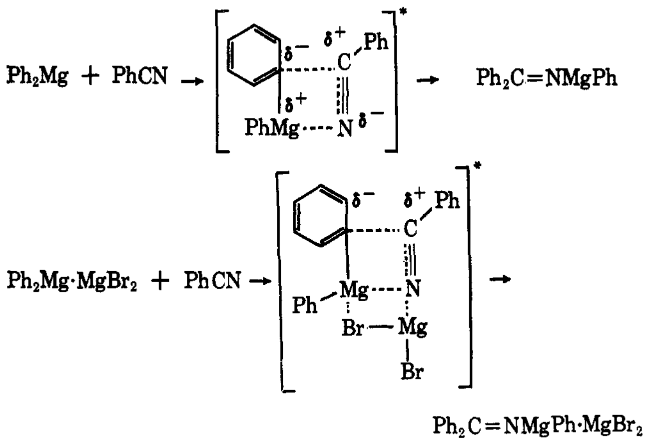
A mechanism which is consistent with the data for the ΔS^* is that in which $MgBr_2$ helps to increase the polarity and hence decrease the order of the transition state by dispersing the charge which develops from the rearrangement of electrons in the activated complex, *e.g.*,[59] Scheme I.

Scheme I



Most Hammett σ values deal with the combined inductive and resonance interactions in a substituted benzene ring.[35] Taft σ^0 values are calculated as inductive effect constants in which no direct conjugative enhancement can occur.[34] If it is assumed that a carbanion attack on the nitrile carbon is a reasonable mechanism for Grignard–benzonitrile reactions, it should follow that only inductive effects on the carbanion should influence the rate of reaction. More specifically, a phenyl carbanion should be composed of two electrons occupying the carbon σ orbital *para* to the point of substitution, and any electronic effect which is due to resonance can operate only by p–π interaction up to the carbon atom involved, *but can not* resonate with a σ sp^2 bond which holds the two electrons. Whereas substituted phenolate ions can have resonance interaction up to the p–π oxygen orbitals, only inductive effects are operative on a phenyl carbanion.

A negative ρ of -2.85 is in keeping with the notion of an attacking carbanion which is activated by electron-releasing groups and conversely is deactivated by electron-withdrawing groups. Citron and Becker[60] found a ρ of $+1.6$ for the reaction of diethylmagnesium and *para*-substituted benzonitriles in THF at 30°, which positive value would be expected for the converse of our reaction.

Acknowledgment.—We wish to acknowledge generous support of part of this work by the National Science Foundation under its Grant NSF-G-14558 (H. E.). We also wish to acknowledge many helpful and stimulating discussions with Professor J. Steigman.

[59] A referee has suggested an alternative mechanism. The effect of $MgBr_2$ on ΔS^* may be to increase the order of the solvent molecules in the ground state so that the solvent medium does not suffer so great a loss in entropy in going to the "frozen" state of the activated complex. In other words, the solvent molecules already are effectively "frozen" to a degree in the ground state by the $MgBr_2$. Therefore, the change in the degree of freedom from ground state to the transition state is less with magnesium bromide present than it is with the neat solvent.

[60] J. D. Citron and E. I. Becker, *Can. J. Chem.*, **41**, 1260 (1963).

The Norbornenyl–Nortricyclyl Radical System

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Received May 23, 1966

The reduction of norbornenyl bromide (**4b**) and chloride (**4c**) and of nortricyclyl bromide (**5b**) and chloride (**5c**) with tri-*n*-butyltin hydride provides the same mixture of norbornene and nortricyclene indicating the existence of common intermediates in the reaction. With triphenyltin hydride, nortricyclyl bromide yields a higher ratio of nortricyclene to norbornene in the absence of solvent than in pentane solution indicating the presence of discrete nortricyclyl and norbornenyl free radicals. Relative rates of reaction of cyclic bromides and chlorides (figures in parentheses) with the tri-*n*-butyltin radical at 45° follow: cyclopentyl, 1.0 (1.0); cyclopent-3-enyl, 1.73; cyclohexyl, 0.62 (0.399); *exo*-bicyclo[2.2.1]hept-2-yl, 0.81; *exo*-bicyclo[2.2.1]hept-2-en-5-yl, 1.40; *endo*-bicyclo[2.2.1]hept-2-en-5-yl, 0.37; and tricyclo[2.2.1.$0^{2,2}$]hept-3-yl, 0.31. Thus no significant degree of anchimeric assistance attends the reaction.

A number of investigations have been carried out to determine whether nonclassical free radicals, analogous to nonclassical carbonium ions, appear as reaction intermediates. Bornyl or norbornyl radicals have been prepared by decomposition of 2-azobornane,[2] in the halogenation of norbornane,[3] in the addition of hydrogen bromide to 2-bromonorbornene,[4] and from the norborn-2-ylcarboxy radical.[5,6] The norborn-2-en-5-yl radicals (**1**) have been generated from the norborn-2-en-5-yl carboxy radical,[5,6] in the decarbonylation of norborn-2-en-5-carboxaldehyde,[7] in the addition of thiols,[8–10a] arenesulfonyl halides,[10b] and other substances[8] to norbornadiene. The uniform conclusion has been that delocalization of the unpaired electron by either σ participation by a neighboring alkyl or π par-

[1] (a) Supported in part by Public Health Service fellowships (4-FL-GM-19,157) to C. R. W. and (1-FL-GM-28,104) to R. J. S. from the National Institute of General Medical Sciences; (b) taken in part from the Ph.D. dissertation of C. R. W., University of New Hampshire, April 1964; (c) to whom correspondence should be addressed at the Department of Chemistry, State University of New York at Albany, Albany, N. Y. 12203.

[2] J. A. Berson, C. J. Olsen, and J. S. Walia, *J. Am. Chem. Soc.*, **84**, 3337 (1962).

[3] E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958).

[4] N. A. LaBel, *J. Am. Chem. Soc.*, **82**, 623 (1960).

[5] M. M. Martin and D. C. DeJongh, *ibid.*, **84**, 3526 (1962).

[6] H. Hart and F. J. Chloupek, *ibid.*, **85**, 1155 (1963).

[7] J. W. Wilt and A. A. Levin, *J. Org. Chem.*, **27**, 2319 (1962).

[8] D. J. Trecker and J. P. Henry, *J. Am. Chem. Soc.*, **85**, 3204 (1963), and references cited therein.

[9] S. J. Cristol, G. D. Brindell, and J. A. Reeder, *ibid.*, **80**, 635 (1958).

[10] (a) S. J. Cristol and D. I. Davies, *J. Org. Chem.*, **29**, 1282 (1964); (b) S. J. Cristol and D. I. Davies, *ibid.*, **29**, 1282 (1964).

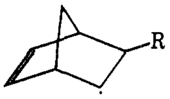
TABLE I

FORMATION OF NORBORNENE AND NORTRICYCLENE IN FREE-RADICAL REACTIONS

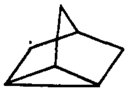
Entry	Source	Hydride[a]	Solvent	Initial concn, *M*	Method[b]	Temp, °C	Over-all yield	**4a**, %	**5a**, %
1	**4b**	Bu	None		A	18–22	100	57	43
2	**5b**	Bu	None		A	18–22	100	55	45
3	**5b**	Bu	None		B	100		60	40
4	*exo* **4b**	Bu	None		B	100		60	40
5	**4b**	Bu	Xylene	1.2	B	90	95	59	41
6	**5b**	Bu	Xylene	1.2	B	90	95	60	40
7	**4c**	Bu	Xylene	1.2	C	90	90	58	42
8	**5c**	Bu	Xylene	1.2	C	90	90	57	43
9	**5b**	Ph	None		*c*	24–27	100	41	59
10	**5b**	Ph	None		*c*	24–27	90	46	54
11	**5b**	Ph	Pentane	0.8	*c*	24–27	87	56	44
12	**5b**	Ph	Pentane	0.8	*c*	24–27		53	47
13			Cumene		D	94		40[d]	60[d]
14			Cumene		D	94		40[d]	60[d]
15			Chlorobenzene	0.8–4.1	E	132	9	44–47[e]	56–53[e]

[a] Bu = tri-*n*-butyltin hydride; Ph = triphenyltin hydride. [b] Method A: the bromide was mixed neat, at room temperature, with an equimolar amount of tri-*n*-butyltin hydride. Method B: a solution of the tri-*n*-butyltin hydride in xylene was added to the appropriate bromide. The solution was sealed in an ampoule and heated at 90° for 49 hr. Method C: the same as method B except 3 mole % azobisisobutyronitrile is added. Method D: the *t*-butyl percarboxylates were heated at 94°, data taken from ref 5. Method E: the aldehyde was decarboxylated in refluxing chlorobenzene using di-*t*-butyl peroxide as the catalyst, data taken from ref 7. [c] See the Experimental Section. [d] Data taken from ref 5; these authors report that the norbornene–nortricyclene ratio equals 2:3. [e] Data taken from ref 7.

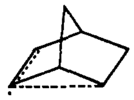
ticipation by a neighboring double bond does not assist the formation of free-radical intermediates. The norbornenyl radical (**1**) and the nortricyclyl radical (**2**) have been shown to be discrete species[9,10] apparently more stable than the nonclassical species (**3**). How-



1



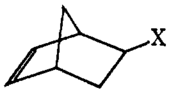
2



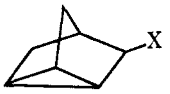
3

ever, in none of the investigations cited have the intermediates been generated from both norbornenyl and notricyclyl derivatives.

The cation corresponding to **1** reacts to give nortricyclenes[11,12] and the anion reacts to give mixtures of norbornenes and nortricyclenes.[13] Those reactions examined to date in which the unsubstituted norbornenyl radical (**1**) is an intermediate have yielded both norbornene (**4a**) and nortricyclene (**5a**) in roughly equal amounts.[5,7]



4a, X = H
b, X = Br
c, X = Cl



5a, X = H
b, X = Br
c, X = Cl

Reduction of alkyl halides by organotin hydrides has been shown to proceed by a free-radical chain mechanism in which reactions 2 and 3 were postulated to be the chain-carrying steps.[14] In step 1, Q· is a radical which may be derived from any of a variety of

$$R_3SnH + Q\cdot \longrightarrow R_3Sn\cdot + QH \quad (1)$$

$$R_3Sn\cdot + R'X \longrightarrow R_3SnX + R'\cdot \quad (2)$$

$$R'\cdot + R_3SnH \longrightarrow R_3Sn\cdot + R'H \quad (3)$$

sources, including the reactants. The reaction frequently proceeds in virtually quantitative yield and, therefore, offered promise as a convenient means of generating radicals **1** and **2** unambiguously from appropriate halides.

Results and Discussion

We examined the course of reduction of norborn-2-en-5-yl bromide (**4b**) and chloride (**4c**) and of tricyclo[2.2.1.0^{2,6}]hept-3-yl (nortricyclyl) bromide (**5b**) and chloride (**5c**) with tri-*n*-butyltin hydride in the first stage of this investigation. Product compositions were determined by gas–liquid partition chromatography (glpc) and the individual hydrocarbons were characterized by comparison of their infrared spectra with those of authentic samples. No reduction products besides **4a** and **5a** were detected. Results are presented in the first eight entries of Table I. Comparison of the pairs of entries 1 and 2, 3 and 4, 5 and 6, and 7 and 8 shows that the product composition is independent of whether the starting halide is the norbornenyl or nortricyclyl derivative. Comparison of the first two entries with the other six shows that temperature has, at most, a slight effect on the product composition. Appropriate comparisons also reveal that the chloride and the bromide give the same results, as do results obtained without solvent and in xylene solution which are indistinguishable. Furthermore, the thermal reactions and those catalyzed by azobisisobutyronitrile provide the same product distribution, a fact which is in accord with our postulate of a free-radical mechanism for the thermal reaction.[14]

These results do not provide an answer as to whether there is a single nonclassical intermediate or a pair of classical radicals.

In terms of the earlier conclusion that discrete radicals are formed in the norbornenyl–nortricyclyl

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(11) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

(12) E. J. Corey, N. L. Bauld, R. T. Lalonde, J. Casanova, Jr., and E. T. Kaiser, *ibid.*, **82**, 2645 (1960).

(13) G. Wittig and E. Hahn, *Angew. Chem.*, **72**, 781 (1960).

(14) (a) H. G. Kuivila, L. W. Menapace, and C. R. Warner, *J. Am. Chem. Soc.*, **84**, 3584 (1962); (b) H. G. Kuvila and L. W. Menapace, *J. Org. Chem.*, **28**, 2165 (1963); (c) H. G. Kuvilia in "Progress in Organometallic Chemistry," F. G. A. Stone and R. West, Ed., Academic Press Inc., New York, N. Y., 1964, p 64.

system, these results mean that this system undergoes interconversion much more rapidly than does hydrogen transfer from the organotin hydride to either radical. Triphenyltin hydride is more reactive in free-radical reactions than trialkyltin hydrides.[14c] This could be due in part, at least, to its being a better hydrogen donor to free radicals. Entries 9 and 10 and 11 and 12 show the effect of dilution on the product distribution obtained in the reduction of bromonortricyclene with triphenyltin hydride. In the neat reaction, nortricyclene is formed in greater amount, and in pentane, norbornene predominates. (Complications due to the addition of triphenyltin hydride to norbornene and, very likely, to norbornenyl bromide deterred us from attempting similar experiments with norbornenyl bromide. See the Experimental Section.) Thus, we appear to be trapping some of the nortricyclyl radical before equilibration with the norbornenyl radical is complete. This effect is far smaller than that observed by Cristol and Davies[10b] in trapping the 3-benzenesulfonylnorborn-2-en-5-yl radicals by halogen transfer from the benzenesulfonyl iodide and bromide, for example. The two sets of results taken together confirm the existence of both norbornenyl and nortricyclyl radicals as intermediates, either of which can be trapped under appropriate conditions.

The last three entries in Table I are included to show that the nortricyclene–norbornene ratio depends very little on the hydrogen donor whether it be organotin hydride, cumene, or norborn-2-ene-5-carboxaldehyde.

We have also examined the relative rates of reduction of several bromides in order to determine whether the bi- or tricyclic systems showed any rate enhancement which would indicate anchimeric assistance. These were carried out by the competition method at 45° with the results displayed in Table II. The fastest rate is less than six times the slowest. Clearly anchimeric assistance of the order of magnitude observed in solvolytic reactions is absent. The relatively small variations are real, however, and merit comment. *exo*-Norbornenyl bromide is about 3.5 times as reactive as the *endo* isomer. This might be attributed to a small degree of anchimeric assistance in the *exo* isomer or to a steric effect. *exo* bromine should be more accessible to the tri-*n*-butyltin radical than *endo* bromine. *exo*-Norbornenyl bromide is nearly twice as reactive as *exo*-norbornyl. This again might be interpreted as due to a small degree of anchimeric assistance by the double bond. It seems more probable that this is due to enhancement in reactivity by the inductive electron withdrawal by the sp^2 carbons of the double bond. This is supported by the significant enhancement in reactivity of 4-bromocyclopentene over bromocyclopentane and is in qualitative accord with electronic effects observed earlier.[14]

Table II

Relative Rates of Reduction of Cyclic Halides by Tri-*n*-butyltin Hydride at 45°

Entry	RX	Relative rate X = Br	Relative rate X = Cl
1	Cyclopentyl	1.0	1.0
2	Cyclopent-3-enyl	1.73	
3	Cyclohexyl	0.62	0.399
4	*exo*-Bicyclo[2.2.1]hept-2-yl	0.81	
5	*exo*-Bicyclo[2.2.1]hept-2-en-5-yl	1.40	1.48
6	*endo*-Bicyclo[2.2.1]hept-2-en-5-yl	0.37	
7	Tricyclo[2.2.1.0^{2,6}]hept-3-yl	0.31	

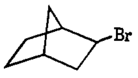
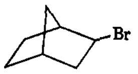
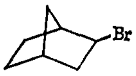
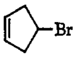
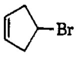
It seemed possible that any anchimeric assistance might be more easily detected if the process of halogen abstraction were one of higher activation energy. To this end the rates of photocatalyzed reduction of cyclopentyl, cyclohexyl, and *exo*-norbornenyl chlorides were compared, and the results are shown in the last column of Table II. The change in relative rates in going from the bromides to the chlorides is negligible. This may be the result of a compensating effect in the transition states. Although the C–Cl bond is stronger than the C–Br bond, the same is true of the corresponding bonds between the halogens and tin. The implication is that there is a high degree of similarity in the transition states for the abstraction of chlorine and bromine by organotin radicals.

Experimental Section

Materials.—Tri-*n*-butyltin hydride was prepared by a previously described method.[15] Cyclohexyl and cyclopentyl bromides were commercially available and were redistilled before use. The tricyclo[2.2.1.0^{2,6}]hept-3-yl bromide (**5b**), bicyclo[2.2.1]hept-2-en-5-yl bromide (**4b**), and bicyclo[2.2.1]hept-2-en-5-yl chloride (**4c**) were prepared as described previously.[11] The precedure of Hanack[16] was used to prepare tricyclo[2.2.1.0^{2,6}]hept-3-yl chloride (**5c**). The bicyclo[2.2.1]hept-2-en-5-yl bro-

Table III

Relative Rates of Reduction of Cyclic Organic Bromides by Tri-*n*-butyltin Hydride at 45°[a-d]

Expt no.	Competitor A	Competitor B	k_B/k_A
1	$c\text{-}C_5H_9Br$	$c\text{-}C_6H_{11}Br$	0.62
2	$c\text{-}C_5H_9Br$	$c\text{-}C_6H_{11}Br$	0.60
	$c\text{-}C_5H_9Br$	*exo* **4b**	1.41
	$c\text{-}C_5H_9Br$	*endo* **4c**	0.37
	$c\text{-}C_5H_9Br$	**5b**	0.26
3		**5b**	0.36
4		**5b**	0.38
	$c\text{-}C_5H_9Br$	**5b**	0.31
	$c\text{-}C_5H_9Br$		0.81
5	$c\text{-}C_5H_9Br$		1.82
6	$c\text{-}C_5H_9Br$		1.64
7	$c\text{-}C_5H_9Cl$	$c\text{-}C_6H_{11}Cl$	0.394
8	$c\text{-}C_5H_9Cl$	$c\text{-}C_6H_{11}Cl$	0.404
9	$c\text{-}C_5H_9Cl$	*exo* **4c**	1.54
10	$c\text{-}C_5H_9Cl$	*exo* **4c**	1.42

[a] The solvent used in all experiments was methylcyclohexane (5 ml). [b] Approximately equimolar amounts of competitors were used in all experiments. [c] Internal standard, toluene. [d] In experiments 5 and 6, 3.78 moles of tri-*n*-butyltin hydride was used. In the other experiments, 7.57 moles of tin hydride was used. The concentration of each of the competing halides was about the same as that of the hydride.

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(15) H. G. Kuivila and O. F. Beumel, Jr., *J. Am. Chem. Soc.*, **83**, 1246 (1961).

(16) M. Hanack and W. Kaiser, *Ann.*, **657**, 12 (1962).

mide was prepared by the method of Schmerling.[17] It contained 66% *endo* **4b**, 25% *exo* **4b**, and 9% of **5b**. The compositions of the halides were checked by infrared spectra and glpc. The use of a 20% silicone nitrile, XF-1155, on Chromosorb 60–80 mesh permitted the separation of the *exo*- and *endo*-norbornenyl and -nortricyclyl halides.

Characterization of Products.—The reactants were mixed together and sealed in glass ampoules under an atmosphere of prepurified nitrogen. The products were separated by preparative glpc. Their infrared spectra were found to be identical with those of the authentic substances.

Determination of Relative Reactivities.—The relative rate constants were determined by allowing the bromides to compete in pairs for an insufficient amount of tri-*n*-butyltin hydride. The competitors and internal standard were placed in the reaction flask followed by 5 ml of methylcyclohexane and tri-*n*-butyltin hydride. The flask was flushed with nitrogen, stoppered, and kept in a constant-temperature bath at 45° until all of the hydride was consumed as indicated by the disappearance of the Sn–H band at about 1815 cm^{-1}. Analysis for unreacted bromide was made by gas chromatography using a 6-ft column packed with 10% diethylene glycol succinate on Diatoport W (60–80). The method of analysis was the same used by Walling and Helmreich.[18] Results obtained by this method afforded the same relative rates when checked by the more commonly used internal standard method described by Keulemans.[19] The former method involves measuring peak heights of the competitors relative to the peak height of an internal standard before and after the reduction. Relative rate constants were computed by the method of Ingold and Shaw.[20] Relative reactivities of the chlorides were determined by irradiating the reactants in Pyrex tubes maintained at 45° in a constant temperature bath with a G.E. 100-w high-pressure mercury vapor lamp for about 10 hr. Analyses were carried out in the same way. Results are given in Table III.

These runs also served as control studies. It was found that the unreacted halides did not undergo interconversion under the reaction conditions. The hydrocarbons did not undergo interconversion under the reaction conditions, either.

Reduction of Nortricyclyl Bromide (5b) with Triphenyltin Hydride.—To 2 ml (7.69 mole) of triphenyltin hydride in 2 ml of *n*-pentane was added 0.245 ml of **5b** with stirring under a nitrogen atmosphere. The reaction mixture was allowed to stand for 2 days, and the hydrocarbon products were removed at reduced pressure into traps at -78 and $-196°$ in tandem. The products were combined and analyzed by glpc yielding the results shown in Table I. The neat reaction was carried out in the same manner. It was observed to be slightly exothermic. Since triphenyltin hydride adds to norbornene the amount of nortricyclene was determined from the gas chromatogram, and the amount of norbornene was taken to be the difference between this value and the initial amount of hydride used.

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[17] L. Schmerling, J. P. Luvisi, and R. W. Welch, *J. Am. Chem. Soc.*, **78**, 2821 (1956).

[18] C. Walling and W. Helmreich, *ibid.*, **81**, 1144 (1959).

[19] A. I. M. Keulemans, "Gas Chromatography," Reinhold Publishing Corp., New York, N. Y., 1957, p 32.

[20] C. K. Ingold and F. R. Shaw, *J. Chem. Soc.*, 2918 (1927).

The Preparation of Some Pyrido and Pyridyl Derivatives of Phenazine and Quinoxaline[1]

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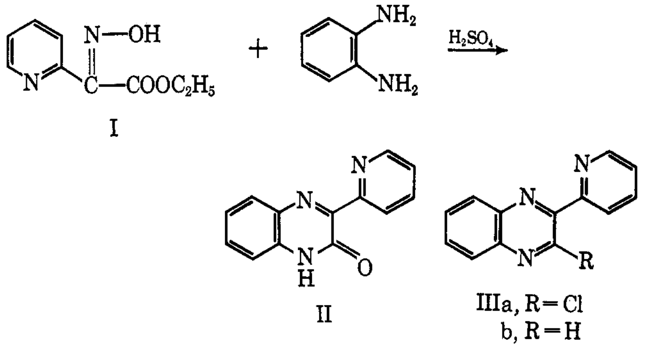
Received May 12, 1966

The Skraup reaction has been used to synthesize several phenazine and quinoxaline derivatives which are expected to form chelates with metal ions. Mono-, di-, tri-, and tetrapyridophenazines were prepared. 2-(2-Pyridyl)quinoxaline has been synthesized as well as some mono- and dipyrido-2- and 3-(2-pyridyl)-quinoxalines. The preparation of some new amino derivatives of phenazine and quinoxaline is described.

Various nitrogen heterocycles having substituent 2-pyridyl groups incorporated in "ferroin" groups[2] have been shown to be effective chelators of the transition elements.[3] In connection with further studies to determine sensitive and selective reagents for the detection of iron(II),[4] we required samples of quinoxaline derivatives that have in common a 2-pyridyl group. Also, pyridophenazines were desired in which the "ferroin" group remains rigid, as in 1,10-phenanthroline, in order to compare the chelating abilities of the pyridylquinoxalines and the pyridophenazines.

CHART I



I

II

IIIa, R = Cl
b, R = H

Pyridylquinoxalines.—For the synthesis of 2-(2-pyridyl)quinoxaline (IIIb), the three-step route shown in Chart I was employed. Ethyl 2-pyridylglyoxylate oxime (I) was condensed with *o*-phenylenediamine in dilute sulfuric acid at 75° to afford a 40% yield of 2-hydroxy-3-(2-pyridyl)quinoxaline (II). This compound exists almost exclusively in the lactam form.[5] Refluxing II with phosphorus oxychloride produced the 2-chloro derivative IIIa. Dehalogenation of IIIa with hydrogen over palladium gave IIIb in fair yield.

The preparation of 2-(2-pyridyl)pyrido(3,2-*h*)quinoxaline (X) is indicated in Chart II. From the condensation of the anil[6] IV with 3-nitro-*o*-phenylenediamine (V) in acetic acid only one of the two possible quinox-

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[1] This work was supported by a grant from the Committee on Research and Publications of Temple University.

[2] (a) F. H. Case, "A Review of Syntheses of Organic Compounds Containing the Ferroin Group," G. F. Smith Chemical Co., Columbus, Ohio (1960); (b) F. H. Case and W. A. Butte, *J. Org. Chem.*, **26**, 4415 (1961); (c) F. H. Case, *ibid.*, **27**, 640 (1962); (d) J. F. Geldard and F. Lions, *ibid.*, **30**, 318 (1965); (e) H. A. Goodwin and F. Lions, *J. Am. Chem. Soc.*, **81**, 6415 (1959), and references cited therein.

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