system at the 6-position facilitates the addition of a third electron to the π-electrons system.[26] However, the only reduction product detected upon hydrolysis was the 5,6-dihydro derivative (VIIc). The isolation of other possible monomeric reduction products was hampered by the facile air oxidation of partially reduced phenanthridines.[27]



XII

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[22] The recent report of dimerization of Schiff bases, such as $C_6H_5CH{=}NCH_3$, with Grignard reagents [H. Thies and H. Schoenenberger, *Arch. Pharm.*, **289**, 408 (1956)] is subject to the basic uncertainty cited in ref. 21. The authors do not state that residual magnesium from the Grignard preparation was absent.

[23] Picrates of the dihydro forms of aza-aromatic heterocycles (secondary amines) generally possess red colors. *Cf.* K. Ziegler and H. Zeiser, *Ann.*, **485**, 174 (1931), and ref. 13a.

[24] *Cf.* H. Gilman and J. W. Morton, Jr., *Org. Reactions*, **VIII**, 258 (1954), concerning the general tendency for the metalation of aromatic systems by organolithium compounds to occur *ortho* to electronegative atoms such as O, N, and S.

[25] This conclusion makes the reasonable assumption that no phenanthridine remains unreacted with at least one metal atom.

[26] *Cf.* ref. 14 for the tendency of the biphenyl molecule itself to assume electrons from metals.

[27] A. Pictet and H. J. AuKersuit, *Ann.*, **266**, 138 (1891).

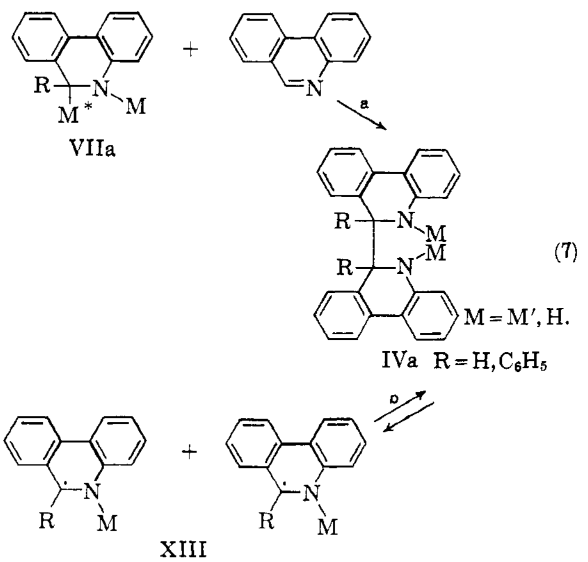
Table I

Alkali Metal–Phenanthridine Ratios in Solution

Compound	Na in toluene M/H ratio[a]	Na in toluene Color	Li in tetrahydrofuran M/H ratio[a]	Li in tetrahydrofuran Color
Phenanthridine	1.55	Violet	1.54	Dark green
6-Phenylphenanthridine	2.28	Dark green	2.19	Dark green
6-*p*-Biphenylylphenanthridine	2.79	Dark blue	2.50	Dark green

[a] The heterocycle concentration was 0.02 mole/l.

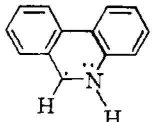
Although it is evident from the product analysis and the metal solubility determinations that metal–heterocycle adducts are involved in these reductions, two possible pathways for the formation of the bimolecular adducts, such as I and IVa, can be entertained. Either the dimetallic adduct VIIa could be formed rapidly from phenanthridine, and the benzylic carbon–metal bond (*) could then add rapidly to a second molecule of phenanthridine (equation 7a)[28]:



or monomeric 1:1 adducts could be formed and undergo subsequent coupling by virtue of their radical character (equation 7b). Furthermore, the latter coupling could take place directly upon the metal surface or species such as XIII R = H) could have a finite existence in the reaction solution. That pathway b predominates in the bimolecular reduction of phenanthridine and that phenanthridine radical–anions do accumulate in solution was demonstrated by examining the initial red solutions formed from sodium and phenanthridine in tetrahydrofuran (THF) by e.s.r. spectroscopy. The pronounced resonance signal observed could be resolved into a spectrum of at least 16 hyperfine components spread over a total width of approximately 30 gauss. This constitutes convincing evidence for the presence of the radical-anion XIII in solution.[29] Even solutions of sodium and 6-phenylphenanthridine in THF gave clear resonance absorptions, although hyperfine structure was not evident. This indicates that a monomeric 1:1 radical–anion of this heterocycle also can exist at low sodium concentrations. Dimetallic adducts of either phenanthridine or 6-phenylphenanthridine would, on the other hand, be diamagnetic and would exhibit no e.s.r. absorption.

Since phenanthridine does form monomeric 2:1 metal adducts, equation 7b is reversible and the dimer IVa can dissociate into radical–anions. The latter could then add additional electrons to form dianions VIIa. The steric bulk of the phenyl group in 6-phenylphenanthridine would undoubtedly hinder the existence of appreciable amounts of its 1:1 dimer, IVb, and thus its 1:1 metal–heterocycle adduct should exist principally as the free radical–anion XIII (R = C_6H_5). Existence as a monomeric species should be even more advantageous with the 6-*p*-biphenylylphenanthridine radical-anion.

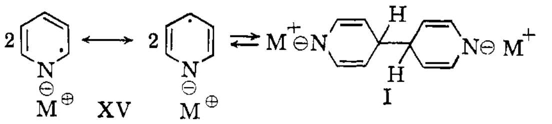
Moreover, the tendency of structures such as IVa to dissociate into free radicals (equation 7b) seems evident even in the hydrolyzed reduction products themselves (IV. M, R = H). The fact that 5,5′,6,6′-tetrahydro-6,6′-biphenanthridyl undergoes facile oxidative cleavage to phenanthridine, rather than the usual aromatization to 6,6′-biphenanthridyl, (*cf.* the behavior of II) and that it disproportionates upon heating to yield phenanthridine and 5,6-dihydrophenanthridine (Chart I) suggest dissociation into radicals (XIV). Such



XIV

a radical would enjoy not only delocalization into the biphenyl π-cloud but it could also utilize the unshared pair on the nitrogen in distributing the unpaired electron spin.

Finally, since this work has demonstrated the intervention of radical-anion intermediates in these metal reductions, the general tendency for bimolecular coupling to occur through the α- and γ-positions of the pyridinoid ring is explicable in terms of the following resonance description of such radical–anions (XV):



(8)

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[28] Benzylmagnesium chloride adds to the azomethine linkage of phenanthridine very readily (ref. 13c).

[29] *Cf.* D. J. E. Ingram, "Free Radicals as Studied by Electron Spin Resonance," Butterworth Scientific Publications, Ltd., London, England, 1958. A detailed treatment of the hyperfine splitting of the phenanthridine radical–anion was not undertaken, since there are undoubtedly more hyperfine components yet to be resolved.

As electronegativity considerations will favor the residence of the negative charge upon the N atom, the greatest probability of finding unpaired electron spin density and hence the greatest likelihood of permitting radical coupling would be at the α- and γ-positions. However, since the dissociation of the dimer into the component radical-anions (equation 8) becomes more probable with benzopyridines and at higher temperatures, as this study has shown, the radical-anions may eventually couple in a manner not involving α- or γ-positions. The resulting dimer may be more stable to dissociation, however. This situation seems to obtain in the metal reductions of pyridine and quinoline at higher temperatures.

Experimental[30]

Preparation of Starting Materials. (a) Phenanthridine.[31]—To polyphosphoric acid obtained from 100 ml. of 85% phosphoric acid and 180 g. of phosphorus pentoxide was added 50 g. (0.25 mole) of 2-formamidobiphenyl. The stirred mixture was slowly heated to 100–120° and 0.50 mole of phosphorus oxychloride was added dropwise so as to avoid frothing. After the evolution of hydrogen chloride had slackened, the reaction mixture was stirred for 5 hr. at 160°. Cautious hydrolysis of the cooled system and treatment with sodium hydroxide solution precipitated the crude organic base. This collected and dried solid was distilled and the fraction boiling at 148–150° (1.7 mm.) was collected. Recrystallization of this fraction from petroleum ether (b.p. 60–90°) gave 37 g. (82%) of phenanthridine, m.p. 105–106°.

(b) **6-Phenylphenanthridine.**—Analogously, 50 g. (0.18 mole) of 2-benzamidobiphenyl, 110 g. (0.72 mole) of phosphorus oxychloride, and 145 ml. of nitrobenzene were stirred at the reflux temperature for 12 hr. After the hydrolyzed mixture was made alkaline with potassium hydroxide, the nitrobenzene was removed by steam distillation. The solid residue was collected and recrystallized from 95% ethanol to provide 42 g. (90%) of 6-phenylphenanthridine, m.p. 104–105° (lit.,[32] m.p. 105–106.5°).

(c) **6-*p*-Biphenylylphenanthridine.**—To 10 g. (0.064 mole) of phenanthridine in 100 ml. of dry ether was added 0.094 mole of *p*-biphenylyllithium[33] in 250 ml. of ether over a 30-min. period. After 4 hr. at the reflux temperature the dark olive-green reaction mixture was hydrolyzed and the precipitated cream-colored solid was collected. An additional quantity of product was obtained by the evaporation of the ether layer. The combined product was refluxed with 60 ml. of nitrobenzene for 1 hr. to oxidize the dihydro state. The nitrobenzene was then distilled under reduced pressure and the remaining solid was recrystallized twice from ethylene glycol dimethyl ether. The pale yellow 6-*p*-biphenylylphenanthridine, obtained in 65% yield, melted at 202–203°.

Anal. Calcd. for $C_{25}H_{17}N$: N, 4.23. Found: N, 4.26.

Preparation of Reduction Products. (a) 5-Acetyl-5,6-dihydrophenanthridine.[27] Phenanthridine was reduced with granulated tin and dilute hydrochloric acid to produce the easily oxidizable 5,6-dihydro derivative, m.p. 124–126°, in 75% yield. This product was readily acetylated in high yield by heating it in benzene solution with acetic anhydride. Removing the benzene, heating the residue with water, and recrystallizing the collected solid from 95% ethanol gave the stable acetyl derivative, m.p. 109–109.5°.

(b) **N,N'-Di(*o*-biphenylyl)oxamide.**[34]—A mixture of 152 g. (0.9 mole) of 2-aminobiphenyl, 52 g. (0.36 mole) of ethyl oxalate and 2 drops of concentrated sulfuric acid was heated at 140–150° in an oil bath until ethanol no longer distilled from the reaction mixture. The reaction residue was digested with 100 ml. of hot methanol and filtered. The insoluble diamide, weighing 31.5 g. (26% yield, base upon ethyl oxalate), was recrystallized from benzene to form colorless needles, m.p. 238–240.5°. The cooled ethanolic extract deposited the monoamide. Subsequent recrystallization of the monoamide from 95% ethanol yielded 31 g. (47%), m.p. 110–113°.

(c) **6,6'-Biphenanthridyl.**—A mixture of 30 g. (0.077 mole) of N,N'-di(*o*-biphenylyl)oxamide, 250 g. of phosphorus oxychloride, 17 g. of stannic chloride, and 200 ml. of nitrobenzene was stirred in an oil bath at 140° for 20 hr. The mixture was distilled under reduced pressure to remove the greater portion of phosphorus oxychloride. After hydrolysis and treatment with sodium hydroxide the nitrobenzene was removed by steam distillation. The crude residue was filtered and the collected solid was then dried. Two recrystallizations from dry pyridine provided 10.5 g. (39% yield) of cream-colored 6,6'-biphenanthridyl, m.p. 342–343°.

Anal. Calcd. for $C_{26}H_{16}N_2$: N, 7.86. Found: N, 7.90. The infrared spectrum of this product was free of any —OH, —NH, or $>$C=O absorption bands; characteristic bands appeared at 1610, 1570 (C=C, C=N), 750, and 720 cm.$^{-1}$.

(d) **5-Benzoyl-6-phenyl-5,6-dihydrophenanthridine.**—6-Phenylphenanthridine could be reduced to 5,6-dihydrophenanthridine in high yield with either lithium aluminum hydride in ether (Soxhlet thimble technique) or tin and hydrochloric acid. The easily oxidizable product was treated with benzoyl chloride and 10% sodium hydroxide solution to form the 5-benzoyl derivative. From 95% ethanol the benzoyl compound crystallized as a colorless, air-stable product, m.p. 182–183°.

Anal. Calcd. for $C_{26}H_{19}NO$: N, 3.88. Found: N, 3.66. The infrared spectrum displayed a characteristic band at 1675 cm.$^{-1}$ (aromatic—$\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}$—) and possessed no band in the 3300–3500 cm.$^{-1}$ (N—H) region.

(e) **6-*p*-Biphenylyl-5,6-dihydrophenanthridine.**—Although quite prone to air-oxidation, this compound could be prepared readily from the reaction of *p*-biphenylyllithium with phenanthridine (*cf. supra*). However, in this case the nitrobenzene oxidation was omitted. Thus the reaction of 14.3 g. (0.080 mole) of phenanthridine with 0.085 mole of the *p*-biphenylyllithium in ether and a 6-hr. reflux period provided upon usual work-up 20 g. (77%) of crude product, melting over the range 140–160°. Recrystallization from absolute ethanol under nitrogen yielded colorless prisms, m.p. 166–167°.

Anal. Calcd. for $C_{25}H_{19}N$: C, 90.05; H, 5.74; N, 4.20. Found: C, 90.06; H, 5.55; N, 4.44.

The infrared spectrum displayed a band at 3400 cm.$^{-1}$ (N—H).

Metal Reduction Products. (a) Phenanthridine and Magnesium–Magnesium Iodide.—Addition of 4.5 g. (0.025 mole) of phenanthridine dissolved in 30 ml. of dry benzene to a mixture of 1.12 g. (0.046 g.-atom) of magnesium metal turnings and 0.014 mole of magnesium iodide in 20 ml. of dry ether resulted in a deep violet solution. The mixture was stirred for 20 hr. at reflux, during which time a solid precipitated. Hydrolysis, extraction with ether and drying of the organic layer yielded after solvent removal a pale

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[30] All melting points are uncorrected. Reactions involving the interaction of phenanthridine systems with metals or with organometallic compounds were conducted under an atmosphere of dry oxygen-free nitrogen.

[31] *Cf.* A. P. Gray, W. L. Archer, D. C. Schlieper, E. E. Spinner, and C. J. Cavallito, *J. Am. Chem. Soc.*, **77**, 3536 (1955).

[32] G. T. Morgan and L. P. Walls, *J. Chem. Soc.*, 2447 (1931).

[33] H. Gilman and G. Dunn, *J. Am. Chem. Soc.*, **73**, 5079 (1951).

[34] L. P. Walls, *J. Chem. Soc.*, 108 (1934).

yellow solid containing reduced phenanthridine and a higher-melting component. Recrystallization from dry pyridine gave 1.0 g. (20%) of pale yellow crystals, m.p. 341–342°. Comparison of this product with authentic 6,6′-biphenanthridyl by means of infrared spectroscopy and mixture melting points proved the two solids to be identical.

(b) **Phenanthridine and Lithium in Tetrahydrofuran (Short Reaction Time).**—A solution of 7.16 g. (0.040 mole) of phenanthridine in 160 ml. of dry, freshly distilled tetrahydrofuran was stirred with 1.39 (0.20 g.-atom) of freshly cut pieces of lithium ribbon. A deep red solution developed almost immediately and after about 10 min. a copious yellow precipitate formed. After the system had been allowed to react with stirring at room temperature for a total time of 90 min., it was treated with 200 ml. of water and 100 ml. of benzene. The dried benzene layer was heated at reflux with 20 ml. of acetic anhydride for 1 hr. Distillation of the solution under reduced pressure gave a viscous residue which was recrystallized from absolute ethanol to yield 1.20 g. (14%) of colorless prisms, m.p. 267–268°. Concentration of the mother liquor and dilution with water allowed 4.0 g. (56%) of phenanthridine to be recovered.

An analytical sample of the high-melting solid from absolute ethanol melted at 268.5–269°. Its infrared spectrum showed an intense C=O band at 1660 cm.$^{-1}$ but no N—H band in the 3200–3500-cm.$^{-1}$ region.

Anal. Calcd. for $C_{30}H_{24}N_2O_2$: C, 81.05; H, 5.44; N, 6.30; mol. wt. 444.5. Found: C, 81.25; H, 5.62; N, 6.54; mol. wt. (Rast) 450. Based upon the preceding analytical data and the chemical behavior cited below, this product is concluded to be 5,5′-diacetyl-5,5′,6,6′-tetrahydro-6,6′-biphenanthridyl.

(c) **Phenanthridine and Lithium in Tetrahydrofuran (Long Reaction Time).**—A solution of 7.16 g. (0.040 mole) of phenanthridine in 160 ml. of dry tetrahydrofuran was stirred under reflux with 1.72 g. (0.25 g.-atom) of lithium pieces for 22 hr. The dark olive-green solution was hydrolyzed and ether was added to extract the organic products. The solid obtained by drying the ether extract and then removing the solvent was dissolved in 20 ml. of benzene and heated with 20 ml. of acetic anhydride for 1 hr. The volatile components were removed and the residual glass was distilled at 0.1 mm. pressure to yield as a main fraction 5.2 g. of viscous pale yellow oil, b.p. 155–165°. This distillate gave only a slight turbidity with an alcoholic solution of picric acid (test for presence of phenanthridine) and its infrared spectrum was essentially identical with that of 5-acetyl-5,6-dihydrophenanthridine. Solution of the viscous oil in warm ethanol and cooling gave colorless prisms, m.p. 107–109°. A mixture melting point with authentic 5-acetyl-5,6-dihydrophenanthridine was undepressed.

(d) **Phenanthridine and Sodium in Toluene.**—The nature of the products depended upon the temperature and the ratio of reactants.

In the first run 3.58 g. (0.020 mole) of phenanthridine and 0.51 g. (0.022 g.-atom) of powdered sodium were stirred in 150 ml. of dry toluene at room temperature for 5 days. Approximately 2 hr. after the start of the reaction an olive-green color developed; eventually the system became greenish black. Hydrolysis, drying of the toluene layer and removal of the solvent gave a mixture of unchanged phenanthridine and reduced products. Digestion with ethanol left 1.65 g. of insoluble residue. This was acetylated with acetic anhydride in benzene solution in the usual fashion to give upon work-up and recrystallization from ethanol 5,5′-diacetyl-5,5′,6,6′-tetrahydro-6,6′-biphenanthridyl, m.p. 267–269° (mixture melting point). As to the possible presence in the product of 6,6′-biphenanthridyl (benzene-insoluble) it should be noted that the 1.65 g. residue dissolved in warm benzene with only a trace of residue.

In the second run 3.58 g. (0.020 mole) of phenanthridine and 0.32 g. (0.014 g.-atom) of sodium were stirred at reflux in 150 ml. of dry toluene for 96 hr. Two hours after the reaction began, a distinct orange color appeared. This soon gave way to a green color and then a greenish black system. Hydrolysis of the reaction mixture gave no gas evolution. From the toluene–water system 0.08 g. of insoluble, cream-colored powder was filtered off, m.p. 340–343°. Recrystallized from dry pyridine this melted at 342–343° and proved to be 6,6′-biphenanthridyl by mixture melting point.

Removal of the solvent from the dried toluene layer, the usual acetylation of the residue and work-up by ethanol digestion of the crude product provided 1.2 g. of colorless prisms, m.p. 235–245°. Recrystallization from a benzene–ethanol pair yielded a substance melting at 246–248°. Admixed with 5,5′-diacetyl,5,5′,6,6′-tetrahydro-6,6′-biphenanthridyl it melted over the range, 220–235°. The infrared spectrum displayed an intense C=O band at 1655 cm.$^{-1}$ and two moderate bands at 1610 and 1585 cm.$^{-1}$ (C=C and C=N), but no band in the 3200–3500-cm.$^{-1}$ region.

Anal. Calcd. for $C_{28}H_{20}N_2O$: C, 83.97; H, 5.03; N, 6.99; mol. wt. 400.3. Found: C, 84.19; H, 5.22; N, 7.02; mol. wt. (Rast) 403. Based upon the preceding analytical data and the chemical behavior cited below, this product is therefore 5-acetyl-5,6-dihydro-6,6′-biphenanthridyl.

Further concentration of the original ethanolic extract from which 1.2 g. of the above product were obtained and dilution with water gave 0.15 g. of colorless 5-acetyl-5,6-dihydrophenanthridine, m.p. 107–109° (mixture melting point).

In the third run 17.92 g. (0.10 mole) of phenanthridine, 2.42 g. (0.11 g.-atom) of sodium pieces and 250 ml. of dry toluene were stirred under reflux for 72 hr. Hydrolysis gave essentially no gas evolution. After a work-up analogous to that in the second run 0.05 g. of 6,6′-biphenanthridyl, 10.1 g. of crude 5-acetyl-5,6-dihydro-6,6′-biphenanthridyl and 0.50 g. of 5-acetyl-5,6-dihydrophenanthridine were isolated.

(e) **Reduction of 6-Phenylphenanthridine.**—Treatment of this heterocycle with equivalent quantities of either sodium in toluene or magnesium–magnesium iodide in ether–benzene gave dark green or violet solutions which upon usual work-up gave an oil. Treatment of the oil with benzoyl chloride and sodium hydroxide solution produced, in both cases, a benzoyl derivative (crude yield, 30–40%), m.p. 182–183° (from 95% ethanol). Admixed with authentic 5-benzoyl-5,6-dihydrophenanthridine it melted undepressed. The residue of the reaction product gave no indication of any dimeric products and proved to be 6-phenylphenanthridine.

(f) **Reduction of 6-*p*-Biphenylylphenanthridine.**—Similarly, treatment of this compound with an equimolar quantity of sodium in tetrahydrofuran for 1 day gave a deep green solution. Hydrolysis and usual work-up furnished a yellow solid. Recrystallization from a methanol–chloroform pair formed almost colorless prisms (27%), m.p. 167–168°. This compound is very air-oxidizable (*cf. supra*). Admixture with authentic 6-*p*-biphenylyl-5,6-dihydrophenanthridine gave no depression in the melting point.

Isolation of 5,5′,6,6′-Tetrahydro-6,6′-biphenanthridyl. (a) **Metal Reduction of Phenanthridine.**—A solution of 17.92 g. (0.10 mole) of phenanthridine and 0.73 g. (0.105 g.-atom) of lithium pieces in 250 ml. of tetrahydrofuran was stirred at room temperature for 24 hr. The dark orange slurry was treated with 200 ml. of water and 200 ml. of benzene. The dried benzene layer yielded upon evaporation a solid which was subsequently digested with 200 ml. of chloroform. The insoluble yellow powder (10.95 g.) melted over the range, 160–175° (capillary inserted at 140°). Recrystallizations from an ethanol-benzene pair yielded short, pale yellow prisms, m.p. 140–170° (inserted at 120°); 175–185° (inserted at 160°); 225–233° (insertion at 215° caused immediate melting and resolidification). Repeated recrystallization in air yielded a product of gradually lowered maximum melting point (180° → 120°). Consequently, the analytical sample was obtained by repeated recrystallization under a nitrogen atmosphere. Although a sharp melting point was never observed for this product, this seems to be due to its inherent oxidizability. A sample of this product could be acetylated in 96% yield to produce the stable 5,5′-diacetyl-5,5′,6,6′-tetrahydro-6,6′-biphenanthridyl, m.p. 265–267°.

Anal. Calcd. for $C_{26}H_{20}N_2$: C, 86.63; H, 5.59; N, 7.77. Found: C, 86.52; H, 5.59; N, 7.47.

The infrared spectrum of the 5,5′,6,6′-tetrahydro-6,6′-biphenanthridyl displayed a sharp band at 3300 cm.$^{-1}$ (N—H) and only a single band in the 1600-cm.$^{-1}$ region (C═C 1615 cm.$^{-1}$), emphasizing the absence of the C═N group.

(b) **Air-oxidation of 5,5′,6,6′-Tetrahydro-6,6′-biphenanthridyl.**—A 3.0-g. sample of the tetrahydrobiphenanthridyl (m.p. 175–185°, inserted at 160°) was divided into halves. One half was heated with 5 ml. of acetic anhydride and 10 ml. of benzene to provide upon usual work-up 1.76 g. (96%) of 5,5′-diacetyl-5,5′,6,6′-tetrahydro-6,6′-biphenanthridyl, m.p. 266–267°. The other half was refluxed in chloroform solution for 4 hr. Cooling precipitated only 5.3% of the original tetrahydro compound. Evaporation of the solvent furnished a 91% yield of phenanthridine, m.p. 100–103° (mixture melting point).

Similarly, treatment of the tetrahydro compound with ferric chloride in ethanol and chloranil in xylene yielded phenanthridine.

(c) **Pyrolysis of 5,5′,6,6′-Tetrahydro-6,6′-biphenanthridyl.**—The 2.0-g. (0.0056 mole) sample was heated under a nitrogen atmosphere at 200 ± 5° for 3 hr. During the first hour no melting was observed. During the second hour a yellow liquid condensed upon the cooler parts of the vessel, but the main portion of reactant did not melt. During the third hour the mass became molten. The pale yellow product was treated with acetic anhydride and benzene. Usual work-up and recrystallization from 95% ethanol gave 0.46 g. of colorless solid, m.p. 105–107°. Admixed with phenanthridine it melted below 90°. This proved to be 5-acetyl-5,6-dihydrophenanthridine (mixture melting point).

Treatment of the original ethanolic mother liquor with ethanolic picric acid gave an immediate yellow precipitate, 1.75 g., m.p. 235–245°. Recrystallization from an ethanol–dioxane pair yielded glistening yellow needles, m.p. 247–249°. This proved to be phenanthridine picrate (mixture melting point).

Saponification of Acetyl Derivatives. (a) **5,5′-Diacetyl-5,5′,6,6′-tetrahydro-6,6′-biphenanthridyl.**—A solution of 1.25 g. (0.0028 mole) of the diacetyl compound and 4.0 g. of sodium hydroxide in 75 ml. of 95% ethanol was refluxed for 1 hr. The precipitated yellow 5,5′,6,6′-tetrahydro-6,6′-biphenanthridyl was collected from the cooled solution, 0.84 g. (82%), m.p. 160–180° (inserted 150°). To attempt dehydrogenation to form 6,6′-biphenanthridyl, this product was heated with 5 ml. of nitrobenzene for 45 min. After the nitrobenzene was distilled, the residue was dissolved in 4 ml. of hot pyridine. Only phenanthridine precipitated. Hence, the pyridine was evaporated to leave a 0.50-g. residue of phenanthridine, m.p. 100–104°.

(b) **5-Acetyl-5,6-dihydro-6,6′-biphenanthridyl.**—A solution of 0.88 g. of the acetyl derivative and 2.5 g. of sodium hydroxide in 50 ml. of 95% ethanol was refluxed for 8 hr. The precipitated tan solid (0.12 g.) was collected and dried, m.p. 342–344°. A mixture with 6,6′-biphenanthridyl melted undepressed. Concentration of the mother liquor gave lower-melting crops. However, when the mother liquor had stood for some time in air, an additional 0.31 g. of 6,6′-biphenanthridyl was obtained.

Reaction of 6-Phenylphenanthridine with Mesityllithium.—To 10.5 g. (0.041 mole) of 6-phenylphenanthridine in 200 ml. of dry ether was added an ethereal solution of mesityllithium [prepared from 8.95 g. (0.05 mole) of 2-bromomesitylene and 0.63 g. (0.091 g.-atom) of lithium in 100 ml. of ether]. During the 48-hr. reflux period the mixture turned from green to black. Hydrolysis precipitated 5.0 g. (48%) of crude dimer. Recrystallizations from a 1:1 methanol–chloroform pair yielded 3.0 g. of pale yellow needles, m.p. 282–283°. Gilman and Nelson reported a melting point of 275–277° and a cryoscopically determined molecular weight of 522. To assure that the present product corresponded to the previously reported product, it was analyzed.

Anal. Calcd. for $C_{38}H_{26}N_2$: N, 5.49. Found: N, 5.48.

The infrared spectrum exhibited prominent bands at 3250 (N—H), 1610, 1595 and 1570 (C═C, C═N), 960 and 940 (twinned), 810 and 790 (twinned), 755 (broad), 725, 700 and 660 cm.$^{-1}$. By comparison the spectrum of 6-phenylphenanthridine showed bands at 1610, 1585 and 1565 (C═C, C═N), 950, 800, 780, 760 (broad), 720, 695, and 665 cm.$^{-1}$. Since it has been observed that 1,2,3-trisubstituted benzenoid rings in the quinoline series—*e.g.*, 5- and 8-substituted quinolines—have their 940-cm.$^{-1}$ quinoline band above 950 cm.$^{-1}$;[35] it is felt that this dimer has a vicinally trisubstituted benzenoid ring (band at 960 cm.$^{-1}$). The dimer therefore seems to be 6-phenyl-6-(6-phenyl-4-phenanthridyl)-5,6-dihydrophenanthridine.

Fusion of the 6-Phenylphenanthridine Dimer with Alkali.—In a nickel crucible 0.24 g. of the dimer was fused with 5.0 g. of pellet potassium hydroxide over a low flame for 10 min. Some colorless solid sublimed onto a cold watch glass covering the crucible. The contents were eluted with water and the residual gum was recrystallized from ethanol. Cooling deposited 0.20 g. (83%) of colorless prisms, m.p. 101–105°. Again recrystallized from ethanol the product melted at 104–106°. A mixture melting point determination showed this to be 6-phenylphenanthridine.

Picrate of the 6-Phenylphenanthridine Dimer.—The dimer, dissolved in a 95% ethanol–chloroform pair, precipitated a yellow picrate when treated with ethanolic picric acid. Attempted recrystallization of this picrate from ethanol, however, yielded back the 6-phenylphenanthridine dimer. The crude picrate could be satisfactorily purified by recrystallizing it from an ethanol–chloroform pair containing picric acid. The bright yellow needles melted at 231.5–232.5°, after washing with cold alcohol and drying.

Anal. Calcd. for $C_{44}H_{29}N_5O_7$: N, 9.47. Found: N, 9.54.

Determination of "Soluble" Alkali Metal–Heterocycle Ratios.—A calibrated, 100-ml. round-bottomed flask, equipped with a three-necked adapter to accommodate a pressure-equalized addition funnel, reflux condenser, and nitrogen inlet, was provided with a magnetic stirring bar, 0.00250 mole of the heterocycle, a tenfold excess of the alkali metal and approximately 100 ml. of dry, freshly distilled toluene or tetrahydrofuran. The system was purged thoroughly with dry, oxygen-free nitrogen and this atmosphere was maintained throughout the experiment. The system was heated with stirring until the concentration of the dissolved metal remained constant. Trial runs had shown that such constancy was reached after 3 days in the case of sodium and toluene, but after only 1 day with lithium and tetrahydrofuran. The system was cooled to 18–20° and volume adjusted by dilution to the calibration mark. After further stirring to permit equilibration 10.0-ml. aliquots were withdrawn and hydrolyzed. The samples were titrated with standardized acid by use of a microburette with a nitrogen atmosphere over the solution being titrated. The colors observed for the metal–heterocycle solutions and the ratios of "soluble" alkali metal to heterocycle, as obtained from the titration data, are given in Table I. Because of the sensitivity of such metal–heterocycle solutions to moisture and oxygen, the volatility of the solvents employed and the possibility of colloidally suspended alkali metal, the observed values for the concentration of dissolved alkali metal would tend to be too high. Such titrimetric determinations of organoalkali compounds usually possess an accuracy of within ±5%.[36]

Electron Spin Resonance Measurements.—Solutions of

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(35) J. J. Eisch, *J. Org. Chem.*, **27**, 1318 (1962).

sodium metal–phenanthridine and sodium metal-6-phenylphenanthridine adducts in tetrahydrofuran were prepared (*ca.* 10^{-3}–10^{-4} *M*) and transferred to e.s.r. sample tubes by means of vacuum-line techniques.[37] The resulting sodium–phenanthridine solution was bright orange-red in color, while the sodium-6-phenylphenanthridine solution was deep green. The e.s.r. absorption spectra were taken on a spectrometer operating at 8996 Mc./sec. The magnetic field was modulated at 90 cycles/sec. Both with the phenanthridine and 6-phenylphenanthridine solutions the spectroscopic splitting factor or g.-value was 2.0054. By the use of phase sensitive detection the absorption spectra were presented as the first derivative of absorption with respect to field as a function of field. Both the sodium–phenanthridine and the sodium-6-phenylphenanthridine solutions gave pronounced, broad paramagnetic resonance absorption signals, definitely indicating the presence of free radical species. The lack of hyperfine components in the spectra of these samples seemed to be due to the transfer of electrons between the sodium–heterocycle adduct and unchanged heterocycle molecules present in the sample. Such electron transfer is known to obliterate hyperfine structure and result in a broadened absorption signal.[38] It was hoped that both higher conversion of the heterocycle into its 1:1 metal adduct and dilution of the sample would reveal hyperfine structure. With the phenanthridine samples this technique was successful. In this fashion a spectrum containing at least eight broad hyperfine components extending over a range of approximately 30 gauss was obtained. Subsequent measurements on more dilute samples indicated the presence of at least 16 components.

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(36) C. W. Kamienski and D. L. Esmay, *J. Org. Chem.*, **25**, 115 (1960).

(37) *Cf.* D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956).

(38) *Cf.* R. L. Ward and S. I. Weissman, *ibid.*, **76**, 3612 (1954), for an ingenious exploitation of such line broadening to determine the rate of electron transfer between the naphthalene radical–anion and naphthalene.

The Formation of Allenes from *gem*-Dihalocyclopropanes by Reaction with Alkyllithium Reagents[1,2]

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Several *gem*-dibromocyclopropanes, prepared by the addition of dibromocarbene to olefins, have been found to give allenes in high yields when treated with methyllithium or butyllithium in ether. The related dichloro compounds are inert to methyllithium but react slowly with butyllithium. In the cases considered there is no indication of carbene intermediates.

gem-Dihalocyclopropanes are readily available from the reaction of a dihalocarbene with an olefin, a reaction discovered by Doering and Hoffmann[4] in 1954 and widely employed by others since that time. Initially, these compounds were reported to be inert to most reagents and did not appear to have great synthetic utility.[5] Later, Doering and LaFlamme[7] found that treatment of certain *gem* dibromocyclopropanes with magnesium in ether gave allenes. The yields were not high (*ca.* 16–35%), but the allenes were reported to be essentially pure. The same investigators also found that these dibromides and the corresponding dichlorides reacted with high-surface sodium to give allenes in higher yields, accompanied, however, by isomers of the allenes.

In the search for a more efficient means to convert these dihalides to allenes, certain of which were desired for other studies, we examined the reaction of alkyllithium reagents with a number of *gem*-dihalocyclopropanes.[2]

Results and Discussion

Several *gem*-dibromocyclopropanes were prepared by the method of Doering and Hoffmann and all could be converted to allenes in good yields with either butyllithium or methyllithium (Table II, Experimental). Utilizing butyllithium in ether at $-10°$, cyclic and internal acyclic allenes were formed with no evidence of isomerization. In those cases in which terminal allenes were formed, the yields were lower and the allenes were extensively contaminated by materials which were assumed to be isomers of the allenes (based on gas chromatographic retention times). Subsequently, it was found that in these cases methyl-

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(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(2) Preliminary report, W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960).

(3) National Science Foundation Summer Fellow, 1959.

(4) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954), and later papers.

(5) The replacement of the halogen atoms by hydrogen by reduction with an active metal in a protonic solvent (ref. 4) appears to be a useful alternative to the Simmons–Smith reaction (ref. 6); *cf.*, K. Hofman, S. F. Orochena, S. M. Sax, and G. A. Jeffrey, *ibid.*, **81**, 992 (1959); S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3235 (1961).

(6) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

(7) W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958).